

MATERIALS SCIENCE

D. Hülsenberg
A. Harnisch
A. Bismarck

Microstructuring of Glasses

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Dagmar Hülseberg
Alf Harnisch
Alexander Bismarck

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With 217 Figures



Springer

Professor Dr. Dr. Dagmar Hülsenberg

Technische Universität Ilmenau, FG Glas- und Keramiktechnologie
Gustav-Kirchhoff-Str. 1, 98693 Ilmenau, Germany
E-mail: dagmar.huelsenberg@tu-ilmenau.de

Dr. Alf Harnisch

Silicaglas Ilmenau (SGIL)
Gewerbering 8, 98704 Langewiesen, Germany

Dr. Alexander Bismarck

Imperial College London, Department of Chemical Engineering
Polymer and Composite Engineering Group (PaCE)
South Kensington Campus, London, SW7 2AZ, UK
E-mail: a.bismarck@imperial.ac.uk

Series Editors:

Professor Robert Hull

University of Virginia
Dept. of Materials Science and Engineering
Thornton Hall
Charlottesville, VA 22903-2442, USA

Professor Jürgen Parisi

Universität Oldenburg, Fachbereich Physik
Abt. Energie- und Halbleiterforschung
Carl-von-Ossietzky-Strasse 9-11
26129 Oldenburg, Germany

Professor R. M. Osgood, Jr.

Microelectronics Science Laboratory
Department of Electrical Engineering
Columbia University
Seeley W. Mudd Building
New York, NY 10027, USA

Professor Hans Warlimont

Institut für Festkörper-
und Werkstofforschung,
Helmholtzstrasse 20
01069 Dresden, Germany

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Preface

Silicon, the second most abundant element on earth, is a well-established material in microsystems technology. Its properties and technical perfection open up an almost unlimited range of applications. Silicon is the main component of most semiconductor devices, but other materials are also applied step by step in microsystems technology so as to obtain some special properties. Glass is one such material that has some special properties.

Glass-making has a history of almost six millennia. However, the science of glass started only around 1830. But even by the end of the sixteenth century (or the beginning of the seventeenth century), glass articles were decorated with very fine gravured patterns in the form of meanders or garlands, combined with other bas-relieved decors [488]. Many of the patterns were made using copper wheels. Frequently the line width was less than 100 μm . Around 1920, glass-cutting tools positioned in pantographs were used for scratching fine lines into waxed surfaces of glass products. The lines were then transferred into the glass by hydrofluoric acid treatment, resulting in permanent patterns. These final patterns consist of lines that are 200 μm wide and deep. Till date, we find glassware such as drinking glasses and candlesticks being decorated using this technique. This method was also used to produce the scaling of clinical thermometers and laboratory glasses. Powder blasting for decorating glass products and treatment with a diamond tool for producing glass scales have been known for more than 50 years and remain the state of the art even today.

Between 1940 and 1950, Dalton, Armistead and Stookey, while working for Corning (USA), discovered that specially composed, UV-sensitive glasses can be micro ‘sculptured’. Partial UV exposure through a mask, followed by thermal and chemical treatments, allow for a defined microstructuring of glasses in a 10- μm range. Unnoticed by the world, the age of glass microstructuring had started, possibly 30 years too early. Only with the rise of silicon technology did microstructuring of glasses become important.

Glass is an amorphous material with a unique property profile. Glasses offer different transparency ‘windows’ for electromagnetic radiation, have

superior chemical stability, are biocompatible, have excellent abrasion resistance and allow for adapting their thermal expansion coefficients to those of other materials. Glasses can be electrically insulating, but they can also be good ion conductors or even semiconductors. The properties of glasses depend strongly on the chemical composition of the glass itself, which can vary widely. The property profile opens a wide range of applications of different glasses in microtechnology. The amorphous character of glasses implies that all its properties are isotropic and that the ability of microstructuring is therefore independent on predefined directions of crystal lattices. Sometimes glasses are the only material that fulfil the specifications for special applications.

As a consequence, and in contrast to silicon, quite different glasses can be used for microstructuring. The producer of microdevices has to select a glass that is suitable for his application and also has a composition that offers the desired property profile. Mostly, the amount of glass ordered is relatively small. Of course, the glass industry is able to produce special glasses, but it is costly to produce very small quantities of glasses with specific composition. It is therefore a disadvantage for the glass producer if a customer demands very small quantities of a glass having a specific composition. For this reason, it would be good to have a theoretical idea of the feasibility of producing a desired glass in a certain small quantity.

Silica coatings, light wave guides, silicon sensor encapsulations and membranes in piezo-driven ink jet printers were the first applications of glass elements in microcomponents. The ability to fabricate extremely thin glass components without additional, geometrical structuring was the only requirement for these early applications. The need for small holes allowing for electrical connections through thin glass coatings to the silicon element soon required additional machining. Initially, these were manufactured by drilling. As of date, almost every geometrical feature that is needed at or near the surface and even in the bulk of the glass element can be made.

However, because of limited communication and knowledge transfer between the glass manufacturer and the microsystems industry, it is hard for the glass manufacturers to estimate the issues and the real demand for microstructured glasses in the microsystems area. Vice versa, the specialist in the microdevices industry cannot assess the full range of possibilities and problems of this amorphous, brittle material. The aim of this book is to link the thinking and understanding of specialists in terms of glass production as well as the fabrication of microdevices. The book attempts to explain the most important fundamentals, methods, features and highlights in the production of glass half products used for microstructuring as well as the microstructuring itself. It does not cover the entire subject matter, because of the growing nature of this field. Rather, the purpose of this book is to provide the newcomer to glasses with enough background to be able to access the specialist literature. Therefore, we start with the basics of glass materials and frequently refer to existing publications so that readers across cognate disciplines can easily understand what happens, for instance, between the ions in the glass

and the ways in which glass processing affects the final properties of glass microdevices. The book's aim is to present an additional source of information on the three aspects, namely, the fundamentals of glass composition and glass processing and the many different methods of its microstructuring. It provides a comprehensive discussion of the various microstructuring methods, with appropriate references to literature, so that the book can be used as a source of information for glass manufacturers, producers of microdevices, engineering professionals with a background in designing (of microdevices) and structuring processes, as well as scientists in general, and students in particular.

The book is divided into two main parts:

Part I deals with the fundamentals of inorganic-nonmetallic glasses and their processing.

Part II explores and explains the principles of geometrical microstructuring of glasses, joining processes and applications.

First (Part I), an introduction to the amorphous state of glasses provides the background to the study of glasses, which is necessary for understanding the unique role of glass in microsystems. This is followed by a description of the characteristics and properties of specific glasses that are important for microsystems. The reader is then provided with information about glass processing, keeping in mind the requirements and specifications of microglass elements.

Part II provides the reader with a general overview of geometrical microstructuring and the special methods used for mechanical, thermal and chemical structuring of glasses. It focuses on methods of glass structuring, using various types of lasers, as well as on structuring of photosensitive glasses. The book also describes in some detail the methods of joining glasses with themselves as well as with other materials, such as silicon. The discussion of the methods is supplemented with relevant applications.

The book focuses mainly on subtractive methods, i.e. the removal of material, and on thermal reshaping methods as well as techniques that allow for the manipulation of locally confined properties. We do not discuss ion or electron beam structuring, because of their limited application in industry; nor do we discuss additive methods such as the deposition of powders or coatings. Silicate glasses form the centre of discussion of the book. We also exclude special microoptics and photonics made from glasses because excellent specialist books are already available, and the reader is referred to them; the processing associated with their manufacture is, however, described in different sections of the book.

We hope that the reader will find sufficient interesting facts and be motivated to use glasses for microdevices. We welcome comments to this work.

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Dagmar Hülsenberg
Alf Harnisch
Alexander Bismarck

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List of abbreviations

Symbol	Description	Unit
α	Thermal expansion coefficient	10^{-6} K^{-1}
α_i	Thermal expansion coefficient of the i th component	10^{-6} K^{-1}
β	Angle of inclination	$^{\circ}$
β	Composition dependent materials transition number	$\text{g cm}^{-2} \text{ s}^{-1}$
β_E	Absorption coefficient	mm^{-1}
β'_E	Non linear absorption coefficient	mm^{-1}
γ	Surface tension	N m^{-1}
$\dot{\gamma}$	Shear rate	s^{-1}
Δ	Loss angle, phase displacement between current and voltage	$^{\circ}$
$\Delta_b H^{\circ}$	Standard enthalpy of formation	kJ mol^{-1}
$\Delta_b S^{\circ}$	Standard entropy of formation	$\text{kJ mol}^{-1} \text{ K}^{-1}$
Δ_{bg}	Widening of trenches/holes	μm
Δ_{bs}	Reduce of width of beams/bars	μm
Δc	Concentration gradient	–
Δg_V	Change of the free volume enthalpy during nucleation	kJ mol^{-1}
$\Delta \text{o.D.}$	Difference of the optical density	–
ΔT	Super or under cooling	$^{\circ}\text{C}$
ε	Strain	%
ε_{Ab}	Threshold energy density for ablation	J cm^{-2}
ε_L	Laser beam intensity, energy density of laser irradiation	J cm^{-2}
ε_O	Electrical field constant	$\text{As V}^{-1} \text{m}^{-1}$
ε_S	Threshold energy density for photo chemical effects	J cm^{-2}

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η	Dynamic viscosity	Pa s^{-1} , dPa s^{-1}
κ	Specific electrical conductivity	$\Omega^{-1} \text{cm}^{-1}$
λ	Heat of two-dimensional condensation	J
λ	Shear deformation rate	–
λ	Thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
λ	Wavelength	μm , nm
λ_{L}	Laser wavelength	nm
ρ	Specific electrical resistivity	Ωcm
ρ	Density	g cm^{-3}
σ	Interfacial tension	N m^{-1}
σ	Normal stress or strength	MPa
σ_{B}	Bending strength	MPa, MN m^{-2}
σ_{f}	Failure strength	N mm^{-2}
σ_{m}	Theoretical stress	N mm^{-2}
σ_{y}	Yield stress	MPa
σ_{z}	Tensile strength	MPa, MN m^{-2}
τ	Optical transmission	%
τ	Shear stress	Pa, MPa
χ	Susceptibility	–
ω	Angular frequency	s^{-1}
A	Area, surface area	cm^2
A	Aspect ratio	–
A_{E}	Optical absorption	–
A_{R}	Fracture area	mm^2
A_{US}	Ultrasonic amplitude	μm
a	Half flaw length	nm
B	Magnetic field, magnetical flux density	T, Wb m^{-2}
B	Chemical binding energy	J mol^{-1}
bg_{i}	Real width of trenches/holes (after thermal treatment and etching)	μm
bg_{s}	Nominal width of trenches/holes	μm
b_{s}	Distance between crossing perforations	μm
bs_{i}	Real width of bars/beams (after thermal treatment and etching)	μm
bs_{s}	Nominal width of beams	μm
C_p	Specific heat capacity	$\text{J K}^{-1} \text{mol}^{-1}$
c	Concentration	–
c	Speed of light	km s^{-1}
c_{Ag}	Concentration of silver ions	%
D	Deformation rate, shearing rate	s^{-1}
D	Energy density	J cm^{-2}
D	Diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$

D	Energy to dissociate oxides	J mol^{-1}
$D_{\min}$	Minimum density of energy	J cm^{-2}
D_s	Relative resp. normalized density of energy	–
d	Machining depth, thickness, crystal size	μm
d_{50}	Grain size of particles: 50% are smaller and 50% greater than this value	μm
d_C	Critical tension depth	μm
E	Young's modulus	GPa
E_η	Activation energy for viscous flow	kJ mol^{-1}
E_B	Energy of binding, effective band gap	eV
E_D	Activation energy for diffusion	kJ mol^{-1}
E_E	Enthalpy of evaporation	kJ mol^{-1}
E_P	Energy for ductile deformation	J
E_{Ph}	Energy of a photon	eV
E_R	Energy for generation of new fracture surfaces	J
F	Area	cm^2
F	Force	N
F_E	Electrical Field strength	V m^{-1}
$f_{L,e}$	Lorentz force density, externally caused	N m^{-3}
G	Shear modulus	GPa
G	Free (or Gibbs) enthalpy	J mol^{-1}
G	Griffith crack propagation parameter	N mm^{-1}
G^*	Activation energy for nucleation	kJ mol^{-1}
G_v	Free volume enthalpy	kJ mol^{-1}
G_O	Free surface enthalpy	kJ mol^{-1}
g	Acceleration due to gravity	m s^{-2}
g	Width of not transparent lines	μm
H	Enthalpy	kJ mol^{-1}
H	Hardness	MN m^{-2}
h	Depth of structures (after etching) or of bottom topography (roughness)	μm
h_c	Cutting speed, speed of the tool	$\mu\text{m s}^{-1}$
h_d	Depth of diffusion	μm
h_f	Feed rate	mm min^{-1}
h_f	Depth of relicts	μm
h_k	Crystallisation depth	μm
I	Intensity of irradiation	W cm^{-2}
I_0	Initial light intensity	W cm^{-2}
i	i th component	–

XVIII List of abbreviations

i	Distance between the median lines of two absorber stripes or transparent perforations, period	μm
i	Imaginary unit	–
J_n	Relative intensity	–
J_E	Electrode current	A
$J_{n\ h=1}$	Relative depth intensity (depth of 1 mm)	–
J_{nges}	Relative total intensity	–
J_{nges}/h	Depth related, relative total intensity	mm^{-1}
$J(T)$	Rate of nucleation (including diffusion processes)	s^{-1}
j	Particle current of diffusing particles from a given volume through an area	$\text{cm}^{-2}\text{s}^{-1}$
$\vec{j}$	Electric current density	A cm^{-2}
K_{IC}	Critical fracture toughness	$\text{MPa m}^{1/2}$, $\text{MN m}^{-3/2}$
KG	Rate of crystal growth	$\mu\text{m min}^{-1}$
k	Boltzmann constant	$\text{J K}^{-1}\text{atom}^{-1}$
M	Molecular weight	g mol^{-1}
m	Mass	g
$\dot{m}$	mass flow	g s^{-1}
m_i	Content of the i th component	–
N	Rate of nucleation without considering the diffusion	$\text{s}^{-1}\text{cm}^{-3}$
N	Number of species	–
N	Number of pulses	–
N_{eff}	Effective number of pulses	–
n	Number of components	–
n	Refractive index	–
n'	Nonlinear refractive index	–
n_0	Refractive index for isotropic materials and linear polarized light	–
n_1	Refraction constant	–
n_2	Absorption constant	–
n_s	Spindle frequency	rpm
o	Width of transparent perforations	μm
o/g	Line ratio, perforation ratio	–
P	Power density	W cm^{-2}
P	Tensile force	N, MN
P_E	Polarization	C m^{-2}
p	Pressure	MPa
Q	Ratio of etching	–
R	Gas constant	$\text{J K}^{-1}\text{mol}^{-1}$
Ra	Arithmetic mean roughness	nm, μm

R_E	Reflection	–
Rz	Surface roughness	nm, μm
r	Radius	mm
r	Griffith flaws radius	nm
r	Nucleus' radius	nm
r_o	Characteristic ion distance	nm
r^*	Critical nucleus' radius	nm
S	Entropy	$\text{J mol}^{-1} \text{K}^{-1}$
s	Proximity space, displacement, deflection	μm , mm
T	Temperature	K, $^{\circ}\text{C}$
T_0	Equilibrium temperature	K
T_g	Transformation temperature	$^{\circ}\text{C}$
$T_{\kappa\ 100}$	Temperature of a material with $\rho = 10^8\ \Omega\ \text{cm}$	$^{\circ}\text{C}$
T_{liqu}	Liquidus temperature	$^{\circ}\text{C}$
T_{melt}	Melting temperature	$^{\circ}\text{C}$
T_{sinter}	Sintering temperature	$^{\circ}\text{C}$
T_O	Annealing point	$^{\circ}\text{C}$
T_R	Room temperature	$^{\circ}\text{C}$
T_U	Strain point	$^{\circ}\text{C}$
TA	Ratio of transmission	–
t	Time	s
t	Duration of a laser pulse	fs
t_d	Time of diffusion	h
t_e	Time of etching	s, min
t_L	Exposure time	s, min
U	Internal energy	$\text{J} \cdot \text{mol}^{-1}$
V	Deformation	%
V	Volume	cm^3
V	Specific volume	$\text{cm}^3 \text{g}^{-1}$
V_M	Molar volume	$\text{cm}^3 \text{mol}^{-1}$
$V_{M, \text{eff}}$	Effective molar volume	$\text{cm}^3 \text{mol}^{-1}$
V_P	Plastically deformed volume	mm^3
v_b	Rate of bubble rising	m h^{-1}
v_c	Cutting rate, speed of the tool	m s^{-1}
v_e	Etching rate	$\mu\text{m min}^{-1}$
v_f	Feed rate	mm s^{-1} , mm min^{-1}
x, y, z	Geometrical coordinates	mm
z	Depth	mm
z	Valence number	–
BHF	Barium hexaferriite	
cw	Continuous wave	
Cps	Counts per second	

CN	Coordination number	
CPM	Colliding pulse mode	
CTE	Coefficient of thermal expansion	
CVD	Chemical vapour deposition	
DC	Direct current	
DIN	Deutsche Industrienorm (in German)	
DNA	Deoxyribonucleid acid	
DSC	Difference scanning calorimetry	
DTA	Difference thermo analysis	
DUV	Deep ultra violet	
EUV	Extrem ultra violet	
HF	Hydrofluoric acid	
HPSN	Hot pressed silicon nitride	
IR	Infrared radiation	
LCD	Liquid crystal display	
LIGA	Lithographie, Galvanoformung, Abformung (in German)	
LMS	Lithium meta silicate	
MEMS	Microelectromechanical systems	
NC	Numeric control	
NIR	Near infrared	
o. D.	Optical density	
PMMA	Polymethylmethacrylate (Perspex)	
PVD	Physical vapour deposition	
RF	Radio frequency	
SAE	Spin agitated etching	
SEM	Scanning electron microscope	
SiSiC	Silicon infiltrated silicon carbide	
TFT	Thin film transistor	
UV	Ultraviolet radiation	
VAD	Vapour axial deposition	
VIS	Visible radiation	
XRD	Röntgen diffractogram, X-ray diffraction	

**Fundamentals of Inorganic Nonmetallic Glasses
and Glass Processing**

Silicate Glasses: A Class of Amorphous Materials

1.1 Structure of Glasses: Ionic Arrangement

1.1.1 Preliminary Remarks

The understanding of the technical processes of geometrical microstructuring of glass components presumes the knowledge of the materials structure, i.e. their microstructure as well as the arrangement of and the interaction between the ions. It is necessary to distinguish between the materials microstructure and the aim of the process to create geometrically defined microstructures in glass components. Chapter 1 addresses the ionic and atomic arrangement in silicate glasses and its effect on the glass properties. The chapter is not exhaustive but explores the areas relevant to geometrical microstructuring.

As we see, the similarity of the terms *materials microstructure* and *geometrical microstructuring of components* signals the practical difficulty to separate them. The better we understand the behaviour of ions in glass, the better equipped we are to technically influence geometrical microstructures in glass components. We will use accessible language to explain the solid-state fundamentals and chemical processes, so that, for example, specialists working in mechatronics can use the book as quick and practical reference.

Concerning the properties of silicate glasses it is very interesting that they are extremely brittle materials but if used in fibre form in reinforced polymers, they provide the composite with strength. It is well known that the smaller the diameter of the glass fibres, the higher their strength. It can be expected that small microstructured glass components with the desired property profile of interest for applications in microtechniques can be produced.

1.1.2 Coordination Polyhedra

Silicates are salts of silicic acids and contain in each case SiO_2 . Silica or quartz glass contains only SiO_2 . All other glasses used for geometrical microstructuring contain also other oxides, such as Li_2O , Na_2O , K_2O , MgO , CaO , BaO ,

B_2O_3 , Al_2O_3 , etc. The principle of electroneutrality governs in the smallest space [225], i.e. the charge of cations is compensated by anions. This can only be achieved if the anions directly surround the cations and screen their charge by their volume and charge and vice versa. The consequence of these geometric requirements is the coordination polyhedra and their 3D network in solid silicate glasses.

The coordination number CN defines the number of ions X (in this case O^{2-}) that surround a central ion A (here $Li^+ \dots Mg^{2+} \dots B^{3+} \dots Si^{4+} \dots$) in the same distance. Provided that the ions can be considered as hard spheres coordination numbers from 3 to 12 can be found in silicate glasses [225]. Figure 1.1 shows schematically all possible geometrical configurations. CN depends on the charge and the radius of the individual ions. Furthermore the deformability especially of the anions and the larger cations should be taken into account [475]. Figure 1.2 shows polyhedra which are common for silicate glasses [439]. Figure 1.2 (left) shows an isolated SiO_4 -tetrahedron, however the schematic does not show the nominal negative charges of oxygen ions. The oxygen is bonded to the silicon in the centre of one tetrahedron and to another silicon from a neighbouring but, not shown, surrounding polyhedron. In case of the MgO_6^{10-} octahedron (right-hand side of Fig. 1.2) each of the O^{2-} -ions obtains nominally $1/3$ electron from the central Mg^{2+} -cation and $5/3$ electrons from the neighbouring octahedra. To compensate the charge fully, if only Mg^{2+} -cations are present, five such additional ions are necessary. CN of oxygen by only magnesium in the neighbourhood is 6. However, if the glass contains different types of cations, they all screen the charge of the oxygen. In this case it is rather complicated to determine CN for oxygen, because the distance between oxygen and the various surrounding cations varies so that the precondition for the determination of CN is not fulfilled. Therefore, it is not common to provide CN for oxygen in glass.

Regardless of glass type short- and long-range ordering of the ions has to be distinguished. The coordination polyhedra represent the short-range order of the glass. They exist in silicate glasses whether or not they are in the melt or solidified (glass) state. The long-range order characterises the periodicity or repetition of distances and angles of neighbouring polyhedra, which provides the basis for a regular lattice in crystals. However, a perfectly homogeneous glass does not possess any long-range periodical order. The absence of any long-range ordering is essential for the amorphous state. Transitions in glass between short-range ordering and emerging long-range ordering will be discussed in Sect. 1.1.4.

1.1.3 Dominating Role of Silica Tetrahedra in Silicate Glasses

In order to understand the role and importance of silica tetrahedra in glass, we should revisit a silicon atom. Silicon contains 14 electrons, which occupy different energy levels or orbitals. The state of an electron in an orbital is given by its four quantum numbers; the primary, azimuthal, magnetic and

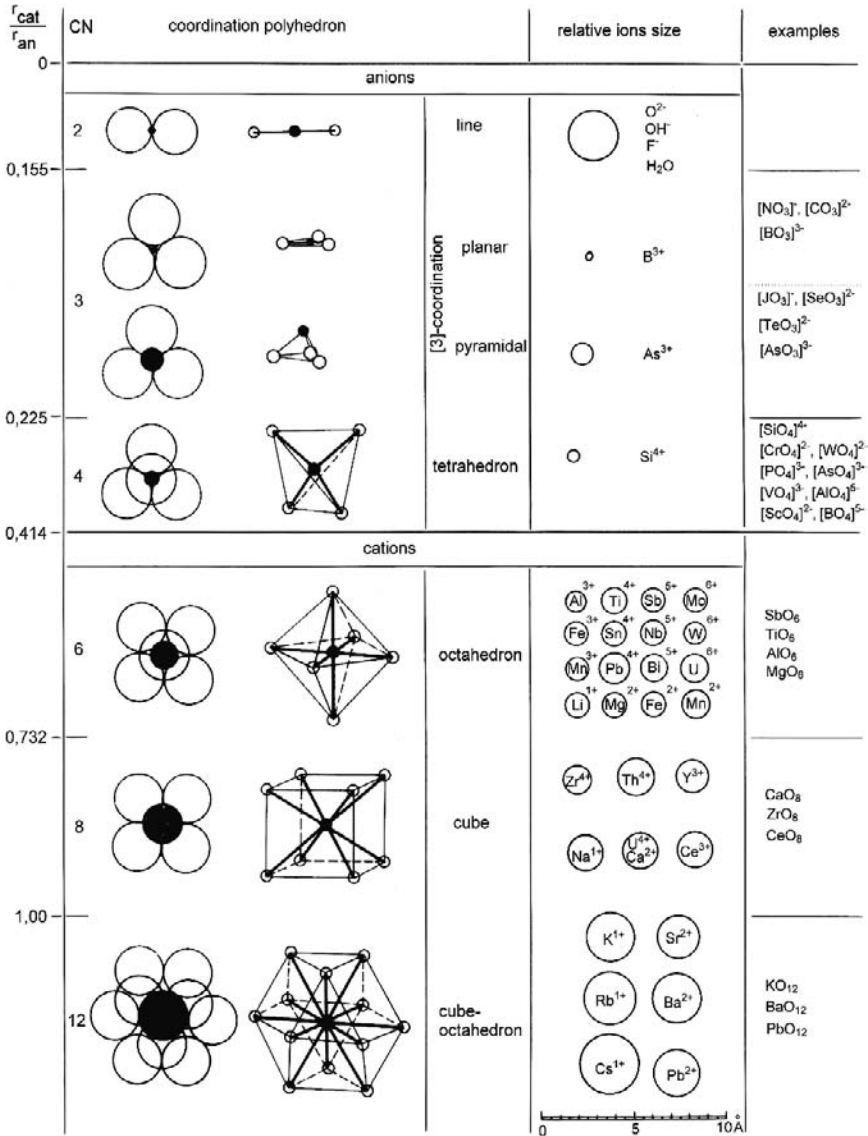


Fig. 1.1. Various coordination polyhedra depending on the ratio of the cation to the anion size and their charge [225]

spin quantum number. Only a small amount of energy is required to transfer an electron from an energy level to another. The valence electrons, i.e. those that occupy the outermost electron orbitals, are those that undergo chemical reactions. Only a small amount of energy is sufficient to rearrange the electrons in the outer orbital, to change especially the azimuthal and spin quantum

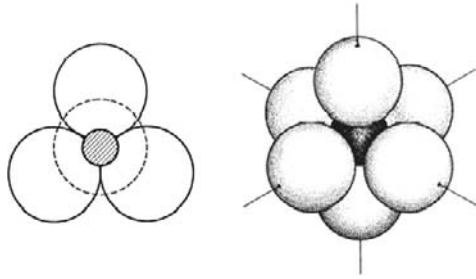


Fig. 1.2. Isolated silica-tetrahedron, (*left*) and MgO_6 -octahedron, (*right*)

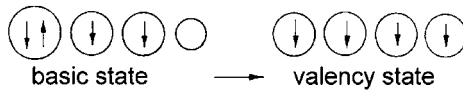


Fig. 1.3. The valence electrons of the silicon atom in the fundamental (*left*) and in the excited (*right*) state [538]

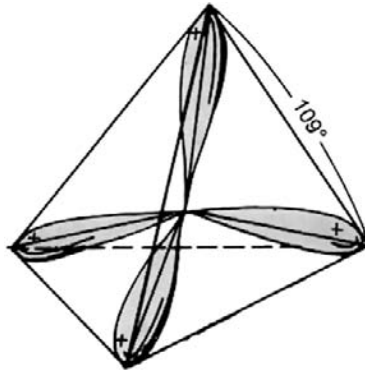


Fig. 1.4. sp^3 -hybrid orbitals of silicon [225]

numbers. A hybridisation process takes place; atomic orbitals form hybrid orbitals [398]. All electrons in the highest energy level of silicon obtain a parallel spin moment, and the electrons in the s -orbital with an antiparallel spin quantum hybridise with the p -electrons to form sp^3 orbitals. All valence electrons occupy hybrid orbitals with equal energy and have parallel spins (see Fig. 1.3). Figure 1.4 shows the excited state of the silicon atom.

These sp^3 -electrons are magnetically equivalent. It follows that the excited state is not stable, so that the sphere like outer shell of the atom deforms into a tetrahedron with the valence electrons in the four corners. The four excited electrons turn towards the energy donors for other molecules, which are in our case oxygen molecules, possessing potential and kinetic energy. The homopolar bonding of the O_2 -molecules is dissolved, and four oxygen

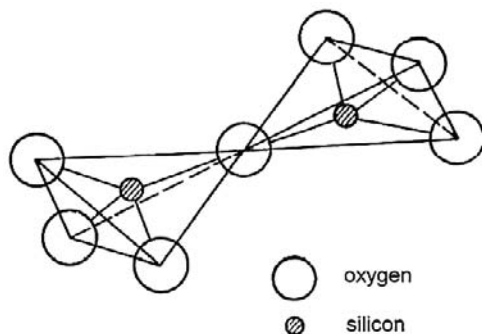


Fig. 1.5. Knotting together of two silica tetrahedra by a bridging oxygen

atoms are fixed to the electrons in the four corners of the former silicon atom (Fig. 1.2, left). Each oxygen atom receives formally one electron, and Si^0 converts into Si^{4+} , see once more Fig. 1.4. However, oxygen anions require two electrons to achieve a stable noble gas configuration. They obtain the second electron from neighbouring silicon ions, which are from themselves the centre of another SiO_4^{4-} -tetrahedron, and the oxygen forms a bridge between two tetrahedra (see Fig. 1.5).

The bridging oxygens join the corners of neighbouring tetrahedra. The Si-O-Si bond angle could become 180° , which however is an exception. Usually the bond angle varies in wide limits and is not constant in glasses, which hinders any long-range ordering. In contrast to the bridging Si-O-Si bond angle, the O-Si-O bond angle at the centre of the tetrahedron is always constant at $109^\circ 28'$, which highlights the short-range order between the associated ions (Fig. 1.4).

Silica tetrahedra are extremely stable. We will only briefly explain this fact. For a detailed explanation please refer to specialist glass materials books, such as Hinz [225], Scholze [449, 450] and Vogel [538].

In order to explain the stability of the silica (SiO_4^{4-}) tetrahedron we have to consider the electronegativity of ions as defined by Pauling [398] (Fig. 1.6). A large difference in the electronegativity of two ions would lead to a predominately heteropolar bond between the ions, which would suggest that in SiO_4^{4-} -tetrahedra heteropolar binding dominates. However, recall the hybridisation of the valence electrons in silicon, which contributes a considerable homopolar character to the bond. Therefore, a mixed binding results in and between SiO_4^{4-} -tetrahedra.

The enormous stability of SiO_4^{4-} -tetrahedra can also be explained in terms of the radius of the ions and their electrical charge, i.e. the electrical field strength of the ions. Table 1.1 provides an overview of some ions radii of interest for silicate glasses. The radii of Si^{4+} and O^{2-} are very different.

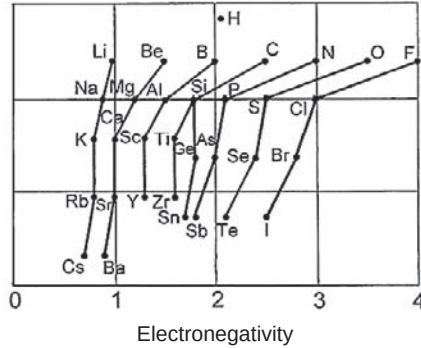


Fig. 1.6. Connection between the electronegativity of the ions and their position in the periodic table of elements [398]

Table 1.1. Radius (nm) of ions important for silicate glasses [224]

I	II	III	IV	Odd series	VI	VII
Li ⁺	Be ²⁺	B ³⁺	Si ⁴⁺	Fe ²⁺	O ²⁻	F ⁻
0.068	0.035	0.023	0.042	0.074	0.132	0.133
Na ⁺	Mg ²⁺	Al ³⁺	Sn ²⁺	Fe ³⁺	S ²⁻	Cl ⁻
0.097	0.066	0.051	0.092	0.064	0.174	0.181
K ⁺	Ca ²⁺	—	Sn ⁴⁺	Cr ³⁺	—	—
0.133	0.099	—	0.071	0.063	—	—
Rb ⁺	Sr ²⁺	—	Pb ²⁺	Zn ²⁺	—	—
0.147	0.112	—	0.120	0.074	—	—
Cs ⁺	Ba ²⁺	—	Pb ⁴⁺	Zr ⁴⁺	—	—
0.167	0.134	—	0.084	0.079	—	—
—	—	—	—	Ti ⁴⁺	—	—
—	—	—	—	0.068	—	—

The electrical field strength F_E is proportional to the valence number z and inversely proportional to the square of the ion radius r (1.1):

$$F \sim \frac{z}{r^2}, \quad (1.1)$$

which explains the strong attractive interaction of Si^{4+} to O^{2-} .

The O^{2-} in the silica tetrahedron did acquire two electrons to establish a stable noble gas configuration, but the additional electrons enhance the repulsive interaction in the outer oxygen shell so it becomes more deformable. As a consequence, the Si^{4+} -cation in the centre of the tetrahedron deforms the O^{2-} -anions. The O^{2-} -anion is deformed by the Si^{4+} -cation like a dented rubber ball. That this fact is correct, one can see in Fig. 1.7. The distance between the nuclei of Si^{4+} and O^{2-} is not equal to the sum of the ions radii ($r_{\text{Si}^{4+}} + r_{\text{O}^{2-}} = 0.042 \text{ nm} + 0.132 \text{ nm} = 0.174 \text{ nm}$, see Table 1.1), but

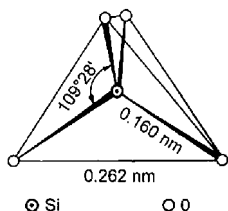


Fig. 1.7. Silica-tetrahedron containing the characteristic bond length and angles [225]

is smaller: 0.160 nm, which confirms that O^{2-} is deformed in the direction to both neighbouring tetrahedra. The bond is almost not polarised. Only the bridging oxygens show this peculiarity. The deformation of the O^{2-} has a further consequence. The four anions screen the Si^{4+} -cation completely so no interaction between the Si^{4+} -centres of neighbouring polyhedra takes place. All these facts explain the extraordinary stability of the silica-tetrahedron.

The silica tetrahedra are linked via bridging oxygen at all four corners, which results in the formation of 3D network of silica tetrahedra. Because of the distribution of the bridging oxygen (Si-O-Si) bond angles this 3D network structure is relatively disordered. As a result of which three, four or even more tetrahedra form hollow rings with interstices of various sizes and shapes in their centre (Fig. 1.8). The shape of the network rings is spherically deformed, and furthermore the number of silica tetrahedra in these rings varies. In order to visualise the 3D network of silica tetrahedra binding in a 2D form, the fourth bridging oxygen anion has to be neglected. A simplified model of a pure silica glass is shown in Fig. 1.8. The fourth bridging oxygen would stick out above and below the paper plane. Figure 1.8 provides a first imagination of the ionic microstructure of silica glass.

Most silicate glasses consist not only of silica, but also many other oxides. Only Ge^{4+} , P^{5+} , and under special circumstances also Al^{3+} and B^{3+} , are surrounded by four oxygens. They occur in the coordination number 4. These cations can substitute Si^{4+} in the tetrahedron. The bond between Ge^{4+} and O^{2-} is not as strong as in case of the Si^{4+} , because of the bigger radius of Ge^{4+} -ions. It is obvious that if B^{3+} , Al^{3+} and P^{5+} substitute Si^{4+} in the tetrahedra the resulting tetrahedra are more or less negatively charged and are therefore not in relating to space equilibrium. The missing or added (compared with Si^{4+}) positive charge has to be compensated. Additional monovalent cations are able to compensate the missing positive charge; P^{5+} -tetrahedra exhibit a double binding. Therefore the tetrahedra are not symmetrical, and this substitution of silica by other oxides reduces the stability of the resulting tetrahedra. Also in these cases the tetrahedra form 3D networks through bridging oxygen. BO_4^{5-} (together with BO_3^{3-}), SiO_4^{4-} , GeO_4^{4-} and PO_4^{3-} -tetrahedra can form glasses on their own. Therefore, these oxides are called network formers. The more network former oxides a glass contains the more stable is the

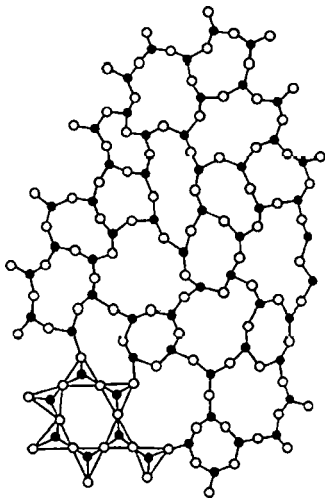


Fig. 1.8. Schematic 2D representation of a network of silica tetrahedra in a pure silica or quartz glass. A fourth bridging oxygen would be located directly below or above the silica [546,574]

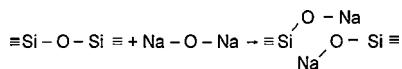


Fig. 1.9. Very simplified model of the effect of the network modifier Na_2O

glass; i.e. the higher its melting temperature, its electrical resistivity and its chemical stability.

If bridging oxygens exist, so must be nonbridging oxygens, but how do they form? Any other cations as the few mentioned above are, if present in a glass, surrounded by more than four oxygens, it could be six, eight or even twelve oxygens. These cations require, in order to obtain charge neutrality (screening), more surrounding oxygens in the glassy network as compared to network former cations. The bond between a cation and oxygen becomes more heteropolar, if the distance between the cation and oxygen increases. This fact is easily explained if monovalent alkaline ions are present in a glass. These ions interrupt the oxygen bridge $\text{Si}-\text{O}-\text{Si}$, which leads if added Na_2O to the formation of two nonbridging oxygens (Fig. 1.9). In order to maintain charge neutrality of the glass each nonbridging oxygen formed must be linked to a Si^{4+} -ion and an additional cation in its surrounding.

Oxides which decrease the connectivity of the glassy network are called network modifier. The higher the amount of network modifiers in a glass formation, the higher the concentration of nonbridging oxygens. The formation of nonbridging oxygens causes the disruption of the direct connection between the tetrahedra, which results in the drastic reduction of the melting

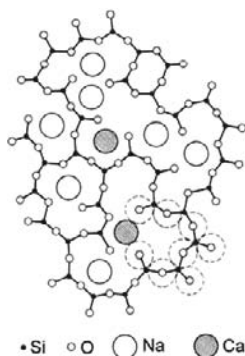


Fig. 1.10. A 2D representation of the structure of a soda lime silicate glass. A fourth bridging oxygen would be located directly below or above the silica [449]

temperature, melt viscosity, chemical stability, electrical resistivity but causes an increase of the thermal expansion coefficient.

Alkaline and alkaline earth oxides are effective network modifiers. The cations Na^+ and Ca^{2+} are usually associated to six or even eight oxygens to achieve charge neutrality. Therefore, they are positioned inside the interstices formed by the network former tetrahedra near the disrupted oxygen bridges (Fig. 1.10).

The free unoccupied volume in the interstices formed by the connected network former oxide tetrahedra determines the basic volume and, therefore, the density of the glass. Any network modifiers that will occupy the empty interstices will lead to an increase of the density of the glasses. The density increase depends of course on the atomic mass and the concentration of the modifier cations within the glass. However, it is not unlimited. The limit depends on the size of the interstices as well as the radius of the network modifier cations. If the network modifier cations are large it will cause the original network to expand, i.e. the volume increases.

If these simplified principles of the ionic arrangement in glasses are understood, also people who do not possess any prior knowledge in glass materials will be able to follow the interrelation between the materials composition and properties of glasses, which is of great importance in connection to geometrical microstructuring of glasses.

1.1.4 Glasses as Supercooled Solidified Melts

Glass melts are liquids. Liquids are characterised by the absence of any long-range order. In liquids consisting of ions the principle of electroneutrality dictates that charge compensation has to take place with the consequence that polyhedra form. The stability of the polyhedra depends on the criteria described in Sect. 1.1.3. Silica tetrahedra are the most stable polyhedra in the melt. The geometrically bulky configuration limits their mobility. In contrast

to bulky tetrahedra, heteropolar bonded alkaline and alkaline earth cations have a relatively high mobility in the melt. These cations often change their position in the different tetrahedron rings. As a consequence, the viscosity of glass melts therefore not only depends on the temperature but, at a given temperature, also depends on the relative concentration of network formers to modifiers and their exact composition. The dynamic viscosity of a glass melt is very high. Commonly processed glass melts have a dynamic viscosity of about 1–10 Pa s at the practical melting temperature. The geometrical shape of the silica tetrahedra causes the high melt viscosity of glasses and makes it impossible for the silica tetrahedra to assume by diffusion or by flowing a minimum energy equilibrium position, i.e. an imaginary lattice place of hypothetical crystals.

During the cooling process the viscosity of the glass melt increases continuously and so the possibility of tetrahedra or single ions to find hypothetical lattice places becomes even less likely. Crystallisation is completely made impossible if the glass melt solidifies. The result is a supercooled solidified melt, which means an amorphous glass. The estimated viscosity of a glass at room temperature is about 10^{18} Pa s. At low temperatures the brittle-elastic behaviour of glasses prevails. The complete dependence of the viscosity on temperature for a given glass is shown in Fig. 1.11. This curve is generally observed for glasses, but for a given glass composition the absolute position of the temperature axis of the viscosity–temperature graph strongly depends on the concentration ratio of network former to network modifier oxides. The more network former oxides, especially SiO_2 , the glass contains the more this curve is shifted to higher temperatures. The slope of the curve depends on the amount and the type of network modifiers present. The more steep the

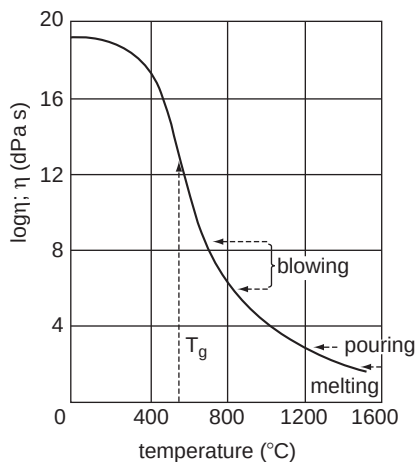


Fig. 1.11. Viscosity as function of temperature for a real soda lime silicate glass with the following composition (mass%): 71.7 SiO_2 ; 0.1 TiO_2 ; 1.2 Al_2O_3 ; 0.2 Fe_2O_3 ; 6.8 CaO ; 4.2 MgO ; 15.0 Na_2O ; 0.4 K_2O and 0.4 SO_3 [449]

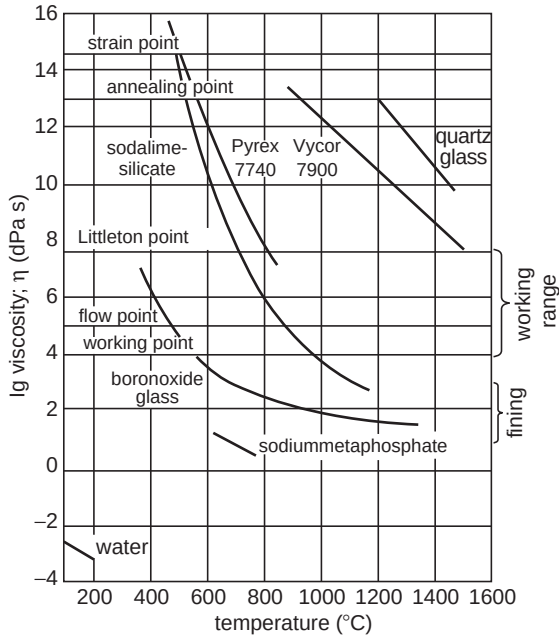


Fig. 1.12. Comparison of viscosity as function of temperature for various traditional glasses of interest to microstructuring [333]

slope of the viscosity–temperature curve, the more CaO the glass contains. An increasing Na_2O causes the curve to flatten. Of course the full explanation of the viscosity behaviour of glass melts is much more complex [420,422,535], but for the first interpretation of viscosity–temperature curves these simple rules might suffice. Figure 1.12 demonstrates the effect of the chemical composition of various glasses on viscosity–temperature curves. All types of glasses, such as alkaline alkaline earth silicate glasses, alkaline-alumino-silicate glasses, borosilicate glasses and pure silica glass are of equal interest for microtechnique applications.

Tailoring the viscosity–temperature behaviour of glasses is of special interest for all technical processes starting with melting, forming, cooling to the preparation of half products and even for geometrical microstructuring. Glass melts are usually processed at viscosities $\eta \approx 10^1$ Pa s. It depends on the necessary temperature of the melt if this processing step is technically challenging and expensive or not. Fining (see Sect. 3.3.1) and homogenisation (see Sect. 3.3.2) of the glass takes place in the melt. Both process steps are responsible for the materials microstructure. Geometrical microstructures in the glass can never be better than the materials microstructure.

Forming follows melt processing. Glasses can be formed by pouring. The melt viscosity during this process should be in the order of $\eta \approx 10^2$ Pa s. Other forming processes such as pressing, rolling, drawing and blowing require melt

viscosities in the range of $10^3 \text{ Pa s} < \eta < 10^{6.6} \text{ Pa s}$ (Fig. 1.11). The temperature belonging to a viscosity of 10^3 Pa s corresponds to the working point. Further hot-forming of glass half products by pressing, drawing etc. often takes place at a viscosity of $\eta \approx 10^5 \text{ Pa s}$, but sometimes also at viscosities higher than $\eta \approx 10^{6.6} \text{ Pa s}$.

Cooling of the glass product follows the forming process. At viscosities lower than $\eta \approx 10^{12} \text{ Pa s}$, i.e. at relatively high temperatures, the glass can still undergo viscous flow. This fact prevents that temperature gradients could cause stresses. They will be immediately dissipated due to viscous flowing. The dissipation rate depends on the temperature. Formed glass products can be cooled down more rapidly at higher temperatures, but have to be cooled slower at lower temperatures. Problems begin to arise at viscosities $\eta > 10^{12} \text{ Pa s}$. Because of the reduced mobility of the silica tetrahedra, the glass melts ability for viscous flow decreases rapidly. The brittle-elastic behaviour increases accordingly. The transformation from a viscous glass melt to brittle-elastic behaviour will take place in the viscosity range $10^{12} \text{ Pa s} < \eta < 10^{13.5} \text{ Pa s}$. In this viscosity region the glass behaves as a visco-elastic solid. Both mechanisms overlap. The viscous behaviour is described by Newton's law (1.2), whereas the elastic behaviour by Hooke's law (1.3).

$$\tau = \eta(T) D \quad (1.2)$$

$$\sigma = E(T) \varepsilon \quad (1.3)$$

τ = shear stress

$\eta(T)$ = coefficient of dynamic viscosity

T = temperature

D = linear shear rate

σ = normal stress

$E(T)$ = elastic modulus

ε = strain

The visco-elastic behaviour of glasses can be described by Maxwell's law (1.4) [383]:

$$\dot{\gamma} = \frac{\tau}{\eta(T)} + \frac{\dot{\tau}}{G(T)} \quad (1.4)$$

$\dot{\gamma}$ = shear rate of an angle γ

G = shear modulus

From (1.4) follows that the dominating deformation mechanism depends on $\eta(T)$ and $G(T)$. It is also clear that a glass at any temperature has always a viscous and elastic contribution to its deformation behaviour. From this follows:

- At viscosities exceeding $\eta = 10^{12} \text{ Pa s}$, the rate at which stresses in glass products dissipate due to viscous flow reduces. Therefore in order to avoid the formation of residual stresses the cooling rate has to be reduced. The

best option to produce stress-free glasses is to anneal the glass at temperatures in the transformation range $10^{12} \text{ Pa s} < \eta < 10^{13.5} \text{ Pa s}$. Viscous flowing becomes negligible if the glass melt is cooled below the strain point T_U at $\eta = 10^{13.5} \text{ Pa s}$. Therefore we repeat: Careful cooling in the transformation range is the best precondition to produce stress-free glass products.

- This transformation range has also direct consequences for glass microstructuring. During heating a glass starts to flow at the just called strain point. Microstructured glass components cannot be used at $T > T_U$. Geometrical structures in the micrometer range would deform.

Most publications concerning glasses, but especially prospects of glass producers, do not publish T_U but prefer the glass transition or transformation temperature, T_g . T_g characterises the transformation range in general and is defined as the temperature at which a glass has a viscosity of $\eta = 10^{12.3} \text{ Pa s}$.

At all temperatures $T_{\text{liq.}} > T > T_g$ the melt is a supercooled liquid. Its viscosity increases with decreasing temperatures. In the transformation range the melt becomes a supercooled, *solidified* glass with an amorphous structure.

1.1.5 Density of the Glass Network

Section 1.1.3 describes the arrangement of silica tetrahedra within a glass. Silica tetrahedra are linked at all four corners and form more or less deformed and disconnected rings of 3–12 tetrahedra, which have interstices of various sizes in the centre of the rings. Small network modifier cations, such as Li^+ and Mg^{2+} , are in principle able to occupy nearly all large and also small interstices in the network and thereby reduce the unoccupied (interstitial or free) volume. However, the larger the cation radius (see Table 1.1) the more difficult it becomes to fill all interstices. As a consequence larger ions tend to occupy only the interstices in large tetrahedron rings. The interstices in small rings could be left unoccupied if a glass contains only big network modifier cations. If a glass consists only of small SiO_4^{4-} tetrahedron rings and large network modifier cations, the glass network would have to expand during melting to accommodate the cations. It follows that the measured density of glasses strongly depends on the amount of network modifiers, their atomic weight and their ionic radius.

Glasses are more commonly characterised by measuring the specific volume V rather than the density $\rho (\text{g cm}^{-3})$. The molar volume V_M , which is defined as the volume occupied by one mole of a glass, is obtained by dividing the materials molecular weight by its density (1.6):

$$V_M = \frac{M}{\rho} [\text{cm}^3 \text{ mol}^{-1}] \quad (1.5)$$

$$M = \text{molecular weight } [\text{g mol}^{-1}]. \quad (1.6)$$

V_M includes the entire free volume of a glass, including the volume of the interstices. Therefore, it is larger than the sum of the volume occupied by

all different cations and the oxygen. Assuming that ions are hard spheres, Hecht-Mijic [201] has defined an effective molar volume $V_{M,\text{eff}}$ which excludes the free volume of the interstices. $V_{M,\text{eff}}$ is very different from V_M . It depends on the actual composition of the glass and the production conditions and has often a surprisingly little total of $\approx 0.5 V_M$. The free or interstitial volume of glasses as well as the interrupts in the silica tetrahedron rings provides an explanation for the remaining deformation of glasses under the tip of an indenter during microhardness tests, for the elastic after-effects of reversible loaded glass bars or springs and for the shrinkage of glass devices during reheating to the transformation range.

Ions have certain mobility in glasses and can move under stress or diffuse at elevated temperature into unoccupied interstices in the glass structure. The ions move only by a few nanometres, sometimes micrometers, which is for most common glass applications not of importance. However, for glass applications in micro devices the ion mobility has to be taken into account.

The density of a glass is not only affected by the chemical composition of the glass and arrangement of the network former (rings!), but also depends on the cooling rate after the products forming. During the cooling of a melt (see Sect. 1.1.4) not only the viscosity increases and the melt transforms from a Newtonian liquid to a brittle-elastic solid, but also its ionic structure changes which is characteristic for any precise temperature of the melt. The structure of the liquid rearranges as the temperature decreases, i.e. the silica tetrahedra become more ordered (but not long-range ordered). The rearrangement of the liquid structure depends on the cooling rate, i.e. how much time is available for this ordering process especially in the Newtonian and the transformation ranges. As a consequence different dense glasses are obtained when cooling a melt faster or slower, see Fig. 1.13. The cooling rate also determines remaining internal (thermal) stresses, which affects the microworkability of glasses in general and the reproducibility of tolerances in micrometer range in particular.

Detailed information about the density of glass melts are given by Pye et al. [414].

1.1.6 Homogeneity of Glasses

The homogeneity of glasses is defined by industrial standards, see also Hoffmann [232]. It is very difficult from the physical point of view to provide a correct definition for a homogeneous glass. What is considered as a homogeneous glass is often difficult to judge and varies with its end-use application. Historically the homogeneity of a glass was defined simply visually. A homogeneous glass is free of any heterogeneities, such as bubbles (blisters, boils or seeds), stones and crystals, striae or cords, which when they are clearly visible are cause for the rejection of the glass. Furthermore colour differences should be avoided if they are visible. On the other hand, however, they might be desired, for instance in antique glass sheets. The size and frequency of

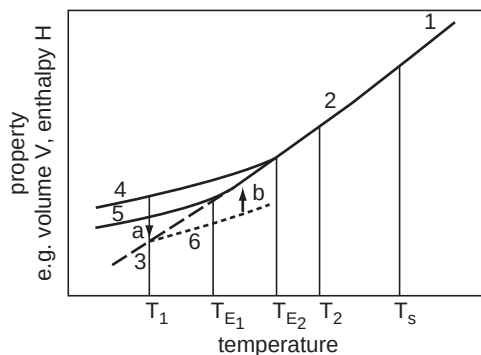


Fig. 1.13. Effect of temperature on physical properties, such as specific volume V or enthalpy H of a glass forming melt [439].

T_s , melting temperature;

T_{E2} , freezing temperature if melt is cooled rapidly;

T_{E1} , freezing temperature if melt is cooled slowly;

1, melt;

2, supercooled melt;

3, equilibrium state of a supercooled melt if cooled extremely slow from T_2 to T_1 ;

4, glassy state if cooled rapidly;

5, glassy state if cooled slowly;

6, property-temperature-curve if glass is heated fast from T_1 to T_2 ;

(a) slow response of glass properties in the direction of the equilibrium

(b) rapid response of glass properties if heated fast

heterogeneities in a commercial glass are classified in several industrial standards. Generally, the size of inhomogeneities has to be below $100\text{ }\mu\text{m}$. Since technical applications become more and more important, the homogeneity of the chemical composition of a glass must be characterised. Chemical inhomogeneities affect for instance the refractive index of glass sheets, the local, electrical resistivity and the thermal expansion coefficient. Bubbles and cords of around $50\text{ }\mu\text{m}$ in size render optical lenses and prisms useless. In optical waveguides on silica glass basis, inhomogeneities in the order of a few micrometers are considered mistakes. The resulting attenuation of light would rise by orders of magnitudes. The detection of such microsized mistakes is very challenging and demands new testing methods.

Glasses to be used for microtechnique applications should have exactly the same degree of homogeneity as glasses used for precision optics, waveguides or for mask blanks. If the required reproducibility of a channel width in a glass has to be $1\text{ }\mu\text{m}$, the allowed inhomogeneity must be smaller than 100 nm . Such stringent requirements demand a new philosophy in glass production, quality control and the handling of glass half products but also novel testing equipment. The experience in the production and handling of microelectronic devices in grey or clean rooms is very valuable.

So far the homogeneity of glasses was only described in terms of a more or less well-understood technical process. But we have to remember (see Sect. 1.1.4) that glass is a supercooled, solidified melt, i.e. a glass is not in thermal equilibrium. The inner energy of a glass is higher as for a chemically equally composed but crystalline solid. However, because of the very high viscosity of a glass at room temperature (almost 10^{18} Pa s) and the extremely low diffusion coefficients of its components, a glass will never crystallise at room temperature. Therefore, a glass can be considered as thermodynamically quastable and should be homogeneous at the ionic level. This assumption of glasses changed with the publication of the first results obtained using transmission electron microscopy (TEM) almost 50 years ago. Vogel and Gerth [541] and Skatulla et al. [471] found that many untreated glasses but also most thermally treated glasses contained nanometer-sized droplets or sponge-like structures. Based on this finding, Vogel and Gerth [542] developed the so-called microphase hypothesis which is nowadays commonly used to explain most effects concerning the microstructure of glasses from a materials point of view. The reader is referred to a more detailed review by Vogel [538].

Figures 1.14–1.16 illustrate such microphase separations in a surrounding glass matrix (large and small droplets and a penetration structure).

All phases shown in the micrographs Figs. 1.14–1.16 are amorphous. Each phase has a different chemical composition and is enriched of one or more chemical components compared to the surrounding phase. Such a phase separation causes the inner energy to decrease and enhances the degree of ordering inside the glass and therefore the thermodynamic stability of the system. The structure of the droplets varies between quite disordered, i.e. only short-range ordering, and cautiously beginning of the long-range ordering, which is fluctuating. The chemical composition of the glass melt and the temperature determine the final composition of the droplets as well as the matrix phase. Figure 1.17 shows a schematic phase diagram for a glass consisting of the components A and B.

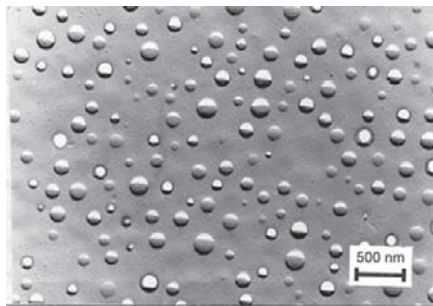


Fig. 1.14. TEM-micrograph of a phase-separated lithium borosilicate glass of the following composition (mol %): 6.45 Li_2O , 21.55 B_2O_3 , 72.00 SiO_2 with a droplet morphology [503]

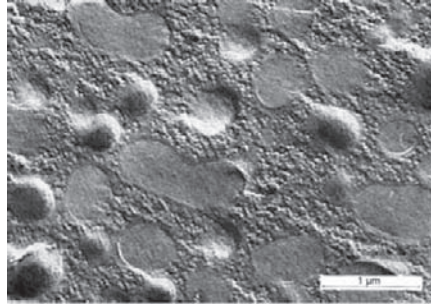


Fig. 1.15. Transmission electron micrograph of a sodium borosilicate glass [470]. Secondary small droplets of a SiO_2 -rich phase are embedded in a sodium borate rich matrix phase. The large droplets are also SiO_2 -rich

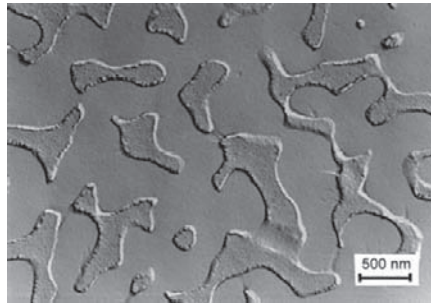


Fig. 1.16. TEM-micrograph of a phase-separated tempered lithium borosilicate glass with penetration structure [503]

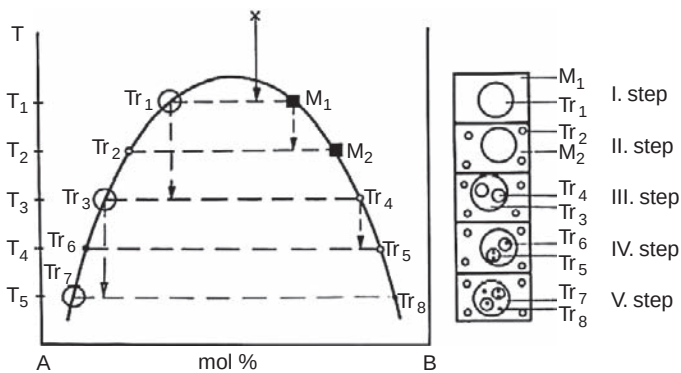


Fig. 1.17. Schematic phase diagram showing the step-like phase separation resulting in more than two phases [537]

Three final possibilities for morphologies exist for such a simple system at room temperature, which depend on the cooling rate from the melt:

- If the melt is cooling very rapidly, so that phase separation cannot occur (no time for diffusion!), the solidified glass will have an almost homogeneous microstructure.
- If melt cools down under natural conditions, so that the diffusion coefficients of the components decrease steadily with decreasing temperature, the solidified glass will have a microstructure very similarly to the one shown in Fig. 1.15 or in the small picture at the bottom right in Fig. 1.17.
- If the melt is cooled very slowly, especially at temperatures $T > T_g$, so that the diffusion coefficients are large enough to allow a continuous compositional change of both phases, then the solidified glass will consist of very large droplets in a homogeneous glass matrix.

In conclusion whether or not a solidified glass is homogeneous or phase-separated depends on the chemical composition of the melt and on the cooling rate. The impact of phase-separated regions on the optical transmission of the final glass is rather small. It becomes only significant if the size of the phase-separated regions exceeds 100 nm. This is also the reason why optical transmission measurements in the visible wavelength range do not provide any information regarding the degree of phase separation. Often the diameter of such droplets ranges from 5–15 nm. Only TEM enables the inspection of such phase-separated microstructures. Moreover also droplets between 15 and 100 nm exist. All these phase-separated domains are able to affect the accuracy of geometric microstructures, such as the width of channels and their wall roughness, in glass.

It may be necessary that the geometric microstructuring of a glass component is performed at temperature above transformation temperature of the glass, or the glass is exposed to elevated temperatures. Perhaps the residence time is long, which could cause the glass to undergo phase separation. This process will affect the properties and sometimes the dimensions of glass components. It should be noted that in general a phase-separated glass has slightly different properties than the chemical equally composed but not phase-separated glass. The importance of phase separation for geometrically microstructured glass components depends on its intended use.

Controlled inducing of the phase separation of a glass is useful for the determined partial crystallisation of glass components and will be described in Sect. 2.3.

1.1.7 Ions, Atoms and Molecules in Interstices of a Glass Network

The network former cations, such as Si^{4+} and B^{3+} that bond to oxygen with a fractional ionic character, form tetrahedra, whereas network modifier cations with very low electronegativities and therefore forming highly ionic

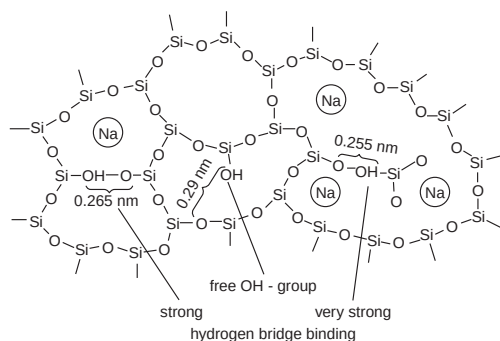


Fig. 1.18. Dissolved water in glass [449]

bonds assume positions inside the interstices formed by the tetrahedra. The bonds between nonbridging oxygens and modifier cations is heteropolar or ionic. However, not only network modifier cations occupy the interstices. Also F^- , H^+ , water (molecular or dissociated $H_2O \rightleftharpoons H^+ + OH^-$), noble gases (He, Ar) or other gasses (O_2 , N_2) and even metal atoms (precious metals or Cu) might also occupy the interstices. Chemical (ionic) or physical (atomic or molecular, especially for gases and precious metals) solutions can be distinguished. In case of water, which is polar or even dissociated, the distinction is not that clear because van der Waals interaction as well as hydrogen bonds occur (see Fig. 1.18). These dissolved gases and water are very different from gaseous inclusions that can be found in bubbles encapsulated in solidified glasses.

Whatever the state of the dissolved gases or precious metals in the glassy network, they greatly affect the glass properties. Dissolved water, whether as molecules or OH^- , has a larger effect on glass properties than any other component. For instance, dissolved water dramatically influences the viscosity behaviour of glass melts (see Fig. 1.19), the infrared transmission of glasses (see Fig. 1.20) or the colour of some glasses. The band due to water adsorption at about $\lambda = 2.8\mu m$ is of major importance for glass applications in the optoelectronic devices and light guidance in near infrared range (NIR).

It may be surprising that precious metals are mentioned here. They are stable atoms. However, they can be incorporated into glass structures. Ions of precious metals, such as Au or Ag, can even act as network modifiers. Only a very small amount of energy is required to reduce the ionic to the atomic state. This reduction occurs if the glass is for instance exposed to UV light and contains electron donors. These glass compositions (see Sect. 1.2.4. and Chap. 6) are photosensitive. Some of these glasses are also known as photoform glasses [498].

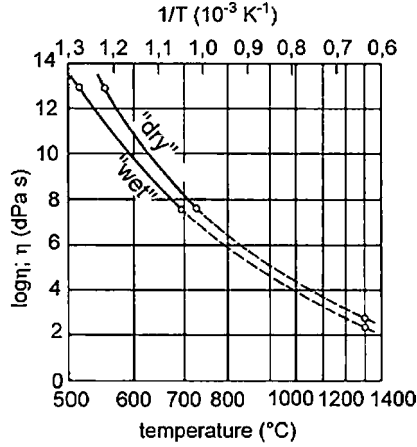


Fig. 1.19. Viscosity as function of temperature of a dry and water containing soda lime silicate glass [448]; dry: melted in N_2 -enriched atmosphere; wet: melted in H_2O vapour enriched atmosphere

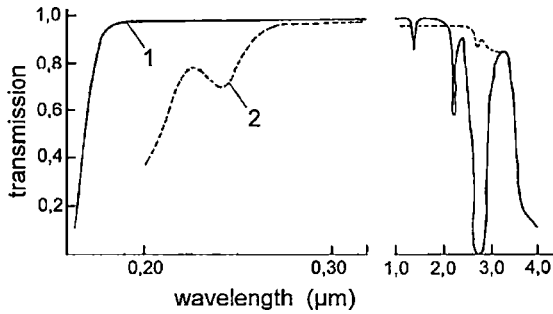


Fig. 1.20. Transmission spectra of two 1-cm thick silica (quartz) glass sheets [142]

- (1) Spectrosil, melted using detonating gas (a hydrogen/oxygen mixture)
- (2) Vitrosil, melted in a plasma flame

1.2 Glass Properties of Importance for Microstructured Components

1.2.1 Pure Silica (Quartz) Glass

As the name states silica glasses contain only SiO_2 and are made up solely by silica tetrahedra. A 2D representation of a silica glass is shown in Fig. 1.18. The silica tetrahedra are linked to other tetrahedra at all four corners by bridging oxygens which form a very strong continuous 3D network. As a consequence silica glasses have extremely high melting and forming temperatures. Such

Table 1.2. Juxtaposition of properties of various borosilicate and quartz glasses

Property	Dimension	Borosilicate glasses	Quartz glasses
Density	g cm^{-3}	2.25 ... 2.45	2.0 ... 2.2
Tensile strength	MPa	80 ... 150	70 ... 120
Compression strength	MPa	600 ... 1,000	1,600 ... 2,000
E-modulus	GPa	65 ... 85	62 ... 75
Thermal expansion coefficient	10^{-6} K^{-1}	3.0 ... 6.0	0.53 ($T = 0 \dots 200^\circ\text{C}$) 0.57 ($T = 0 \dots 1,000^\circ\text{C}$)
Thermal conductivity	$\text{kJ m}^{-1} \text{ h}^{-1} \text{ K}^{-1}$	2.0 ... 3.8	4.8
Electrical resistivity	$\Omega \text{ cm}$	$10^{14} \dots 10^{18}$	$10^{18} \dots 10^{19}$
Dielectric constant	—	4.5 ... 8	3.7 ... 3.9
$\tan \delta$	10^{-4}	20 ... 40	10^3 Hz : 5 10^6 Hz : 1 10^9 Hz : 1 10^{10} Hz : 4
$T_{\kappa 100}$	$^\circ\text{C}$	125 ... 360	≈ 600
Transparent range	nm	350 ... 750	from UV to IR

glasses have an excellent chemical stability and electrical resistivity and a very high hardness. Furthermore, silica glasses have a low thermal expansion coefficient and dielectric losses. However, such glasses are quite hard to work. Table 1.2 juxtaposes some important properties of various quartz glasses with the properties of some borosilicate glasses of different compositions.

Considering the electrical, chemical and optical requirements for microstructured glasses, quartz glass should be the most widely used glass for such applications. However, that is not the case. Because of its lack of workability quartz glasses are more commonly used as tools in the production of microcomponents rather than the microstructured device itself.

Every UV-lithography equipment using any kind of laser-radiation ($\lambda = 308, 248$ and 193 nm) utilises quartz glass optics and blanks for the chromium masks. A high optical transmission is especially important for the ArF-excimer-laser with a wavelength of $\lambda = 193 \text{ nm}$. Quartz glass reaches its actual transmission limit and is in direct competition with fluorspar (CaF_2) single crystals. Figure 1.21 shows the UV transmission spectra of different quartz glasses used in lithographic tools. Current research concentrates on the development of quartz glasses transparent for the radiation of the F_2 -excimer laser ($\lambda = 157 \text{ nm}$).

Besides applications as tools for microstructuring silicon and other semiconductors, quartz glass is important in microoptics and for light waveguides. For the latter application, the transmission in the near IR-range ($\lambda = 1.3$ or $1.55 \mu\text{m}$) is of greatest importance, see Figs. 1.20 and 1.21. In order to

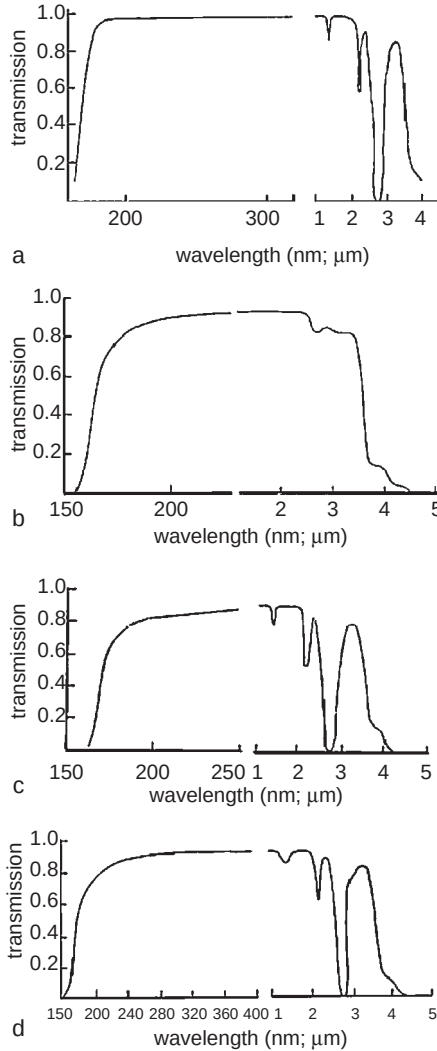


Fig. 1.21. UV- and IR-transmission spectra of the following quartz glasses [142]: (a) Spectrosil (Thermal Syndicate Ltd., UK), (b) Tetrasil (Quartz et Silice, France), (c) Suprasil (Heraeus Quarzschmelze, Germany) and (d) Code 7940 (UV grade) (Corning Glassworks, USA)

guarantee the highest optical transparency all impurities have to be excluded. The accepted maximum amount of impurities depends on the intended application, but is usually not higher than a few ppm. Figure 1.22 illustrates the extent to which Na_2O impurities affect the electrical resistivity of a quartz glass.

The high chemical stability of quartz glass is advantages for many applications. In particular, quartz glasses are extremely resistant against many

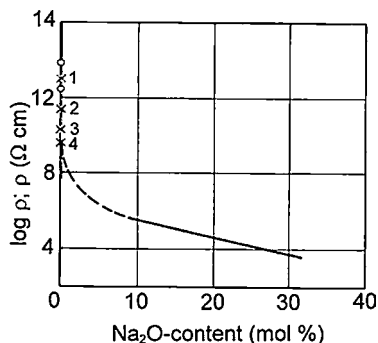


Fig. 1.22. Specific electric resistivity at 300°C of quartz glass as function of Na₂O concentration [449]. The origin of x -axis corresponds to a pure quartz glass (100% SiO₂ and 0% Na₂O). The numbers correspond to the following amounts of Na₂O: 1 = 0.04 ppm, 2 = 0.6 ppm, 3 = 4.0 ppm and 4 = 20 ppm

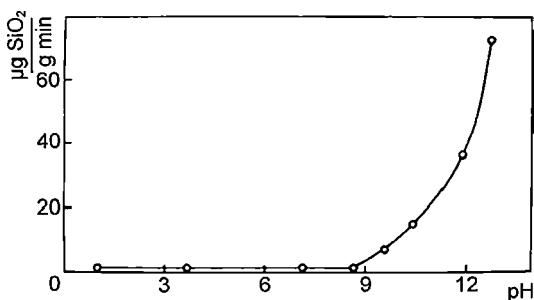


Fig. 1.23. Effect of pH on the rate of silica extraction from vitreous silica powder at 80°C [132]

different types of acids. The reason for the remarkable chemical stability is the absence of any network modifier cations. Any other glass that contains highly mobile network modifier cations, especially alkaline ions, will react with diluted acids via an ion exchange mechanism with the hydronium ions (H_3O^+). The aqueous liquid could attack the glass network directly until the concentration ratio of the components of the glass equals that in the solution. This process is known as congruent dissolution. However, layers of the dissolution product can form on the surface of the glass which will affect the subsequent dissolution rate. For quartz glasses this ion-exchange reaction cannot take place because of the absence of any network modifier. Only the presence of an alkaline lye can trigger off the reactivity of quartz glass. OH^- has almost the same ionic radius as O^{2-} so the hydroxyl ion of the dissociated alkaline lye can replace O^{2-} , which causes the conversion of a bridging oxygen into a nonbridging OH^- which subsequently leads to the destruction of the silica network. Figure 1.23 demonstrates the effect of pH on the loss of SiO₂ during the exposure to dilute aqueous solutions.

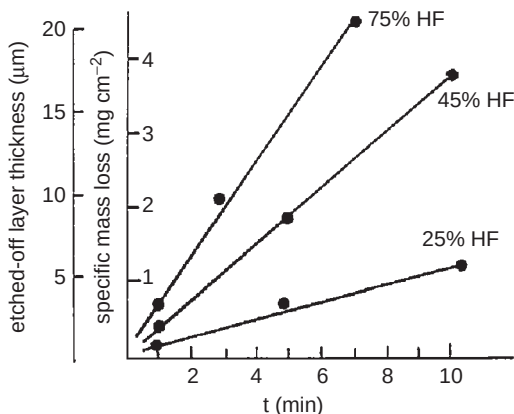


Fig. 1.24. Etched layer thickness and specific mass loss of a quartz glass sheet exposed for various times to different concentrations of hydrofluoric acid

Besides its excellent chemical stability quartz glass is very strongly attacked by hydrofluoric acid. HF in aqueous solution dissociates into H_3O^+ and F^- . It is not the hydronium ion which causes any problems, but the F^- . The ionic radius of O^{2-} is 0.132 nm, while that of F^- is 0.133 nm. From the geometrical point of view F^- can easily substitute O^{2-} . However, F^- is monovalent. The substitution of O^{2-} by F^- breaks the oxygen bridges of the silica network and eventually the SiO_4^{4-} -tetrahedron is fully converted to SiF_4 with no links to glass network. Therefore, the glass corrodes in diluted hydrofluoric acid. Quartz glasses indented for applications as lenses or mask blanks can be easily polished in diluted HF. Figure 1.24 shows the thickness of the etched layer of a quartz glass as function of the HF concentration and time.

Quartz glass is often used because of its superb temperature stability for applications in which geometrical dimensions are of outmost importance. Thermal expansion coefficient of $\alpha \approx 0.5 \times 10^{-6} \text{ K}^{-1}$ is very small in comparison to other glasses (Fig. 1.25) and in particular to that of metals and polymers.

The thermal expansion coefficient α of silica glasses depends on the following parameters:

- Content of impurities in the glass
- Cooling rate used during the solidification of the glass
- Temperature range for determining of α
- Measuring principle and equipment used to determine α

Figure 1.26 shows the thermal expansion coefficient α as function of temperature. α is slightly positive, zero or at very deep temperatures even negative. Furthermore, each testing method gives different results.

For some applications, especially if dimensional stability is a must, a zero expansion is desired. However, it will cause problems if quartz glass is joined to

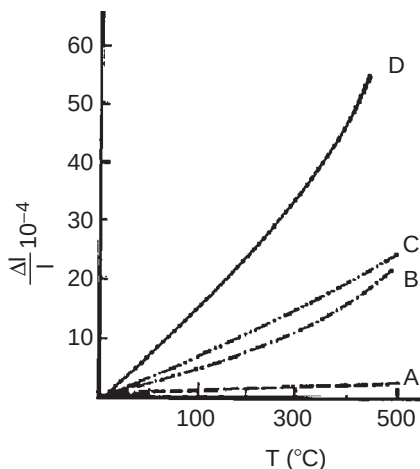


Fig. 1.25. Thermal expansion of a quartz glass (A) in comparison to a Pyrex-type borosilicate glass (B), a borosilicate tungsten-sealing glass (C) and a common soda lime silicate glass (D)

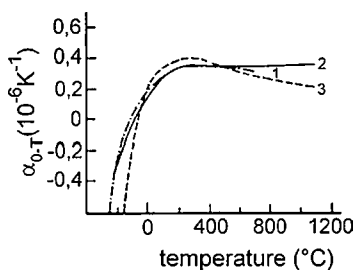


Fig. 1.26. Thermal expansion coefficient α as function of temperature, measured using different methods in three laboratories: State Optical Institute (GOI) Leningrad (1), Sosmann [478] (2) and Otto and Thomas (3) [4]

materials with a high thermal expansion coefficient. Cooling after hot joining or high-temperature applications will result in considerable thermal stresses. Corning Glass Works recently developed a TiO_2 -doped silica glass (called ULE (ultralow expansion)) that has almost a zero thermal expansion coefficient at room temperature. Gulati [186] reports the mechanical properties of telescope mirror blanks made from ULE after a special surface treatment.

1.2.2 Alkali Alkaline Earth Silicate Glasses

Alkali alkaline earth silicate (or soda lime silicate) glasses are the most commonly used and oldest known glasses. They contain mainly SiO_2 and a small amount of Al_2O_3 as network former oxides. The network modifiers are the alkali oxides Na_2O and K_2O and the alkaline earth oxides CaO and MgO .

Some undesired impurities in commercial glasses are Fe_2O_3 , Mn_2O_3 and other polyvalent $3d$ -elements. These impurities also act as network modifiers and affect the colour of the glasses. The large content of network modifier oxides of almost 25% in most relevant glasses means that nearly 1/4 of the total amount of oxygen is nonbridging. These nonbridging oxygens soften the glass structure and result in a huge reduction of the glass transformation temperature and the temperature of the melt. Furthermore, these glasses have much reduced chemical stability, hardness and electrical resistivity as compared to quartz glasses. The thermal expansion coefficient increases. At given temperatures, reduced viscosity comparatively also means that the glass is much easier to work. The effect of the network modifier oxides on the glass properties depends on their amount, on their ion radius and valence, their coordination number CN in the glass (see Sect. 1.1.) as well as their electrical field strength (see (1.1)). Moreover, mixtures of various alkali oxides produce anomalies in the viscosity behaviour of such glass melts as well as the thermal expansion and electrical resistivity of solidified glasses, which is caused by the interaction between various alkali oxides. This effect is called the mixed-alkali effect [152]. Such a composition dependence of glass properties makes it easy to choose the right glass for an intended application. However it makes it necessary to use always the same glass of the same supplier to manufacture special microcomponents.

The viscosity behaviour as function of temperature of a soda lime silicate glass was already shown in Fig. 1.11. Soda lime silicate glass can be processed using machines in a temperature range from 1000°C to 700°C . However, these glasses can already be formed at temperatures as low as 650°C by a glass blower using a desk gas burner (a so-called lamp).

The actual viscosity–temperature behaviour of such glasses depends on its composition. Figure 1.27 shows the fact that the addition of divalent cations replacing silica in a sodium-silicate-glass drastically reduces the temperature required to achieve a viscosity of $\eta = 10^3 \text{ dPa s}$. The addition of B_2O_3 or more Na_2O also results in a reduction of the temperature to obtain a melt in this viscosity range. However, when adding Al_2O_3 having CN 4 for Al^{3+} it results in an increase of this temperature. Such information is important for the melting and forming of the glasses. However, the addition of these oxides affects only marginally the temperature to obtain a viscosity of $\eta = 10^{13} \text{ dPa s}$. At this viscosity the transformation from viscous fluid to a brittle-elastic solid takes place.

The complete glass transformation range can be determined by measuring the thermal expansion of a glass as function of temperature using a dilatometer. Figure 1.28 shows a characteristic curve. The curve can be divided in three obvious parts. In the parts at low and high temperatures the curve can be approximated by a straight line. The temperatures at which the thermal expansion curve deviates from linearity are called T_U , the strain-point at $\eta = 10^{14.5} \text{ dPa s}$, and T_O , the annealing-point at $\eta = 10^{13} \text{ dPa s}$. These characteristic temperatures form the boundaries of the curved glass transformation

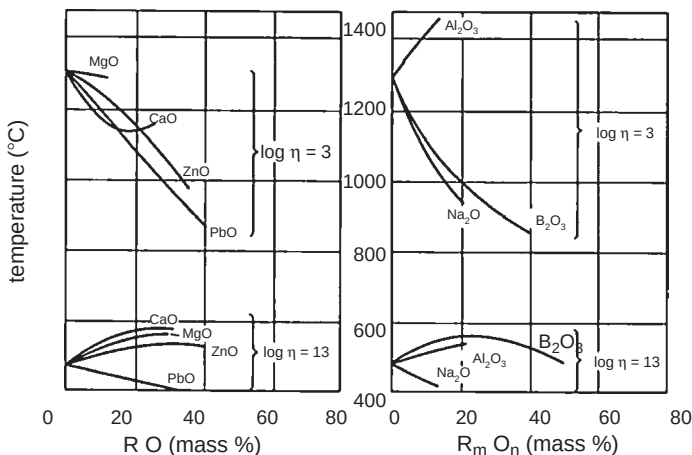


Fig. 1.27. Effect of the chemical composition of a glass with a composition of 18 mass% Na_2O and 82 mass% SiO_2 after replacing SiO_2 partially by x mass% of other oxides on the temperature required to achieve a viscosity of $\eta = 10^3$ or 10^{13} dPa s [163]

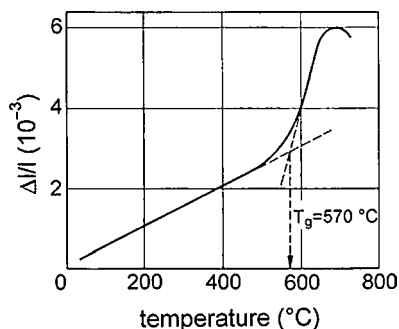


Fig. 1.28. A characteristic curve obtained according to DIN 52324 demonstrating the determination of the glass transition temperature T

range, whereas the glass transition temperature T_g is a fictive temperature (Fig. 1.28). The temperature at the maximum of the thermal expansion is called the dilatometric softening temperature T_d , which is an artefact of this measuring method. Knowledge about this transformation range is of great importance to obtain a stress-free glass product. The glass has to be cooled very slowly through this temperature range as already previously noted.

As a further consequence microstructured glass components cannot be used at T exceeding T_U . Micron-sized holes and channels, sharp edges or walls will deform by viscous flowing of the glass. Microstructured alkali alkaline earth silicate glasses can be safely used up to temperatures of about $350^\circ C$ (see also Fig. 1.27, it shows the temperatures of the annealing point

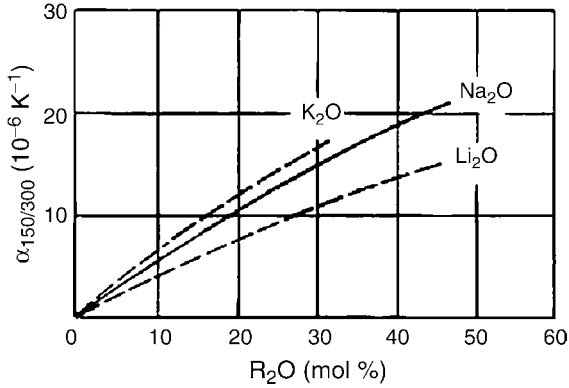


Fig. 1.29. Thermal expansion coefficient between 150 and 300°C for binary alkali silicate glass as function of glass composition. The zero-point of the x -axis corresponds to a pure SiO_2 glass [461]

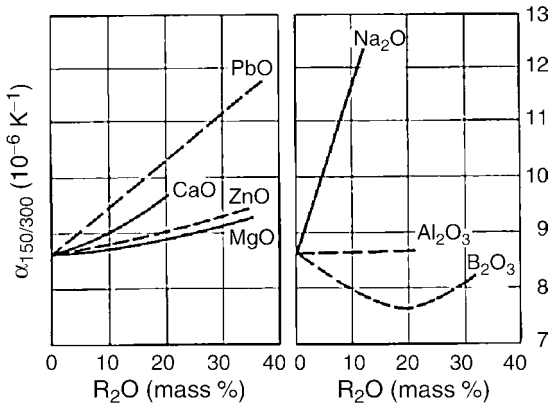


Fig. 1.30. Thermal expansion coefficient of a glass containing 18 mass% Na_2O and 82 mass% SiO_2 after replacing SiO_2 partially by x mass% of other oxides [163]

T_O at $\eta = 10^{13}$ dPa s, what is the upper boundary of the transformation range).

The exact chemical composition of alkali alkaline earth silicate glasses does not so much influence the maximum service temperature of these glasses. However, it will very much affect the thermal expansion behaviour of the final glass product. Figures 1.29 and 1.30 illustrate the effect of a changing chemical composition of the glass on the thermal expansion coefficient.

Replacing silica by alkali oxides causes the thermal expansion coefficient α of the resulting glass to increase. The addition of alkali oxides produces more nonbridging oxygens, which break the connectivity of the glass network, which soften the structure of glass. The addition of alkaline earth oxides leads

only to a small increase of α , whereas Al_2O_3 does not affect α . The effect of B_2O_3 on α depends on the amount added to the glass composition and will be discussed in Sect. 1.2.3.

Because each oxide contributes to the thermal expansion of a dense glass we can calculate α using a simple rule of mixtures (1.7) on the basis of tabulated coefficients [7, 564]. However, the tabulated α values are only valid in a narrow composition range.

$$\alpha = \sum_{i=1}^n \alpha_i m_i \quad (1.7)$$

α = thermal expansion coefficient of glass consisting of n components

α_i = thermal expansion coefficient of the i th component

m_i = amount of the i th component

n = number of components

The thermal expansion coefficient α of alkali alkaline earth silicate glasses varies from 7 to $10 \times 10^{-6} \text{ K}^{-1}$ depending on the actual chemical composition of the glass and is many times greater than for silica (quartz) glass.

Besides the chemical composition the size of the cooled glass devices also depends on the cooling rate in the transformation range (Fig. 1.31). Therefore the cooling rate plays also a part if a joining between an alkali alkaline earth silicate glass with another material exhibits inner stresses.

The specific electrical resistivity of alkali alkaline earth silicate glasses at room temperature is still high enough (ranging from 10^{10} to $10^{12} \Omega \text{ cm}$) for them to be electrical insulators. However, with increasing temperature the electrical resistivity decreases. A material is classified as insulator if the specific electrical resistivity exceeds $10^8 \Omega \text{ cm}$, which is only given for alkali alkaline earth silicate glasses if the temperature does not exceed about 150°C . This temperature is the maximum service temperature for alkali alkaline earth

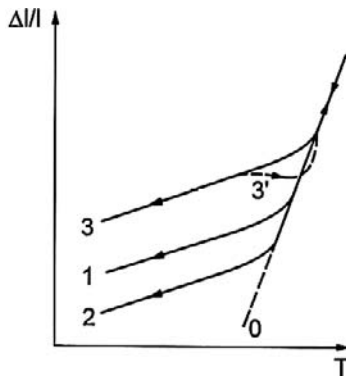


Fig. 1.31. Thermal contraction and expansion curves of glasses [449] (0) when in thermal equilibrium, or when cooled at a standard cooling rate (1), very slowly (2) or quenched (3) or when reheated after quenching (3')

silicate glasses if insulating properties are required. The electrical resistivity of these glasses is determined by the type and amount of network modifier oxides.

Because of their relatively good processability, their optical transmission properties and the sufficient chemical stability these glasses are frequently used to encapsulate microelectronic devices and for microfluidic systems. However, for these applications alkali alkaline earth silicate glasses are competing against aluminosilicate and borosilicate glasses (see Sect. 1.2.3.). Alkali alkaline earth silicate glasses are most commonly used as flat sheet glasses for windows and windscreens, bulb glass but also as container glass (hollow ware) for wine, beer and other bottles.

Unfortunately the addition of large amounts of alkali oxides to silica leads to a reduction of the chemical durability of the resulting glass. Although commercial alkali alkaline earth silicate glasses are used as bottles and other containers for liquids, these glasses are compared with silica glass rather susceptible to dissolution in water and chemical reactions with acids and alkaline lyes.

Water undergoes autodissociation, and if acids and alkaline lyes are dissolved in water they dissociate according to equations ((1.8), (1.9) and (1.10)):



The protons H^+ in hydronium ions are very mobile and can easily exchange so they diffuse very fast. Ion exchange takes place between the protons from the aqueous phase and network modifier cations, particular if these are monovalent. With progressing exposure time of the glass to aqueous solution the diffusion distance for the ions increases, which will slow down the reaction of protons with a glass. An equilibrium state is finally established after the formation of micrometer-sized surface layers of reaction products, which will additionally slow down subsequent dissolution. Parallel to the dissolution process water molecules migrate into the glass. Since the ion exchange or dissolution process is diffusion controlled the penetration depth of the protons increases only with the square root of exposure time. Figure 1.32 shows the concentration profile of sodium ions near the surface of a soda lime silicate glass. Migrating water molecules cause the slight deviation from the square root like distribution of Na^+ near the glass surface. Furthermore the Na^+ concentration at the surface does not quite approach zero.

The solution conditions strongly influence the rate of glass dissolution. Is the aqueous solution in contact with the soda lime silicate glass basic (i.e. high pH what means high OH^- concentration), bridging oxygens, i.e. the $\text{Si}-\text{O}$ bond, is directly attacked and substituted by OH^- , because of its very similar ion radius to the oxygen, which will lead to the formation of nonbridging oxygens. $\text{Si}(\text{OH})_4$ will form if all four oxygens in a SiO_4^{4-} -tetrahedron are

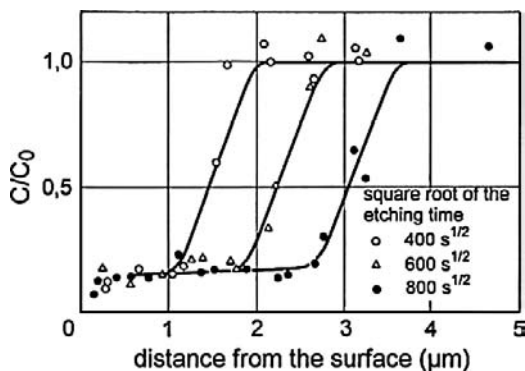


Fig. 1.32. Concentration profile of sodium ions expressed as relative values c/c_0 in a soda lime silicate glass of the following composition (mol%): 20 Na_2O –6 CaO –74 SiO_2 during exposure to 0.1N HCl at 60°C [451]

replaced by OH^- and eventually dissolve into the surrounding alkaline lye. This mechanism of the glass dissolution is a true chemical reaction which occurs at a constant rate and has no saturation limitations. Therefore, the attack on glass is stronger in alkaline lyes as compared to acids.

In pure water itself the corrosion of a glass occurs according to both mechanisms. The small dissociation product of water of 10^{-14} , and therefore, the small proton concentration means that glasses are relatively stable in water. Furthermore, the ion exchange between proton and network modifier cations and the simultaneous formation of a layer of reaction products slows down the dissolution rate. However, if the ratio between the glass area and the solution volume is very large, the release of alkali ions into the water will cause a relatively rapid rise of the solution pH which in turn will result in an increase in the dissolution rate of the glass.

All these remarks are very important for applying alkali alkaline earth silicate glasses in microdevices. Nevertheless, absolutely regarded in comparison with other materials, also these glasses are chemically resistant.

1.2.3 Silicate Glasses Containing Other Network Forming Oxides

The following section will describe glasses that contain, besides silica, also Al_2O_3 or/and B_2O_3 in significant amounts. The ion radius of Al^{3+} and B^{3+} , see Table 1.1, is very similar to that of Si^{4+} so that silicon can be easily substituted by Al^{3+} and B^{3+} . However, because of the different valence, i.e. aluminum–oxygen or boron–oxygen tetrahedra have an excess negative charge of -1 , the presence of monovalent cations in such glasses is required to guarantee charge neutrality. These associated cations have top presence in the immediate vicinity of these tetrahedra. Al^{3+} and B^{3+} can only exist in coordination number $CN\ 4$ in presence of a sufficient amount of alkali cations.

In this case they act as a network former and contribute to the network stability, which will positively affect many properties of importance for glass applications. However, simultaneously the addition of Al_2O_3 and B_2O_3 to the glass composition will result in a significant increase of the viscosity at a given temperature.

On the other hand, if the glass composition contains not enough quantities of alkali network modifier cations in order to compensate the missing valence, then B^{3+} and in particular Al^{3+} will also act as network modifier. In this case B^{3+} will be in *CN* 3 and Al^{3+} in *CN* 6. It is obvious that special glasses containing both oxides consist of an optimum composition. These glasses are of particular interest for microcomponent applications.

The effect of an increasing concentration of Al_2O_3 in a glass composition on the viscosity and the thermal expansion coefficient of the resulting solidified glass was already described above (see Figs. 1.27 and 1.30, respectively). The thermal expansion coefficient α , the density ρ and the refractive index n are not very much affected by the presence of Al_2O_3 in the glass. The reason for addition of Al_2O_3 in many glass compositions is its positive impact on the mechanical and chemical properties as well as the processability of the glass. Moreover, the presence of higher alumina concentration suppresses or eliminates phase separation, see Sect. 1.1.6., and devitrification, which is the growth of undesired crystals. All desired effects only exhibit if Al^{3+} is surrounded by four oxygens. That means, in many glasses 1–5 mass% Al_2O_3 are allowed. If the glass consists of more Al_2O_3 , then a part of Al^{3+} exhibits in *CN* 6 and changes the properties completely. Traditional apparatus glasses are typical aluminoborosilicate glass products with a good chemical stability (hydrolytic class, see industrial standard DIN 12 111, between 1 and 3 depending on the exact chemical composition of the glass) and an attractive heat strength.

Borosilicate glasses are generally of more interest for microcomponents. In these glasses the B_2O_3 content does not generally exceed 12.5 mass%. Any excess of B_2O_3 will negatively affect the final properties of the glass because it converts to B^{3+} in *CN* 3. The influence of B_2O_3 on the viscosity and the thermal expansion of the glass are shown in Figs. 1.27 and 1.30, respectively. Figure 1.30 clearly shows that an excess of B_2O_3 leads to a significant increase of the thermal expansion coefficient. The excess amount of B_2O_3 results in the formation of a softer glass network.

The addition of Al_2O_3 and/or B_2O_3 to the glass composition significantly improves the chemical stability and durability of the glass. Figure 1.33 shows the reduction of the mass loss of a sodium silicate glass after the addition of Al_2O_3 or B_2O_3 after exposure to a diluted acid, weak base soda or distilled water. Because of the excellent chemical stability, Al_2O_3 containing borosilicate glasses are traditionally used for the manufacture of chemical apparatuses. The chemical composition of some important commercial aluminoborosilicate glasses are shown in Table 1.3. All these glasses have an

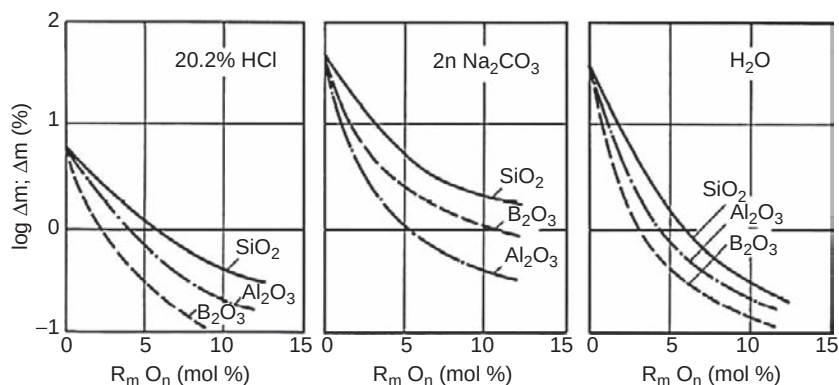


Fig. 1.33. Mass loss of a sodium silicate glass containing [mol %] 25 Na_2O – 75 SiO_2 after exposure to 20.2% HCl , 2N Na_2CO_3 or distilled water. The Na_2O in the glass composition is partially replaced by SiO_2 , Al_2O_3 or B_2O_3 [112]

Table 1.3. Composition [mass %], thermal expansion coefficient $\alpha(10^{-6} \text{ K}^{-1})$ and transformation temperature T_g ($^{\circ}\text{C}$) of some common commercial aluminoborosilicate glasses used for manufacturing laboratory apparatuses [449]

Glass	Duran 50	Pyrex 7740	Supremax	G 20
Producer	Schott Mainz	Corning	Schott Mainz	Schott Jena
SiO_2	79.7	80.3	57.5	75.5
B_2O_3	10.3	12.2	9.0	9.0
Al_2O_3	3.1	2.8	20.0	5.0
Na_2O	5.2	4.0	0.5	5.3
K_2O	–	0.4	–	1.2
CaO	0.8	0.3	5.0	0.4
MgO	0.9	–	8.0	–
BaO	–	–	–	3.6
–	–	–	–	–
$\alpha_{20/100}$	3.2	3.25	3.3	4.8
$\alpha_{20/300}$	3.2	3.3	3.7	4.9
T_g	568	565	715	569

acid and a hydrolytic class of 1 according to the industrial standards DIN 12 116 and DIN 12 111, respectively.

Borosilicate glasses are also (like silica glass) very susceptible to attack by hydrofluoric acid. The mechanism is the same as for quartz glass and is described in Sect. 1.2.1. HF is used for polishing, to etch holes, cavities and channels. HF treatments are preferred tools in microtechnology.

The optical properties of borosilicate glasses are important if the glasses are to be used to encapsulate silicon chips or for microfluidic systems, e.g. the customer wants to observe chemical reactions or in case of DNA the fluorescent radiation. For such applications the glass has to be transparent in the visible,

near IR and very near UV wavelength range of the electromagnetic spectrum. This can be achieved only for an impurity and technically defect-free borosilicate glass. The refractive index n of borosilicate glasses is similar to that of soda lime silicate sheet glasses. It ranges from 1.50 to 1.51 and depends on the Na_2O and B_2O_3 content of the glass.

Because of their great importance especially for borosilicate glasses it seems to be necessary to make some remarks concerning the mechanical properties of glass generally and of microcomponents.

Glasses are brittle-elastic solids at room temperature and show perfect Hookian behaviour (see (1.3) and (1.4)) when external stresses are applied. Their elastic or Young's modulus E is influenced by the dimensionality and connectivity of the glass structure. The higher the connectivity of the glass network the higher is the theoretic elastic modulus of the glass. It increases as materials structure changes from a chain to a layered to a fully interconnected 3D network structure. We have learned that network modifiers cause the formation of nonbridging oxygens and breaks in the tetrahedra rings. This of course influences the network stability, which allows easier displacement of atoms and ions and therefore causes a reduction of the theoretic elastic modulus.

Before a glass breaks the binding energy of the chemical bonds has to be overcome by the applied stress to create two new fracture surfaces. Therefore, the stress required to break a bond is proportional to the energy required to create these fracture surfaces, which is given by (1.11):

$$\sigma_m = \sqrt{\frac{E\gamma}{r_0}} \quad (1.11)$$

σ_m = theoretical stress required to create two fracture surfaces

E = elastic modulus

γ = tension of these new surfaces

r_0 = characteristic ion distance

The theoretic fracture stress corresponds to the theoretic strength. When calculating the theoretical strength of glasses using (1.11) and comparing it to measured values of the fracture strength we find discrepancies of sometimes of 2–3 orders of magnitude. What might be the reasons for such discrepancies?

From the chemical structure we would expect that alkali alkaline earth silicate and borosilicate glasses should possess lower fracture strength as compared to quartz glass. But in practice we find no such difference. Other factors, such as flaws and cracks, mostly starting from the surface of a glass, and other defects such as small stones, crystals and cords influence the real strength of glass products more than the chemical structure of the glass. The fracture strength is affected also by applied surface treatments, the surrounding environment and the method to determine the strength. The just reported defects create stress concentrations especially at the ends of cracks or flaws. Figure 1.34 shows a schematic of a crack under stress.

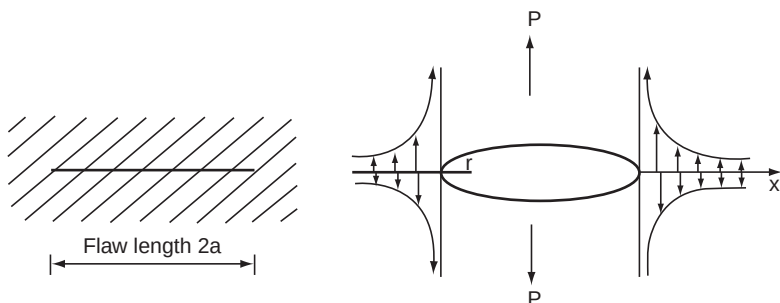


Fig. 1.34. Stress concentrations arising at the ends of flaws. (*Left*) the unstressed flaw in a glass probe and (*right*) a flaw stressed in tension and the resulting stress concentration profile

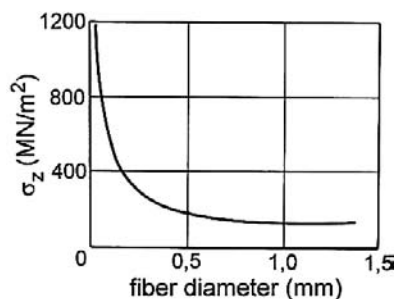


Fig. 1.35. Tensile strength σ_z of glass fibres and rods as function of their diameters [424]

The stress concentration arising near flaws present in the glass may be many times greater than the average stress in the surrounding glass. So it is not surprising that not the average stress but the peak stress concentration arising around flaws end cause sudden and catastrophic failure of the glass. The peak stresses must be compared to the bond strength which explains the difference between the theoretical and real strength of glasses.

It becomes evident that one single crack at the surface of a glass product can lead to the failure under load. Therefore, the real strength of glasses is relatively independent on the glass composition and cross-sectional area of the glass part. It is also clear that the strength found in practical applications depends on the number and length of flaws in a glass product. Since the probability to find flaws in large glass products is higher, their strength is mostly smaller than in smaller parts. It follows that glass products with small cross-sectional areas exhibit higher strength. This advantage is utilised in glass microcomponents and glass fibres. Common sheet glasses have bending strengths in the range of 60–80 MPa, but the measured strength for very thin glass fibres can be as high as 1 GPa. Glass fibres are the most commonly used reinforcement for polymers. Figure 1.35 illustrates to what extent the tensile strength of glass fibres or rods depends on its diameter.

Back to the flaws themselves, (1.12) was derived (see Bartenev [21]) to express the real strength of a glass as function of the flaw length:

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi a}} \quad (1.12)$$

σ_f = failure strength

E = modulus of elasticity

γ = surface tension

a = half of flaw length or critical crack length for crack growth

The elastic modulus is an intrinsic material property, and the tension of the fracture surface is only slightly affected by the glass composition. Flaws, however, are due to external factors. Flaws are easily introduced by abrasion with harder materials, by chemical attack or thermal stresses. Since most flaws start at the glass surface it should be possible to improve the strength of glass products by removing the flaws. Flaws can be removed completely or at least their length shortened below the critical length required for a crack to grow by polishing. Glasses can be polished mechanically, by chemical etching or in flames, which heals flaws by viscous flow in the surface region (see also Sect. 3.3.4). Figure 1.36 highlights the remarkable improvement in strength after the removal of surface flaws. The measured strength increases, but the variability of the results is due to some remaining flaws and cracks with a variable depth.

Microstructured glasses undergo in almost every case some kind of chemical treatment, so it can be expected that their strength should be higher as compared to common sheet glass. The mostly small dimensions of microstructured glass components mean that the probability for flaws to occur is limited and furthermore the chemical etching later removes most flaws by the removal of surface damaged layers.

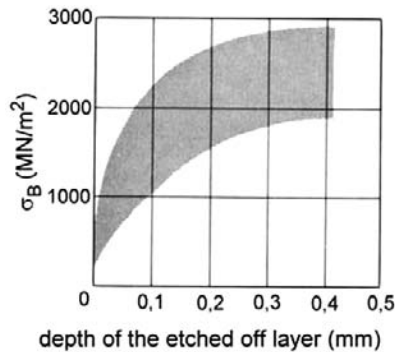


Fig. 1.36. Bending strength σ_B of Pyrex glass as function of material removed after chemical polishing/etching in 15% hydrofluoric acid. The *grey* region corresponds to the scattering of the measured values [412]

Borosilicate glasses have gained great importance for microfluidic systems and for the encapsulation of silicon devices, because of their thermal expansion coefficient particularly of Pyrex-type glasses. The thermal expansion coefficient is $\alpha = 3.3 \times 10^{-6} \text{ K}^{-1}$ up to temperatures about 300°C and sometimes up to 400°C . If Pyrex-type glasses have to be bonded to silicon by anodic bonding temperatures of 400°C are required. At this temperature silicon has almost the same thermal expansion coefficient as the glass and so stress free joining is possible. Anodic bonding allows direct joining of a suitable borosilicate glass to silicon provided that:

- The required joining temperature does not cause damage to the doped silicon chips due to enhanced diffusion processes.
- The joining temperature is high enough for diffusion processes in the glass which causes the formation of a strong SiO_2 interphase between silicon and glass.
- The ion conductivity of the glass at the joining temperature is high enough to use a DC current in order to direct the diffusion process.

Pyrex-type glasses fit this demands. Na^+ ions provide the electrical conductivity, but the glass also contains small amounts of Al_2O_3 which prevents the unwanted phase separation (see Sect. 1.1.6). The homogeneous microstructure of a Pyrex glass is shown in Fig. 1.37.

In many cases temperatures as high as 400°C cannot be used to join silicon with glasses. In such cases glasses with much higher ion conductivity at lower temperatures are desired. In order to increase the ion conductivity in glasses, Straube [503] came up with the idea to replace Na^+ by Li^+ in glass compositions. The ion radius of Li^+ is much smaller compared to Na^+

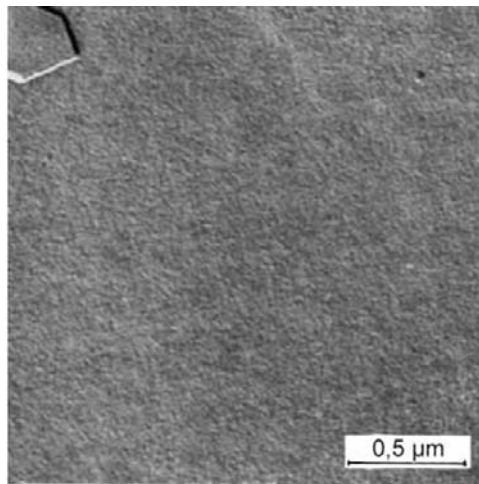


Fig. 1.37. TEM-micrograph of a Pyrex-type glass [537]. The Mo-oxide crystal partially seen in the *top left* corner demonstrates the resolution

Table 1.4. Chemical composition (mol %) of a lithium borosilicate glass suitable for anodic bonding to silicon at 250°C [503]

SiO ₂	B ₂ O ₃	Al ₂ O ₃	Li ₂ O	FeO	TiO ₂
73.77	16.27	2.40	6.45	0.66	0.46

(see Table 1.1) which should make result in higher mobility of Li^+ . However, on the other hand the electrical field strength increases (see (1.1)), with the result of a stronger binding of Li^+ in the network and a lower mobility. This raises the question which mechanism will be predominating. The aim was to develop a glass with a thermal expansion coefficient very similar to that of silicon at joining temperature to be used. Furthermore, the joining temperature should be as low as possible, which requires much higher ion conductivity at lower temperatures as for Pyrex-type glasses. The glass should be suitable for microstructuring. And finally, such a glass should be chemically at least as stable as Pyrex-type glasses and transparent.

It is evident that the ion conductivity of a glass strongly correlates with its chemical stability, i.e. the higher the ionic conductivity the less durable the glass. Both properties are influenced by the extent and type of phase separations. The increase of the Li_2O content at the expense of SiO_2 changes the microstructure of the phase-separated glass from a ‘droplets in matrix’ morphology (see Fig. 1.14) to a penetration structure with an interconnected morphology (see Fig. 1.16). The ion conductivity of Li_2O containing glasses increases significantly with temperature, which is caused by the enrichment of Li_2O in the one of the two interconnected phases. Table 1.4 summarises the chemical composition of a glass which allows for low temperature anodic bonding at 250°C. Furthermore, the thermal expansion coefficient of this glass is compatible to silicon, and it has a good chemical stability. The basic glass composition consists of SiO_2 , B_2O_3 , Al_2O_3 and Li_2O . This glass can be easily etched and is optically transparent just like Pyrex-type glasses.

The basic composition without the dopands FeO and TiO_2 fulfils almost all requirements outlined above, however can the glass be easily microstructured? The dopands FeO and TiO_2 were added in order to allow for microstructuring by laser ablation using the Nd-YAG laser in its basic mode ($\lambda = 1,060 \text{ nm}$). The optical transmission curve of the doped lithium borosilicate glass is shown in Fig. 1.38. This glass can be microstructured without problems. The glass has a slightly brownish colour because of the absorption band in the visible wavelength range, but is still transparent.

1.2.4 Photostructurable Glasses

Principle

Glasses can interact in various ways with radiation. Different types of radiation exist: particle (such as ions) and electromagnetic radiation. The electromagnetic spectrum ranges from high-energy radiation, such as γ and X-rays over

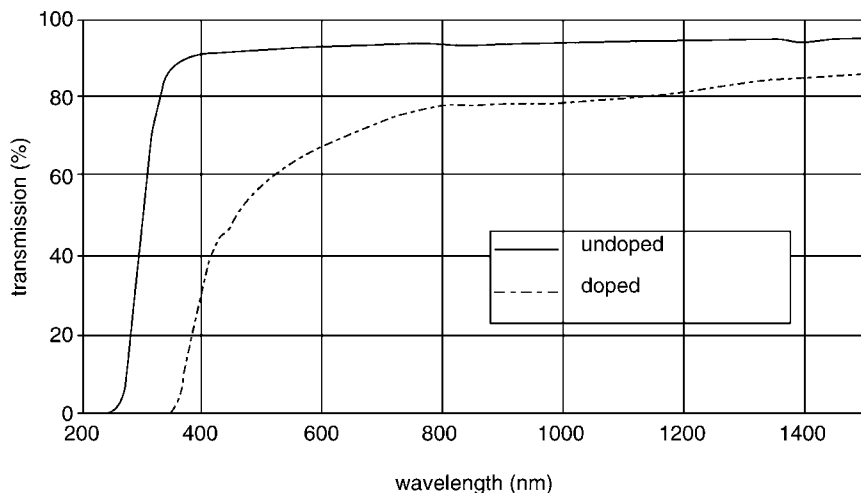


Fig. 1.38. Optical transmission spectrum of an undoped and a FeO (0.66 mol%) and TiO₂ (0.46 mol%) doped lithium borosilicate glass (its composition is shown in Table 1.4) [503]

the EUV-, UV-, visible (VIS) to the low energy IR-, microwave and radio radiation. Each type of radiation has its own characteristic energy range. Therefore, it is obvious that different interactions can take place between a glass and the radiation, depending on the actual wavelength of the radiation. The different electrons in a material, i.e. the electrons in the different orbitals, interact with a certain type of radiation which may lead to different thermal, chemical and possibly optical effects. The chemical and optical effects are of interest for photosensitive glasses, which occur if a sensitive glass is exposed to UV- and VIS-radiation.

For instance it is known for a long time that some older window glasses become slightly coloured by continuing irradiation with sunshine, which is also known as solarisation. Black/white TV-panels turned grey if they were exposed to γ -radiation. Of course these effects are undesired, but they can now be prevented by using optimised glass compositions. Other glasses containing rare earth metal oxides begin to fluoresce during and continue to do so after exposure to UV radiation. This effect is technically useful. Some special glasses, for instance doped with Nd³⁺, emit light after continuous exposure to (or pumping) coherent laser radiation.

And again another effect observed in Ce³⁺ containing glass when exposed to UV radiation of a certain wavelength is a light induced valence change. Ce³⁺ is oxidised to Ce⁴⁺. If precious metal ions, such as Ag⁺, Au⁺ but also Cu⁺ are present in the vicinity of Ce³⁺ in the glass they will be reduced by this photoelectron to atoms. This process can be thermally assisted. At higher temperatures as the diffusion of these atoms is enhanced, they will agglomerate

to form clusters. If these clusters grow to a certain size, about 4 nm [245,365], a darkening of the glass is observed. The colour of the glass depends on the concentration and the final dimensions of the metal atom clusters. The colour of the glass can range from yellowish, greenish, brownish, reddish brown to red in different intensities but they can also be grey or almost black.

If the initial UV exposure of the glass takes place through a mask, pictures and images can be produced in special doped glasses. Dalton discovered this effect in 1941 [407]. The directed development of corresponding products was later published by Stookey [496]. Nowadays this effect is of interest to suppress light transmission in glass microdevices in certain places.

Precious metal clusters in glasses can also be beneficial for the microstructuring of glasses. Ag clusters, formed during the UV exposure, and thermal treatment of photosensitive glasses, can act as heteronuclei for the thermally initiated growth of $\text{Li}_2\text{O} \cdot \text{SiO}_2$ (lithium-metasilicate LMS) crystals. LMS crystals have solubility that is 54 times higher than the solubility of the non-crystallised glass phase in hydrofluoric acid [128]. During a HF treatment the LMS crystals are preferably dissolved, leaving holes or channels of a geometry that was predefined by design of the mask used during UV exposure. This procedure is protected in many patents [9,497]. The commercial exploitation of the process started during the years of the Second World War [497]. Stookey [501] wrote a historical review about it.

This complex procedure which is the basis for geometrical microstructuring of photosensitive glasses is not allowed to be confused with silver clusters in $\text{Na}_2\text{O-ZnO-Al}_2\text{O}_3\text{-SiO}_2$ glasses (doped with silver, cerium and fluorine). These silver clusters act – during thermal treatment – as nuclei for NaF crystals growth reducing the refractive index suitable for Bragg gratings and high-power lasers, see Glebov [176].

Droplets, Silver Clusters and Lithium-Metasilicate Crystals

In principle it should be possible to grow crystals with a higher solubility than the surrounding amorphous phase in various glasses. Such glasses are SiO_2 -rich with a small amount of Al_2O_3 , in which the Al^{3+} is in CN 4 [201]. However, they are B_2O_3 free [399]. If any such crystals form, they act as placeholder for the holes and channels to be etched. The crystals size determines the smallest dimensions of the geometrical structures that can be obtained via etching, i.e. the crystal size determines the smallest channel width and its wall roughness. The wall roughness personifies the negative of the dissolved crystals. Therefore, very small crystals in the range of 100–500 nm in diameter are desired. This size range corresponds to the size of droplets in a glass matrix that form during phase separation as described in Sect. 1.1.6 (see Fig. 1.39). If these droplets have a suitable chemical composition, it should be possible to transform them into crystals which could easily dissolve in HF.

In conclusion, a glass with the tendency to develop many small droplets during the phase separation could be used as a template providing the droplet

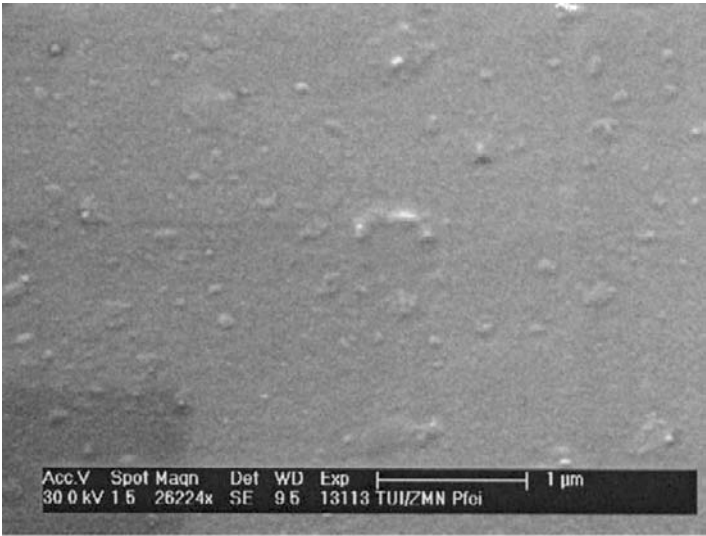


Fig. 1.39. Scanning electron micrograph [220] of the photostructurable glass FS 21, which was developed by Brunsch [75] at the TU Ilmenau

Table 1.5. Glass compositions which allow for the formation of LMS crystals [399]

Oxides	Glasses, composition (mass %)			
	1	2	3	4
SiO ₂	77.5	79.0	80.0	73.5
Al ₂ O ₃	10.0	7.5	4.0	10.0
Li ₂ O	12.5	9.0	12.5	12.5
Na ₂ O	–	2.0	–	–
K ₂ O	–	2.5	2.5	4.0
ZnO	–	–	1.0	–

phase and has the ability to crystallise. Some Li⁺ or Ba²⁺ containing silicate glasses form small droplets via phase separation and furthermore, the crystals with desired high solubility in HF form in the droplet phase. In practice, glasses used for these purposes consisting of Li₂O, Al₂O₃ and SiO₂ have prevailed against other compositions. These glasses contain besides Li₂O also other alkali oxides, such as Na₂O and K₂O (see Table 1.5).

The glasses of the compositions shown in Table 1.5 have the tendency to develop LMS crystals during thermal treatment by homogeneous nucleation at temperatures of around 600°C [306]. However, these glasses are not photosensitive and, therefore, are not useful for geometrical microstructuring. But the addition of very small amounts (far below 1%) of optical sensibilisators and thermal stabilisators these glasses turns photosensitively. The dopands used are Ce₂O₃ and Ag₂O, which act as electron donor and acceptor pairs. Ce³⁺ is used because of its UV absorption band and Ag⁺ because it is easily reduced

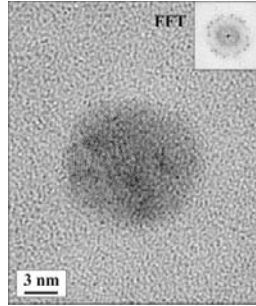


Fig. 1.40. HR-TEM micrograph of a 12 nm silver cluster in FS21 glass given by Hofmeister [365] (FFT: Debye reflexes)

to Ag. However, Ag atoms have a relatively high thermal mobility even at temperatures close to room temperature. In order to reduce the mobility of Ag, i.e. to suppress an undesired silver nucleation in the entire glass piece, and at the same time to suppress the undesired homogeneous nucleation and crystallization of LMS about 600°C, so-called thermal stabilisators such as SbO and SnO are added to the glass.

Ag-clusters start to form via aggregation at temperatures above 350°C, which is depending on the silver concentration in the glass (Brokmann, [67]). Such Ag clusters were detected by Hofmeister and reported by Mrotzek [365]. At higher temperatures, around 500°C, due to the much increased mobility of the Ag atoms the clusters grow to diameters of about 7 nm. Such a silver cluster (particle) produced at 550°C having a diameter of 12 nm is shown in Fig. 1.40. Ag clusters of at least 7 nm in diameter are required for acting as heteronuclei to induce the formation of LMS crystals. If these silver particles happen to be situated in-sight a droplet of a composition suitable for LMS crystallisation then they induce the crystal growth [365], see Figs. 1.41 or 9.10.

Technically advantageous is that the temperature of starting LMS growth induced by *heterogeneous* nucleation occurs at around 550°C, which is still 50 K below the onset of *homogeneous* LMS crystallization [306], which enables the decoupling of the two nucleation processes. The precise nucleation temperatures, however, depend of course on the composition of given glass.

In his original patent Stookey [497] protected suitable compositions of photostructurable glasses and the principles of photostructuring, however, the terms ‘microstructuring’ or ‘micromachining’ were still unknown. Instead he used glass ‘sculpturing’. The technology of the glass sculpturing and the glass trademark were coined by Corning ‘Fotoform’. Fotoform glass is now no longer manufactured. Schott Glas in Mainz/Germany later developed ‘Foturan’ and Hoya-Glass in Tokyo/Japan ‘PEG 3’. Some important properties of Foturan[®] and PEG 3[®] are summarised in Table 1.6.

Both glasses have very similar property profile. However, unfortunately their thermal expansion coefficients do not match with that of silicon or other materials used for manufacturing microsystems. If thermally joined to silicon

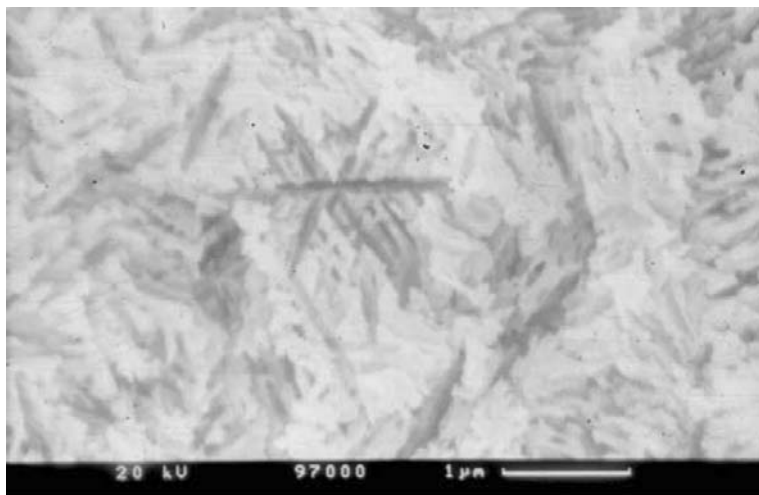


Fig. 1.41. SEM micrograph of partially crystallised areas in the photostructurable glass FS 21 after UV exposure and tempering for 1 h at 590°C. The LMS crystals were dissolved in 2.5% HF [446]

Table 1.6. Properties of two photostructurable glasses Foturan [453] and PEG 3 [239]

Property/unit	Foturan	PEG 3
$\alpha/10^{-6} \text{ K}^{-1}$	8.6	8.4
E/GPa	78	81
$T_g/^\circ\text{C}$	465	465
$\rho/\text{g cm}^{-3}$	2.37	2.34
$n/-$	—	1.511
$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	1.35	0.8

(or other materials) high thermal stresses result if cooled down, which impedes many useful applications.

Tailoring the Thermal Expansion Coefficients of Photostructurable Glasses

In order to remove the problem of the mismatch of the thermal expansion coefficients a family of photostructurable glasses was developed in the Department of Glass and Ceramics Technology of the Technische Universität Ilmenau/Germany. All these glasses can be microstructured using a modified UV lithographic procedure. Brunsch [75] developed the photostructurable glass FS 21. The composition and some properties are summarised in Table 1.7. The thermal expansion coefficient of FS 21 is significantly higher than that of Foturan and PEG 3 and comparable to that of cast iron and steel.

Just like the commercially available photostructurable glasses, FS 21 also has an intense Ce^{3+} -absorption band with a maximum between

Table 1.7. Composition and properties of the microstructurable glass FS 21 [75,190]

	Dimension	
Main components		
SiO ₂	mass %	74.29
Al ₂ O ₃	mass %	7.20
Li ₂ O	mass %	11.61
Na ₂ O	mass %	2.74
K ₂ O	mass %	4.16
Dopands		
AgNO ₃	mass % above 100 %	0.18
Sb ₂ O ₃	mass % above 100 %	0.40
SnO	mass % above 100 %	0.07
CeCl ₃ · 7H ₂ O	mass % above 100 %	0.065
Properties ^a		
α _{20–400}	10 ^{−6} K ^{−1}	10.6 ± 0.13
T _g	°C	450
T _{κ100}	°C	134
ρ ₂₀	10 ⁹ Ω cm	5.63
ρ ₂₀₀	10 ⁹ Ω cm	4.74
n		1.522
Acid resistance class		2
Alkali resistance class		2
ρ	g cm ^{−3}	2.3758
λ ₂₅	W m ^{−1} K ^{−1}	1.19
λ ₁₅₀	W m ^{−1} K ^{−1}	1.5
λ ₃₀₀	W m ^{−1} K ^{−1}	2.06

^a The subscripts indicate temperatures (°C) at which the properties were determined

300 nm < λ < 320 nm (Fig. 1.42). After exposure to light of this wavelength the intensity of this band decreases dramatically or it disappears completely.

In order to determine the temperature range in which the silver-induced heteronucleation and growth of LMS-crystals occurs differential-scanning calorimetry (DSC) was used. DSC measures the specific heat flow. DSC curves provide information about glass transformation temperature, phase transitions and the character of chemical reactions. Figure 1.43 shows the DSC heating curve of FS 21. The glass transition or transformation from the brittle-elastic to predominant viscous behaviour occurs at $T_g = 450^\circ\text{C}$. The broad exothermic peak with a maximum at 640°C is due to the formation of LMS crystals. The onset temperature of 552°C is in good agreement with the previously reported 550°C .

Starting from the photostructurable glass FS 21, Ehrhardt [128] varied the glass composition to tune α . Photostructurable glasses with a higher or lower thermal expansion coefficient compared to FS 21 are demanded. Figure 1.44

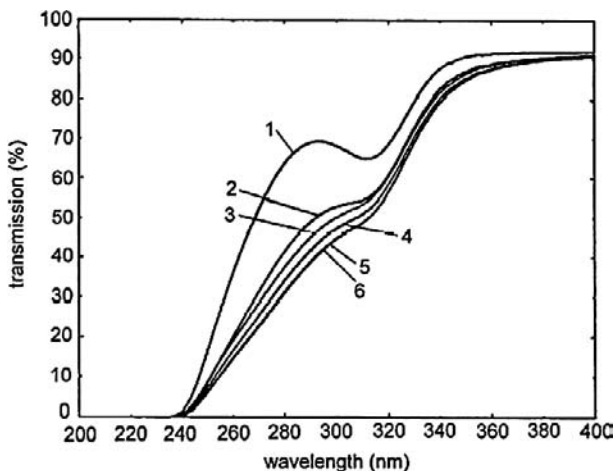


Fig. 1.42. UV transmission spectra of photostructurable Ce^{3+} -doped FS 21 glass sheets of $500\mu\text{m}$ thickness [446] before and after UV exposure in the absorption maximum using a modified mask aligner; exposure time to UV (1) 0 min, (2) 5 min, (3) 10 min, (4) 15 min, (5) 20 min, (6) 25 min (curve 6 is identical with curve 5)

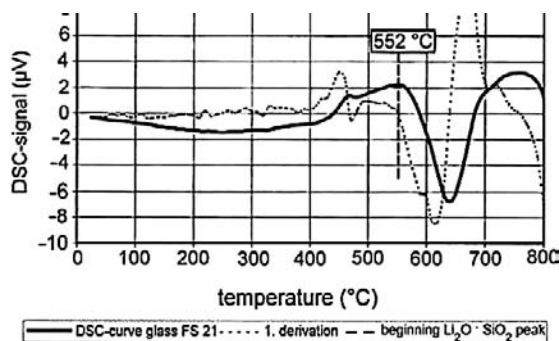


Fig. 1.43. DSC-curve and its first derivation of untreated FS 21 glass powder. Heating rate: 5 K min^{-1} . The LMS crystal growth starts at 552°C [201]

shows the tested compositions as straight lines in the simplified ternary phase diagram: alkali oxides – Al_2O_3 – SiO_2 .

As described above (Sect. 1.1.3), it is well known that if the amount of network modifier oxides is increased in a glass composition so does its thermal expansion α . On the other hand if the amount of network former oxides is increased, then α decreases. This relationship offers a possibility to tailor the thermal expansion coefficient. However, at the same time we have to keep in mind, that photostructurable glasses can only be composed in a relatively narrow composition range (Fig. 1.45) by doping the glass with Ce_2O_3 , Ag_2O , Sb_2O_3 and SnO . Outside this narrow composition range (see

hatched area in Fig. 1.45) UV-induced Ag clusters do not occur and therefore will not act as heteronuclei for the LMS crystallisation. Other crystallisation mechanisms, such as homogeneously induced crystallisation during reheating or spontaneous crystallisation during cooling, predominate outside this composition range (Fig. 1.45), or other crystal structures form, which will not allow the defined microstructuring of the resulting glasses. Therefore, Ehrhardt [128] changed the ratio of the alkali oxides as well as the total amount of the dopands starting from the original composition of FS 21, which enabled her to extend the composition range of photostructurable glasses.

There is a further possibility to influence α . A straight line connects the SiO_2 -corner of the phase diagram with the $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$ composition on the opposite side of the triangle (Figs. 1.44 and 1.45). According to the mathematical intercept theorem, all compositions on this line have the same ratio of $\text{Li}_2\text{O} : \text{Al}_2\text{O}_3 = 1 : 1$, but a variable SiO_2 content, which varies from 0–100%. Following this line we find several chemical compounds with defined crystalline phases, which have remarkable properties because of their near zero even negative thermal expansion coefficient which depends on the crystal axis and temperature. Table 1.8 provides selected information about these compounds. Moreover, these crystal phases are able to form mixed crystals with even more complicated crystalline lattices and thermal expansion coefficients. Silica O, Keatite and Virgilite are examples for such mixed crystals. If the

Table 1.8. Thermal expansion coefficient of the crystal phases $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2$ ($x = 2, 4, 6, 8$)

Phase	$T(^{\circ}\text{C})$	$\alpha(10^{-6} \text{K}^{-1})$	Axis	Source
Eucryptite $x = 2$	0, ..., 1,200	−8.7	Random in a ceramic	[353]
	About 800	−17.6	c	[399]
	About 800	+18.2	a, b	[399]
	20, ..., 700	−9.0	Random	[399]
	20, ..., 1,000	−6.4	Random	[399]
Spodumene $x = 4$	0, ..., 1,200	+1.0	Random in a ceramic	[353]
		+0.9	Random	[538]
	About 1,200	+0.9	Random	[399]
Li-Orthoclase $x = 6$		+0.5		[538]
	0, ..., 1,200	+0.7	Random in a ceramic	[353]
Petalite $x = 8$	0, ..., 1,200	+0.5		[353]
		+0.3		[538]
	About 1,200	+0.3	Random	[399]

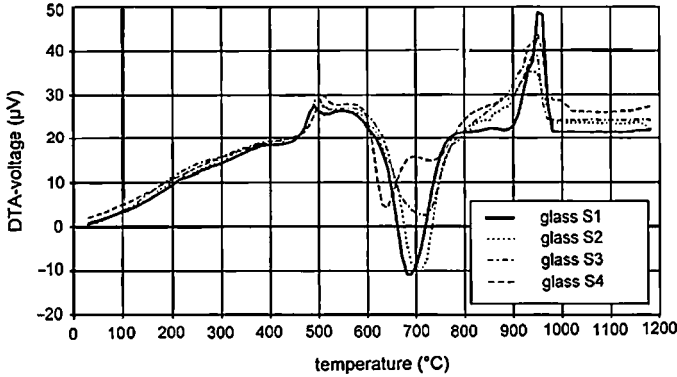


Fig. 1.46. DTA-curves of the four glasses corresponding to the compositions S1, S2, S3 and S4 (direction R1 in Fig. 1.44) [128]

average thermal expansion coefficient of a material is the sum of the individual thermal expansion coefficients contributed by each component (1.7.), then crystalline phases in a glass composition with a near zero or even negative α should result in a decrease of the average α of a partially crystallised glass.

In order to produce photostructurable glasses with tailored thermal expansion coefficients we need to choose a suitable glass composition, for example along the compositions lines R1 and R2 in Fig. 1.44. At first, LMS crystallisation is induced in these glasses for controlled microstructuring, which may be followed by inducing the crystallisation of, for example, virgilite, at higher temperatures to adjust the thermal expansion coefficient α [128].

The DTA curves of the glasses S1, S2, S3 and S4 with the compositions in direction R1 in Fig. 1.44 are shown in Fig. 1.46. An endothermic peak between 450 and 550°C corresponding to the glass transformation temperature (T_g) can be seen for all glasses. T_g increases with increasing Al_2O_3 content. The exothermic peak corresponds to the LMS crystallisation, but it is shifted to slightly higher temperatures for the glasses S1 and S2 as compared to the glass FS 21 (see also Fig. 1.43). Other exothermic peaks are not detected for these glasses. The glasses S3 and S4 have a higher Al_2O_3 content, which enhances the likelihood of virgilite crystallisation. For the glass S3 the crystallisation peaks of LMS and virgilite overlap, whereas they are clearly separated for glass S4. As seen, it is possible to induce the crystallisation of virgilite in both glasses (S3 and S4) after microstructuring via an additional thermal treatment. Virgilite containing glasses have a lower thermal expansion coefficient. The endothermic peak between 900 and 1,000°C signals melting processes.

An increased SiO_2 content (direction R3 in Fig. 1.44) in the glass composition, starting from FS 21, should result in a decreased α . The effect of the possible crystallisation of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ on the thermal expansion of the glass was unclear. Pavluškin [399] gives $\alpha_{20/600} = 11 \times 10^{-6} \text{ K}^{-1}$ for lithium disilicate crystals, which is very similar to α of FS 21 meaning

Table 1.9. Compositions (mass %) of photostructurable glasses with different thermal expansion coefficients [128]. The numbers correspond to the compositions shown in the simplified phase diagram in Fig. 1.44

Number	1	2	3	4	FS 21
SiO ₂	67.90	65.00	70.00	67.50	74.29
Al ₂ O	7.20	7.20	13.00	16.50	7.20
Li ₂ O	8.71	11.61	10.62	10.02	11.61
Na ₂ O	6.42	6.42	2.51	2.37	2.74
K ₂ O	9.77	9.77	3.81	3.60	4.16
Ag ₂ O	0.0308	0.0308	0.123	0.123	0.123
Ce ₂ O ₃	0.0083	0.0083	0.033	0.033	0.033
Sb ₂ O ₃	0.20	0.20	0.40	0.40	0.40
SnO	—	—	0.07	0.07	0.07
α (10^{-6} K ⁻¹)	13.10	13.69	9.91	9.58	10.60
			(glass)	(glass)	
			7.74	5.99	
			(part. cryst.)	(part. cryst.)	

that the thermal expansion behaviour would not be affected. Contrary to this observation, the thermal expansion coefficient of partially crystallised Foturan [453] increased by the crystallisation of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ compared to the amorphous material. This discrepancy can be explained by the different compositions of Foturan and FS 21, which of course results in different α (see Tables 1.6 and 1.7). Furthermore, the thermal expansion behaviour of $\text{Li}_2\text{O} \cdot \text{SiO}_2$ crystals is anisotropic. Ehrhardt [128] determined the thermal expansion coefficients α for $\text{Li}_2\text{O} \cdot \text{SiO}_2$ -single crystals. α in c -direction is $14.82 \times 10^{-6} \text{ K}^{-1}$ and perpendicular to it $9.31 \times 10^{-6} \text{ K}^{-1}$, whereas α of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ has only (isotropically) $8.37 \times 10^{-6} \text{ K}^{-1}$. Resulting, the variations of glass compositions in direction R3 have not remarkably influenced the thermal expansion of the partially crystallized glasses.

Considering all investigated compositions of photostructurable glasses for technical microstructuring applications we recommend the compositions given in Table 1.9. These glasses can be joined to other materials by thermal fusion, diffusion bonding or microgalvanic methods. All methods are described in Chap. 10.

Chemosensitive Photostructurable Glasses

The high amount of alkali oxides in FS 21 could cause chemosensitivity. If submersing one site of a glass piece (sheet) into an ionic solution and applying direct electric current, a potential difference between both surfaces of the glass piece occurs. This potential difference depends on the chemical composition of the solution, e.g. pH or Na^+ content, and the ion conductivity of the glass. If the potential difference is high enough for measuring the

glass is chemosensitive. A combination of both, the ability to microstructure glasses and chemosensitivity, would allow the design of chemical microsenors on glass basis which could be used as discrete devices or be an integrated part of glass microfluidic systems. Silicon-based ion-sensitive field effect transistor (ISFET) chemical microsenors (see also Bergveld [44]) have certain disadvantages, such as their intrinsically poor long-time stability. Traditional pH-sensors with glass electrodes are too large and require large quantities of fluid to realise measurements. They can therefore not be used in microfluidic, analytic systems.

The glass that is traditionally used to fabricate pH-sensors is ion conducting and has a relatively low electrical resistivity. If this glass is in contact with an electrolyte solution and an electrical potential is applied across the glass, an ion current will flow. The measured voltage between the working and an additional reference electrode is a measure of the potential difference at both boundaries between the electrolyte and the working electrode on the one side and the reference electrode on the other side. The potential difference depends on the pH of the solution and the reactions occurring at the glass-solution boundary. The low electrical resistivity of the glass allows the easy interpretation of the measured potential differences. In practice, frequently, a potential difference, which depends on the pH is measured (see Eisenman [131]). The pH-sensitive glass has the optimal composition, if the function voltage against pH is linear over a wide pH-range and has a steep slope.

Initial experiments with FS 21 have confirmed that the glass is indeed chemosensitive. However, these experiments have also demonstrated that the glass is not only sensitive to H^+ but also simultaneously to Li^+ , Na^+ and K^+ . In order to improve the ion selectivity in such a way that the glass is only sensitive to either H^+ or any of the alkali ions over a wide concentration range while maintaining the ability for microstructuring via UV lithography the glass composition had to be optimised. To obtain optimised photostructurable glass membranes with low electrical resistivity, the mixed-alkali effect (see Sect. 1.2.2) must be considered. An increase of the Li_2O amount in presence of K_2O or Na_2O in the glass, starting from FS 21, resulted in an increased ion conductivity of the membrane more so for the glasses containing K_2O [251]. Furthermore, Hülsenberg and Kallenbach [251] found that proton selectivity (pH sensitivity) could only be achieved for $Li_2O-Al_2O_3-SiO_2$ glasses, which contained K_2O but no Na_2O . In this case the actual amount of Al_2O_3 and K_2O influences the pH-characteristics more than Li_2O . Following this investigation, Hecht-Mijic et al. [204] optimised the glass composition to improve the pH selectivity of the FS 21-based glasses. They kept the ratio of alkali oxides to SiO_2 constant but varied the Al_2O_3 content. With decreasing Al_2O_3 content (see Fig. 1.47) the slope of the voltage as function of pH curve increased and the dependency became more linear over a wider pH range. Furthermore, the glass composition was only selective to protons. Considering the currently available hardware, the voltage signal obtained from these glasses is large enough so that the glasses can be utilized for microtechnical applications.

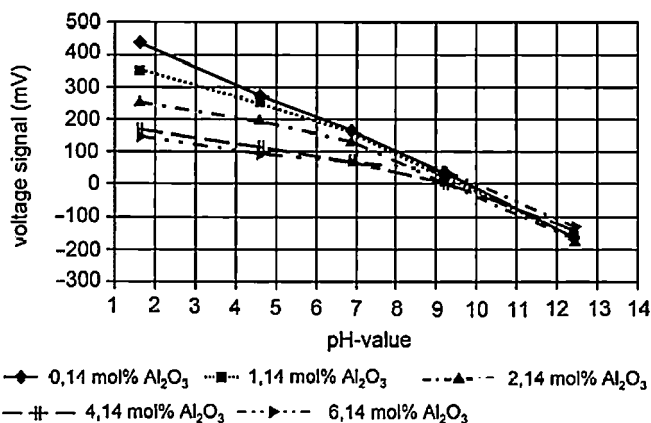


Fig. 1.47. Voltage as function of pH for alkali oxides- Al_2O_3 - SiO_2 glasses with varying Al_2O_3 content used for pH measurements [251]

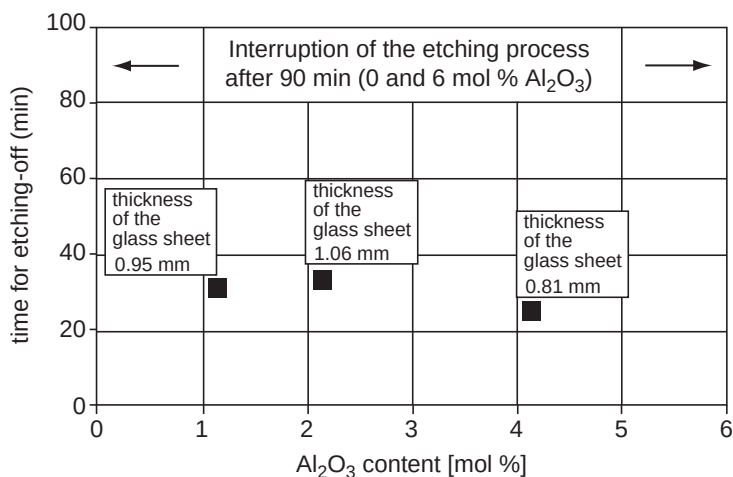


Fig. 1.48. Etching time required to etch holes through 1 mm sheets of microstructurable glass as function of the Al_2O_3 content [251]

Unfortunately, however, the suitability of the glass for microstructuring decreases with decreasing Al_2O_3 content, see Fig. 1.48. The glasses with Al_2O_3 contents ranging from 1 to 4 mol% Al_2O_3 can be easily microstructured, i.e. very low etching times are required. But the highly pH-sensitive glass, which does not contain any Al_2O_3 is not that susceptible to etching. Therefore, the potential user has to choose a composition according to the intended use that fits the required property profile.

Photostructured, Light Wave Guiding Glass Devices

It is a well-known fact that ion exchange near the surface of a glass product can influence the mechanical strength of the glass [81, 188, 221, 368] as well as its refractive index [107, 236, 570]. Especially the latter is of importance if the glass is to be used to guide light waves through microstructured glass devices. Light waveguides, such as optical fibres, are based on the principle of total internal reflection. This requires materials consisting of a core with a higher refractive index and a cladding with a lower refractive index, which could be air. However, in this case the optical waveguide would be susceptible to surface flaws of the glass.

Optical light guiding paths in microstructured glass elements can be created in two ways either by the reduction of the refractive index at the surface of the device, for instance of a microstructured glass spring, so that the light may be coupled in at one end and may be coupled out at the other or by increasing the refractive index inside a microstructured glass component. It is relatively easy to reduce the refractive index near the surface of a glass component via an ion exchange reaction. This can be achieved by submersing the already microstructured glass device into a molten salt, which contains the desired cations for the ion exchange. In order to prevent the deformation of the microstructured glass at the elevated temperatures required for ion exchange reaction this has to take place at temperatures below the strain point T_U of the glass (see also Sect. 1.14 or Hecht-Mijic [201]). This, of course, limits possible available salt melts. However, in most cases molten Li^+ -, Na^+ - or K^+ -nitrate salts can be used.

FS 21 contains three alkali cations, Li^+ , Na^+ and K^+ , so we have to consider which type of exchange could take place. Li^+ ions are very mobile and would preferentially be exchanged, however large K^+ ions are also present. A treatment in molten NaNO_3 should result in exchange of both cations. Figure 1.49 shows exemplarily the ion exchange behaviour of FS 21 after exposure to a NaNO_3 melt. Of course the results depend on the actual exchange temperature and time.

As can be seen in Fig. 1.49 FS 21 rapidly depletes of Li^+ near the surface during the exposure to a NaNO_3 melt and simultaneously enriches in Na^+ . As expected the concentration of K^+ near the surface is only marginally affected. This ion exchange influenced both the optical density near the surface and the internal stresses. As a result of the ion exchange, the refractive index near the surface is reduced by about 0.01 [201], which is sufficient for applications in microglass springs as light waveguides and also for fibre optical waveguides for applications in the communication (see Fig. 1.50).

The mechanical properties of photostructurable glasses allow the fabrication of spring-like mechanical sensor devices, because of their linear stress-strain behaviour (see also Sect. 11.1.1). However, for such applications it is necessary to detect the distortion of these devices. Real microstructured glass springs or other microstructured glass components could be used

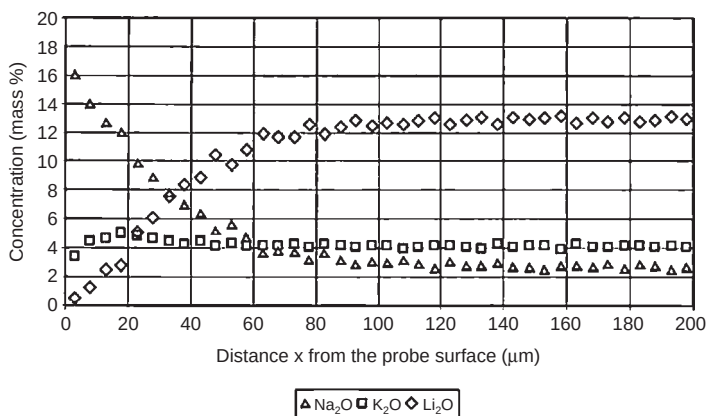


Fig. 1.49. Concentration profile of Li_2O , Na_2O and K_2O near the surface of FS 21 after exposure to a NaNO_3 melt at 360°C for 210 min [201]

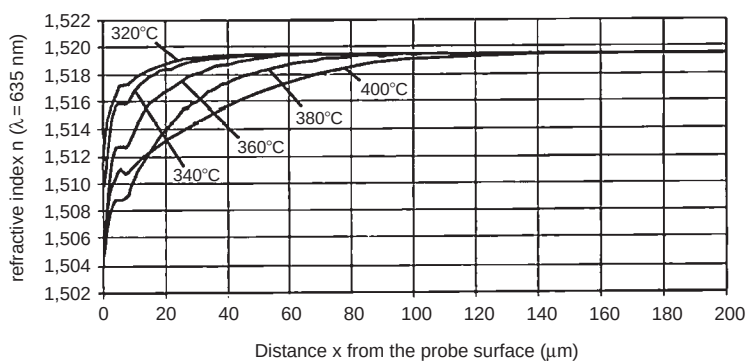


Fig. 1.50. Refractive index at $\lambda = 635$ nm near the surface of microstructured, Na^+ exchanged FS 21 glass devices [201]. The exchange temperature was varied between 320 and 400°C and the residence time in the melt was 210 min

directly to detect their distortions if they contain well-defined ion exchanged regions.

The refractive index near the surface of a FS 21 glass component can be increased by an ion exchange in a KNO_3 melt (Fig. 1.51). The increase of the concentration of the large diameter K^+ ions leads to an increase in the optical density of the glass near the surface, but it also causes increased compression stresses. Both effects cause an increase of the refractive index. However, it is very surprising that the refractive index directly at the surface decreases below the value of the bulk glass. In conclusion it is possible to integrate light guiding paths directly into microstructured FS 21 glass components.

The ion exchange treatment can have an additional beneficial effect on the glass properties. If suitable salt melts and ion exchange conditions are

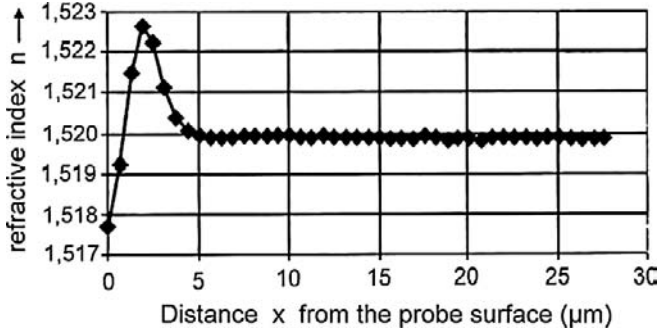


Fig. 1.51. Refractive index profile at $\lambda = 635$ nm near the surface of FS 21 glass after exposure to a KNO_3 melt at 430°C for 120 min [251]

chosen, compressive stresses arise near the surface of the glass. The compressive strength of glasses is ten times higher as compared to the tensile strength (see Sect. 1.2.3). Therefore, it can be expected that such an ion exchange will not only improve the optical performance but also the mechanical properties of microstructured glass devices. Ludwig [338] tested the bending strength of microstructured FS 21 glass bars ($30\text{ mm} \times 1\text{ mm} \times 1\text{ mm}$) after an ion exchange treatment in a KNO_3 melt at 345°C for 30 min. A surprisingly high-bending strength of 780 ± 60 MPa was measured. This value is more than $10\times$ higher as the bending strength of common window sheet glass, see also Hesse et al. [222].

Thermodynamic Phenomena in Glass

2.1 Binding Enthalpy

Whatever method – mechanical, thermal or chemical – we use, microstructuring of glasses is always intrusive, which means bonds between anions and cations are being broken, and this requires energy. The actual energy required for the process of microstructuring has to exceed the theoretical binding energy and must also cover the needs for the applied process conditions and losses.

Section 1.1 describes the ionic arrangement and structure of glasses. The presence of short-range order, as represented in the structure coordination tetrahedra, but absence of long-range ordering, which results in the random arrangement of the coordination polyhedra in the glassy network, makes it rather difficult to formulate generally valid statements about energetic phenomena in glasses. If we indeed want to define a certain value for the binding energy even for a glass with a well-defined composition, we have to consider that this would only represent a mean value with a wide distribution.

From a practical point of view, only processes operating at constant pressure are of interest for glass microstructuring. Therefore, we should not use the term “energy” to describe energetic phenomena in the glassy network. It is better to use enthalpy (2.1):

$$H = U + pV \quad (2.1)$$

where H is the enthalpy, U the internal energy, p the pressure and V the specific volume.

The Gibbs–Helmholtz equation links the enthalpy H with the (Gibbs) free enthalpy G which is the available energy in chemical systems at a given absolute temperature (2.2)

$$\Delta G = \Delta H - T\Delta S \quad (2.2)$$

where S is the entropy.

Table 2.1. Thermophysical parameters of some common glasses [261]

Glass	Enthalpy $\Delta_b H^\circ$ at standard conditions (kJ mol ⁻¹)	Entropy $\Delta_b S^\circ$ at standard conditions (J mol ⁻¹ K ⁻¹)
Sodium calcium silicate	-810	45.6
Pyrex	-1080	44.0
Fused silica	-908	43.4

Both, enthalpy and entropy at standard conditions for chemical elements and compounds are tabularised [50]. Using these values Jacquorie [261] calculated H and S at standard conditions for a sodium calcium silicate, a sodium borosilicate and a pure silica glass (Table 2.1).

These actual values of H , S and G depend on the actual temperature (2.3) and (2.4) and affect as a consequence the free enthalpy G (2.5):

$$H_{(T)} = H_0 + \int_0^T C_p dT, \quad (2.3)$$

$$S_{(T)} = \int_0^T \frac{C_p}{T} dT \quad (2.4)$$

$$G_{(T)} = H_0 + \int_0^T C_p dT - T \int_0^T \frac{C_p}{T} dT \quad (2.5)$$

where C_p is the specific heat at constant pressure and H_0 the enthalpy at standard conditions.

These energetic parameters are valid for one mole of a given glass composition and represent an integrated median value over all types of bonds in the glassy network. These values do not provide accurate information about the binding enthalpy between for instance oxygen and silicon in a glass, because it cannot be distinguished whether the oxygen is bridging or a nonbridging. If the oxygen is nonbridging the bond is heteropolar and requires the presence of another cation in the vicinity, which also affects the strength of the neighbouring bond between oxygen and silicon. A value for the Si-O-Si binding enthalpy does not contain any information about the binding enthalpy between O^{2-} and the other cation. Therefore, in order to estimate the binding enthalpy between special anions and cations, the problem reduces frequently to a comparison of the differences in the electrical field strength ((1.1) and Table 1.1).

More than 50 years ago, Sun [508] defined the chemical binding energy B of a given glass composition (2.6) using the exact chemical composition (mol%), the energy D required for dividing/dissociating the oxides, which are represented in the form RO_y where $y = n/m$ in R_mO_n , into their atoms in

the gaseous state as well as the coordination numbers CN (see Sect. 1.1) of the cations in the oxides.

$$B = \sum_{i=1}^n \frac{D_i}{CN_i} \quad (2.6)$$

Surprisingly, for most studied glass compositions the value B is very close to 420 kJ mol^{-1} . Perhaps this value could offer a clue to understand energy, which is theoretically required for microstructuring glasses. The actual energy value that is required for the process, however, must include the additional kinetic energy contributions, as well as those required to overcome the energy which is holding all the ions in exact positions, with fixed distances and angles. It follows that all processes to microstructure glasses have to overcome an initial activation energy and require energy for removing the ions from their original position (that means for transportations).

2.2 Mechanisms of Materials Transport in Amorphous Homogeneous Solids

2.2.1 Viscous Flow

The temperature dependence of viscosity of a soda lime silicate glass (Fig. 1.11) was already discussed previously and its relevance to glass processing, especially to obtain stress-free glass products was also explained. The viscoelastic behaviour of glasses can be described by Newton's (1.2) and Maxwell's law (1.4). Very comprehensive reviews of the subject matter have been published by Scholze [450] and Brückner et al. [74]. Pye et al. [414] give tables which allow for calculation the viscosity of glass melts in dependence on composition and temperature.

During the process of microstructuring, glasses are often exposed to elevated temperatures, which is true in the case of laser treatments and modified UV-supported lithography. Viscous flow occurs if the applied temperatures exceed the transformation temperature T_g of the glass (Sect. 1.1.4). The glass is especially susceptible to viscous flow at the edges of micrometer-sized holes and channels, if the stress driven by the surface tension γ of the glass (melt) acts towards the bulk of the device. Microstructured edges will deform easily if surface tension stress is high, the viscosity low and the residence time at elevated temperatures long enough. In order to be able to estimate the impact of viscous flow on the final appearance of the microstructured device it would be helpful to be able to describe the flow process at the atomic level.

A glass melt, just as the solidified glass itself, does not possess as explained before any long-range ordering. If a melt is sheared what forces it to flow, then initially the bond angles between the polyhedra will change and bonds are stretched up to a point at which eventually the chemical bonds will break. Thermal and mechanical energy is required to heating the glass, to interrupt

the chemical bonds and eventually to overcome attractive Coulomb interactions and finally to allow the ions, polyhedra or clusters to move freely, which depends on temperature and applied shear stress.

Broken bonds, but not the same, immediately reform again after the melt experienced some deformation. The reformation of bonds leads to a recovery of chemical binding energy. This process is repeated as long as stress is applied. Thermal energy is only required to break the chemical bonds and to overcome attractive Coulomb interactions, but the glass melt starts to flow because of applied external stress acting on the glass or because of surface tension gradients. The temperature dependence of the viscosity of glass melts can be described by or fitted to an Arrhenius expression (2.7):

$$\eta = \eta_0 \exp (E_\eta / RT), \quad (2.7)$$

where η is the viscosity, η_0 a constant, E_η the activation energy that must be overcome to induce viscous flow, R is the gas constant and T the absolute temperature in K. The so-called Arrhenius plot $\log \eta$ vs. $1/T$ should result in a straight line. This would be the case if E_η would be a constant, which is rarely observed. In most cases, Arrhenian behaviour is only observed at very high temperatures where melts are very fluid or near the glass transformation range. However, E_η is very much smaller for fluid melts than for high viscosity melts near the glass transformation range. In the range between the limiting Arrhenius regions, E_η is a function of temperature. Avramov [13] determined the activation energy from the slope of the Arrhenius plot of viscosity against the reciprocal temperature and discussed the results near the transformation temperature. A typical Arrhenius plot for soda lime silicate glass is shown in Fig. 2.1. The slope of this curve, i.e. the activation energy, at temperatures

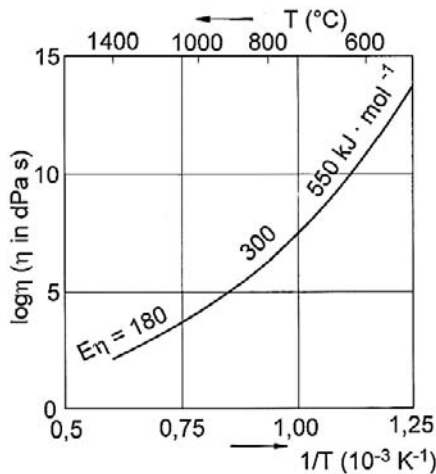


Fig. 2.1. Arrhenius plot $\lg \eta = f(1/T)$ for a soda lime silicate glass in the temperature range above the glass transformation (original data see Fig. 1.11)

above T_g is relatively large (550 kJ mol^{-1}), but it still allows for deformations to occur. It is important for thermal bonding of different glasses to each other or between microstructured glass wafers to silicon (anodic bonding). In the first case the bonding temperature must not exceed the annealing temperature (a higher temperature would indeed favour the desired diffusion between both glass devices, but simultaneously the undesired deformation of the microstructures) and in the second case it has to remain below the strain point in order to avoid diffusion processes in the doped silicon wafers.

Viscous flow in microstructured glass devices, which is responsible for the rounding of edges and the deformation of walls, occurs during the postcrystallisation of UV-sensitive devices which is performed to improve their mechanical properties (see Sect. 1.2.4). Certain technical provisions are required to prevent the undesired deformation of glass devices.

2.2.2 Diffusion

Diffusion describes the movement of atoms, molecules or ions through matter, i.e. gases, fluids or solids. Diffusion is their movement driven by a concentration gradient from a region of higher concentration (or chemical potential) to lower concentration, which gives the process directionality. Any type of fields/gradients, such as mechanical stresses, temperature gradients, magnetic and electric fields, can also influence the direction of diffusion. Chemical, thermal or mechanical gradients are the most common drivers for diffusion in microstructured glasses. The kinetic energy of the diffusing species increases exponentially with temperature. Diffusion coefficients behave in a similar manner, i.e. diffusion processes in glasses can be neglected at room temperature but become significant at temperatures in the glass transition range and above it. Diffusion is a thermally activated process, so the temperature dependence of diffusion coefficients can be described by means of an Arrhenius expression (2.8) which holds at temperatures $T > T_g$:

$$D(T) = D_0 \exp\left(\frac{-E_D}{RT}\right), \quad (2.8)$$

where $D(T)$ is the diffusion coefficient of a species at a given temperature, D_0 is pre-exponential diffusion constant at standard conditions, E_D is the activation energy for diffusion to occur and R the gas constant. The diffusion constant D_0 depends on the underlying diffusion mechanism and the diffusing species; i.e. atoms, molecules, ions or ionic clusters. The diffusion of charged species is affected by electrostatic interaction between the species and the surrounding matter. Therefore it is not the same if e.g. silver or oxygen exists in a glass as atoms or ions. Experimental diffusion coefficients of ions represent only mean values. The values can vary by an order of magnitude even for supposedly identical glasses, which is due to real differences in the glasses because of the absence of any long range order. Diffusion coefficients

of individual ions depend strongly on the valency and the radius of the ion but also on the surrounding matter. It is impossible to predict diffusion coefficients of ions, such as Na^+ , K^+ and Ca^{2+} , in a glass without providing any information about the glass composition. Ions diffuse only remarkably at temperatures exceeding the glass transformation temperature. The diffusion in bulk glasses of ions (or atoms) takes place utilising interruptions and interstices in rings formed by the silica tetrahedra. Ion diffusion may occur via self- or interdiffusion. Self-diffusion is the diffusion of an ion which is the primary component of the glass whereas interdiffusion or ion exchange occurs when a glass containing a certain mobile ion is in contact with a source of a different mobile ion (e.g. from molten salt). This process is of significant interest for many technical applications. If the diffusing ionic species have different sizes, it also means that mobility in the glass is different, which causes differences in the diffusion rates of these ions, and that will result in the development of a temporary electric field in the glass. This field, on the one hand, will slow down the diffusion of the faster ion but, on the other hand, will accelerate the diffusion of the slower ion until the diffusion rates are equalised.

The interdiffusion process between glass containing a mobile ion, such as K^+ , in contact with a source of different mobile ions with a valency, such as Ca^{2+} , requires that two K^+ diffuse per one diffusing Ca^{2+} ion because of electroneutrality reasons. However, if we recall what we learned about coordination numbers (see Sect. 1.1), we understand that such an ion-exchange process rarely takes place. However, an ion exchange between various monovalent ions, such Li^+ , Na^+ and K^+ , is often used to modify for instance near surface properties of glasses or to strengthen glasses. The ion radii of various monovalent ions vary significantly (see Table 1.1), which determines their space requirements in a glass, i.e. larger ions require larger interstices in the tetrahedra rings. Interdiffusing K^+ , having a large mass, leads to an increased optical density and, therefore, increased refractive index (see also Fig. 1.51). If a K^+ is exchanged for a smaller ion, which can occupy smaller interstices, this causes significant compressive stresses near the surface region.

Most commercial ion exchange processes take place by exposing a (microstructured) glass device to a bath containing the melt of suitable salt. The diffusion (ion exchanging) temperature has a major influence on the final result. At $T > T_g$ additionally viscous flow processes might occur which lead to the deformation of the rings of tetrahedra. Whereas at $T < T_g$ the interdiffusion of large cations into the glass containing smaller primary ions causes compressive stress which influences the optical and mechanical properties of glass devices, however, an ion exchange at $T > T_g$ causes flowing and will affect the thermal expansion coefficient in the outer devices layers, which will again influence the refractive indexes and mechanical stresses, but in a different way as at $T < T_g$. As described in Sect. 1.2.4, it is possible to produce light guiding paths in microstructured glass springs [201] by ion exchange process but also to improve the mechanical strength of glasses by the compressive stresses arising from ion exchange [338]. An ion exchange by interdiffusion

Table 2.2. Interdiffusion coefficient $D_{\text{Na}^+ \leftrightarrow \text{Li}^+}$ as a function of temperature for FS 21 glass [201]

$T(^{\circ}\text{C})$	$D_{\text{Na}^+ \leftrightarrow \text{Li}^+} \text{ (} 10^{-10} \text{ cm}^2 \text{ s}^{-1} \text{)}$
320	2.12
340	3.21
360	5.00
380	12.99
400	17.58

below the strain point of the glass will guarantee that the diffusion process is not accompanied by a deformation of the glass device. Hecht-Mijic [201] measured and calculated the interdiffusion coefficients (Table 2.2) for an exchange of Na^+ against Li^+ in FS21 glass in a NaNO_3 -melt as function of temperature.

This exchange process of Na^+ against Li^+ in FS21 can be described by an Arrhenius expression up to the strain point of FS21 at 383°C and again at $T > T_U$, however now having a different slope. This behaviour signalises a strong correlation between the transport mechanisms in glasses by viscous flow and diffusion.

Baumgart [25] investigated almost the same glass composition as Hecht-Mijic [201]. However, the silver dopand was introduced into the glass via an ion exchange in an Ag/NaNO_3 melt. The measured and calculated diffusion coefficients at 405°C are shown in Table 9.4. In this case the diffusion rate of Ag^+ controls the ion exchange rate. The diffusion profiles can be described by Fick's laws (2.9) and (2.10):

$$j = \frac{dN}{A dt} = -D_o \frac{\delta c}{\delta x} \frac{1}{V}, \quad (2.9)$$

$$\frac{\delta c}{\delta t} = D_o \frac{\delta^2 c}{\delta x^2}, \quad (2.10)$$

where j is flux of the diffusing species, i.e. the number of species diffusing from a given volume in 1 s through an area of 1 cm^2 , N is the number of diffusing species, A the area, V the volume, t the time, D_o the diffusion constant, $\delta c/\delta x$ is the concentration gradient of the diffusing species in the direction x .

The ion exchange process occurring between the salt melt and the glass surface is determined by the composition/concentration gradient across the surface, the chosen temperature and the diffusion time. The diffusion rate is controlled by the larger, i.e. slower diffusing ion.

The growth of LMS crystals around Ag -nuclei in photosensitive glasses, as described in Sect. 1.2.4, is also a diffusion process. The Ag particles are homogeneously distributed throughout the glass (matrix and droplets, see Fig. 1.39 and Mrotzek [365]), however, only the Ag clusters in the droplets become nuclei for the growth of $\text{Li}_2\text{O} \cdot \text{SiO}_2$ crystals (LMS) because the chemical composition of the droplets is similar to that of LMS and, therefore, the

diffusion distances are short. The equations describing the nucleation (2.18) and crystal growth process (2.19) account for the importance of the diffusion via the inclusion of the activation energy E_D for diffusion.

Moreover, the joining of glass devices to glasses and/or to other materials are diffusion-controlled processes which are accompanied by flow. Commonly, the joining procedure is supported by pressure, sometimes even by applying a direct electrical field, for instance during anodic bonding of sodium–boron–silicate glass to silicon.

If two wafers of the same glass are joined, self-diffusion occurs. The process is accelerated by elevated temperatures, at or somewhat above the annealing point T_0 . This joining process has to be optimized considering the desired quality of the bonding face and possible deformations of microstructures that can occur around T_0 at the applied pressures to enhance the bond formation. At lower temperatures, around the strain point T_U , the glass device could be destroyed because of stress peaks or tilting. In order to keep the deformation of microstructures within an acceptable level the applied bonding pressure should not exceed 0.02 MPa and the temperature not $T = T_0 + 50 \text{ K}$ [190].

As stated above, the ion diffusion can be enhanced by the application of a direct electric field. In most glasses electrical current is conducted by ion movement and, therefore the strong correlation between the diffusion coefficients of ions and electrical conductivity of glasses is not surprising. Any applied electrical field (alternating or direct) acts as driving force which determines the diffusion direction. If the diffusion way of the ions is long, any applied direct current will cause the glass to decompose via electrolysis. However, the decomposition of the glass can be minimized by controlling the temperature, pressure and applied direct electric field. The anodic bonding between glass and silicon will take place via the diffusion of Na^+ and O^{2-} .

The diffusion length of ions in an applied alternating electric field is only in the range of ion distances. The diffusion direction changes with the frequency of the alternating field. If the frequency is high enough, the ions will not leave their positions; they will only oscillate around the position at rest, which causes inner friction thereby generating enough heat to melt glass electrically (see also Sect. 3.4.1). In this case, i.e. at elevated temperatures, the diffusion is driven mainly by chemical concentration gradients. Section 3.4.1 deals with technical methods for homogenisation of glass melts. Diffusion processes help the homogenisation of glass melts by reducing chemical composition gradients $\delta c / \delta x$ (2.9) and (2.10) in the melt.

It is obvious that the diffusion processes influence almost all glass processing steps ranging from melting to postmanufacturing as well as all the properties of glasses at different temperatures. The higher the temperature the more apparent become the desired or undesired diffusion processes. At $T > T_g$ diffusion as well as flow occur simultaneously, which is beneficial during homogenisation of glass melt or during thermal bonding.

2.3 Enthalpy of Partial Crystallisation

Partial crystallisation of glasses has been described by many authors, see for instance Vogel [538], Scholze [449] and Hinz [225]. The process comprises both steps: the nucleation and the crystal growth.

The free enthalpy G (see also (2.2)) for nucleation of a supercooled glass melt consists of two terms, the volume and the interface term G_v and G_0 (2.11):

$$G = G_v + G_0. \quad (2.11)$$

G_v describes the formation of the long range order arrangement in the melt, i.e. the nucleation, which is an exothermic process and lowers the free enthalpy; this is counteracted by an increase in interface energy G_0 which is caused by the creation of new boundaries between the amorphous and the long range ordered regions. Both terms may be reduced to specific values, which are expressed for a spherical nucleus with (2.12) and (2.13):

$$G_v = -\frac{4}{3}\pi r^3 \Delta g_v, \quad (2.12)$$

$$G_0 = 4\pi r^2 \sigma \quad (2.13)$$

where r is radius of the developing nucleus, Δg_v the change of the free volume enthalpy during transformation from the disordered into the ordered state and σ the interfacial tension.

Using (2.12) and (2.13) to complete (2.11) it results in (2.14):

$$G = -\frac{4}{3}\pi r^3 \Delta g_v + 4\pi r^2 \sigma. \quad (2.14)$$

Δg_v and σ are temperature dependent. Guessing values for Δg_v and σ the following qualitative diagram can be drawn for $G(r)$ at a constant temperature (Fig. 2.2).

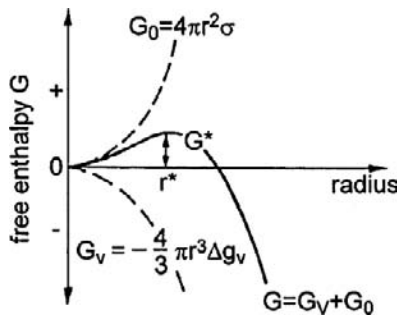


Fig. 2.2. Free enthalpy G of a developing nucleus depending on the actual radius of the ordered volume

The resulting curve for $G(r)$ exhibits a typical maximum. It can be determined in (2.15) by taking the first derivative $dG(r)/dr$ and setting it equal to zero:

$$G^* = \frac{16\pi\sigma^3}{3\Delta g_v^2}, \quad (2.15)$$

where G^* is the activation energy for nucleation. The activation energy G^* signifies the amount of energy required to create a nucleus with a critical radius. If the cluster (region of long range ordering) is very small the interfacial energy term will dominate so the cluster is unstable. Only if the size of the cluster exceeds the critical radius r^* (which is equal to $2\sigma/\Delta g_v$), it becomes stable because the interfacial energy term ceases to dominate and the nucleus has the chance to grow with one's own might. The critical nucleation enthalpy G^* originates from the supercooling of the melt. Nucleation takes only place at $T < T_{\text{liqu.}}$, i.e. via supercooling the melt, see (2.16):

$$G^* \approx \frac{1}{(T_{\text{liqu}} - T)^2}. \quad (2.16)$$

The critical radius of a nucleus r^* decreases with an increasing degree of supercooling. The principle curve is shown in Fig. 2.3 [538]. The smaller the r^* the more stable nuclei can develop. As consequence the rate of nucleation N depends on the degree of supercooling ($T_{\text{liqu}} - T$) and on the activation energy G^* for nucleation, see (2.17):

$$N = N_0 \exp -(G^*/kT), \quad (2.17)$$

where N is the rate of nucleation, N_0 is a pre-exponential factor and is equal to N at standard conditions, k the Boltzmann constant and T the absolute temperature.

However, (2.17) is only an approximation. This equation does not account for the kinetic barriers, which are a result of the number of ions, that have

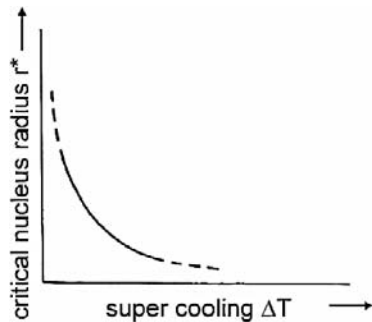


Fig. 2.3. Variation of the critical nucleus radius r^* with the supercooling ΔT of the melt [538]

to be moved and reorganised in a given volume necessary for a crystal with a certain composition to form from a disordered melt (see also Sect. 2.2.2). The process of nucleation is better described by (2.18):

$$J(T) = J_0 \exp - (G^* + E_D)/kT, \quad (2.18)$$

where $J(T)$ is the rate of nucleation including the diffusion of ions, J_0 is equal to J at standard conditions and E_D is activation energy of diffusion. Both quantities, G^* and E_D , depend on temperature, but in an inverse fashion. Therefore, the resulting curve $J(T)$ at $T < T_{\text{melt}}$ displays a maximum. Annealing a glass at a temperature corresponding to J_{max} results in the formation of as many nuclei as possible.

The above discussed expressions described the process of homogeneous nucleation. In this case the nucleus forms spontaneously in the supercooled melt and, therefore, the nuclei at which crystallisation eventually occurs are of identical composition with the later crystal. This process has the precondition that nucleation does not occur on bubbles (they are absent) or any other surface and boundaries. On the contrary, heterogeneous nucleation occurs at any surfaces in contact with the melt, such as impurities and the container walls. These nuclei are called heteronuclei. Heteronuclei are already in contact with the glass melt and the boundaries are established, so that only small or no work is required to create them, which means that G^* in (2.18) becomes very small or disappears altogether, which makes it easier for crystals to grow and lowers the temperature range in which crystallisation occurs. This effect is utilised in UV-induced crystallisation in the UV-sensitive glass FS 21 (Sect. 1.2.4). In this special glass Ce^{3+} loses an electron by UV radiation. This one is collected by Ag^+ which changes to a silver atom. This $\text{Ag}^{\pm 0}$ has a higher diffusion constant than Ag^+ (see Sect. 2.2.2) and is able to form Ag-clusters at relatively low temperatures. If they are big enough (critical radius) they become nuclei. Ag-nuclei, which act as the substrates for LMS growth, develop at temperatures almost 100 K [365] below the temperature at which normally homogeneous nucleation occurs (around 600°C) [306], if the glass is annealed once more.

The crystal growth can be described by following the arguments which were outlined above, however, in this case the ion transportation processes by diffusion must be considered much more. Frenkel [151] derived in (2.19) an expression for the crystal growth rate KG:

$$KG = A \exp(-1/kT)(E_D + (CT_0/\lambda\Delta T)), \quad (2.19)$$

where A and C are constants, k is the Boltzmann constant, T the absolute temperature, E_D the activation energy for diffusion, T_0 an equilibrium temperature for the crystal growth, λ the heat of two-dimensional condensation and ΔT the degree of supercooling.

All ions diffusing towards the growing nucleus are deposited at lattice points with the smallest G_0 , which explains the dendrite like growth of some

crystals (Fig. 1.41). The diffusion process is driven by chemical and thermal gradients.

The processes occurring during partial crystallisation of glass are not only of importance for the crystallisation of LMS in the UV-radiated regions of UV-structurable glasses (see Sect. 1.2.4), but also for the localised crystallisation of any glasses which can be used to tailor the properties of the material in confined “micro” areas. The partial crystallisation can be induced by means of local heating. The energy supplied has to be large enough to enable crystallisation but should be low enough to avoid the melting of surrounding glass. A focused laser beam is a suitable energy source to induce local crystallisation. The crystallisation should be performed at the temperatures optimal for both, the nucleation and crystal growth. However, temperature control within a glass is rather difficult when using the laser beam. Nevertheless, the energy supplied by the laser must provide the latent heating of the glass up to the crystallisation temperature but also the activation energy for crystallisation. Tammann [512] has found that the curves describing the nucleation process $J(T)$ and the crystal growth $KG(T)$ overlap (Fig. 2.4.).

A glass can be heated to a temperature which enables both processes simultaneously, i.e. nucleation and crystal growth. In order to use laser heating, the laser radiation has to be absorbed by the glass. A laser with a suitable wavelength for a given glass composition has to be chosen. Laser-induced crystallisation can be achieved in various ways; (1) the entire glass sample is heated close to the crystallisation temperature and only the activation energy required to induce crystallisation is supplied by the laser. However, this is technically very challenging. (2) Two lasers are used; an unfocused laser to heat the glass and a focused laser to induce crystallisation. Or (3) only one but well-controlled laser is used. Using laser-induced crystallisation, crystallisation patterns can be *written* by using a microdriven sample stage, which moves relative to the laser.

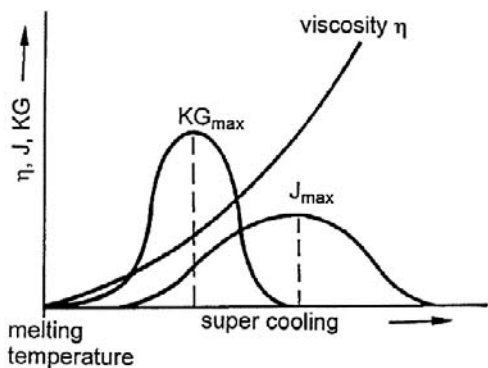


Fig. 2.4. Effect of the degree of supercooling below the melting temperature on the viscosity and rates of nucleation and crystal growth

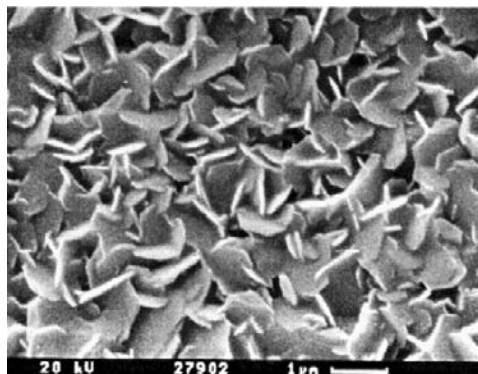


Fig. 2.5. Regions of barium hexaferrite crystals created in a $\text{BaO}-\text{B}_2\text{O}_3-\text{Fe}_2\text{O}_3$ glass by laser-induced crystallisation [250]

Figure 2.5 shows an example of patterning a glass using laser-induced crystallisation. The original glass consists of BaO , Fe_2O_3 and B_2O_3 in such amounts that $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ (BHF) can crystallise. BHF has hard magnetic properties. By melting and rapid quenching of the melt between two counter rotating, cooled rolls black glassy foils form. The wavelength λ of 1,064 nm of a Nd-YAG laser is strongly absorbed by the glass foils. Magnetic patterns can be *written*, created by laser-induced BHF crystallisation into the glass, if a controlled XYZ-stage is used. The resulting BHF-crystals are single crystalline and, therefore, magnetic as soon as they form.

A similar procedure was made recently by Honma et al. [237]. The authors used glasses in the system $\text{BaO}-\text{TiO}_2-\text{GeO}_2-\text{SiO}_2$, which are suitable for fresnoite-type crystallisation. The applied heat source was a cw-YAG (yttrium-aluminum-garnet) laser.

2.4 Enthalpy of Melting and Evaporation

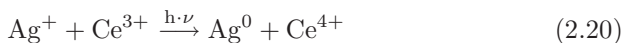
Glasses can be microstructured also by means of ablation. Material is heated until it evaporates. Laser radiation can be used to supply enough heat to vaporise glass. Since glasses do not possess long range order (crystalline structures), they have no well-defined melting and evaporating temperatures, i.e. glasses do not undergo first-order phase transitions. Instead of a well-defined melting point, the viscosity of a glass changes continuously as function of temperature (Fig. 2.1). The slope of the viscosity-temperature curve decreases with increasing temperature. *Practical* experiences indicate that a glass is homogeneously melted without bubbles if it has a viscosity of about 10 Pa s. The slope of the viscosity-temperature curve of a sodium lime silicate glass (Fig. 2.1) at this temperature is only 180 kJ mol^{-1} , which is much lower than the chemical binding energy $B \approx 420 \text{ kJ mol}^{-1}$ at room

temperature. The apparent discrepancy between both values is explained by the slow continuous softening of the glass in the whole temperature range above the transformation temperature. Therefore, it is not possible to define the melting enthalpy; instead the activation energy of viscous flow at different temperatures has to be estimated.

The same holds true for the evaporation enthalpy of glasses. A precise value for the evaporation enthalpy of a one-component glass, such as quartz glass (SiO_2) can be defined. However, already for a two-component glass, such as $\text{Na}_2\text{O-SiO}_2$ or $\text{K}_2\text{O-SiO}_2$, the evaporation enthalpy cannot be clearly determined anymore because of the presence of different types of chemical bonds, such as Na-O and Si-O (see Sect. 1.1.3). Na_2O evaporates at lower temperatures than SiO_2 . Nevertheless, Kröger and Sörström [312] published evaporation enthalpies E_E for a binary $\text{Na}_2\text{O-SiO}_2$ glass of $E_E = 290 \text{ kJ mol}^{-1}$ and for ternary $\text{Na}_2\text{O-CaO-SiO}_2$ glasses of $E_E = 355\text{--}545 \text{ kJ mol}^{-1}$. In case of the ternary $\text{Na}_2\text{O-CaO-SiO}_2$ glass the evaporation enthalpies exceed the chemical binding energy at room temperature. The most chemical bindings are broken; the glass evaporates.

2.5 Redox Equilibria

The redox equilibrium, see (2.20)



was already discussed in Sect. 1.2.4. If a glass contains multivalent elements as main components or as dopants the possibility that redox reactions occur has to be considered. If such reaction occurs within a glass it will affect all its properties.

The redox equilibria are of great importance for the following processes:

- Heterogeneous nucleation in photostructurable glasses
- Electrical conductivity/resistance of glasses containing lead oxide
- The colouring of glasses
- Refining processes, see also Sect. 3.2.1

Whether or not redox reactions can occur in glasses depends in the first instance on the valency of the ions present but is strongly influenced by the:

- Coordination number of the multivalent element (see Sect. 1.1)
- Neighbouring coordination polyhedra of the polyvalent ions [538]
- The melting temperature and residence time of the melt
- Chosen raw materials to produce the glass [365]
- Occasionally the addition of reducing or oxidizing agents to the melt
- Relative humidity of the atmosphere, the presence of crystal water in the raw materials and the water content of the batch

It is also obvious that all of the above are interrelated. Detailed reviews of redox processes in glasses can be found in the literature [29, 43, 371, 414, 538].

Because of interactions between various redox pairs it is rather difficult to understand the redox processes occurring in glasses. This requires specially designed experiments of well-defined glass compositions, see also Rüssel [433]. Redox processes in glasses are very difficult to generalise. It is virtually impossible to transfer experiences from one glass composition to another.

Melting and Forming Glass Half Products for Microstructuring

3.1 Processes During Batch Melting

A ‘batch’ in microelectronic processing describes an array of chips on a silicon wafer, which is processed at the same time. In glass melting, a ‘batch’ describes a homogeneous mixture of all raw materials used in a predefined mass ratio. The premixed batch is placed in a melting vessel¹ together with cullet of the same composition. During the initial heating the premixed raw materials undergo a series of chemical reactions and physical changes before melting. However, turning this melt into a homogeneous liquid requires further processing such as the removal of bubbles, called fining, homogenisation and conditioning.

This section provides a brief overview of the processes occurring during the initial heating of the batch and its conversion to a melt in the vessel up to the highest temperature. As stated in Sect. 2.4, this temperature must not be confounded with a physically well-defined melting temperature of a crystalline material. The melting temperature as defined by a glassmaker during batch melting represents from a technical point of view the temperature corresponding to the lowest viscosity during the melting process. A low viscosity liquid is required to allow bubbles to rise through the melt in an acceptably short time.

The physico-chemical reactions that occur during the batch melting comprise different types of heat consuming reactions, such as the release of moisture and crystal water (from for instance caoline) from the batch; first solid-state reactions between the different raw materials; and the decomposition of carbonates, causing the release of CO₂ and the formation of eutectic melts. The eutectic melts form by reactions between network modifier and a

¹ A melting vessel containing several tonnes of glass is called tank, and the one containing only some kilograms is called pot, or it is a special Pt-lined crucible adapted to the requirements of optical glasses and glasses for the microstructuring.

part of the network forming oxides. The glasses mainly used for microstructuring applications, as described in this book, are silicates, and the following ternary eutectic systems are important:

$\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ [362]

$\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ [361]

$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ [431]

The lowest ternary eutectic temperatures for these systems are around 800°C; however, because of the presence of other oxides, which lower the eutectic temperatures, in most batches initial partial melting of the batch occurs in the temperature range from 600 to 700°C. The raw material particles react with each other at the contact points and melt eutectically. Slowly thin melted surface layers are formed. The capillary action arising by the formation of melted surface layers pulls the batch particles together causing particles to sinter, that means to agglomerate and to entrap remaining air, H_2O vapour and CO_2 , which is the reason for the formation of relatively large (in the order of 1–4 mm) gas bubbles. At the end of the initial batch melting it still contains the following:

- Solid sand grains with an eutectically melted surface
- An eutectic melt formed by the reaction between the network modifier containing raw materials with the sand particles
- Large gas bubbles

As the temperature increases, the dissolution rate of network forming particles, such as sand and alumina, increases. SiO_2 does not really melt, but is corrosion-melted in a temperature-assisted reaction between SiO_2 and the surrounding eutectic melt. For this reason, the final melting temperature is not 1713°C (that of pure SiO_2), but significantly lower, often about 1300°C, which however depends on the glass composition. This corrosion-like process is diffusion controlled, which means that the larger the specific surface area of the sand particles, see (2.9), the larger the contact area for mass transfer and so shorter the diffusion ways; i.e. the larger the sand particles, the slower the melting process. Natural occurring sand has a grain size ranging from 100 to 500 μm . Larger particles should be removed for instance by sieving.

In the case of eutectic melting of the sand particles, the driving SiO_2 concentration gradient is that between the sand and the composition of the surrounding eutectic melt. SiO_2 leaves the sand surface, which leads to an increase of the SiO_2 content in the melt at the solid/melt boundary, which in effect reduces the concentration gradient of SiO_2 . To accelerate the SiO_2 transport into the melt its flow behaviour is very important. The eutectic dissolution of SiO_2 leading to the increase of the silica concentration in the melt causes its viscosity to increase rapidly, which further reduces the dissolution rates. To compensate this effect the temperature and the residence time in the melting vessel has to be increased.

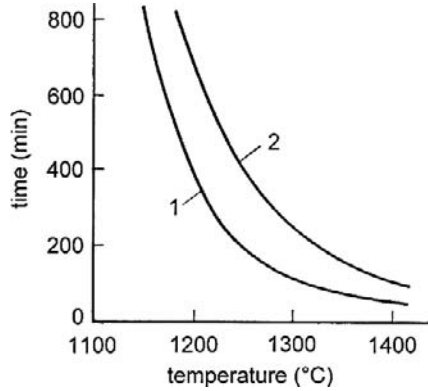


Fig. 3.1. Dependence of the required residence time on the temperature for batch melting of quartz sand having a particle size range of 125–150 μm (1) and 250–430 μm (2) in a 16.5 Na₂O–10 CaO–73.5 SiO₂ [mass %] glass (Nölle, 1978)

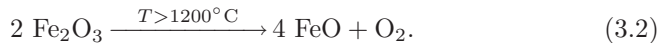
A very generalized equation describing the solution of quartz sand in the glass melt was derived by Nölle [383] (3.1):

$$\dot{m} = \beta A \Delta c, \quad (3.1)$$

where $\dot{m}$ is the mass flow rate of SiO₂ from the quartz particle into the eutectic melt, β is the composition-dependent transition number of a material, A is the surface area and Δc is the concentration gradient.

Figure 3.1 summarises how the temperature and the particle size of quartz sand determine the required residence time for batch melting of a sodium–calcium–silicate glass (described in Sect. 1.2.2.).

During this phase of the melting process, high melting salts, such as for instance Na₂SO₄, decompose releasing SO₃, which causes large bubbles and - indirectly - stirring. Oxygen is produced if the raw materials contain iron oxide as impurity or other oxides of polyvalent elements (see Sect. 1.2.3) by a shift of the redox-equilibrium to the more reduced site, which alters the state of oxygen from chemically bound to physically dissolved, as given in the reaction (3.2):



Such redox reactions of oxides of polyvalent ions cause the formation of very small oxygen bubbles, called seeds (which should not be mistaken with nuclei, often called seeds), because the solubility of molecular oxygen in the melt is very much smaller than that of atomic oxygen.

At the end of this stage the melt has the following properties:

- All raw materials are completely molten, which means that all long range orders that existed in the raw materials particles are destroyed
- The viscosity of the melt is very high compared with other liquids, because of the high SiO₂ content of the desired glass

- The chemical composition of the melt is inhomogeneous because of insufficient mixing of the components by diffusion and flow
- Furthermore, the melt contains large and also very small gas bubbles

To eliminate bubbles and chemical inhomogeneities, a fining and homogenisation step has to be followed. These process steps are described in the following section considering the problems that may occur if a microstructured glass device shall be produced.

3.2 Special Problems that Have to be Observed During Fining, Homogenizing and Conditioning the Melt

3.2.1 Microbubbles

Fining is the removal of gaseous inclusions, i.e. large bubbles that formed in the interspaces between the original raw material particles and also small seeds, from a melt. To understand the problems of fining, the solubility of gases in glass as a function of the temperature and the SiO_2 content of the melt has to be considered. The solubility of gas in a glass melt decreases with increase in SiO_2 content and increasing temperature, which supports the degassing of the melt during fining. In some cases, the solubility of noble gases in glass melts can also be of interest, which is described by Opyd et al. [389, 390]. Rongen et al. [427] have investigated the influence of water vapour, helium gases, air and combustion gases on the melt fining.

Large bubbles have to be eliminated from glass melts as they are considered mistakes in almost all commercial glass products (except for antique glass for lamps or windows). Large bubbles can be removed during the fining process by the buoyancy caused by the density difference between the gas and the liquid at the fining temperature, which causes the bubbles to rise upwards to the surface of the melting level (so-called mirror); i.e. the larger the bubbles, the larger the buoyancy. Because the density difference is not very much dependent on the temperature, the buoyancy itself is not so temperature dependent. To estimate the velocity of rise of bubbles in a melt, the viscosity at fining temperature has to be considered. The higher the viscosity of a melt the higher is the inner friction between the bubbles and the melt. The velocity of bubble rise v_b can be calculated using the following equation (3.3):

$$v_b = \frac{gr^2\Delta\rho}{3\eta}, \quad (3.3)$$

where r is the radius of a bubble, $\Delta\rho$ is the density difference between gases and glass melt, η is the melt viscosity and g is the acceleration due to gravity. A bubble with a radius of $r = 3 \text{ mm}$ and a density difference between the melt and the gas phase of $\Delta\rho = 2.4 \text{ g cm}^{-3}$ at a melt viscosity of $\eta = 10 \text{ Pa s}$ gives

a bubble rise rate $v_b = 26 \text{ m h}^{-1}$. A bubble of this diameter needs roughly 2 min to move from the bottom of a 1 m tank through a melt to the surface. However, if a bubble has a radius of $r = 0.3 \text{ mm}$ it moves only upwards with a rate of $v_b = 26 \text{ cm h}^{-1}$, which means it takes almost 4 h to rise to the surface, which sets a practical limit for the fining operation. The removal of smaller bubbles and seeds by simply waiting is just not feasible and must be assisted technically.

However, it is the number of small bubbles, i.e. seeds, present in a glass that determines whether this glass is suitable for microstructuring or optical applications. It is well known that seeds can be removed by the addition of small amounts of raw materials to the batch such as chlorides, sulphates or nitrates, called fining agents, which decompose at temperatures between 1200 and 1400°C releasing large amounts of gases that form large bubbles. These large bubbles rise rapidly upwards collecting the seeds on the way to the surface of the melt. Also, As_2O_3 and Sb_2O_3 are effective and commonly used fining agents. They release gases by undergoing redox reactions. Pigeonneau [405] explains the possible connections between gases dissolved in the glass melt, bubbles and redox reactions in the melt. The author derives a model that describes the gas content of the bubbles in dependence on the residence time at fining temperature.

The process can be completed by a bubbling from the outside of the melting vessel, that means, large bubbles can simply be introduced into the tank or crucible by bubbling compressed air through holes at its bottom. The large bubbles that form and rise upwards again collect the seeds, which are shown in Fig. 3.2. A further possibility for driving small bubbles out of the melting tank is proposed by Faber et al. [140]. They use high power ultrasound for an accelerated fining.

The fining of special glasses can also be assisted by applying centrifugal forces to the melt. Equation (3.3) must be extended by a factor that gives the enlargement of the acceleration compared with the acceleration due to gravity. This type of fining is used for quartz glass.

In exceptional cases, the formation of seeds can be prevented by thin layer melting. In this case one layer of the batch is melted after the other, which however results in rather small throughput rates. A typical example that utilises this principle is the chemical vapour deposition (CVD) of pure or doped SiO_2 for light-guide fibre preforms [167].

If the bubbles do not rise fast enough through the melt, it can be supported additionally by melt flow in the melting vessel, which will help to move the bubbles to the surface. This process is described in the following section.

Figure 3.3 makes clear the work performed by a rising bubble against the highly viscous glass melt, which causes the bubble to deform elliptically. Bubbles in a glass which are deformed in such a way as shown in Fig. 3.3 can usually be found in ill-fined melts. Aiuchi et al. [2] have derived drag laws for various bubbling conditions to describe this phenomenon.

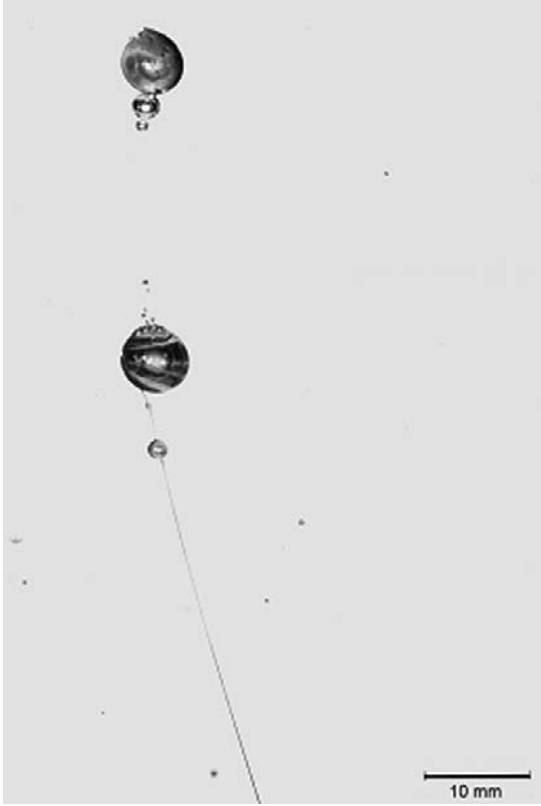


Fig. 3.2. Rising large fining bubbles collect small bubbles. Coalescence causes the buoyancy to increase, which allows transporting small bubbles faster to the melt surface [539]

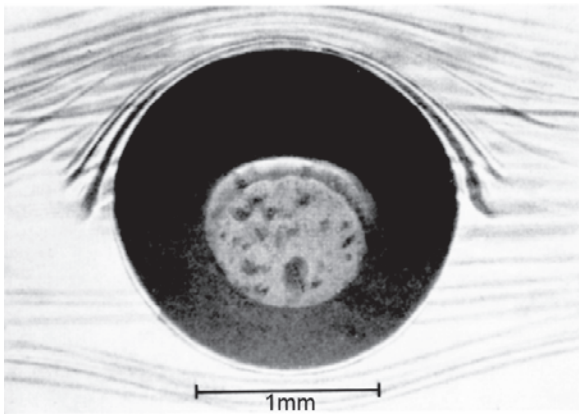


Fig. 3.3. Bubble moving upwards deforms striae claddings [46]

In most cases a combination of all the methods described above allows for the effective elimination of seeds. If it is not possible to avoid the formation of seeds or remove them satisfactorily, it is still possible to increase the fining temperature, which will result in a reduced melt viscosity. However, the temperature cannot be increased without limits as the melt will start to evaporate. In particular, the light oxides, such as boron oxide, tend to evaporate.

If the gas bubbles reach the surface of the melt bath, then they must be able to push through the melt/air interface, which requires additional energy.

The appearance of exactly round bubbles in the cooled glass is due to the following phenomenon, which is called reboil. The gas solubility in the melt is temperature dependent. It increases with decreasing temperatures, which causes very small bubbles to disappear during cooling by solution. However, seeds start forming again from an apparently bubble-free material during reheating because of the smaller solubility of gases in glass melts at higher temperatures. The seeds forming under these conditions are so small that the buoyancy will not result in any upwards movement, and therefore remain perfectly round. Larger bubbles do not form during this stage to assist the removal of these seeds. Reboil occurs in not well temperature-controlled feeders, i.e. in the junction between melting vessel and the forming equipment or during thermal bonding of glass wafers.

Large bubbles are usually not a problem for microstructuring as they are already removed during glass production, or the following quality control is leading to the rejection of the product. Small bubbles, however, are often invisible with the bare eye, and so it might be possible that glass wafers containing seeds are used for microstructuring. Seeds can usually be detected only under a high-resolution microscope. Testing glass-half-products prior to any microstructuring is recommended to avoid the rejection of the product.

3.2.2 Microinhomogeneities

The melt produced in the initial stages of the batch melting is chemically very inhomogeneous because of insufficient mixing of the raw materials and of the batch during melting and the reactions between the melted glass and the surrounding refractory materials (undissolved stones). Therefore, a processing step follows the fining to homogenise the chemical composition of the glass melt. This homogenisation process is of particular importance for microstructuring as its success depends on the local chemical composition of the glass piece. Locally, chemical variations of the glass melt affect all properties of the solidified glass. In window sheet glass this localised chemical inhomogeneities can result in visible gross defects, such as cords or striae, which are regions having a chemical composition different from the bulk material, resulting in local refractive index variations. In glasses used for microstructuring, such inhomogeneities would result in locally different etching rates of the glass or the variable ability of the glass to partially crystallise.

Two processes contribute to the homogenisation of the glass melt: melt flow (Sect. 2.2.1) and diffusion processes (Sect. 2.2.2). Temperature enhances both processes, which suggests performing the homogenisation at the temperature used for fining. However, the energy costs are prohibitive, and therefore homogenisation is usually performed at temperatures of about 100 K below the fining temperature corresponding to a melt viscosity of about 100 Pa s. Some degree of chemical homogenisation of the melt was already achieved during the fining process by the mixing action of the rising bubbles. However, the production of an acceptably homogeneous glass requires additional homogenisation methods and time for diffusion. The initially heterogeneous character of the melt, i.e. the presence of concentration gradients, drives the diffusion process. However, the diffusion coefficients are strongly dependent on the temperature and the valency of the diffusing ions. In particular, the highly valent cations, such as Ti^{4+} and above all Zr^{4+} , have very small diffusion coefficients. Therefore, simply waiting long enough is impracticable technically for chemical homogenisation to occur via diffusion.

An increasing melt flow may destroy the cords and striae by elongating them, what simultaneously results in an increased contact area between them and the surrounding bulk glass, which results in an increased diffusion rate (see (2.9)). The longer and narrower the cords and striae, the less visible they become. If the thickness of the cords and striae falls below the wavelength of visible light they become invisible for the naked eye, which might be sufficient for window sheet glass but it is certainly not for optical glass or glasses used for microstructuring. In microstructuring, micrometre-sizes features have to be fabricated, which requires that any inhomogeneities, if present, are in the nanometre range. The effect of laminar flow on elongation of cords is shown in Fig. 3.4.

Temperature gradients are useful in producing laminar flow in the glass melt. They arise in all types of melting vessels and cause density gradients in the melt. Such gradients cause on the other hand buoyancy, which acts like a thermally induced stirrer. The higher the temperature gradients the more intensive is the stirring action. The following three figures show the flow patterns induced by thermal stirring in a pot melt (Fig. 3.5), a flame-heated

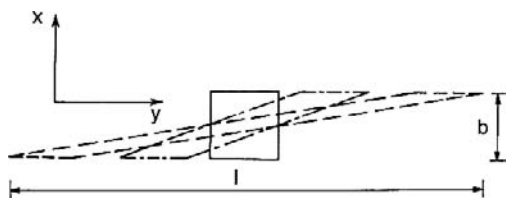


Fig. 3.4. Elongation of chemical inhomogeneities, such as cords and striae, by laminar flow (Nölle, 1978)

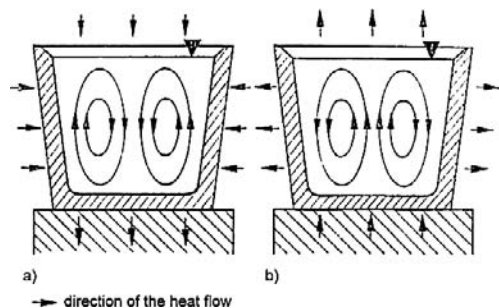


Fig. 3.5. Laminar flow in a glass melting pot during heating (a) and cooling (b)

tank furnace (Fig. 3.6) and in the vicinity of the electrodes of an all electric melting furnace (Fig. 3.7).

The buoyancy caused by the density gradients may be assisted by mechanical stirring using a paddle stirrer. Because of the aggressive environment of glass melt the agitators corrode very rapidly, which results in impurities, such as stones and additional cords for instance in case of a mullite or ZrO_2 -containing stirrer, or small Pt-particles that can act as heterogeneous crystallisation nuclei or affect the transmission of optical glasses. This is state of the art for optical glass products. More recently, mechanically assisted homogenisation became more important for sheet glass used in flat television screens or in photovoltaic devices and of course for the preparation of glasses for microstructuring.

Osmanis et al. [393] used external magnetic fields to create additional Lorentz forces in all electric melt tanks, feeders or bushings for glass silk production. This Lorentz forces act as magnetic stirrers because these forces induce additional flow (Fig. 3.8) and influence the temperature gradient in the melt and thereby improve mixing [253]. This principle can be used in special melting equipment to produce very homogeneous glass products.

A glass suitable for microstructuring must be as homogeneous as possible. Great efforts are actually made to model and simulate what happens during all steps of the glass melting process, see Thielen et al. [516], Fasilow and Symoens [143], Van Nijnatten [533].

3.2.3 Conditioning: Thermal History of Glasses

The viscosity of melt during the homogenisation is too low to form glass products. At the homogenisation temperature the melt has a viscosity of 10^2 Pa s, which only allows for melt casting into a mould. To be able to form stable glass products by other means the melt viscosity has to increase, which is achieved by cooling the melt by about further 100 K from the homogenisation temperature. A melt viscosity of about 10^3 Pa s usually allows glass forming (Figs. 1.11 and 1.12). However, not only the average viscosity of the melted

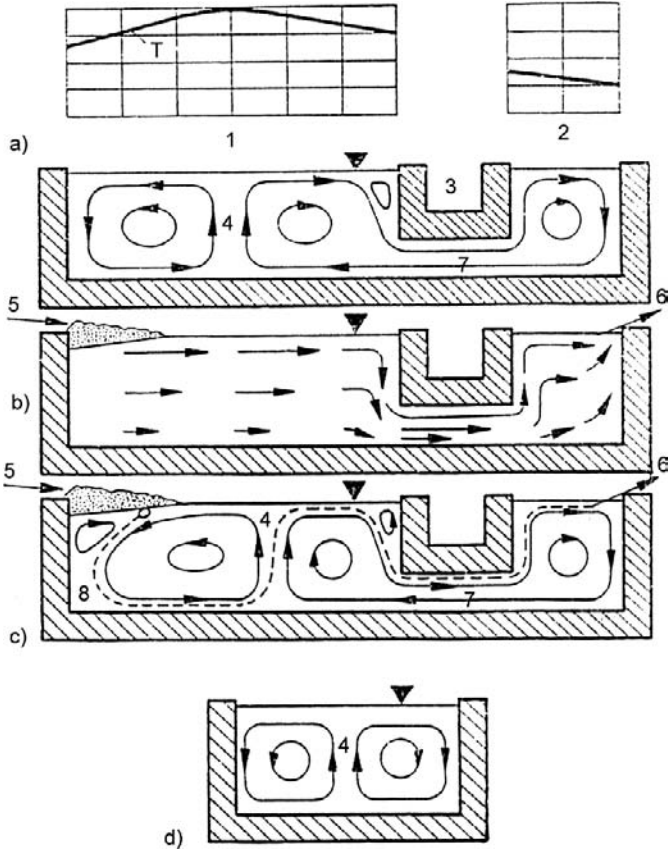


Fig. 3.6. Laminar flow in a two-room (for melting and conditioning) flame-heated tank. The spring zone has the highest temperature, see the upper picture. (a) Flow induced by temperature gradients, (b) flow induced by mass taking out, (c) both processes overlap, (d) shows the cross-section, (1) shows the temperature profile in the melting vessel, (2) the temperature profile in the conditioning vessel, (3) the throat, (4) the spring point, (5) the charge/batch, (6) the point where the melted glass gathered, (7) the back flow and (8) the route of a raw material particle without mixing (short circuit)

glass volume is important, a homogeneous melt viscosity of 10^3 Pa s has to be guaranteed all over throughout the melt, which means that no temperature gradient should be present. This situation is very different from that of the homogenisation process. As a consequence, the part of the equipment for conditioning has to be separated from the part in which the homogenisation takes place. This part of a melting furnace is called conditioning tank, which is shown at the right-hand side in Figs. 3.6 and 3.7. In the conditioning tank, the glass is cooled down in such a way that possibly no temperature and

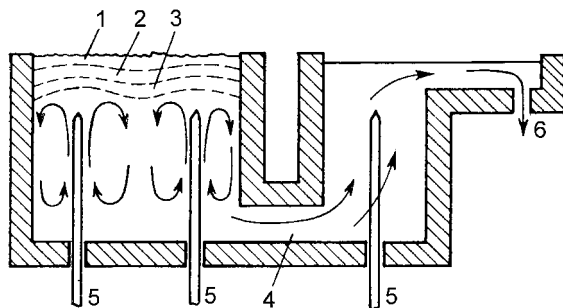


Fig. 3.7. Laminar flow around the electrodes in an all electric melt tank (Nölle, 1978), where 1 represents the batch, 2 the zone of batch melting, 3 the zone of melt fining, 4 the throat, 5 the electrodes and 6 the point where the melted glass is removed

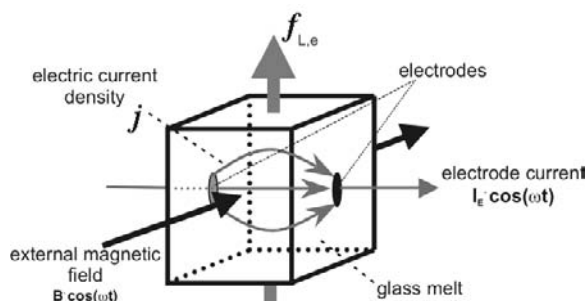


Fig. 3.8. Schematic presentation of Lorentz force density $\vec{f}_{L,e}$ in alternating current $I_E \cos(\omega t)$ heated glass melts crossed with an alternating external magnetic field $B \cos(\omega t)$ with the same frequency; where $\vec{j}$ is the electric current density in the glass melt and ω the angular frequency of the electric current and the magnetic field [253]

chemical composition gradient result that should guarantee the melt viscosity of 10^3 Pa s throughout the vessel.

During the conditioning period, further but slower diffusion processes aiding the homogenisation of the melt continue to occur. However, at the same time undesired partial crystallisation might occur in so-called dead, cooler corners of the conditioning tank. The Tammann curves (curves of J and KG) overlapped with the viscosity–temperature curve (Fig. 2.4) are useful to estimate the problematic temperatures at which nucleation and crystal growth can occur. The temperatures are similar to those required for forming, however, slightly below the conditioning temperature. Therefore, the favourable temperature conditions for undesired crystallisation could arise in the dead corners of conditioning tanks, such that nuclei form and/or even crystals grow, which will not affect the product as long as the melt stays in the cooler corners of the conditioning tank. If, however, more molten glass is required

during the forming process, the nuclei or crystals can flow out of the dead corners and end up in the glass product, causing mistakes and rendering the glass part useless for microstructuring. Glassmakers call this process devitrification. Most glasses have only a small tendency for devitrification. The melting methods are usually optimised to avoid dead cooler zones in the process. Figures 3.9 and 3.10 provide examples of devitrified glasses, showing the crystals in the glass and at the product surface.

The residence time of the melt in the conditioning tank (and later in the feeder) also affects the ordering of the glassy network, i.e. the interstitial volume of the silica tetrahedra rings, see Sect. 1.1.5, as well as the distribution of network modifier cations and the inclusion of gases. The longer the conditioning time the denser the glass structure becomes and approaches to equilibrium.



Fig. 3.9. Devitrite $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ crystals in a soda-lime-silicate glass having the characteristic shape of a shavingle-brush [539]

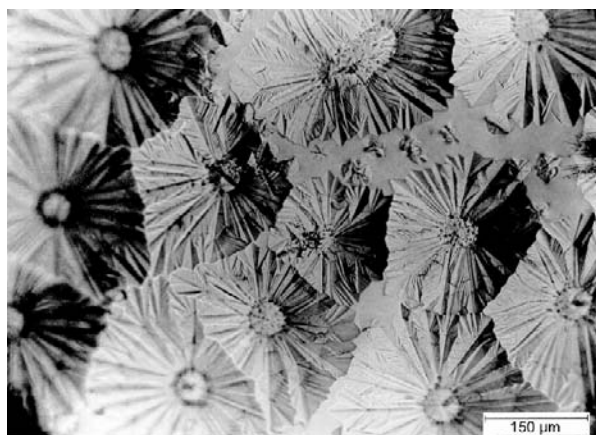


Fig. 3.10. Tridymite crystals at a glass surface [539]

The difficulty to allow for the appropriate residence time in order to establish a thermodynamic equilibrium but avoid undesired devitrification is even more important during the forming and the cooling of glass pieces. The slower the cooling rate during the forming of a glass part, the smaller is the thermal expansion coefficient of the final piece and also the shrinkage during post-processing, which is particularly important for the production of flat TV-screens and microstructured glass devices. A slow cooling rate also leads to a decrease in the electrical conductivity, a higher refractive index and dielectric constant of the final glass product. Also the phase separation (see Sect. 1.1.6) is influenced by the conditioning time. All these effects are commonly lumped together and called thermal history of a glass, which must be considered for potential glass applications in microstructuring.

3.3 Equipment for the Production of Glass Half Products

3.3.1 Melting

This section is intended to provide only a brief overview of the melting of a final glass product starts with the preparation of the batch, i.e. the weighting and mixing of raw materials, because an ill-mixed batch is often the reason for inhomogeneities in the glass. The homogenised batch is transported and stored before filling the tank. In the case of a tank melt the filling takes place automatically via a charging gear, which is controlled by a glass-level controller in the tank. To guarantee a steady glass supply for the forming process, the glass level in the tank should not vary. Depending on the size and shape of the glass products, variations of the glass level in the basin of the tank of around ± 1 mm can be tolerated. The batch is charged onto the molten glass in case of flame-heated tanks or on top of the still to be melted batch if all electric melt tanks are used (Figs. 3.6 and 3.7). Once more, the batch must be homogeneously mixed. In general, the batch is charged together with cullet of the same composition in order to accelerate the heating and melting of the raw materials. One has to take into consideration that some raw materials tend to get dusty and to evaporate, and must consider this fact with weighting.

The five stages of the melting process as described in Sects. 3.1 and 3.2 occur in the melting equipment. These processes occur in chronological order in a discontinuously working pot furnace (Fig. 3.5), or parallel in different places in the continuous tank furnaces. Many types of melting furnaces are used. A specific example of a continuously working furnace is shown in Fig. 3.11.

Both tanks of the cross-fired furnace (Fig. 3.11) are standing on steel supports and the walls are fixed by rods. The flames generated by the burners (3) cross the melt level at a right angle to the melt stream in the melt basin (1) and leave the room above the glass level through the opposite burner port. The

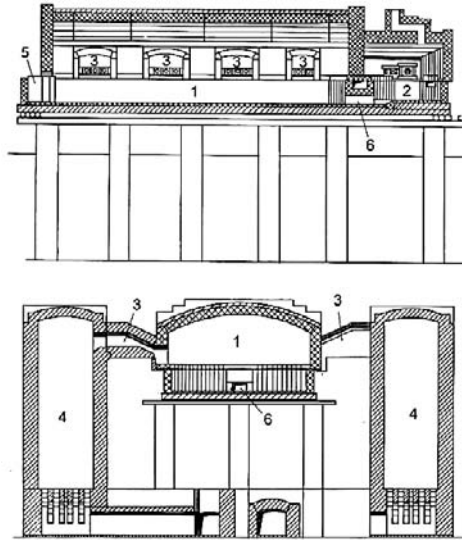


Fig. 3.11. Two-house fuel oil heated cross-fired furnace having two tanks for melting and conditioning or working (Nölle, 1978), where 1 is melting basin, 2 is the conditioning zone (working chamber), 3 is the burners, 4 is the regenerator or checker chamber, 5 is the doghouse or charging station and 6 is the throat

direction at which the flame heats the batch is switched about every 30 min. The hot exhaust gases before being discharged via the chimney pass through the checker chamber (4) where the heat is used for heating the refractory bricks that store the heat, thereby cooling the exhaust gas to a temperature around 700°C. This is still high enough for a following preheating batch or cullet before the exhaust gases reach the chimney. When the flame direction is switched, the cold air used for the combustion reaction passes the heated refractory bricks. Now these refractory bricks preheat the combustion air by heat transfer. This regenerative system saves energy. Besides this, the air used in combustion can also be preheated in the recuperator. It is a heat exchanger fit for high temperatures, which allows recovering waste heat from the hot exhaust gases. It acts continuously with separated, crossed streams of heated exhaust gases and cold combustion air.

Because the combustion of natural gas or oil takes place with air, its nitrogen part oxidises to the problematic NO_x . The amount and precise composition of NO_x strongly depend on the preheating temperature of the air and the combustion temperature. Beerken [30] deals with possibilities to reduce the NO_x emission.

The flame arrangement may be cross-fired, as shown in Fig. 3.11, or like an U. In this case two burner ports are positioned at the end face of the tank. The flame comes out of one burner port, heats the melt, returns at the wall

over the throat (this is the connecting channel between the melting basin and the working chamber) and leaves the tank through the other burner port.

The melt flow is driven by two processes: the withdrawal (gathering) flow and the convective flow, which is caused by buoyancy (Fig. 3.6). The batch materials are charged and undergo, see also Sect. 3.1, various physico-chemical reactions in the initial heating process, followed by melting, fining (which possibly takes place in the middle of the melting basin where the thermal spring zone is) and homogenisation. Then the material flows through the throat and is conditioned in the working chamber. Often, bridge walls can be found in the basins that assist the melt homogenisation by changing the flow patterns.

Another glass melting method utilises the ion conductivity of the melt at elevated temperatures. Most commercially available glass products are electrical insulators at room temperature, because most ions except the small monovalent ions, such as Li^+ , Na^+ or Ag^+ , are so strongly bound and are hardly able to diffuse at room temperature. However, the ionic conductivity of glasses increases with increase in temperatures, especially above the transformation range (see Sect. 1.1.4). The diffusion coefficients of ions increase and allow for the charge transport via ion diffusion. The electrical resistivity (the inverse of the conductivity) as a function of temperature for silicate glasses decreases drastically with increase in temperature (Fig. 3.12).

If the specific electrical resistivity of the glass at elevated temperatures drops below a threshold of about $40 \Omega \text{ cm}$, the glass becomes a practically

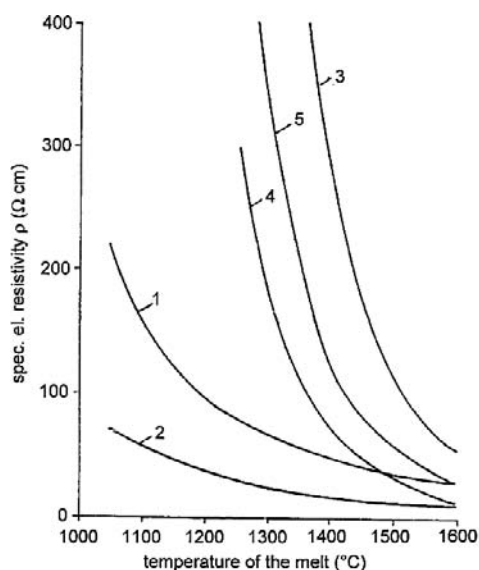


Fig. 3.12. Specific electrical resistivity of a Pyrex-type glass (1), Neutral-glass 4.9 (2), alkaline free Alumo-Boro-Silicate glass (3), E-fiber glass (4) and an alkaline poor Alumo-Boro-Silicate glass (5) melt as function of the temperature [486]

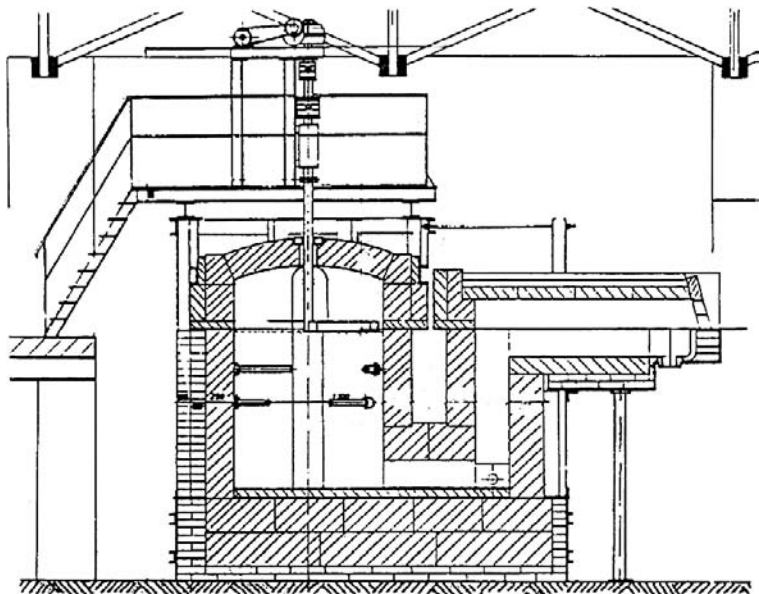


Fig. 3.13. An all-electric melt furnace with side electrodes in two levels [551]

useable electrical conductor. The heat generated by applying an electric field between electrodes positioned directly in the glass can be used to melt it. An all-electrically heated tank furnace is exemplarily given in Fig. 3.13.

An all-electric melting furnace (Fig. 3.13) consists of a melting basin (left), a throat (middle), a working or conditioning chamber (right) which is followed by a feeder. The electrodes are positioned horizontally in two planes, which allows for a good temperature control. Because of this particular arrangement the glass flow deviates from that shown in Fig. 3.7. The batch is charged through the centre of the crown and distributed by a rotating blade covering the melting glass completely.

The type of melting equipment used depends on the glass composition, the required melting temperature, the quality specifications and the amount of glass produced. Often small, discontinuously working pots or special electrically heated furnaces with Pt-crucibles already fulfil many requirements. However, a detailed description is beyond the scope of this book. The reader is referred to the following review books [5, 486, 526].

Some remarks about feeders are necessary, because its function assists the conditioning of glasses. An ill-controlled feeder might even cause reboiling (see Sect. 3.2.1). The main task of the feeder is the transport of the molten glass from the working chamber of the furnace to the forming machine. The length of the feeder varies between 1 and 10 m. The transport of the flowing melt is based on the principle of communicating containers. If the melt stream attains the forming station, its viscosity should be 10^3 Pa s (see Sect. 3.2.3).

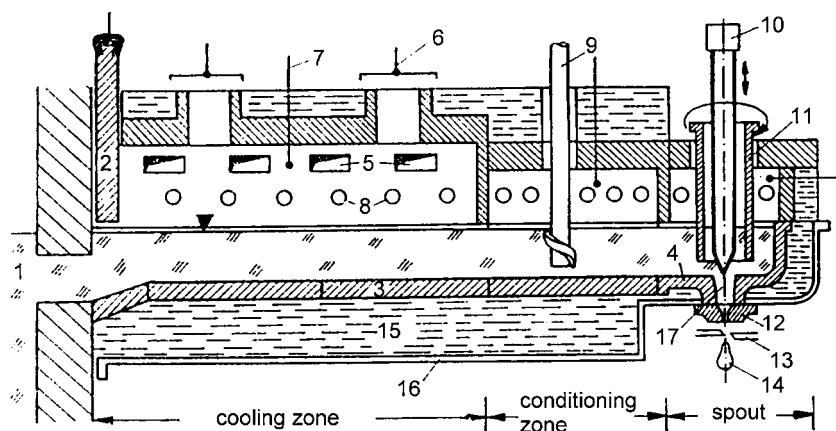


Fig. 3.14. Longitudinal cross-section through a gob feeder, where 1 is the connection between working chamber of the furnace and feeder channel, 2 is the feeder gate, 3 is the refractory bottom of the channel, 4 is the feeder nose/bowl, 5 is the entrance of cooling air and 6 its exit, 7 is a thermocouple, 8 are heating rods or a burner, 9 is a stirrer, 10 is the plunger, 11 is a revolving tube, 12 is the orifice ring or bushing, 13 is a pair of scissors, 14 is the gob, 15 is the thermal insulation, 16 is the steel framework and 17 is the spout

Therefore, the actual temperature in the conditioning tank of the furnace is about 30 K higher than that in the feeders head in order to compensate for cooling of the melt during its transport.

The used forming process depends on the desired glass product. The melt stream, with a certain glass mass in a given time and of a uniform viscosity, must leave the feeder as a broad ribbon for making sheet glass, as a continuous rope for making tubes or as drops (gobs) for press forming or blown products. The provision of a melt stream with a uniform viscosity is rather difficult. Figure 3.14 shows a schematic representation of a gob (drop) feeder, consisting of the entrance, a channel with the cooling and conditioning zones and the so-called spout.

The flowing melt at any place within the channel is directly surrounded on three sides by refractory bricks and on top by air, which results in different temperature gradients in all directions. The temperature gradient can be compensated by careful heating and good thermal insulation. However, the problem amplifies near the spout where the melt is surrounded on four sides by refractory bricks, causing the temperature gradient to increase. To achieve as homogeneous a temperature profile throughout the melt as possible the plunger moves in a revolving tube to form gobs. A temperature gradient in the gob results in a viscosity gradient, which affects the shape tolerances of products. Lets recall (1.2), $\tau = \eta(T)D$, and assume that the gobs form under the action of constant gravity, then it becomes obvious that the melt flows in

the hotter zone of the glass volume more rapidly than it does in the cooler zones, which gives rise to undefined shapes and mass distribution of the gobs. Temperature gradients in the gobs cause different wall thicknesses of the hollow glass articles formed. The use of screw plungers reduce this problem and allow for precise dosing of the ejected glass volume.

In the case of ribbon feeders, the problems are thickness deviations in the ribbon cross-section, wedge-shaped sheets and warp in the final product. In particular, deviations in the thickness of glass sheets or wafers affect the printing of thin film transistors on glass sheet or of masking the glass wafers negatively (see Sect. 1.2.4), which can give rise to gaps causing geometry deviations in UV lithography.

These short remarks about the feeder should illustrate its signification for production of high quality glass half products fit for microstructuring.

3.3.2 Forming

In principle all glass-forming methods can be used to produce glass half products for microstructuring. Because of the high demands on the reproducibility and tolerance of any geometric shape most glass products are machine made. Handmade glass products are still used but only for specialty and decorative glass articles because of the limitations with respect to homogeneity and geometrical tolerances. To improve the quality, i.e. the tolerances and optical finish, many glass products used in microsystems have to be ground and polished, which increases the production costs. Moreover, the chemical behaviour of the produced surfaces is of interest. Any polishing that follows the production process will also lead to the modification of the surfaces of the produced glass articles.

From all conceivable methods to shape glasses for microsystems, press forming and the float technology for flat glasses are the most important techniques used, which is followed by drawing of rods, tubes or thin glass; rolling and blowing of specially shaped products are also applicable. In exceptional cases and if necessary, only small quantities of the so-called optic-technology is used, which consists of casting a block, followed by cutting, grinding and polishing the glass into the desired half product.

Pressing

Pressing of glasses is widely used to produce large quantities of glass commodity products, such as tableware or traditional TV panels. Each article is formed individually in temperature-resistant cast-iron or steel moulds with extremely smooth surfaces. Its inner surface is post-processed by coating, eroding or polishing. The mould is split and consists of a metal form defining the outside form (wall) of the glass piece and the bottom form, which can be used also like a push-up, and a plunger, which defines the insight shape. Figure 3.15 shows a schematic illustration of a pressing tool. To compensate

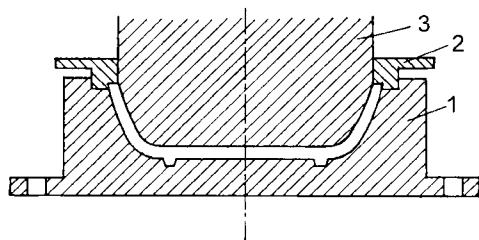


Fig. 3.15. Schematic illustration of a tool for the production of bowls via press forming. 1 is the mould, 2 is the pressing ring and 3 is the plunger

for the varying volume of not exactly dosed gobs and to limit the upper edge of the product, a spring cage and a pressing ring are used. The mould can be mounted on the desk of a single station or on a multistation rotating (carousel) table. The gobs fall from the feeder bowl into the mould, where they instantly flow under gravity. The plunger moves down and presses the melt into the predefined shape.

Pressing glasses is very sensitive to the process temperatures of the mould and the plunger. On the one hand, above a certain temperature, the so-called sticking temperature, the glass will stick to the mould. This process is very complex and depends on the compositions of metal mould and the glass, its viscosity during pressing and the actual interfacial tension. During pressing, the temperature of the mould must not exceed the sticking temperature. On the other hand if the mould is too cold the surface of the glass melt will cool very quickly. If the melt passes the strain point (see Sect. 1.1.4) it embrittles. As a result small cracks may form and render a glass wafer useless for microstructuring.

If the applied pressure increases too rapidly during the pressing of a glass melt, it will not have enough time to flow and fill the mould, which will also result in brittle failure (flaws) at the glass product surface. Nölle [383] explains this using Maxwell behaviour (1.4).

Another important aspect during glass pressing is the overlap between the pressure–time cycle with the temperature–time curve. The residence time of the glass melt under pressure is an important fact to consider. If a glass article is pressed into the desired shape it must be allowed to solidify via cooling before the mould is opened. The pressure cannot be released and the mould opened until the viscosity of the glass melt exceeds $10^{6.6}$ Pa s (see Fig. 1.11), so that any undesired deformations by gravity will not occur.

Temperature fluctuations can occur during the flow of glass melt inside the mould. This and surface tension effects might give rise to the formation of flow patterns, which is followed by “waviness” in the glass causing uneven surfaces and thickness variations of the finished part. This is usually not a problem for kitchen and tableware, but it is for microdevices.

Often press forming is used to produce articles with thick walls. During the cooling step higher temperature gradients develop through thick glass parts than through thinner ones, which results in thermal stresses. The formation of thermal stresses can be prevented by very slowly cooling (see Sect. 3.3.3).

Float Technology

Flat or plate glass was quite originally made by casting a glass melt and rolling it out into a sheet. The surface condition of the rollers and the table determined the quality of the produced glass surfaces. Also, the sheet glass made by the Fourcault method has to be ground and polished in order to achieve parallel surfaces with an optical finish. This, however, makes this process rather uneconomical.

The float method to produce perfectly flat sheet glass was developed by Sir Alastair Pilkington of Pilkington Brothers Ltd. in 1952. For a detailed review of the entire story the reader is referred to the literature [383, 437, 524]. Nowadays, this technology dominates the production of flat clear, tinted and coated sheet glass for applications in the building and automotive industry. The float technology is now used for the production of flat LCD- and plasma-TV screens and flat glass used for encapsulation of electronic devices. The float methods allow for the continuous production of very smooth flat glass sheets of a width of more than 3 m and thicknesses ranging from 0.4 to 25 mm. To avoid the undesired devitrification as described in Sect. 3.2.3, it is necessary to adapt the chemical composition of the glass sheets and the temperature–time–running of the process. Hrma et al. [240] have investigated the problems and given recommendations in this connection. Figure 3.16 shows a schematic of the process.

In the float process a glass melt is poured continuously from a furnace onto the surface of molten tin, where it floats because of the density difference. The floated glass melt spreads to form a ribbon with a defined thickness and

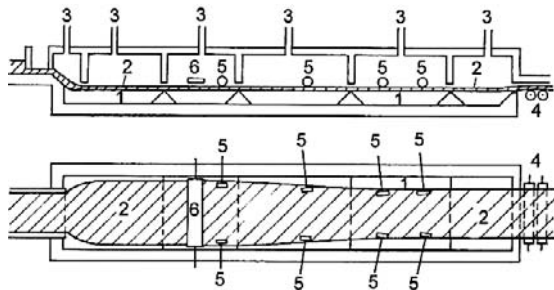


Fig. 3.16. Schematic of the Float-method for the continuous production of perfectly flat and ‘polished’ sheet glass [383]. 1 is tin bath, 2 is the glass ribbon, 3 are inert gas entrances, 4 are the transporting rolls to the lehr, 5 are the edge rolls and 6 a cooler for the edges

perfectly smooth surface. After controlled cooling the glass produced has a “polished” surface with perfectly parallel sides. The continuous process allows for very high production rates, which can exceed in case of window sheet glass to more than 800 t per day. A few smaller tanks are used if sodium-borosilicate flat glass such as Borofloat [148] or flat screen glass for TVs is produced.

The glass tanks are heated by using 8–10 natural gas cross-firing burner pairs, which guarantee the desired temperature and temperature distribution. Any mistakes in the batch cannot be corrected after the melt passes the melting tank. The molten glass flows out from the conditioning zone of the glass melting furnace through a controlled slit, runs down the inclined refractory plane onto the tin bath. The melt viscosity must be as low as 10^3 Pa s, because the melt is supposed to spread over the entire tin bath until it reaches an equilibrium thickness. The equilibrium thickness is determined by the density difference between the glass and molten tin, as well as the glass/tin and glass/atmosphere interfacial tensions. In most cases the equilibrium thickness is about 7 mm [383]. However, Schaeffer [437] states that it varies between 4 and 5 mm. The final thickness of the glass sheet can be adjusted by the speed at which the solidifying glass melt is drawn off from the tin bath. The glass ribbon on the tin bath is drawn by rollers that are positioned on both its edges (Fig. 3.16, position 5). The rollers are serrated top wheels fixed onto a driving shaft. Depending on the direction (angle) of the shaft and the rotation speed of the rollers the glass ribbon can be thickened or also stretched. The equilibrium thickness can be maintained if the rollers are installed rectangular to the ribbon direction. The ribbon becomes narrower and thinner if the rollers are turned in the flow direction as shown in Fig. 3.16, because an additional drawing takes place. The longitudinal flow rate enlarges. If the rollers are directed vice versa (to the slit), then the thickness and breadth expand; the moving rate of the ribbon falls. The flow of the molten glass is laminar and follows the principle of geometric similarity. The amount of the flowing glass is always determined by the glass mass passing the slit and is not affected by the direction in which the rollers turn.

The tin bath has a length of up to 50 m and is divided in several sections, which is required because cooling towards the end of the tin bath is necessary. By the time the glass is drawn on the tin bath the viscosity must have reached roughly 10^{10} Pa s. The glass sheet still flows but can not be deformed by the action of gravity.

The tin melt bath is operated in inert atmosphere to prevent its oxidation. A N_2/H_2 mixture is commonly used. The side of the ribbon directed to the tin is smoothed by the direct contact between the glass and the molten tin. In general, no interaction or diffusion processes take place between the glass and the tin. However, in practice tin ions are found up to several micrometre deep inside the glass. The interdiffusion occurs because the oxidation of tin is not completely prevented; furthermore, the glass melt contains some oxidizing compounds. The fact becomes important if these glass sheets are to be used

for the production of electronic devices. In contrast, the opposite glass side is tin free and also very smooth as it is fire polished.

It seems to be clear that each temperature difference in the cross section of the slit or the tin bath influences the thickness distribution of the sheet. This has to be in consideration, e.g. for the anodic bonding of borosilicate glass with silicon, see Sect. 1.2.3, or if printing thin film transistors on substrate glasses.

After passing the tin bath, transport rollers lift the glass ribbon into the lehr, which is a special oven used to anneal glass. Its length can exceed 100 m. The viscosity of the glass melt is slightly lower in the region of the rollers than in the transformation range, about 10^{10} Pa s, so that the ribbon can be transported from the tin bath into the lehr without destruction. The length of the lehr is determined by the production rate, the temperature of the glass mass and desired cooling rate to prevent thermal stress or shrinkage during thermal post-processing.

Other Methods to Produce Flat Sheet Glass

Flat glass can be made using a variety of other techniques besides the float technology. The other techniques are used if the required glass composition is very difficult to handle or if small lots have to be produced.

Small quantities of flat glass can be manufactured by starting off to produce initially a cylinder by using a blow pipe. In a first step, this cylinder is elongated by swinging the pipe and then blown out to the correct dimensions. Afterwards, the cylinder is separated from the blow pipe, placed on a substrate, cut open and rolled on the substrate producing a flat glass sheet. However, this method produces glass sheets that are neither perfectly smooth nor with absolutely constant thickness.

An actual technology to fabricate sheet glass is the overflow-fusion down-draw method, which was developed by Corning Glass Works. A schematic of the process is shown in Fig. 3.17. In this process a melt stream is forced over the edges of a platinum vessel (trough) and thereby divided into two parts. The melt flows over the trough faces and eventually both streams recombine and fuse again to a single stream just below the trough. The surfaces of the free falling melt are only in contact with the surrounding atmosphere. The great importance of the correct choice of the radius on the top edges and of the tip angle at the bottom of the trough is emphasized by Lin et al. [332]. They found that a tip angle near 20° is necessary for steady flow and good fusion of the molten glass streams.

This process allows for the fabrication of glass sheets with freely formed, very smooth surfaces. The thickness of the produced glass sheet is determined by the pull-down rate. The glass sheets produced by this method are used as substrates for liquid crystal displays (LCD). The process is described in much more detailed by Fujita [153].

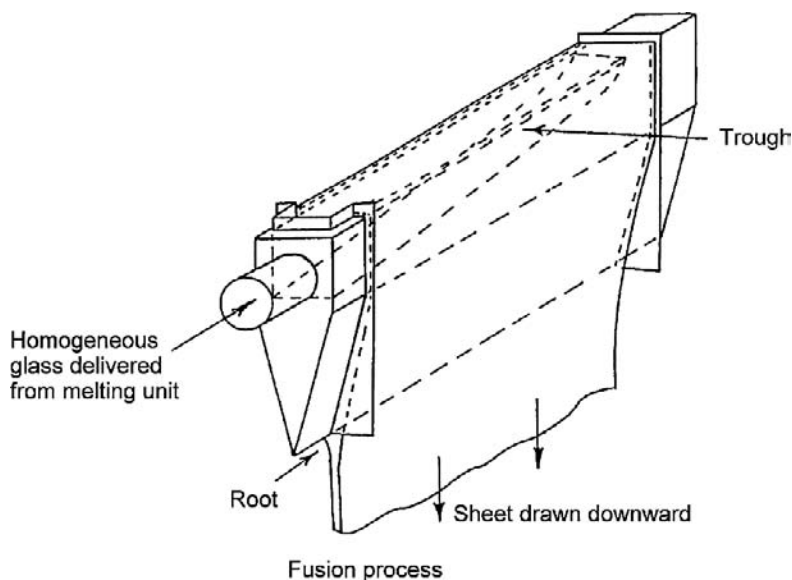


Fig. 3.17. Schematic of the overflow-fusion downdraw process [121]

Drawing of Tubes and Rods

We are going to briefly describe methods that allow for the production of glass half products for the later drawing of micrometre-sized tubes and rods, which are frequently used in the microsystem technique. Glass rods and tubes are usually drawn directly from the melt. The drawing direction can be horizontal if a Danner pipe (rotating mandrel) is used, vertically upwards using a rotating bowl and a nozzle (Schuller principle), or vertically downwards simply through a nozzle, the so-called Vello method. This method is preferred to produce tube and rod half products for further drawing. In the Vello method the nozzle is positioned in the feeder spout (see Fig. 3.14) having a liner in the centre, which partially blocks the orifice and forces the melt to flow around it. If the liner is connected to a blow pipe a tube can be produced if air is blown into the liner, which stabilises the inner diameter of the tube. The liner is removed from the nozzle for drawing round, quadratic or triangular rods. In the later cases the nozzle shows a special shape. Giegerich and Trier [170] provide a good review of the processes involved in the production of glass tubes and rods.

Fibre Drawing

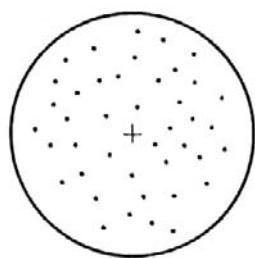
Glass fibres are extensively used in many applications, ranging from thermal insulation to reinforcements in polymer composites. Glass fibres, wool or textile fibres can be produced using a variety of processes [334,524]. Continuous fibres can be drawn in analogy to the Vello method directly from the melt

or from remelted glass marbles. The molten glass is extruded simultaneously through many small nozzles in the bottom of a rectangular vessel (very small tank), called bushing, and then is drawn down into fibres with diameters of typically 4–20 μm . Before the fibres are gathered into a single strand the individual fibres are passed through a finishing or sizing bath. Finishes or sizes are applied to allow for better handling of the fibres or to improve the wetting behaviour and compatibility of the fibres with prospective composite matrices. A detailed description of the process of fibre drawing with particular emphasis on the various parameters, especially the necking-down limits, was provided by Stehle and Brückner [491]. They also developed a model that allows for the calculation of the necking-down limits [492]. In particular, applied to phosphate glass fibres, Munoz et al. [373] tested the influence of viscosity and drawing speed on the fibre diameter. They postulated the great importance to control the hydrostatic pressure in the bushing resp. nozzles. The hot fracture mechanism during the glass fibre drawing is discussed by Brückner et al. [73]. The structural and mechanical properties of glass fibres depend on the fibre dimension as well as on the parameters used during the drawing process [395].

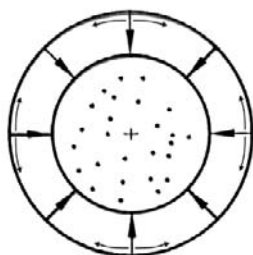
3.3.3 Cooling of Formed Glass Products

During forming, a supercooled glass melt is able to flow (see (1.2)). Externally applied shearing stresses during forming and stresses arising due to temperature differences are compensated by melt flow, which depends on the viscosity of the melt. The situation changes if during cooling the temperature at the product surface drops into the transformation range, at which the brittle-elastic behaviour of glasses starts to dominate. During the cooling of glass parts the major problem is the temperature gradient between the surface and the bulk material. Initially, the surface will turn brittle-elastic while the bulk material is still able to flow, which still allows for stresses to be reduced by melt flow. However, permanent stresses occur in radial and tangential directions as soon as the bulk of the glass passes the transformation range and turns brittle-elastic during further cooling. Figure 3.18 visualises the development of stresses during cooling.

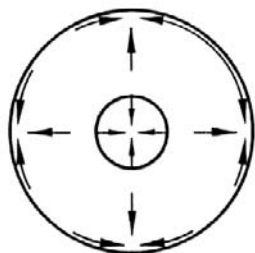
Instantaneous failure of the glass product can occur if the stresses developed during cooling exceed the strength of the glass product. This fact is clearly evident and the broken product will be thrown away. However, more problematic for the application of glass in microsystems is the case when cooling results in the introduction of uncontrolled permanent stresses that do *not* result in the instantaneous failure of the glass part. Such permanent stresses cause a certain degree of anisotropy of the glass properties, which leads slowly to dimensional changes of the product by structural relaxation processes during subsequent processing, and result also in failure due to static fatigue, stress birefringence and refractive index gradients, which are undesirable for many applications and render glasses useless for microstructured glass devices. As

1st phase

- relatively homogeneous temperature distribution at $T > T_g$
- no permanent stress is present
- glass is flowing

2nd phase

- surface: $T < T_g$; bulk: $T > T_g$
- volume in the surface region contracts
- glass in the bulk can still flow
- temporary, tangential tensile stresses develop at the surface
- temporary, radial compressive stress directed towards the bulk develops

3rd phase

- $T < T_g$ homogeneous throughout the glass
- bulk of the sphere cools and wants to contract
- solidified cold surface prevents the contraction in the bulk leading to
- permanent compressive stresses at the surface and radial tensile stresses

Fig. 3.18. Schematic illustration of the development of permanent stress during cooling of a glass sphere

a consequence temperature gradients during cooling should be avoided completely, but this is rather impractical. Therefore, a precise cooling process is used that allows for the removal of thermal stresses. This process involves holding the glass for a certain time at a precise temperature corresponding to the annealing point, which is followed by a very slow temperature reduction in the transformation range (see Sect. 1.1.4). The principle of such an annealing or precision cooling process is shown in Fig. 3.19.

In the production of glasses, the cooling process takes place continuously in lehrs or in discontinuously working chamber kilns. In industrial production, a lehr has a moving belt to transport the glass through the oven at controlled speeds. The lehr is divided into different subsections with its own heat sources, which enable to carefully regulate the temperature gradient. The temperature

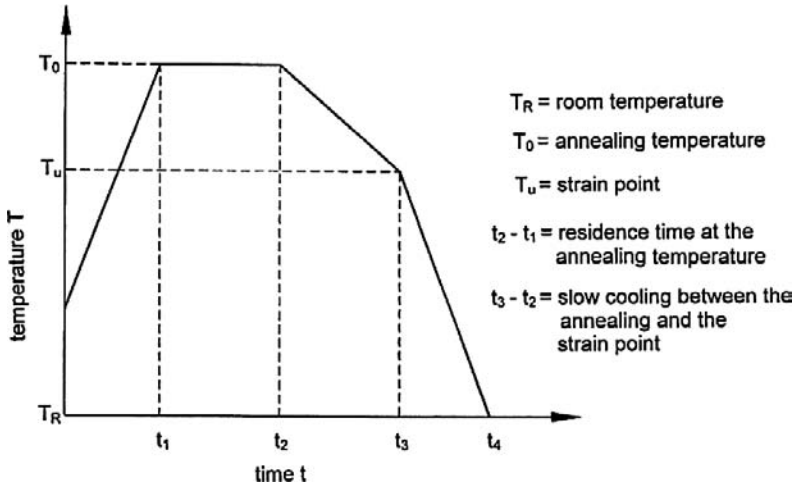


Fig. 3.19. Temperature–time–curve of a cooling process with residence time at the annealing temperature to remove permanent stresses

distribution in the oven is of most importance in order to obtain stress-free devices. To guarantee the desired temperature locally and in dependence on time, the electric heating is preferred.

As already mentioned in Sect. 3.3.2, the production of sheet glass for LCDs and flat TV requires special attention during cooling. The processing of thin film transistor (TFT) layers, electrical guides and bond of pixel layouts require temperatures that often exceed T_U . Shrinkage may occur if the glass is not in thermal equilibrium at the process temperature, which causes the glass to become denser and thermodynamically more stable during post-processing. The glass might shrink by only 50–100 μm if the length of the sheet is about 1 m, but this is too much for producing reproducible electronic connections in microelectronics. To avoid this shrinkage the glass sheets have to be cooled much more slowly as described earlier.

3.3.4 Surface Treatment of Glass Parts

The forming method used to produce a glass part determines the geometric tolerances of the half products as well as their surface properties and characteristics, which include the surface roughness, waviness, warp and its wettability. These properties determine whether a glass product is suitable to fulfil the stringent requirements for applications in the microsystems technology. Thickness deviations within a given glass substrate and between different parts of the same lot cause complications for the application of float glass sheets, pressed and rolled plate glass. Imperfect packing can cause damage and flaws as well as undesired surface reactions leading to surface changes during

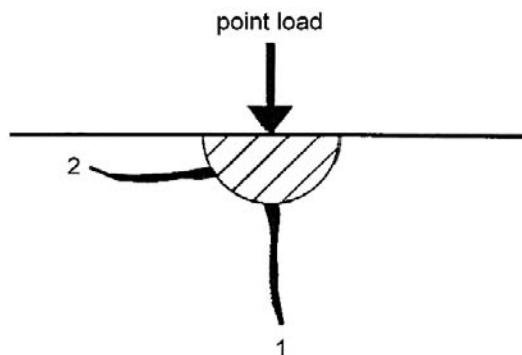


Fig. 3.20. Longitudinal (1) and lateral (2) cracks caused in a glass by a point load

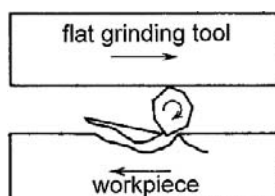


Fig. 3.21. Chipping of a glass platelet during mechanical grinding

transportation. Therefore, before actually using the glass for microstructuring processes it requires a surface pretreatment. Such surface treatments of glass wafers include mechanical, chemical and thermal methods. The sole aim of such surface treatments is to improve the thickness tolerances and surface properties of the half-product.

The mechanical surface treatments consist of grinding, lapping (smoothing) and polishing. For a detailed description of the processes involved the reader is referred to the literature [184, 284, 550] or Sect. 5.2.2. The brief description that follows is only related to surface treatments in general.

The mechanical treatment of glass involves the use of fine powders to remove scratches and flaws. The Hertz pressure half sphere (Fig. 3.20) is helpful to explain the grinding process. As soon as the glass surface is loaded, elastic and inelastic deformations occur. Figure 3.20 shows the volume picking up the load. The load causes normal stresses and tangential shear stresses within the glass. The highest shear stresses occur in the volume near the glass surface, see Fig. 3.20, position 2. If the applied stresses exceed the local strength of the glass flaws occur, and the material will start to fail. The following process of breaking is described in Sect. 1.2.3, see also Fig. 1.34. Whether longitudinal cracks or tangential shear failure occurs depends on the tool and actual technical process used to cut or grind the surface. If the points load causes lateral failure, then chipping occurs, i.e. the formation of shell-like glass platelets (Fig. 3.21).

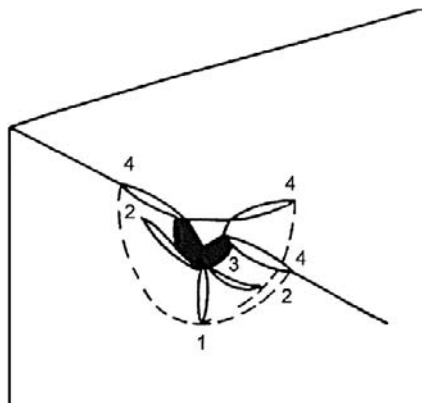


Fig. 3.22. Schematic illustration of the formation of longitudinal (1), lateral (2) and radial (4) cracks in the surrounding of a Hertz pressure half sphere (3) in glasses

The roughness of the ground surface is comparable to the dimensions of the chips that are formed during the process. However, simultaneous to the chipping, new longitudinal failure and radial cracks form as shown in Fig. 3.22.

The number and depth of the longitudinal cracks depend strongly on the size of the abrasive particles used for grinding. The most frequently used abrasives in grinding operations are synthetic diamonds, and also silicon carbide and corundum. Figure 3.23 illustrates to what extent the size of the abrasive particles affect the resulting roughness and the crack length below the surface layer.

Any grinding causes damage to a layer with a certain thickness below the surface, which is illustrated in Fig. 3.23. This damaged surface layer affects the mechanical properties of the glass. Nevertheless, only grinding allows for the production of glasses with the desired μm -tolerated thickness and parallelism from pressed plate glass. The amount per time of glass removed from the part depends on the hardness of the glass and increases with increase in abrasive particle size and the relative speed between the abrasive and the glass surface.

As mentioned earlier, the grinding is followed by lapping and polishing. Grinding using abrasives with a diameter of around $50\mu\text{m}$ and a relative speed of $15\text{--}35\text{ m s}^{-1}$ enables the fast removal of any undesired material or unevenness. However, it also causes as said before most damages in the form of crack formation to the underlying glass volume.

The grinding process is followed by lapping or smoothing in order to reduce the surface roughness and to remove critical cracks, which could cause brittle failure of the glass device. However, subcritical flaws still remain. The abrasive particles used during this process have diameters ranging from 5 to $10\mu\text{m}$. The lapping speed is smaller than 3.5 m s^{-1} .

Finally the glass part is polished in order to reduce the surface roughness below a value of 10 nm . The polishing powders used have a particle size of

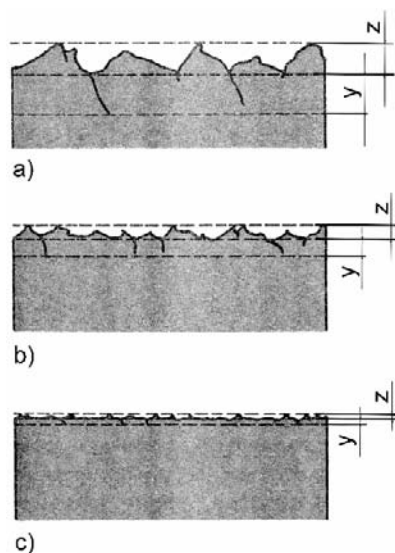


Fig. 3.23. Schematic representation of the cross-sections of ground glass substrates, which were ground using abrasives with a grit of (a) no. 25, (b) no. 10 and (c) F 20. y represents the depth of the crack containing region and z the peak-to-valley roughness of the surface

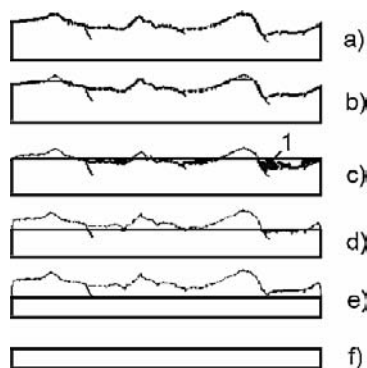


Fig. 3.24. Schematic of the processes involved in mechanical polishing, (a) smoothed surface after lapping containing dents and flaws, (b) removal of the large unevenness, (c) filling of dents and flaws with removed silica gel (1), (d) removal of the interim layer, (e) removal of the damaged surface layer and (f) the polished surface

around $1\mu\text{m}$ and are less hard. Commonly used abrasives for polishing are Cr_2O_3 , CeO_2 , Fe_2O_3 and $\text{Al}(\text{OH})_3$. During the polishing process material is not only removed but flaws and cracks will be filled by ‘smearing’ the removed material into the voids (Fig. 3.24). Because of the use of basic polishing

suspensions, the removed material is almost a pure silica gel. Any other glass components will have been leached away (see also Sects. 1.2.2–1.2.3), which affect the surface composition of any polished glass. Its surface composition is different from its bulk composition. In general, chemical stability of a glass increases through polishing.

Chemical etching using hydrofluoric acid also allows producing polished glass surfaces. This method is particularly useful to polish very hard glasses, such as quartz glass. Figure 1.24 illustrates the material's removal during etching of quartz glass in HF. Chemical surface treatments are not solely used to polish surfaces to reduce its surface roughness, but also for cleaning a surface prior to coating or joining glasses. The compounds used to clean glass surfaces vary and are selected having the following process step in mind. Acetone plays an important role but also other chemicals are used.

The thermal post-treatment of glass half products is driven by surface tension effects, which will result in sometimes undesired secondary effects such as warps, borders or bulb edges. However, if this is not a problem or bulb edges are even desired, than fire polishing is a method of choice. In fire or flame polishing only a thin surface layer of the glass half product having a thickness of about $20\mu\text{m}$ is rapidly heated so that it has a viscosity of around 10^5 Pa s , which is low enough to allow the glass to flow under the action of surface tension and cause flaws and cracks to heal. Beside the post-treatment of any glass substrates fire polishing is an integrated part of the float technology (Sect. 3.3.3) in which the top side of the continuous glass ribbon is fire polished.

**Geometrical Microstructuring of Glasses
and Applications**

Introduction to Geometrical Microstructuring

4.1 Principles

Microtechnology or microtechnique deals with the assembly or manipulation of matter or features near the micrometre size range. Microtechnology is a broad term and includes microelectronics, micro-electro-mechanical systems, microstructuring techniques, micromechanics, microfluidics, microoptics, microactuators and sensor technique. Microtechnology allows for the generation and fabrication of complex microsystems with various functions and a high degree of integration. Microtechnology started with the development of microelectronic circuits in the 1960s, having a massively improved performance, higher functionality and much better reliability, which allowed to reduce cost and shrink the size of electronic devices. In the 1980s, microstructuring techniques were developed to enable the generation and assembly of geometrical structures of some hundred micrometres in three dimensions. Microstructuring is to date state of the art [267].

Microstructures can be assembled using a variety of techniques, which are summarised in Fig. 4.1. Magnetical microstructuring is important particularly for assembling actuators and sensors. Electrical microstructuring approaches are used in all areas of microtechnology, but especially for creating microsystems that require the generation of complex elements, the transport and processing of information and the supply of energy. Optical microstructuring techniques are important in information technology as well as in sensors and measuring techniques. Other microstructuring technologies are required in biological and chemical applications.

Geometrical microstructuring is key because of its importance for MEMS. It allows for the fabrication of functional components. However, the design and processing are very demanding. It is obvious that materials used in geometrical microstructuring have to fulfil certain specifications. The property profile of the materials determines not only the design but also the processes that have to be used for microstructuring (see Fig. 4.2).

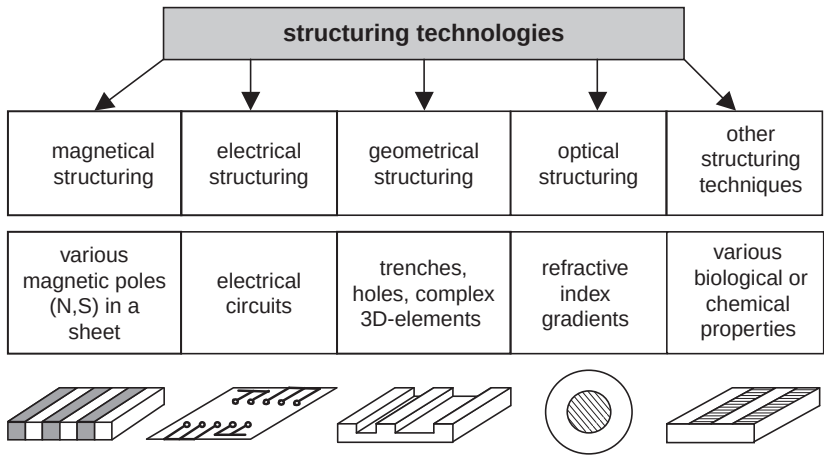


Fig. 4.1. Structuring technologies used and examples of application

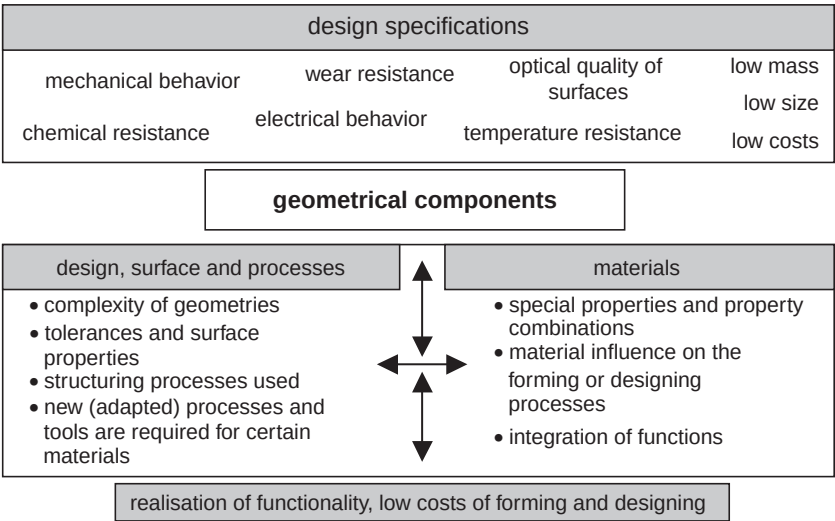


Fig. 4.2. Interrelation between materials, designs and processes of functional components

Geometrical structuring technologies can be grouped into categories depending on whether material is removed or added (Fig. 4.3).

Depending on the depth and width of the structures to be created, which depends also on the ability to control the process, the features are two or three dimensional. A one-dimensional process allows only treating the substrate surface.

Additive technologies for structuring rely on materials deposition procedures, such as sputtering, physical vapour deposition (PVD) and chemical

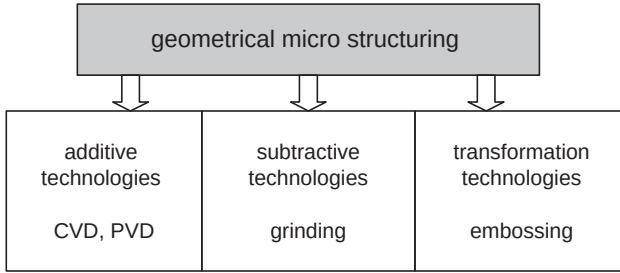


Fig. 4.3. Classification of geometrical technologies for microstructuring

vapour deposition (CVD), which are often used to create one-dimensional features. The use of masks during the deposition procedure allows creating structured thin layers, which is the so-called two-dimensional (2D) structuring technology.

Subtractive technologies are used to remove material from the substrate to be structured. Material can be removed from a substrate by mechanical, thermal or chemical processes. Subtractive technologies can be used to remove material from the entire surface (one-dimensional), such as for instance in grinding or polishing processes, but it is also possible to selectively remove material to create two- or three-dimensional structures by means of etching or machining using tools. To selectively remove material, masking techniques are commonly used for instance in photo-structuring of glasses. However, focused laser or ion beams can also be used to remove material for structuring.

Transformation technologies are reshaping processes, such as embossing or post-drawing, in which no material is added or removed. Transformation technologies can only be used if the material is ductile or able to undergo viscous flow. A material can for instance be heated up to temperatures that allow for viscous flow (see Sect. 2.2.1) or a liquid precursor can be used during the forming followed by curing (setting or hardening) the material, such as UV-curing of polymers or thermal curing of epoxy resins. Transformation technologies often require an original or a negative of the structures that shall be produced, such as the embossing tool, coining die or forming punch.

Furthermore, geometrical microstructuring techniques can also be classified according to the dimension of structures created. 1, 2, 2.5 and 3D structuring technologies are known (Fig. 4.4).

4.2 Interrelations Between Material Properties and Geometrical Structures

Isotropic materials, such as glasses, show the same response during a structuring process, for instance during etching, in all directions, which will not be the case for anisotropic materials, such as single crystal silicon or aligned

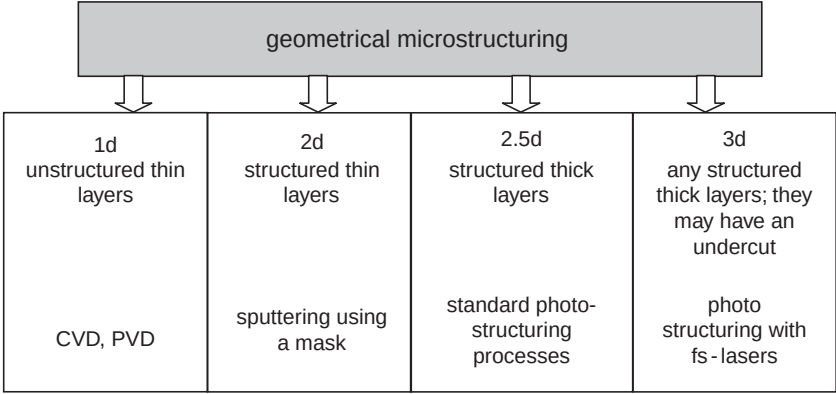


Fig. 4.4. Classification of geometrical microstructuring technologies according to the number of dimensions of the structures created

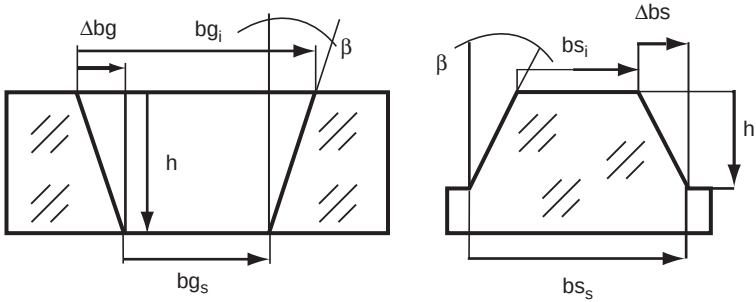


Fig. 4.5. Definition of geometrical parameters of structures, where bg_s is the nominal width of trenches, bg_i is the real width of trenches, bs_s is the nominal width of bars, bs_i is the real width of bars, h is the depth or thickness of a structure, Δbg is the widening of structures, Δbs is the reducing of width of bars and β is the angle of inclination

fibre reinforced materials. Such materials may well show different etching or dissolution rates in all three dimensions. For instance, the etching speed of single crystalline silicon in alkaline solutions depends on the exposed crystal facet, which results in anisotropic etching. Such effects are widely exploited in microstructuring applications, such as the anisotropic etching of silicon in silicon micromechanics.

The structuring parameters illustrated in Fig. 4.5 are used to describe the geometry of structures, although not all of these parameters are relevant to all structuring technologies.

The following equations (4.1–4.5) describe the parameters and their inter-relation mathematically.

Widening of structures

$$\Delta \text{bg} = \frac{\text{bg}_i - \text{bg}_s}{2}, \tag{4.1}$$

Aspect ratio

$$A = \frac{h}{\text{bg}_i}, \tag{4.2}$$

Reducing of width of bars

$$\Delta \text{bs} = \frac{\text{bs}_s - \text{bs}_i}{2}, \tag{4.3}$$

Angle of inclination

$$\beta = \arctan \frac{\Delta \text{bg}}{h} \quad \beta = \arctan \frac{\Delta \text{bs}}{h}, \tag{4.4}$$

Etching ratio

$$Q = \frac{h}{\Delta \text{bg}} \quad Q = \frac{h}{\Delta \text{bs}}. \tag{4.5}$$

The technologies mainly used for geometrical structuring of materials that are relevant to fabricate microsystems can be classified as follows:

- Mechanical processes (including the use of focused ion or laser beams if used to remove material)
- Chemical processes (including complex processes combining of various methods to remove material as well as plasma processes)
- Beam processing or beam-assisted processing
- Thermo and thermo-mechanical processes

Table 4.1 contrasts the various categories of geometrical structuring technologies. The application occurs with respect to various process parameters and costs. Methods that enable batch processing are not suitable for single prototyping applications. The process costs are determined by the purchase price of equipment as well as the operation costs, which include handling (i.e. time to load and unload), process time and materials costs. Because of the high demands on precision and tolerances of microsystems the process equipment is usually rather expensive. Only mass production makes such processes economically profitable and allows recovering the costs.

One of the major issues of structuring processes is the sometimes limited applicability of the process for structuring a wide range of substrates. Table 4.2 summarises the applicability of the various categories of processes for structuring various materials.

Table 4.1. Comparison of geometrical structuring technologies with respect to various processing aspects

Process	Mechanical	Chemical	Beam	Thermo-mechanical	Plasma
Suitable for batch processing	–	++	–	++	+
Suitable for single prototyping	+	–	+	–	0
Purchase costs	+	0	–	0	–

+ suitable, 0 neutral, – not suitable

Table 4.2. Suitability of structuring processes for geometrical structuring of various classes of materials

Technology	Mechanical, such as machining using tools	Chemical, such as wet etching	Beam processing, such as laser structuring	Thermo- mechanical such as drawing and embossing	Plasma assisted processes, such as sputtering and CVD
Glasses	—	+	+	++	0
Ceramics	0	0	+	+	+
Metals, alloys	++	+	+	0	+
Polymers	+	—	+	++	+
Semiconductors	—	++	0	—	++
Compounds	—	—	+	—	0

+ favourable, 0 neutral, — not favourable

Metals can be structured using almost all structuring technologies. Polymers can also be machined and structured using a wide range of techniques. However, chemical etching cannot be used to structure polymers. A range of microsystems is fabricated using thermo-mechanical moulding technologies, such as injection moulding or embossing, which are very efficient technologies. Glasses and ceramics cannot be micromachined mechanically in a sufficient extent, but they can be easily structured using chemical and plasma technologies. Glasses can also be structured using thermo-mechanical processes because of the continuous nature of the viscosity–temperature behaviour (see Fig. 1.11). Semiconductors are the most widely used materials in microtechnology. The standard micromachining technologies, including chemical processing and plasma technologies, were initially developed for the geometrical structuring of these materials.

Beam technologies can be used to structure for any kind of material. They are the most economical techniques used for the geometrical structuring of composites. The major disadvantage of beam-based technologies is that features are created in series, which results in the long fabrication times.

4.3 Some Remarks about Lithography

Lithography is very commonly used for micromachining and for mass production. Most lithography techniques generally require a pre-fabricated photomask or masking layer as a master from which the final pattern is copied. These process masks must possess high chemical resistance so that they can withstand an etching step that creates the structure. Lithographic techniques are used because they allow precise control over the shape and dimensions of the objects to be created. Furthermore, patterns can be created over the entire surface of a substrate simultaneously. However, lithography requires

flat substrates and it cannot effectively be used to create features that are not flat. Lithographic methods can be divided into the following techniques, which depend on the beam used:

- Optical lithography
- Laser lithography
- Electron beam lithography
- Ion beam lithography
- X-ray lithography

Optical lithography and X-ray lithography are the most important techniques used to create more dimensional geometrical structures with a large depth profile. X-ray lithography is mainly used for the LIGA technology (LIGA is an abbreviation derived from the German words **L**ithographie (lithography), **G**alvanoformung (electroforming) and **A**bformung (moulding)). This technology is used for the production of microstructured polymer, ceramic and metal components. The advantages of this technology are that it enables the fabrication of high aspect ratio structures with very small angles of inclination and very low surface roughness. The main disadvantage, however, are the high costs involved. Unfortunately, this technology is not suitable for the geometrical microstructuring of glasses. Optical lithography used for the geometrical structuring of glasses will be discussed later in more detail.

In semiconductor lithographic structuring commonly a thin surface layer, called photoresist, is applied to the substrate surface. This layer is exposed to mostly UV light through a mask, which induces chemical changes to the photoresist, and then removed, laying open the underlying substrate which can now be etched. In these applications the photoresist consists of the active material, whereas in the case of photosensitive glasses (Sect. 1.2.4 and Chap. 9) and polymers the material to be structured itself is active.

Three main types of optical lithography are used as illustrated in Fig. 4.6. The major differences between these techniques are the position of the mask. The first step in lithography is always the alignment of mask and substrate.

Contact exposure and proximity exposure lithography use the principle of shadow projection, which means that the shadow created by the mask is not exposed to the intense light source. The scale of the mask and exposed image is one to one. As the name says, in contact exposure the mask is in a direct contact with the substrate, which guarantees a very good resolution of the structural details. However, the mask is undergoing high wear. The optical resolution that can be achieved is determined by the wavelength of the light used, i.e. the shorter the wavelength the higher the resolution. This fact causes the trend to use shorter wavelengths in lithography.

In proximity exposure, the mask and substrate are not directly in contact. Instead the mask is aligned with the substrate in close proximity at small distance, which is usually in the order of 5–40 μm . On the one hand, this reduces the maximum possible resolution of structural details, i.e. the larger the distance between the mask and the substrate the lower the optical resolution.

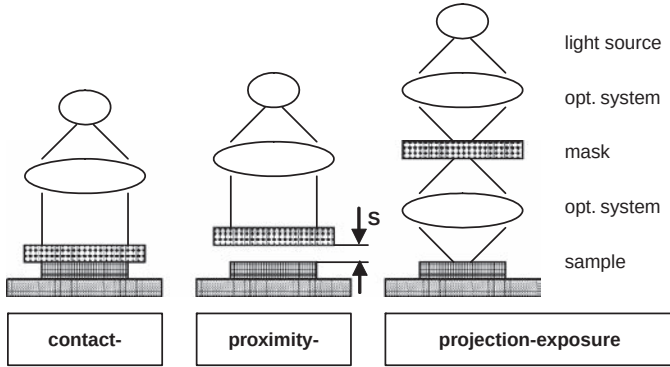


Fig. 4.6. Optical lithography techniques; s , proximity space

On the other hand, the wear of the mask is experiencing during handling significant lower.

In projection exposure lithography, an optical system is used to project the image created by the mask onto the substrate. In this case, masks with a larger scale can be used, because the optical system allows scaling down the image. Usually systems with mirror optics are preferred for higher-scale substrates and lens optics for lower-scale substrates (up to 6 in. diameter of substrates). Again, the resolution that can be achieved depends on the wavelength of the light and the numerical aperture. Decreasing the wavelength and increasing of numerical aperture lead to an increased optical resolution. However, the major problem is the depth of focus as it will strongly diminish with increasing numerical aperture.

Nowadays, wafer steppers are used for the lithographic structuring of large diameter wafers at high resolution. This equipments use the step and repeat principle. Only small area of the substrate of about 1 cm^2 is exposed to the mask in a single step. Afterwards, the substrate is moved to the next area followed by a subsequent exposure step and so on, which will be repeated until the entire wafer is exposed to the mask.

On the one hand, the high optical resolution depends on the thickness of the photoresist and requires a thin resist layer. On the other hand, to guarantee a good stability of the masking layer throughout the subsequent processing and in order to be able to compensate more easily for differences in the layer thickness, chemically modified or thicker layers of the chemically active photoresist are required. To address these issues, new processes, such as the DISIRE-process, Tri-level process and phase shifting masks, have been developed. For further improvement of the optical resolution, excimer lasers and light sources operating in the extreme ultraviolet (EUV) range are used. For more detailed information about lithographic and rapid prototyping techniques the reader is referred to the literature [167, 342, 354, 360, 407, 511].

Sotomayor-Torres [479] gives an overview of alternative lithography methods.

Mechanical Structuring Processes

5.1 Introductory Remarks

Mechanical structuring is achieved by the action of mechanical forces. Cutting, ultrasonic machining, powder blasting and water jet milling are mechanical structuring processes. Mechanical structuring processes are concurrent operations in which a step follows another (serial processes). The only exception is powder blasting using a mask and ultrasonic machining with a complex tool. The advantages of these concurrent operations are the high degree of flexibility at a reasonable low cost. Many different shapes can be produced simply by changing the tool or the process programme of the cutting machine. Mechanical structuring technologies are excellent for prototyping and can be easily applied in conjunction with other structuring technologies [155]. However, the disadvantages are the relatively low precision when compared with the lithographic processes and the low productivity.

5.2 Micromachining by Cutting

5.2.1 Description

Cutting of glasses by grinding and polishing of plane surfaces and spherical lenses has a long tradition (see also Sect. 3.3.4). In contrast to this ‘microcutting’, the fabrication of geometrical features with dimensions in the micrometre range, is a relatively new technology. Weck et al. [552] state that only non-ferrous metals and some polymers can be machined recommendably by microcutting processes using diamond tools. The most common cutting processes are milling, drilling, turning and grinding. All processes can be used for microfabrication. An overview of mechanical microfabrication processes, the range of tools used as well as the shapes and features that can be machined is shown in Fig. 5.1.

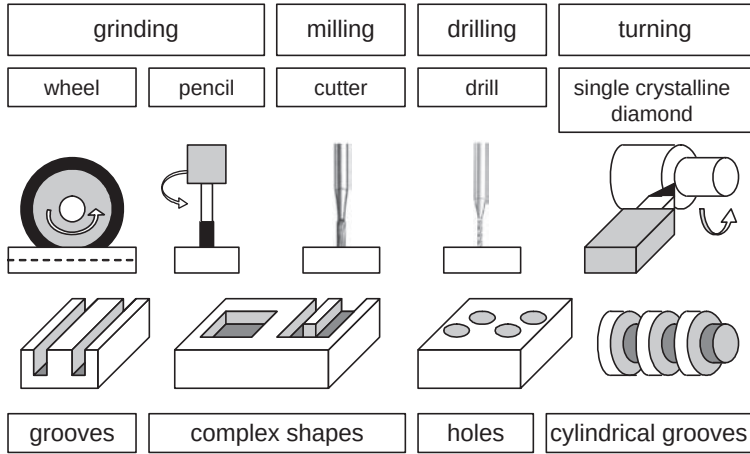


Fig. 5.1. Overview of microcutting processes, the tools used and machined shapes

Milling, drilling and turning can be used to machine ductile metals and polymers. However, in the case of brittle materials special cutting processes are required. Tönshoff et al. [520] described various techniques that enable the abrasive machining of silicon, which is a hard and brittle material. Processes for machining of flat silicon surfaces as well as for micromachining features are presented. With modification, these processes can be transferred to machine glasses. Ultrasound-supported machining is commonly used for the structuring of brittle materials. Grinding using a geometrically well-defined tool, such as a grinding wheel (dicing) or an abrasive pencil, is the most commonly used mechanical micromachining process for brittle materials. Depending on the tool used and the movement of the machines, various different shapes can be machined (Fig. 5.1).

Mechanical cutting processes offer many advantages as the following:

- The possibility to create an unlimited number of shapes
- A wide range of different shapes can be fabricated by only changing tool or the numerical programme of the machine in combination with the optimized machining parameters
- The endless spectrum of materials, isotropic as well as anisotropic, that can be machined using the same equipment and tools
- The geometry of features created depends only on the geometry of the tool used and its movement but not on the crystal orientation, e.g. compared with the anisotropic etching of silicon
- The possibility to machine a small number of parts at reasonable low costs, which depend on the degree of flexible automation of the machine and its handling system
- The possibility to create very smooth machined surfaces

However, the major disadvantage of such mechanical structuring processes is that they do not lend themselves for mass production.

5.2.2 Chip Formation During Machining of Glasses

In this section some aspects are shortly repeated, which are nearly the same in case of mechanical treatment of any surfaces with loose (not bound in a tool) grains, see Sect. 3.3.4. All cutting processes follow the same principle of removing material; a cutting edge, such as diamond particles or the edges of a tool, penetrates into the material, which results in the formation of a complex three-dimensional stress field within the material. Under normal conditions glass is a hard and brittle material; however, as discovered in the early 1900s, under low load conditions glass can be microplastically deformed, which allows to make a groove without the generation of visible cracks [411, 514]. The phenomenon is better described as ‘inelastic’ or ‘permanent’ deformation caused by the local compression of the rings of silica tetrahedra (Fig. 1.8) and not as plastic flow caused by sliding or creeping as in really ductile or plastic materials. However, this behaviour is traditionally described as plastic or ductile and we will do it, too.

During the penetration of an indenter into a hard and brittle material, such as glass, initially the material deforms elastically, which with increasing penetration depth is followed by a ‘plastic’ deformation [323, 347] (see also Fig. 3.20). The plastic deformation is associated with a bulge formation in the surrounding area, compressive stresses and compression in the material below the penetrating body [323]. The compression of the material below the indenter causes in the surrounding area tensile stresses, which are determined by the force equilibrium. A further increase in the applied load, accompanied by an increase in penetration depth, results in the initiation of cracks [323, 450]. If a Vickers pyramid is used as indenter, cracks start forming at the diagonal of the indenter [294]. Also many other properties of the glass will be changed around a Vickers indentation, e.g. the nucleation activity in a $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$ glass [94] or the density [300].

The effects occurring during scratching of a glass surface are very similar. If the applied normal force remains below a critical level it is possible to generate a crack free track, i.e. the glass displays a nearly ductile behaviour. However, the glass will display brittle behaviour if the applied force exceeds a critical level. The different effects are illustrated in Fig. 5.2. In the transition range both quasi-plastic and brittle behaviour occur simultaneously [469].

Mishnaevsky [357] distinguishes three stages during the process of machining brittle materials, which are (a) ductile materials deformation, (b) cracking and formation of a crushed material zone and (c) chip spalling. A mathematical model for describing the cutting of brittle materials was presented. Chiu et al. [93] also observed the various stages during orthogonal machining of glass pieces. They also describe a transition range, which they called semi-ductile-mode machining.

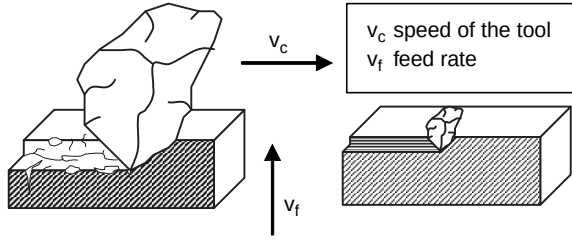


Fig. 5.2. Brittle (*left*) and ductile (*right*) behaviour during mechanical treatment of glass

Klocke and Hambrücker [283] defined a viscous shearing or flow zone and calculated the temperature field in the contact zone between a grinding grain and a glass surface. For a certain treatment they calculated the temperature at the surface to be around 700 K. The temperature in the material decreases with increase of away from the surface.

Schinker [443] explained the increase in temperature during high speed machining of optical glass not only by the external but also by the internal friction caused by the shear stress superimposed by the compressive stress field along the shear planes in the plasticized material. The sliding of material layers against themselves causes friction, which produces heat-supported plasticization.

Other authors (for instance [89,175,284]) observed the formation of curved continuous chips analogous to those created in metal cutting. These chips display often shear marks on the back.

Giovannola and Finnie [175] discussed the balance between failure strength σ_f and hypothetical yield stress σ_y of the material. For normal brittle behavior σ_f is smaller than σ_y , which results in the formation of a crack if a stress is applied. In order for flow to occur prior to brittle fracture, σ_f should be greater than σ_y , which is possible at a local scale, especially at the tip of a tool which causes high-temperature promoting flow. This fact substantiates the assumption that a critical load exists at which a transition from plastic flow to brittle fracture will occur [321].

Other authors (such as [47, 49, 378, 413]) took the view that the depth of penetration is the most decisive parameter causing the transition between ductile and brittle behaviour. Bifano et al. [47, 48] defined a critical border tension depth d_C , see (5.1):

$$d_C = 0.15 \left(\frac{E}{H} \right) \left(\frac{K_{IC}}{H} \right)^2, \quad (5.1)$$

where E is the Young's modulus, H is the hardness and K_{IC} is the critical fracture toughness. All brittle materials, for example semiconductors, glasses and ceramics, display in principal the same behaviour [291]. Especially, K_{IC} strongly affects the critical border tension depth [294]. The critical border

tension depth decreases from more than 50 nm for zirconium oxide ceramic to about 5 nm for silica glass.

Initially a model to predict the transition from ductile to brittle behaviour of brittle materials as a function of the machining parameters, i.e. the tool radius and tool feed, for turning was developed. However, concluding from scratch tests using single-grain diamonds and various cutting geometries, Sinhoff [469] recommended the use of the border stress condition to predict the transition from ductile to brittle behaviour, which means that not only the depth of penetration of a diamond grain is important, but also its geometry because it influences the characteristics of the generated stress field. Moreover, the cutting feed, the cooling lubricant used and its flow rate influence the temperature field.

Sheldon and Finnie [462] investigated the effect of particle size on wear during the impact of a stream of solid particles onto a substrate. They found a transition from the behaviour typical of a brittle solid to that of a ductile material occurs when the particle size of the abrasive was decreased.

Tanikella and Scattergood [513] studied the microcutting of borosilicate glass using a Vickers indenter. The fracture damage was produced above a well-defined crack initiation threshold. The damage varied with load, cutting speed and indenter orientation. Celarie et al. [87] observed the same characteristic of nanoscale damage in glass-like metallic materials. The materials were studied in nanometer scale by atomic force microscopy at a stress-corrosion crack tip.

Yoshida and Ito [571] and Gee et al. [162] presented the use of ductile machining processes to produce optical parts with aspheric surfaces. The glass to be machined strongly influences the outcome. This is because the glass composition determines the final properties of a glass (see Sect. 1.2). Peter [403] demonstrated by means of indentation experiments that glasses with an appreciable amount of network modifiers will display ‘ductile’ behaviour, whereas fused silica could only be compacted and fails in a brittle manner. Koenig and Sinhoff [295], Sinhoff [469] and Schinker and Döll [445] also discussed the influence of glass properties on the shaping behaviour. They investigated various glasses containing different amounts of network modifiers. A high amount of network modifiers, see also Sect. 1.1.3, affect the material’s properties in two ways. Cracks can easily be formed in a glass with a high content of network modifiers because of the reduced covalent bond character in the material due to the presence of larger amounts of non-bridging, heteropolar bound oxygens. But simultaneously a high amount of network modifiers leads to an increase in plasticity, because of weak points in the glass network. The plastic deformation takes place favourably in the case of a higher content of non-bridging oxygen ions, respectively, at a lower content of network forming oxides.

Weyl et al. [560] and Weyl and Marboe [561] explained the differences in the plasticity of various glasses and crystals by the temporarily incomplete screening of the cations present in the glass. They interpreted the ions as deformable elements with a varying configuration of electrons. In the case of

the penetration of an edge into a brittle material a stress field results below it. Consequently, charged ions move with respect to each other. The deformation will be inhibited if repulsion forces increase because of a reduced proximity between equally charged ions. If a critical load is exceeded the ions will move passing each other. This process is mainly determined by the polarisation of the ions. An increase of the polarisation of the ions results in decreasing of repulsion forces. This process might offer an explanation for the observed high plasticity of glasses having a high content of ions with high polarisation, such as lead oxide containing glasses. A detailed examination of the shaping behaviour of various glasses can be found in the literature [469].

Fused (or vitreous) silica is special within the family of glasses, as it contains only a single chemical component and has highest degree of crosslinking, because all oxygens are bridging oxygens (see Sects. 1.1.3 and 1.2.1). Crack formation in pure silica glass is difficult but at the same time its plasticity is very low. If a point load is applied to fused silica, the observed deformation is minimal and rapid crack formation occurs. However, the crack growth stops after a short distance because the load is distributed via all the bridging oxygen links in the network.

The fracture behaviour of glasses is also influenced by humidity. An increase of the relative humidity results in an increase of fracture velocity. Wiederhorn [562] provided an explanation of the mechanism of the impact of moisture on the fracture behaviour. Michalske and Freiman [356] discussed the molecular mechanism of stress corrosion in vitreous silica, which depends on the environmental conditions. The increase in the fracture velocity in glasses with increase in environmental moisture content is due to the chemical reaction between glass with water at the crack tip. The transport rate of water to the crack tip influences the fracture behaviour. These effects are of particular importance for the mechanical shaping of glasses in the presence of aqueous lubricants.

The discussion of energetic effects during the machining of brittle materials offers another perspective to monitor the grinding regime [47, 48]. They developed a model to describe the dependence of the grinding energy on the material removal regime. The energy required for crack formation (E_R), see (5.2), and the energy required for ductile deformation (E_P), see (5.3), are defined as

$$E_R = GA_R, \quad (5.2)$$

$$E_P = \sigma_y V_P, \quad (5.3)$$

where σ_y is yield stress, V_P is the plastically deformed volume, G is the Griffith crack propagation parameter and A_R is the surface of the crack or fracture.

Bifano et al. [48] found that the grinding energy will stay relatively constant during grinding in ductile-regime but will decrease following a power-law relationship with an increase in material removal rate during brittle-regime grinding. During brittle shaping the energy required for crack formation is

smaller than the energy needed for ductile deformation ($E_R < E_P$). Therefore, a penetrating edge results in brittle chipping and crack formation. This process is determined by the energy required for initiation of a crack and to drive crack growth. The initiation of cracks is mainly influenced by the presence of defects in the material and their position, size and orientation. The complex stress field in the material (tensile stress, shear stress, hydrostatic stress) is decisive for the growth of the cracks initiated.

During an other machining the energy for ductile deformation is lower than the energy for crack formation ($E_R > E_P$), which is expected for small machining depths since both V_P and A_R are a function of the machining depth d ($V_P \sim d^3$, $A_R \sim d^2$). It is also possible to reduce the yield stress or respectively the viscosity.

The penetration of an edge results in the formation of shear and hydrostatic stresses. A sliding of dislocations at room temperature is impossible because of the chemical bonds in glasses. As mentioned above machining causes the local temperature increases, which in turn results in a decrease of the local viscosity of the glass enabling a viscous flow of the material. The low thermal conductivity of the glass in the range of $\lambda \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$ affects the locally heated zone. The viscous flow is mainly determined by the local thermal behaviour near the cutting edge and the viscosity–temperature behaviour of the glass. This model is in agreement with the model based on the degree of binding in the glass network and can also explain the differences between various glasses. Komanduri et al. [302] provided a comparison of various material removal mechanisms.

Chiu et al. [92] investigated the chipping process in brittle materials subjected to an uniformly loaded edge by using finite element analysis. During the formation of a chip it may bend, which changes the loading at the growing crack tip resulting in nonlinear effects. Their numerical analysis of the chipping showed that the crack reaches a maximum depth to deviate back to the surface causing spalling.

5.2.3 Machine Tools

One major advantage of the microcutting processes is the flexibility provided by the machining tools. Drilling, milling and grinding are possible using the same relatively inexpensive machine tools [235]. However, the disadvantages are the positioning accuracy and cutting speed of the machine and its stiffness.

Conventional machine tools allow a resolution of less than 0.01 mm, which is not far from satisfactory for the fabrication of geometrical structures for microtechnological applications. Ultraprecision machine tools allow for a resolution in the range of nanometres; however, the work pieces have macroscopic dimensions that make them rather inflexible. However, micromachining tools offer an alternative. These special tools have small dimension of working area, and the mass of the moving components is also small. Provided the machine

has an accurate measuring system, a resolution of $0.1\mu\text{m}$ with a positioning accuracy of $1\mu\text{m}$ can be achieved. Using these machines, structures with geometrical dimensions down to $10\mu\text{m}$ can be fabricated [558].

The major problem of microcutting processes is the availability of spindle drives to guarantee useful cutting speeds. Useful cutting speeds of wheels for microgrinding of brittle materials vary between 50 and 100 m s^{-1} [159, 233, 234, 257]. Grinding wheels with a diameter of around 50 mm (commonly used in dicing) combined with a high frequency spindle ($50,000\text{ rpm}$) allow for cutting speeds of more than 100 m s^{-1} . But in the case of an abrasive pencil with a diameter of 1 mm combined with an air-driven turbo spindle enabling $175,000\text{ rpm}$, a cutting speed of only less than 10 m s^{-1} can be realised. The problem amplifies if abrasive pencils with even smaller diameters, in range of $100\mu\text{m}$, are used. In this case cutting speeds of less than 1 m s^{-1} can be achieved, which is very low for any useful cutting processes.

5.2.4 Grinding Using Abrasive Pencils and Wheels

Grinding is the most commonly used mechanical cutting process for brittle materials. Grinding can be performed using loose particles or with geometrically well-defined tools. Grinding using loose abrasive powders is very often used in optical processing of planar surfaces and curved lenses. However, this process can not be used to create well defined microstructures and, therefore, is not discussed in detail.

Geometrically defined tools for microgrinding are wheels or abrasive pencils (see Fig. 5.1). Using abrasive pencils many geometrically well-defined features, such as grooves, holes or even more complex shapes, can be created. The complexity of the features created can be increased if numerically controlled (NC) machines are used. The size of the tools used for grinding determines the dimensions of the structures that can be created. Abrasive pencils with diameters as small as $50\mu\text{m}$ are nowadays available [555], whereas the particle sizes of abrasives range from 2 to $10\mu\text{m}$. Tolerances of about $1\mu\text{m}$ of structures with minimum lateral dimensions of around $50\mu\text{m}$ and a depth of $100\mu\text{m}$ can be fabricated using these tools. The machined surfaces can have surface roughness in the range of $R_z < 0.5\mu\text{m}$. Brittle materials can be machined at cutting speeds of $2\text{--}5\text{ m s}^{-1}$ and feed rates of $5\text{--}10\text{ mm min}^{-1}$ [233, 234].

Very fine abrasive pencils with diameters less than 0.2 mm , small grain sizes and various geometries cannot be manufactured using the conventional electroplating methods of diamond grits. As an alternative coated abrasive pencils can be made. The body of these pencils is made from cemented carbide. A diamond layer of approximately $10\text{--}15\mu\text{m}$ is deposited onto the body by means of CVD. The pencil bodies must be cleaned and seeded prior to the CVD coating. The CVD coated layers are very homogeneous and consist of a high number of small diamond crystals of uniform size with sharp edges. CVD on complex pencil geometries is possible and yields coatings with superb

quality. CVD can be used to coat micromachining tools used for grinding, milling and drilling [156–158].

Lapping tools are usually steel cylinders that are produced by high precision turning. The grain size of a lapping agent, often boron carbide is used, is one order of magnitude smaller than the dimension of geometrical structures machined.

If grinding wheels are used, grooves of varying width, cross-section and depth are the only geometrical features that can be fabricated. However, pyramidal and columnar shapes can be fabricated by a clever arrangement of the grooves to be cut [233, 234]. It is possible to profile the wheels with single point diamond dressers or dressing plates. Wheel grinding of brittle materials is commonly performed at cutting speeds of $60\text{--}80\text{ m s}^{-1}$ and feed rates of $600\text{--}900\text{ mm min}^{-1}$.

Namba and Abe [378] investigated the grinding conditions of 11 different optical glasses. They were able to differentiate three grinding modes: a fracturing mode, mixed ductile/brittle fracture mode and ductile mode. All glasses could be ground in the ductile regime. The grinding forces generated depend on grain size of the wheel, the feed per wheel revolution, the depth of the cut and the glass material itself, whereas the roughness of the machined surface is only a function of the grain size of the wheel, the feed per wheel revolution and the glass composition.

Dicing is a special kind of grinding operation used in semiconductor device manufacturing to separate the processed wafers into individual silicon chips, which is performed either through thickness cut or repeated cutting using a cut depth less than the wafer thickness. An improved productivity and higher quality output of this process is very much desired. The productivity of silicon chip separation could be improved by reducing the width of the cut, i.e. reducing the dicing wheel width, meandering and minimising the chipping of the edges. The ductile regime for cutting is preferred. Currently, dicing wheels of widths between 20 and $60\text{ }\mu\text{m}$ are applied in the semiconductor industry. Metal bound wheels (electroplated diamond blades) with grain sizes between 3 and $6\text{ }\mu\text{m}$ are state of the art. Cutting speeds varying from 60 to 120 m s^{-1} at feed rates of $10\text{--}150\text{ mm s}^{-1}$ are used for dicing. In MEMS fabrication a device consists often of a combination of materials, such as silicon with a pyrex glass covering. To be able to cut these material combinations resin bound tools are preferred, and the feed rate has to be decreased to 3 mm s^{-1} [159].

The major influences on the quality of cutting and the productivity of the dicing process have been examined by [159, 255]. The most critical wear problem during dicing is radial wear of the blade during cutting. The protrusion should be as low as possible to improve the stability of the blade but should be as high as possible to increase the productivity of the process. The wear of the blade increases proportionally with the dicing length. It is possible to minimise the radial wear to less than $1\text{ }\mu\text{m}$ during the machining of $1,000\text{ mm}^3$ silicon [233, 234].

Dicing technology is not only a technique to separate silicon wafers into individual chips, it is also possible to produce mechanical function components, e.g. resonators [160].

The surface quality during machining of brittle materials can be improved by reducing the depth of a cut of each single grain. The major factor influencing the surface quality is the grain size of diamonds in the wheels. The feed rate affects the surface quality only at lower speeds. Compared to the effect of grain size, the spindle feed influences can be ignored if normal machining conditions are used [291]. Ichiro [255] found that increasing the rotational blade speed is the most effective way to optimise the productivity and the quality of the machined parts. The above mentioned problem of spindle drives limits this possibility. The results of an examination of surface cracking during standard grinding processes are presented by [509].

In ultrasonic-assisted grinding, conventional grinding kinematics are superimposed by an additional high-frequency oscillation, which helps to overcome existing technological limitations when grinding hard and brittle materials using diamond tools [485,530]. The process variants are illustrated in Fig. 5.3. Ultrasonic vibration can be induced by the vibration of the work piece or the tool. If the later one is fact, the spindle running has to transmit the ultrasonic vibrations to the tool. The ultrasonic frequency is in the range of 20 kHz and has an amplitude of several micrometres. The major advantage of ultrasonic-assisted grinding is the reduction in the processing forces, which enables higher feeding speeds leading to an increased machine output and less damage of the machined parts. Because of the reduced processing forces the wear of the tools is also reduced.

In the case of surface grinding the material is removed by the diamond grains at the periphery of the grinding wheel, which is reciprocating rapidly over the workpiece as it is gradually lowered to the final depth of the cut.

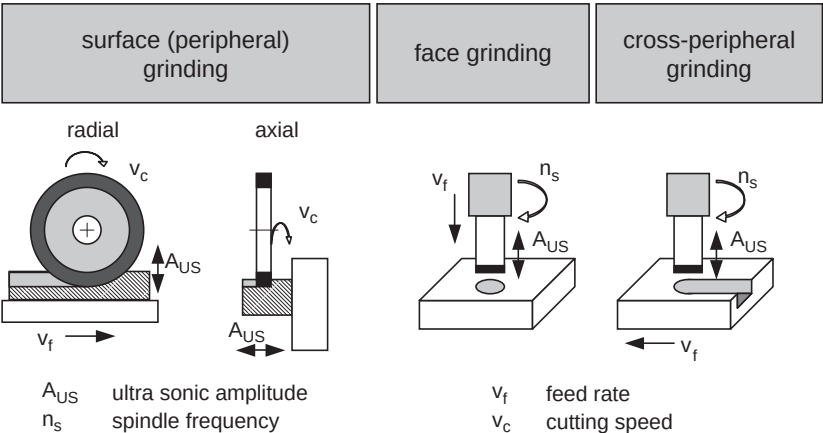


Fig. 5.3. Process variants in ultrasonic-assisted grinding

Two variants are commonly used: pendulum grinding and creep feed grinding. Creep feed grinding uses a formed grinding wheel that is plunged into the workpiece, thereby producing the finished part in a single pass. Creep feed grinding is characterised by low feed and very high working forces that are generated during the process. This results in big contact length of a grain and low chip thickness. In creep feed grinding assisted by radial ultrasonic vibrations, the normal and tangential forces increase significantly slower as compared with normal grinding [485]. In face grinding the grains at the front of the tool are important, whereas in cross-peripheral grinding the chipping takes place at the grains at the periphery of the tool.

Because of the pulsed grain engagement during ultrasonic supported grinding, the mechanical load on workpiece and tool increases but the thermal load decreases in comparison to conventional grinding. The high mechanical load causes splintering of the grains, which consequently leads to the perpetual generation of new edges. This effect increases the sharpness of the tool and reduces the friction between tool and workpiece. An increase of the ultrasonic amplitude results in a steady machining process and an increase of material removal rates [530]. However, lower temperatures and the higher engagement depth result in a reduction of the plastic deformation and a more brittle behaviour of the glass during ultrasonic machining.

5.2.5 Microdrilling

Microdrilling is a cutting process to fabricate circular holes. To date microdrills with diameters as small as $20\text{ }\mu\text{m}$ are available [233, 234]; however, $20\text{-}\mu\text{m}$ diameter drills are rarely used. The cutting speed achieved during microdrilling is only 0.02 m s^{-1} at a spindle frequency of 180,000 rpm (air bearing spindle). This low cutting speed means that the process is not suitable for an economic fabrication of parts. The durability of the tools and feed rate are very low. Normally the tools in microdrilling have diameters in the range between 1 mm and $100\text{ }\mu\text{m}$ [233, 234]. Drilling of brittle materials is possible using drills with these diameters [156, 157, 235]. Microdrills made from cemented carbide, in general, also for ductile materials, are coated with a thin diamond layer. CVD-processes are usually used to deposit the diamond coating with a thickness ranging from 5 to $15\text{ }\mu\text{m}$ because of the independence on the geometry of the tool. These coated drills have been successfully used for the drilling of brittle materials, such as ceramics and glasses.

An entirely new concept for the drilling of brittle materials is a vibration-assisted process. It is realized by a special machining tool. This drilling tool uses the effect of magnetostriction of a special material integrated in the spindle. This material reacts by a length variation in the case of magnetical excitation, which generates lower forces during drilling and smaller chipping, leading to a better contact and circulation of lubricants [555]. Further research efforts are directed at the optimisation of geometry of the microdrills and feed rate [156, 157, 235].

5.2.6 Microturning

Microturning of brittle materials is a very interesting method to shape optical surfaces. Commonly used machine tools are ultra precision tools. For example, a stiffness of $30 \text{ N } \mu\text{m}^{-1}$ at a maximum spindle frequency of 100,000 rpm is required and the radial run-out tolerance has to be below $0.2 \mu\text{m}$. For the detection of position of interferometers with a resolution of 10 nm are used. The shaping of non-rotation symmetrical workpieces is possible using assisting tools, such as the so-called ‘fast-tool-servo’ [288].

The process is mainly influenced by the feed rate. To obtain optically smooth surfaces, feed rate must be reduced down to about $1 \mu\text{m}$ per revolution. The formation of compressive stresses in front of the tooling edge is desired in order to plasticise the material in this zone. The very low chipping depth is in the range of rounding of the diamond tool used for turning and, therefore, a run in time is preferred [288].

Uhlmann et al. [531] examined the use of single crystalline and polycrystalline diamond as well as a CVD-diamond layer for the shaping of ceramics. They found that the wear rate increases with increasing penetration depth of the tool, increasing cutting speed and increasing feed rate. Polycrystalline diamond was most durable during the turning process, which is due to its tendency to splinter the work piece. The machined surfaces with the best quality, i.e. lowest roughness, were obtained if tools with CVD-diamond layers were used. Using other materials as an edging material for the tools, such as cubic boron nitride, or performing the machining in special atmospheres is just not suitable for industrial applications [284].

As already mentioned above, a useful alternative to reduce the wear during the turning process to shape brittle materials, such as glasses or semiconductors, is to utilise ultrasonic-assisted diamond turning [363, 364, 460]. The principle of ultrasonic-assisted turning is shown in Fig. 5.4. Conventional ultraprecision turning machine tools can also be used in ultrasonic-assisted turning. It is only necessary to adapt an ultrasonic module at the place of the conventional tool holder. This ultrasonic module is independent on the standard machine tool and allows for superimposing of the lateral tool movement with a high-frequency ultrasonic vibration (Fig. 5.4a). In ultrasonic-assisted turning the effective resulting cutting speed is given by superimposing the

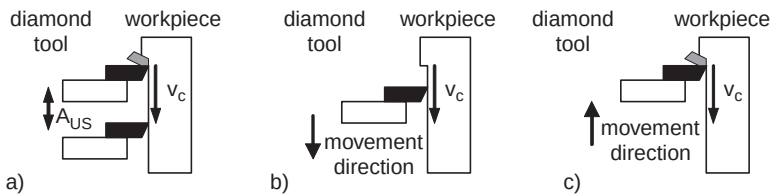


Fig. 5.4. Ultrasonic-assisted turning. The process steps (a), (b) and (c) are explained in the text. A_{US} is the ultrasonic amplitude and v_C is the cutting speed

constant rotation speed with the speed of the high frequency oscillation. It is essential for ultrasonic-assisted turning that the maximum oscillation speed is higher than the constant rotational speed of the workpiece. Only in this case the edge of the tool can be lifted off. It requires that work piece and the tool edge move in the same direction (Fig. 5.4b). If the direction of oscillation is changed and the tool and workpiece move in the opposite direction, then the edge penetrates into the material again (Fig. 5.4c). The lifting off reduces the effective contact time and consequently the wear of the tool. In ultrasonic-assisted turning of optical glasses the oscillation frequency, ultrasonic amplitudes and depth of the cut are around 40 kHz, up to 5 μm and in the range of 2–4 μm , respectively at feed rates between 3 and 7 μm .

Ductile machining of glasses to achieve optically smooth surfaces ($R_a < 10\text{ nm}$) is possible in a wide range of parameters. The feed rate is the most influential parameter determining the surface quality, whereas the depth of a cut is not so important. The resulting surface damage is also strongly dependent on the glass composition used [284]. The major advantages of ultrasonic-assisted vibration cutting are smoother machined surfaces and deeper critical depths during ductile cutting [460]. Furthermore, complex glass contours can be manufactured directly using a diamond tool if combined with an ultrasonic oscillation. This was shown for the manufacturing of microglass lenses with high accuracy of the shape and perfect surface quality [284–287].

5.3 Ultrasonic Machining

5.3.1 Principle

Ultrasonic machining, also known as ultrasonic impact grinding, uses ultrasonically induced vibrations of irregular abrasive particles, such as boron carbide, suspended in water, in a narrow gap between the vibrating tool and the workpiece to remove material from the workpiece (Fig. 5.5b). The particle suspension is pumped through or sprayed into the narrow gap (the work space) between the tool and the workpiece [517]. The suspension is used to move the particles through the cavity of the workpiece while cooling it and discharging the material from the workpiece. The cavity produced in the workpiece has the same geometry as the tool. Figure 5.5 illustrates the principle of ultrasonic machining.

A high frequency generator triggers a piezoceramic sonic modifier. The sonic modifier oscillates with the frequency of stimulation (normally around 20 kHz) at a low amplitude of around 5 μm . The amplitude of the ultrasound can be amplified by coupling the sonic modifier with a transformer and sonotrode. These elements are tuned to the frequency and the amplitude intensified to 20–40 μm . The sonotrode also acts as locator for the tool [281, 282]. The tool is joined with the sonotrode by brazing, sticking or press-bonding.

A movement in z -axis determines the feed rate. The suspended abrasive particles are accelerated by the longitudinal movement of the tool in the

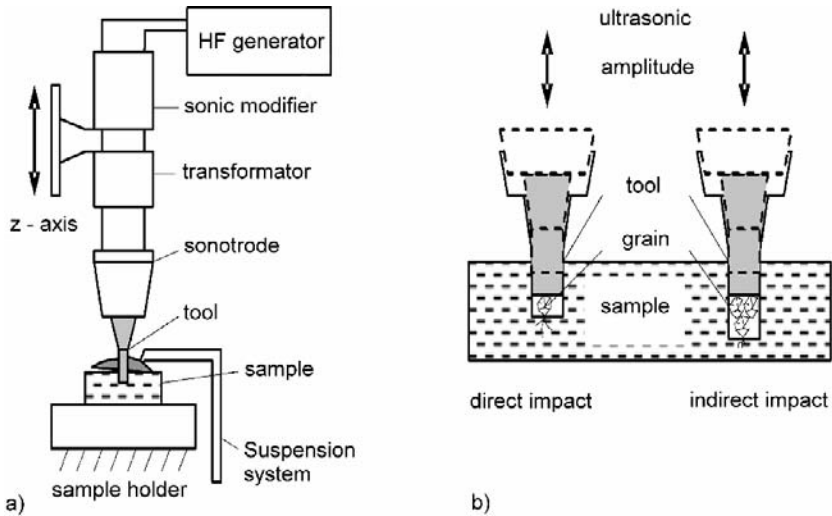


Fig. 5.5. Schematic of ultrasonic machining (a) and different impacts (b)

direction of the workpiece. The impact of these particles initiates microscopic cracks in the brittle workpiece surface, which eventually will result in chipping. The width of gap between the workpiece and the tool is extremely important as it determines the impact process (Fig. 5.5b). If on the one hand the distance between the edge of the tool and the workpiece has the same dimension as the abrasive particles, direct impact results, i.e. the particles are pushed by the tool into the workpiece causing direct energy transfer leading to maximum ablation rate. If on the other hand the work space is significantly larger than the particle size only indirect impact results. The energy is transferred via a number of particles and decreases with increasing width of the work space causing the ablation to decrease. The roughness of the machined surface is therefore very much dependent on the width of the work space. Klocke et al. [289] found that if the width of the work space is in the range of d_{50} of abrasive particles, the surface roughness of the machined workpiece is largest. The resulting surface roughness decreases with increasing work space width.

The process to create certain features in a workpiece can be optimised by the appropriate choice of the abrasive particles [289]. The ultrasonic machining process can be performed using a constant feed rate or a constant force. Fine geometrical features can be best fabricated using constant small feed rates because of the minimal forces allowed for optimised shaping conditions.

The advantages of the ultrasonic machining are that it can be used to machine a wide spectrum of brittle materials causing minimal surface damage to the workpiece. The technique is very flexible to create free geometries of structures and generates low chipping forces. Applying high loads on the tips of abrasive particles in contact with a glass surface will lead to the initiation of cracks.

Two types of ultrasonic machining are currently used: ultrasonic sink and ultrasonic path machining. In the case of sink machining the ablation rate is highest in front of the tool. At the sides of the tool the ultrasonic amplitude in normal direction to the surface is rather small, which results in a rolling of the abrasive particles so that the particles cause no direct impact in the work piece. A review of ultrasonic machining can be found in the literature [517].

The wear of the tool is an important factor affecting the quality of geometrical structures fabricated. Wear can occur on the tool in length, at the edge, the sides and the local features of the tool. The front face of the tool is the part of the tool that is mainly subjected to wear, which is followed by wear in length. It is possible to reduce the wear of the tool for instance by selecting better materials, such as polycrystalline diamond instead of plain classical steel [296]. They found a reducing of wear in lengths of several orders of magnitude. Also the edge and side wear were significantly diminished. The tool wear in ultrasonic machining negatively affects the machining accuracy, which makes it is necessary to account for and to compensate the wear during machining.

5.3.2 Effect of the Abrasive Particles

The action of ultrasonic-activated abrasive particle suspension determines the materials removal rate, which is affected by the particles itself, their size and concentration in the suspension. The ideal abrasive particles have high hardness and high compressive strength, a lot of sharp edges and usual fracture behaviour [281, 282]. The use of diamond particles allows high ablation rates because of their enormous hardness. However, they are expensive. Boron carbide is an alternative material, which allows an ablation rate of 90% as compared to diamond grains at a significant lower cost. Silicon carbide can also be used; however its ablation rate is even lower than those for boron carbide.

The most commonly used suspension medium is water. Particle concentrations in the range of 25–35 mass % are optimal to achieve the highest ablation rates. An increase of particle size of the abrasive results in an increased ablation rate and also an increased roughness of the machined surfaces. In the praxis often particles of size between 40 and 50 μm (F280) are used. During the machining the quality of suspension deteriorates with increasing time of use because of the accumulation of worn-down abrasive grains and rubbed-off material.

5.3.3 Effect of the Workpiece Materials Composition

The materials composition of the workpiece is the major factor that determines the ablation rate. The ablation rate increases with increasing brittleness of the material. The critical fracture toughness is commonly used to characterise the effects of brittle crack formation in a material. Klocke and Hilleke [281, 282] provided a relationship between the critical fracture toughness of

Table 5.1. Ablation dependent on the critical fracture toughness

Material	Critical fracture toughness (MPa m ^{1/2})	Ablation (mm ³ min ⁻¹)
Glass	1.5	864
Al ₂ O ₃	2.5	160
SiSiC	3.8	70
HPSN	6.0	40
ZrO ₂	9.1	20

various materials and the observed ablation rate (Table 5.1). Materials with larger critical fracture toughness usually have smaller ablation rates. Therefore, ultrasonic machining is especially useful to structure brittle materials with low critical fracture toughness such as glasses. Nowadays ablation rates between 20 and 40 mm min⁻¹ are achieved, which is in the same order of magnitude of grinding processes.

5.3.4 Equipment for Ultrasonic Machining

The operational parameters of oscillating system are important for the minimisation of tool wear, because deviations in the amplitude and oscillation rates affect the quality of geometrical structures and increase the wear rate. The wear rate when working with rotational symmetrical tools can be further reduced by applying an additional rotation to the tool, which will lead to an improved precision of geometrical structure to be machined.

Ultrasonic sink machining can be used to create geometrical features with a diameter as small as 200 μm. It is also possible to use complex tools to generate a complex shape in a single step process. Tools having several tips are commonly used to improve the efficiency, which is particularly useful for ultrasonic drilling of glass wafers for MEMS applications or for the encapsulation of silicon chips by anodic bonding, which requires drilling many cylindrical holes in a predefined pattern.

Ultrasonic path machining enables the generation of engraved free contours by using a simple tool geometry whose movement is numerically controlled by the machine. Such engraved structures can be created by a layer or a depth treatment. In layer treatment, the depth of the materials layer removed is in the order of the oscillation amplitude of tool, which allows only for materials ablation by the abutting face of the tool. The complex shape of a certain depth is engraved by repeated machining. In depth treatment the depth of each materials layer removed is significantly larger than the oscillation amplitude of the tool. In this case ablation also takes place on the sides of the tool. However, it is necessary in this case that the tool is rotating to prevent uneven tool wear.

For certain applications, for instance in microfluidic devices, the surface quality of ultrasonic machined holes is insufficient. Diepold and Obermeier

[108] examined the smoothing of ultrasonically machined holes using wet chemical etching. A NiCr–Au layer was used as etch mask and hydrofluoric acid as etching solution. Depending on the concentration of the hydrofluoric acid etch rates up to $11.5 \mu\text{m min}^{-1}$ could be achieved. The resulting surface quality was not found affected by the concentration of hydrofluoric acid. An etching time of 3 min using 33% HF was found to be optimal to smooth ultrasonically machined holes.

5.4 Powder Blasting

5.4.1 Principle

Powder blasting or abrasive jet machining is a simple and very fast mechanical erosion method for the fabrication of geometrical structures in brittle materials [36,61,472,474]. The effect of a particle impact on the material removal rate from the surface of brittle materials is discussed in literature [462]. The main advantages of powder blasting are the high erosion rates, which are much higher than those obtainable by wet or dry etching processes, low process forces and thermal pollution of the workpiece. Using different powders and masks, features in the range of few millimetres down to tenth of micrometres can be realised and the process can be used for nearly all brittle materials.

During powder blasting the powder is injected into an air jet, which accelerates the abrasive particles to a velocity near the speed of sound. Commonly used pressures are up to 6 bar. The kinetic energy of the impacting particles depends on the velocity and the mass of the particles. Varying the kinetic energy of the particles impacting the workpiece has different effects. The particles can cause hammering, consolidating, polishing, grinding, purifying, roughening, lapping, deburring, drilling or cutting.

Many powders, such as Al_2O_3 , SiC, SiO_2 , WC, diamond or glass particles, are used for blasting operations [61,62,147,474], but the most commonly used is Al_2O_3 powder [37,38,472,557] because it has sufficient properties at a low price. SiC offers a high hardness, very good thermal and chemical stability and very sharp edges. Glass powders are used to purify and solidify surfaces. However, for the depth structuring of brittle materials glass powders have only limited applicability.

The powder particle size used for blasting strongly depends on the aim of the operation. The spectrum of abrasive size ranges from 3 to $200 \mu\text{m}$ [472], but the most widely used particle size is in the order of $30 \mu\text{m}$ [37,38]. It was found that channels with steeper walls could be made if $9 \mu\text{m}$ instead of $30 \mu\text{m}$ particles were used [557]. Slikkerveer [472] found that the impact energy and not the particle size is the most critical process parameter. He investigated particle sizes ranging from 9 to $200 \mu\text{m}$ and particle velocities varying from 20 to 300 m s^{-1} . At a given velocity the impact energy increases with increasing

particle size. An increase of impact energy of the abrasive particles leads to a significantly higher erosion rate and a larger surface roughness.

The principle of hard particles indentation into the workpiece surface is shown in Fig. 3.20. The effects occurring at a surface during particle impact are discussed by Slikkerveer et al. [473]. The enormous stress below the indenting particle causes elastic and plastic deformation of the brittle substrate. If the fracture threshold is exceeded, initially short, median or deep cracks are initiated perpendicular to the surface followed by lateral cracks parallel to the surface in the depth of the plastic deformation zone. The lateral cracks must connect in order for material removal from the surface to occur.

The erosion rate depends on the material properties of the workpiece, its Young's modulus, hardness and fracture toughness and also on the process parameters, such as the hardness, size, shape, kinetic energy and number of particles hitting the surface of the workpiece. Evans et al. [139] investigated the effect of the particle impact of various abrasive materials into different target materials. The blasting process of various brittle materials was examined and modelled by several teams [79, 139, 374]. A non-linear dependence of the material removal rate on the hardness, elasticity and fracture toughness of the workpiece was found. Generally, it was found that the removal rate increases with decreasing of fracture toughness K_{IC} of the workpiece, whereas no uniform trend was found for the elasticity and hardness.

The results obtained by Buijs [79] are especially important for glass machining. Various glasses were examined and an increased removal rate was found for glasses with higher density and Young's modulus but lower hardness. A model for the prediction of the evolution of an eroded surface was presented by Slikkerveer et al. [474].

The most commonly used powder blasting processes are the mask process using just an unconfined powder jet, and microblasters that utilise a well-defined and confined powder jet.

5.4.2 Masking Process

To create structures using a powder blasting process a mask partially protecting the workpiece is required. The principle of masking is shown in Fig. 5.6. During the powder blasting step the air/particle stream is scanned over the masked surface to produce uniformly the depth and geometry of the desired structures. The diameter of the nozzle through which the powder jet is normally ejected is in the range between 6 and 12 mm. Because of the very abrasive nature of the powder jet the nozzle is commonly made from a high wear-resistant material, such as tungsten carbide. The major advantages of the masking process are the possibility to generate a number of geometrical features and structures with complex designs at a high resolution simultaneously. Furthermore, powder jets allow for high erosion rates in the order of 1 mm min^{-1} . The biggest disadvantage is the additional effort required to fabricate the mask.

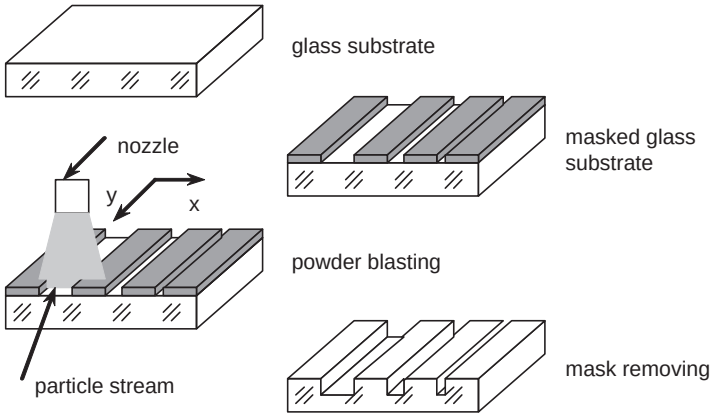


Fig. 5.6. Powder blasting using the masking process

The manufacturing of the masks can be done in several ways. Commonly used metal masks are produced by laser cutting or by wet chemical etching. These masks have a considerable thickness because of the plastic deformation they undergo during the impact of the abrasive particles. Metal masks are only available for the fabrication of larger geometrical features. The lower feature size is limited to approximately $50\text{ }\mu\text{m}$. However, these masks can be used repeatedly. The vertical erosion rate of a steel mask is about $2.4\text{ }\mu\text{m min}^{-1}$ as compared to the erosion rate of glass, which is about $110\text{ }\mu\text{m min}^{-1}$. The lateral erosion rate of the steel mask is even lower at $0.2\text{ }\mu\text{m s}^{-1}$ [38]. The wear rate during powder blasting of various mask materials was investigated by Slikkerveer et al. [474].

Prior to the powder blasting a pre-fabricated mask has to be attached to the substrate (see the right-hand side of Fig. 5.7), which can be however problematic. If the mask is simply clamped onto the substrate, particles could enter the space between mask and workpiece and therefore cause significant damage to the substrate, which might also result in additional stresses causing the mask to deform. These problems can be reduced by clamping the mask magnetically, gluing or cementing it to the substrate.

For making finer structures, i.e. below $50\text{ }\mu\text{m}$, rubber masks that can be photo-patterned are directly formed on the substrate surface. A continuous rubber layer is laminated directly to the substrate surface. Afterwards, the layer is exposed through a mask to UV-light (in analogy to the photolithography), which induces crosslinking in the exposed material. During the development step the uncrosslinked areas of the rubber are removed (see left-hand side of Fig. 5.7). The advantage of this technique is that the mask is directly transferred to the glass [472], but these masks can only be used once.

Wensink et al. [556] compared a variety of masking materials. The best results for powder blasting of structures with dimensions larger than $50\text{ }\mu\text{m}$ have been achieved using BF 400, which is an elastic negative photoresist foil.

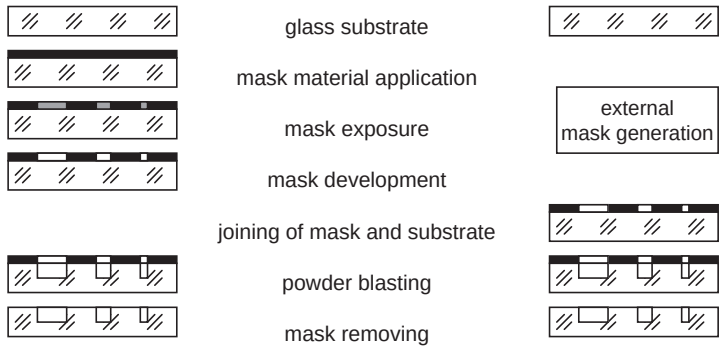


Fig. 5.7. Illustration of masking processes for powder blast structuring

If the dimensional tolerances had to be less accurate, thicker metal plates attached to the surfaces by a wax seal were favoured.

To combine the high resolution of directly transferable rubber masks with the high wear resistance offered by metals, metal masks can be directly created on the substrate by electroplating. Copper can be easily electroplated and furthermore offers a good resistance against powder blasting. The adhesion between the electroplated metal and the workpiece can be optimised by plasma-assisted cleaning of the glass substrate and the deposition of an intermediate titanium layer. The deposited copper layer is patterned using a lithographic process. Such copper layers allow powder blasting using $9\text{ }\mu\text{m}$ particles at velocities of 200 m s^{-1} . The ratio of the wear rates between Pyrex glass and copper is 30 [557].

A geometry dependence of the eroding depth during powder blasting was found for feature with sizes above 1.5 mm [36]. If the opening of the mask is too small with respect to the abrasive particle size, the intrusion of particles is prevented. The angle of impact of the abrasive particles at the side walls decreases as compared to those ones impacting the middle of the structure perpendicular. This will eventually lead to the formation of a V-shaped channel, causing the erosion rate to drop. The smaller the channel the sooner this will occur. This effect is called blast lag [557]. The best way to reduce blast lag is the use of smaller particles [557].

A $60\text{-}\mu\text{m}$ -wide channel was realized with an aspect ratio of 2.5 with a particle size of $9\text{ }\mu\text{m}$ and a powder velocity of 180 m s^{-1} using a $50\text{ }\mu\text{m}$ wide copper mask.

Belloy et al. [36, 38] investigated the oblique powder blasting, in which the jet of abrasive particles is directed to the masked workpiece at an angle different from normal incidence, which opens the way to new underetching effects and perspectives in the 3D microfabrication. A symmetrical shape is created if the abrasive particles impact the surface at normal incidence. An oblique particle impact, however, i.e. at an angle away from 90° , leads to the formation of an asymmetrical erosion profile. More material is removed in the

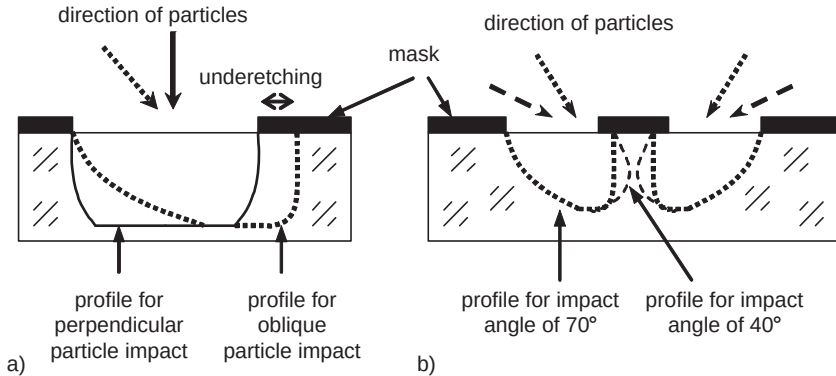


Fig. 5.8. Schematic illustration of (a) a profile of an oblique powder-blasted structure in glass using an eroding beam with an incidence angle different from 90° compared to normal impact. (b) The shape of the feature created dependent on directions of particle impact

direction of the particle stream (Fig. 5.8a). Depending on the process parameters and the process time one-sided (mechanical) underetching is obtained. The underetching is defined as the distance between the mask edge and the substrate wall directly with respect to the glass-mask interface (Fig. 5.8a). In the case of an oblique abrasive jet not only direct impact takes place, but also secondary impact particles contribute to the underetching. Secondary impact is caused by incoming abrasive particles that are rebounded by the bottom of the structure. They are eroding the wall of the glass structure under the mask additionally. Underetching is observed to be more important for small impact angles. The underetching and also the depth of the powder-blasted structures increase with increasing blasting time. The incident angle of the particle jet is the main parameter that determines the inclination of side walls. If jet incident angle is in the range of 60° – 70° only a very small wall slope results, which allows for creating nearly vertical sides of the structure. A pillar shape with a diameter of $100\mu\text{m}$, a depth of $700\mu\text{m}$ and an aspect ratio of 7 has been created [38]. More curved shapes can be created by decreasing the incident angle (Fig. 5.8b). The utilisation of this underetching effect enables to generate free standing structures at a surface [38].

Titre plates and micromixers as well as microfluidic devices and microchips are examples of microstructures that have been created using powder blasting process. The microstructuring of hard magnetic composite layers, microfluidic glass chips, electrophoresis chips, cantilever beams having various masses made from Pyrex glass have been described in [35,36]. Furthermore, the suitability of powder blasting for the micromachining of accelerometer devices in glass was also demonstrated [39]. In this case a double-sided eroding process was used. Iron masks are fixed on both sides of the glass substrate using a wax seal. The upper side of the substrate is exposed to the eroding jet to define the

global contour of the sensor. The side below is exposed to the eroding jet in order to thin the cantilever. Powder blasting is also used for the fabrication of channel plates for Zeus panels, a special type of flat and slim display. Lighthart et al. [331] compared powder blasting to other structuring processes.

5.4.3 Microjet Powder Blasting

Microjet powder blasting does not require a mask, instead the abrasive powder jet is ejected directly through a fine nozzle, which restricts the spread of the particle stream. The microstructures, whose features depend on the beam geometry, are directly ‘written’ into the substrate by the relative movement between microblaster and substrate (Fig. 5.9). The simplicity of the microblasting process and the high flexibility allowing to create any geometry of structures are major advantages. The disadvantages are the low productivity of the process caused by its serial character and the impact of the nozzle wear on the resulting geometrical structures. Powder microblasting can be favourably used to create 3D structures and special surface shapes as well as for cutting processes.

A model for the material removal during microjet powder blasting from the technological point of view was presented in the literature [61,62]. The material removal rate in microjet powder blasting depends on the Young’s modulus of the workpiece, its fracture toughness and also on the energy required to create new surfaces. The process rate depends also on the impact energy of the particles, which as mentioned depends on the velocity and the mass of the eroding particles. The velocity profile in the open jet, after leaving the nozzle, changes from an approximately rectangular shape immediately behind the nozzle to an exponential profile with increasing distance away from the nozzle. The particle velocity inside the jet is higher in comparison with the velocity of particles at the boundaries of the jet. The velocity at the centre of the jet remains almost constant, but the width of the centre area decreases with increasing distance from the nozzle. Bothen and Kiesewetter [62] discussed also the local concentration distribution of particles in an open jet, which allows calculating the local and temporal profiles of the shapes to be created. The maximum for the eroded volume and abrasion depth depends on the distance between the nozzle and the substrate.

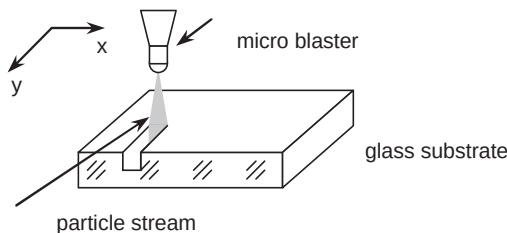


Fig. 5.9. Microjet powder blasting

5.5 Water Jet Processing

Water jet milling or cutting is a machining process that is particularly suitable for materials that are difficult to cut, such as hard and brittle materials like glasses, ceramics and composites. The process was developed in the late 1960s. Water jet milling was not directly developed for micromachining applications. Commercial water jet systems have often a processing table that is several square metres big; however, the precision of the process is significantly better than a millimetre. To cut materials using a water jet the water is pressurised up to 400 MPa. The impacting water jet causes shearing, cracking, erosion, cavitation, delamination and plastic deformation within the workpiece subjected to the jet. The main advantages of water jet milling are that it causes no thermal and only a low mechanical load during processing and that it offers a great deal of flexibility with respect to the geometry to be created as well as materials to be processed. The technique requires only a simple jet and workpiece positioning and good CAD/CAM coupling. Water jet milling subjects the tools to very little wear. A description of the cutting process with fluidic jets of small diameters is given by Cadavid-Giraldo [86].

Three principles of the water jet processing are distinguished (Fig. 5.10). In conventional pure water jet milling, also called hydrodynamic machining, simply pure water jet is used for cutting. The velocity of the water jet reaches 900 m s^{-1} and nozzle diameters can be as small as 0.1 mm . For precision machining dimensional tolerances of $50 \mu\text{m}$ with a minimum width of grooves and bars of $200 \mu\text{m}$ are possible.

In abrasive water jet processing, also called hydroabrasive machining, abrasive particles are added into the water jet. The particles increase the erosive effect of the jet. Normally the abrasive is added by the suction generated by

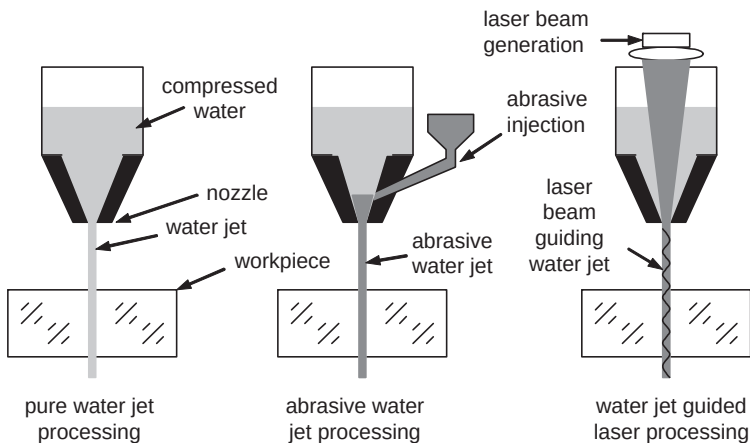


Fig. 5.10. Methods of water jet milling or cutting

the water into the mixing chamber. The water acts as an accelerating medium for the particles. The jet is formed by a nozzle made from tungsten carbide because of the extremely high wear that experiences [199, 260].

Abrasive water jet processing is controlled by more than 16 parameters [578]. An increase of ejection pressure causes the particle velocity to increase. Hashish [199] provides a concrete description of the influence of the water jet pressure on the abrasive machining. A lot of material parameters influence the effectiveness of the cutting process of brittle materials, such as the fracture toughness and grain size (in case of ceramics). Zeng and Kim [575] presented a model for the water jet cutting of brittle materials. The geometry of the cutting space depends on the process and jet parameters and also on the pre-existing geometry of the structure. Considering all these effects the cutting process for a defined contour was modelled and optimised [216–218].

In water jet guided laser processing, the focused beam of an Nd:YAG laser is coupled into the water jet. The concept of the water jet guided laser is to couple a pulsed laser beam into a narrow water jet, that means, a laser beam is focused into the nozzle of a water jet while passing. The focus of the laser beam is stretched (between 30 and 100 mm) depending on diameter and pressure of the water jet. This fact allows working nearly independent on the focus position in difference to the conventional laser machining process. The water jet ejected from the nozzle guides the laser beam by means of total internal reflection at the water/air interface to the workpiece, thereby acting as a stable fluid waveguide [209].

The water jets are ejected with pressures in the range between 20 and 500 bar, but laminar flow of the water jet is important. It is possible to couple a laser power of more than 50 MW cm^{-2} into a water jet of approximately 0.1 mm diameter. This kind of processing combines the advantages of laser machining and water jet machining. During a laser pulse for a duration of parts of a millisecond, the high intensity laser beam melts the material and vaporises the water in the direct vicinity. The water jet provides continuous cooling of the workpiece during the action of laser pulses and keeps the thermal damage of surrounding material to a minimum. In the break between two pulses the water jet impacts the working space. The water jet also removes the material eroded by the laser ablation because of its high momentum. The presence of a water film on the machined workpiece also prevents process debris from adhering to the machined surfaces.

The laser enables to separate the workpiece with almost perpendicular side walls compared to the inclined walls that the action of a conventional water jet produces. This is especially interesting for the precision machining of microsystems [211]. Water jet guided laser processing enables to produce cuts of width of 0.05 mm with tolerances of about 0.01 mm. Very thin substrates and also those with a thickness of 3 mm can be cut.

The process is used for the machining of silicon, for example for the cutting of solar cells [210], but it was also successfully tested for many other hard and brittle materials, such as ceramics. However, for the machining of glasses its high transmission in the range of the Nd:YAG laser wavelength of around 1,060nm causes problems. A successful basic approach is the development of absorption adapted glasses [503] (see also Fig. 1.38) or the applying of frequency doubled Nd:YAG lasers.

Chemical and Complex Structuring Processes

6.1 Chemical Etching

6.1.1 Introductory Remarks

Chemical etching enables geometrical structuring of workpieces by removing the material using chemical or electrochemical reactions [430]. Chemical etching processes can be performed in the liquid (wet etching) or gaseous phase (dry etching). Pure electrochemical processes, however, are only important for the etching of metals and will not be discussed here.

The visible ablation of material during the etching process is effected by chemical interphase reactions. In addition to the chemical interphase reactions, physical interactions, e.g. diffusion, adsorption, streaming, impact, are also involved in the complex process of etching. In the sequence of the manifold influences the effect of the lowest speed is controlling the complete process [430].

To utilize chemical etching processes for the geometrical structuring of materials, it is necessary to ensure a selectivity of the etching process, which again is possible by using an etch mask (Fig. 6.1). The masking process uses a protective layer on the surface of a workpiece. These protective layers have to be structured and the areas of the workpiece not to be removed protected against chemical attack. Historically, wax was often used for masking the workpieces. However, the main problem of waxes is their limited chemical stability; nevertheless, structures in the range of micrometres can be created. The structure is basically drawn into the wax layer, which is rather labour intensive and not suitable for complex geometries. Nowadays, photoresists are used for the structuring of the protective layer, which can be performed by lithography (see Fig. 4.6). The problem of photoresists is their limited chemical stability and also the adhesion between the layer and the substrate surface, which affects the success of the structuring process especially during the etching process in HF solutions. Metal layers can also be used as etching mask. In this case, the metal layer or a system of metal layers is deposited

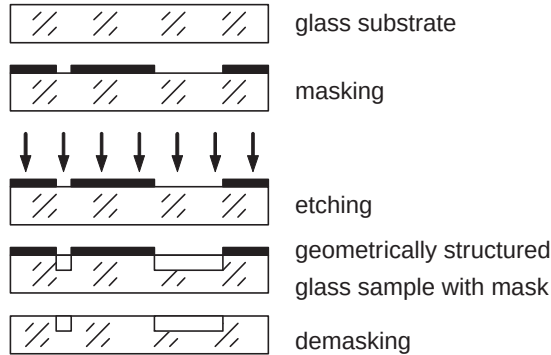


Fig. 6.1. Masking processes for the chemical etching of glass

onto the surface. Afterwards, a photoresist is coated onto the metal layer, which is lithographically structured. Then the structure is transferred into the metal layer, for instance by dry etching followed by the removal of the photoresist, and only then the underlying workpiece can be structured wet chemically. Finally the metal layer will be removed.

A special masking process is to use an anodically bonded silicon wafer [99]. In this case a borosilicate glass wafer (workpiece) is anodically bonded to a structured silicon wafer (mask) and etched in a solution of HF. Tests have shown that it is possible to etch cavities of depth up to 500 μm . The etching mask has a sufficient chemical resistance and a very good adhesion to the glass surface. The advantages of this process are the suitability to create microsystems and the possibility for deep etching with a small degree of underetching.

Another important criterion for the appropriateness of chemical etching processes is the degree of anisotropy of the features created. Various etching methods and etched materials generate etched structures with different profile, which can be isotropic or anisotropic (Fig. 6.2). In isotropic etching the speed of etching is the same in all directions, which is the case for glasses. As a result of isotropic etching all geometrical structures will have rounded side walls. The maximum possible aspect ratio is 0.5, because the material removal rate in the z -direction (i.e. the resulting depth) is the same as in all other directions (x - and y -direction and of both sides) (Fig. 6.2).

In contrast to the isotropic etching, anisotropic etching can be achieved only if the materials properties of the workpiece are not isotropic, for instance for single crystalline silicon. For anisotropic materials the etching rate is different in different directions, i.e. crystal planes. In Fig. 6.2, the different crystallographic planes are described by Miller indices. If anisotropic materials are structured by chemical etching, the geometry of the resulting structures is dependent on the orientation of the crystal planes, which will result in inclinations of the side walls (Fig. 6.2). In single crystalline silica, the 100 and 110

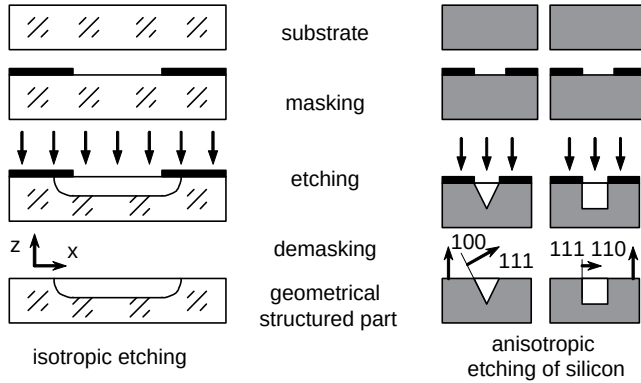


Fig. 6.2. Structures after isotropic (*left*) and anisotropic (*right*) etching

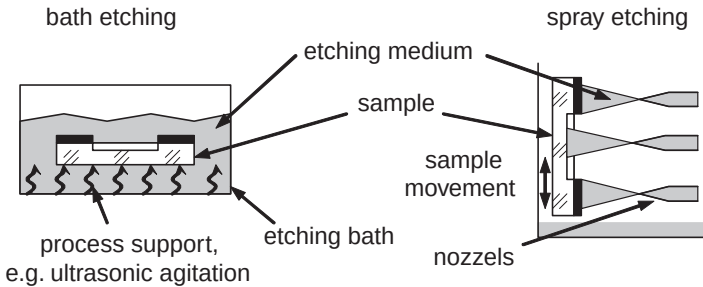


Fig. 6.3. Types of wet-chemical etching

planes have a higher solubility than the 111, which causes the etching process to stop [342]. A comprehensive description of the different etching processes in microsystems technology and a compostructure of recipes for different materials is given by Köhler [298].

6.1.2 Wet-Chemical Etching

Two types of wet-chemical etching processes are commonly used: bath etching and spray etching (Fig. 6.3). In bath etching the sample is placed inside a bath containing the etching medium. The medium must be continuously stirred so that fresh and reactive etching medium is always in contact with the work-piece surface and the reaction products are removed from the reaction zone. Commonly the etching process is supported by microstreaming of the etching fluid, for instance by ultrasonic agitation.

As the name says, in spray etching the etching medium is sprayed onto the surface of the sample by an array of nozzles. To optimize the uniformity of the process the sample is moved. Normally many samples are placed on a rotating table and processed simultaneously. The etching rate of the spray etch

process compared with the bath etch process is much higher, because of the permanent streaming etching solution, which removes the reaction products of the etching process very quickly from the surface and allows fresh reactive etching solution to attack the material. This effect is very dependent on the dimensions of geometrical structures to be created. For very small features a macroscopic stream of etching medium will not be able to enter the small spaces, which affects the materials transfer rates causing the etching rate to decrease.

For the etching of glasses, only hydrofluoric acid or other HF containing aqueous solutions can be used. HF reacts in presence of water with the glass surface. The etching rate strongly depends on the chemical composition of the glasses. Silica glass consists only of SiO_4^{4-} tetrahedra connected at all four corners to four other SiO_4^{4-} tetrahedra via bridging oxygens (see Fig. 1.8 and Sect. 1.2.1) creating a three-dimensional network. It is necessary to break these bridging oxygen bonds in order to destroy the complex network structure to dissolve the material. The dissolution of vitreous silica in aqueous HF solution can be described by the following reactions. At first silica reacts with HF forming silicon tetrafluoride and water, see (6.1):



In a subsequent reaction, (6.2), SiF_4 reacts with HF to form H_2SiF_6 , which is not soluble in HF solutions.



For multicomponent glasses the reaction mechanism are much more complex. Additional alkali fluorides, alkali earth fluorides, aluminium alkali fluorides and other compounds arise having very different dissolution rates during the reaction; (6.3) shows an example.



A detailed description of the mechanisms of the dissolution process of glasses in HF and the effect of the glass composition can be found in the literature [482,483]. He described the general mechanism of solubility of glasses, the role of fluorine containing species F^- , HF and HF_2^- as well as the catalytic action of H^+ on the etching rate of glass. Various different etching media containing different additives were used and the effect on the surface morphology and etching behaviour was investigated.

For practical glass etching three processes are commonly used: smooth, matt and depth etching. The processes are described in Table 6.1.

The influence of the addition of various acids to HF-based etching solution on the dissolution of $\text{Na}_2\text{O}-\text{MgO}-\text{CaO}-\text{SiO}_2$ glass has been investigated [484]. Stjernström and Roeraade [495] described a process for the fabrication of microfluidic glass systems. They used standard microscope slides

Table 6.1. Processes used for the etching of glass

	Smooth etching	Matt etching	Depth etching
Specific	Surface treatment, deposition of alkali fluoride should be prevented	Transmutation of the etching products with etching salts into insoluble silicon fluorides	Very aggressive solution and high etching rates
Process	Multiple dipping into the etching fluid followed by rinsing with water	Silicon fluorides deposited at the surface stop any further etching resulting in matting	Dipping process into a bath or painting using paste of the etching medium
Solutions	Solutions of HF with additives of other acids, such as H_2SO_4 , intensive agitation of the bath, elevated temperature	Low concentrated solutions of HF with alkaline fluorides or ammonium fluoride additives	Solutions of HF

made from soda-lime silicate glass as substrates for the etching experiments. The microscope slides were carefully cleaned and coated with a positive photoresist, which was structured and hard baked. The masked glass was etched using buffered HF solutions containing additionally HCl. The addition of HCl prevented the formation of alkaline earth fluorides with low solubility on the surface of the workpiece during the etching process, which results in a significantly reduced roughness of the wall surfaces created. The photoresist, however, was not sufficiently stable in buffered HF solution, but when concentrated HCl was added to the etching medium the stability of the photoresist mask improved allowing etching times of up to 1 h at room temperature. In this time structures with a depth of approximately $70\text{ }\mu\text{m}$ were created. Such depths are sufficient for applications in microfluidic systems.

Shimizu and Iwakuro [463] examined the influence of an improved wettability and adhesion of photoresist, initiated by O_2 plasma treatment, and the addition of surfactants into the etching fluid on the etching of thin SiO_2 layers, resulting in a more consistent etching behaviour. The improved etching behaviour was due to the prevention of bubble formation at the microstructures, allowing for a better exchange of the etching solution in the patterns.

A mask-free etching process for the etching of the commercially available glasses BK7 and SK5 (Schott) was developed by Kyung and Lawandy [317]. A localised increase in the solubility of the glass was found in the case of an UV exposure. A conventional UV-lamp and alternatively (for comparison) a frequency-doubled Nd:YAG-laser with a wavelength of 532 nm were used. The UV-exposure of the glass results in multi-photon process-generated absorption

centres in the glass [318]. The authors demonstrated that the glasses etched while exposed to UV had much smoother surfaces than the samples etched normally. Rapid and easy micropatterning was demonstrated on commercially available borosilicate glasses containing at least 10 mass % B_2O_3 by exposure to UV light (255 nm) through a mask. Using this process it was possible to create structures with a width of $35\text{ }\mu\text{m}$ and a depth of approximately 250 nm.

A modified process, the so-called spin-agitated-etching (SAE), was developed by Kyung and Lawandy [318]. In this case the substrate is mounted on a desk rotating with 3,000 rpm in an ultrasonically agitated 12% HF solution. This process allows for a significantly deeper and more selective etching, enabling to create structures with a depth of up to $3\text{ }\mu\text{m}$. The surfaces produced are much more uniform. The result is mainly influenced by the vigorous agitation caused by the rotation, and the ultrasound preventing build-up of insoluble by-products on the surface during the chemical etching.

Henkel et al. [214] demonstrated the application of wet chemical etching of glass (BOROFLOAT 33, Schott Jena, thickness 0.7 mm) to produce a chip module for the manipulation of fluids. The used etch mask was a Ni/Cr layer of 150 nm thickness. The complete chip consists of two sheets with half channels joined by anodic bonding.

Youn and Kang [573] described a maskless patterning technique by combining nanoindentation with HF isotropic etching.

To etch chalcogenide glasses it is possible to use alkaline solutions as an etchant. A selective etching is achieved by photoinduced changes in the structure of the glasses. The etching contrast depends on the glass composition, type and concentration of etchant and the incident light energy [391].

6.1.3 Dry Etching

Dry etching methods refer to the removal of material from a workpiece by the exposure to a gaseous or vapour phase. Dry etching processes are often used in microtechnology for the etching of thin layers. These processes are very precise but the etching rates are low. Material is removed from the surface of the workpiece by physically bombarding the material with ions that are generated for instance in a plasma or chemically by a reaction between the materials surface and a reactive gas species or a combined effect. The most meaningful classification of dry etching methods distinguishes the effective etching mechanism (see Table 6.2) [85, 298, 342, 354]. Three basic classes of dry etching techniques can be distinguished: sputter etching, reactive ion etching and vapour phase etching.

In sputter etching (ion etching or ion beam etching) the workpiece is placed into a plasma reactor. The removal of material is a real physical process. A plasma is defined as a partially or fully ionised but spatially neutral gas, which contains electrons, ions and eventually uncharged species. Such species are atoms, molecules and radicals. A plasma is ignited using for instance an RF power source generating ions that are accelerated towards the workpiece

Table 6.2. Classification of dry etching techniques

Process	Mechanism of effect	Selectivity	Profile of geometry	Pressure (Pa)
Ion beam etching	Physical	Poor	Anisotropic	<0.01
Ion etching	Physical	Poor	Anisotropic	1–10
Reactive ion beam etching	Physical/chemical	Good	Anisotropic to isotropic	<0.01
Reactive ion etching (RIE)	Physical/chemical	Good	Anisotropic to isotropic	1–10
Plasma etching	Chemical/physical	Good	Isotropic to anisotropic	10–100
Barrel etching	Chemical	Excellent	Isotropic	100

surface of the material being etched. Commonly used plasma feed gases are inert gases, such as argon. Material is removed from the surface by a sputtering process. If the kinetic energy of the ions is high enough, they can ‘kick’ atoms out of the workpiece without undergoing any chemical reaction, which results in a poor selectivity and a high anisotropy of the etching process.

In reactive ion etching and reactive ion beam etching, both physical and chemical processes take place at the workpiece surface. In this case the active etching species generated are reactive ions, such as O^+ or F^- . Whether chemical reactions, resulting in the formation of gaseous compounds, or the sputtering effect dominates can be adjusted by choosing the etching medium and controlling the process parameters. In a plasma free radicals are also generated, which can undergo surface reaction in plasma etching. If the chemical modification of the workpiece surface is undesired, the workpiece can be moved out of the plasma chamber so that the most reactive species had the time to recombine prior to hitting the surface.

On the contrary vapour phase or barrel etching is a purely chemical etching process. The active species resulting in the material removal are free radicals, for instance F^* . The material removal is due to chemical reactions between these highly reactive species and the workpiece surface, resulting in an excellent selectivity allowing for a complete isotropic etching geometry.

Additionally to the above mentioned processes, magnetically enhanced and chemically assisted processes have been developed. Further information can be found in the literature [342].

The etching result is mainly governed by the reactor used and the geometrical requirements. For the barrel etching a special cylindrical reactor is used. However, in this reactor the workpiece is shielded from the plasma discharge by means of a perforated metallic cylinder, allowing the active species, i.e. the ions or radicals, to draw by the vacuum into the cylinder where the etching process takes place. This reactor arrangement hinders the formation of an accelerated and orientated ion stream being directed towards the substrate, which commonly would cause an anisotropic etching profile.

For ion, reactive ion and plasma etching commonly a parallel plate plasma reactor is used. In this type of reactor two electrodes are arranged in parallel. The workpiece is mostly positioned on the bottom electrode. Commonly used are low-temperature plasmas, which are non-equilibrium plasmas. The plasma contains only a small amount of ionised gas (degree of ionisation is 10^{-6} to 10^{-5}), a few percent (2–20%) free radicals and emits very highly energetic, ultra-violet (VUV) light. Glow-discharges are used to create the plasma in the space between the plates. This discharge is very effective to create high density inert and reactive ions and also free radicals by dissociating molecules through electron bombardment and photochemical processes. The generated active species in the plasma are accelerated towards the substrate. The chemically reactive components in the plasma depend on the feed gas used. The physical component contributing to the material removal in plasma processes depends on the applied acceleration voltage and the geometry of the reactor. If the workpiece is positioned on the smaller electrode plate, such as in ion etching, the acceleration of ions is greater as compared to positioning the workpiece on the larger electrode plate, which is commonly done in plasma etching. The degree of anisotropy of the structures created varies accordingly (Table 6.2).

The systems used for ion beam and reactive ion beam etching consist of a two-chamber reactor that spatially separates the generation of reactive species and ions in the plasma process and the etching of the substrate. The advantage of such a system is that the ion energy, ion stream density and the free angle of impact of the accelerated ions can be adjusted separately. However, the disadvantage is the significant higher technical involvement of such a process.

Only fluorine containing gases, such as CCl_2F_2 , CF_4 , SF_6 and C_2F_6 , are commonly used to etch glasses. A variety of reactive radicals, such as CF_2^+ , are formed in the plasma. A comparison of various plasma sources and different process parameters is given by Tsukada et al. [529], Sugawara [506], Goyal et al. [179].

The rate of material removal in dry etching techniques is generally low and strongly dependent on the process parameters. If the material removal is overwhelmingly physical, the etching rate is typically in the range of some 10 nm min^{-1} ; however, if chemical processes are prevailing, it can be as high as some 100 nm min^{-1} .

As for wet etching process masking of the workpiece is also required for the dry etching process. The masking processes are highly dependent on the type of etching process used. If on the one hand physical processes of material removal prevail, the selectivity between the etching rate of mask material and workpiece is rather low, that is why thick masking layers are required. If on the other hand chemical etching prevails, the selectivity between the etching rates of mask material and workpiece is high. In this case, the masking layer is not required to be very thick, but it must have a very high chemical resistance.

Table 6.3. Comparison between wet and dry etching processes

Parameter	Dry etching	Wet etching
Etch rates	Slow ($<0.1 \mu\text{m min}^{-1}$)	Fast ($>1 \mu\text{m min}^{-1}$)
Selectivity	Poor to good (dependent on the special process)	Good
Control of etch rate	Simple	Difficult
Operating parameters	Many	Few
Equipment cost	Expensive	Inexpensive
Materials	Only certain materials	All
Integration to production	Good	Poor
Directionality	Highly directional	Isotropic: highly directional Anisotropic: dependent on crystal directions
Adhesion of the mask	Not critical	Critical
Submicron features	Applicable	Not applicable

Mask structures are commonly fabricated using lithographic processes. The most frequently used masking materials for the etching of glasses are aluminium, chromium/gold, alumina, gold, silicon nitride and photoresists. However, polymer layers have also been used as etching masks for the structuring of glasses [101]. The structured mask is produced by embossing. A small layer of the polymer remains at the bottom of the embossed polymer structures. This, however, does not constitute a problem for the process since this layer is rapidly removed at the beginning of the dry etching.

A comparison between wet and dry etching processes will help to select a particular process for a given application. Table 6.3 juxtaposes the process parameters and etching results of wet and dry etching processes [342]. Dry etching processes are very precise and allow for the integration into a production line; however, the etching rates are rather low. Recently, however, Goyal et al. [179] reported a high speed inductively coupled plasma (ICP) reactive ion etching process for Pyrex glass with a maximum etch rate of $0.75 \mu\text{m min}^{-1}$. The etch rate is mainly influenced by the distance between substrate and plasma source, the ICP power, the flow rates of reactants and the operating pressure.

Hence, dry etching processes are particularly useful for the precision etching of thin layers in microelectronics. Wet etching allows for high etching rates and is suitable for the depth etching in micromechanics and microsystem technologies, which require low and medium batch sizes.

6.2 Other Thermal, Chemical and Electrical Structuring Processes

6.2.1 Glass Products with Controlled Porosity

VYCOR Principle

Originally the VYCOR[®] process was developed to produce a glass with a composition and properties similar to quartz glass (see Sect. 1.2.1) but much cheaper as compared to other production technologies for quartz glass [142, 385]. The process sequence of the VYCOR[®] process (without the last sintering step) is shown in Fig. 6.4. The composition of the initial glass and the process parameters are chosen such that the resulting porous, leached glass body consists in excess of 98 mass % of silica. The remainder is sodium borate. Originally, the saleable silica-like glass was obtained by sintering the porous pre-product. However, nowadays the porous half-product is desired.

Besides etching of masked glass substrates, see Sect. 6.1, the leaching of phase-separated glasses, see for instance Figs. 1.14–1.16, is completely another process and also allows for the fabrication of microstructured glass bodies. A schematic of the process to fabricate a porous glass membrane, which was developed from the classical VYCOR[®] process, is shown in Fig. 6.4.

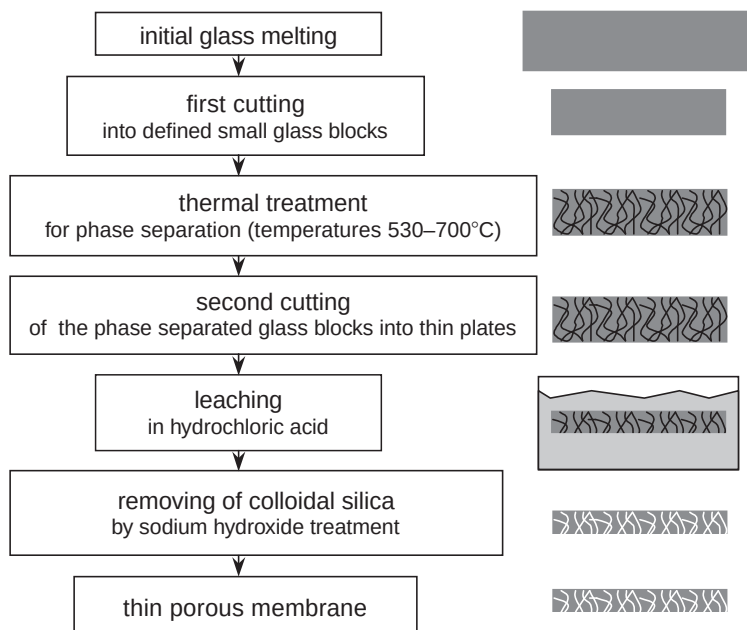


Fig. 6.4. Schematic for the production of porous glass membranes

A $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass precursor is melted and formed [264, 385]. The precursor is then cut into blocks, and a thermal treatment follows to induce phase separation. The thermal treatment takes place in a temperature range between 530 and 700°C. A phase separation as illustrated in Fig. 1.16 takes place and a SiO_2 -rich (consisting of more than 98% SiO_2) phase forms. This SiO_2 -rich phase has a very high chemical stability. The other phase consists of an alkali borate phase and can very easily be dissolved in an acid solution.

Depending on the chemical composition of the initial glass and the thermal treatment conditions, various types of material structures can be realised during thermally induced phase separation. It is for instance possible to create a droplet structure in which one phase is geometrically isolated in drops and the other forms the surrounding matrix (in analogy to Fig. 1.14). A penetration structure can also form. In this case both phases form a three-dimensional network similar to a sponge (shown in Fig. 1.16). This type of phase separation is necessary to produce microporous glass products. Furthermore, it is possible that transition structures occur, which fall in between the drop and penetration structures (Fig. 1.15). The processes occurring during phase separation and the development of various material structures are briefly described in Sect. 1.1.6. A detailed discussion can be found in the literature [263, 538].

Before the removal of the more soluble minor phase, the glass is shaped by mechanical cutting into thin plates. This is important to define the membrane thickness and reduce the sample thickness to enhance the effectiveness of the leaching process.

The alkali borate phase is commonly removed by leaching in hydrochloric acid, which dissolves selectively this phase but does not damage the SiO_2 -rich phase. If a three-dimensional penetration structure was formed during the phase separation process, it is possible to solve the alkali borate phase completely, so that the second phase forms a porous membrane [263, 264]. Depending on the actual process conditions used, an additional sodium hydroxide leaching to remove any remaining colloidal silica from the pores of the membrane might be necessary. The pore diameter and pore volume can be tailored by adjusting the composition of the initial glass as well as the process parameters of the thermally induced phase separation and the leaching step. Such porous silica membranes find applications in chemical sensors [348], chemistry, medicine and in microreaction vessels [42, 213]. The modified VYCOR® process has been further modified to generate mesopores inside the porous glass. In this case the macropores of a porous glass form the scaffold for the deposition of finely dispersed silica inside the porous medium [135].

Porous glasses can also be produced by inducing partial crystallisation in the glass rather than a phase separation and utilising the difference in solubility between the glass and crystalline phase. This process is similar to the photostructuring process (see Chap. 9).

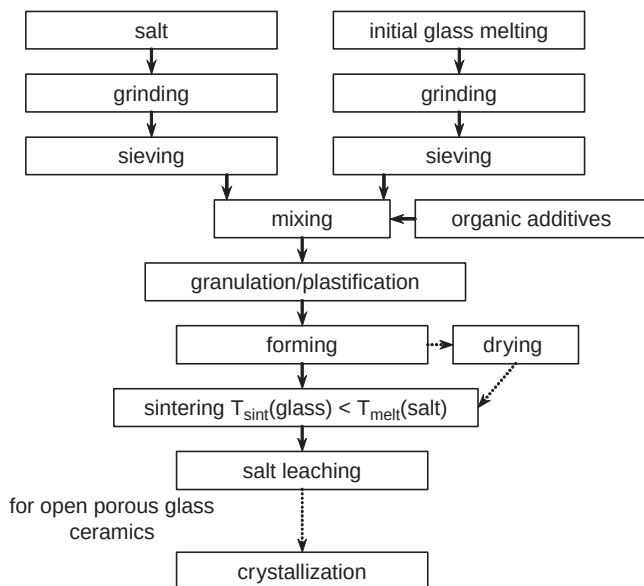


Fig. 6.5. Schematic flow diagram of the filler process

Filler Principle

The filler principle or process can be used to produce open porous glass or glass ceramic bodies with a defined pore diameter and volume. The advantages of the filler process as compared to the conventional sintering of glass powders are that it is possible to produce glasses with porosities of up to 80% possessing an open porous structure. The process allows for close control of the pore volume, pore size and distribution, and the specific surface area of the glass can be tailored. The filler process is illustrated in Fig. 6.5. A more detailed description of the filler process can be found in the literature [466].

The process starts with the melting of a glass, which is rapidly cooled leading to stressed glass. This stressed glass is ground to a powder. An inorganic, highly melting, chemically soluble salt is used to act as a template for the pores. Both the ground salt and the glass powder are sieved to obtain the desired particle size fraction. The ground glass powder has to have a smaller particle size than the salt to stabilize the sintered body. Commonly an average particle size of the glass powder in the range of 1–60 μm is required. The particle size and the amount of the salt that will be added to the glass determine the pore size and pore volume of the sintered glass body. The resulting porosity of the glass body can be adjusted to vary from 20 to 80 vol %. By tailoring the porosity of the glass device its specific gravity can range from 2.5 to 0.4 g cm^{-3} , which depends also on the density of the glass. The average pore diameter can be adjusted from 5 to 300 μm by selecting the appropriate

particle size of the salt. A bimodal pore size distribution can be obtained if two different salt particle sizes are used [466].

In the following step the glass powder, salt and additives, which are required to optimise the later forming, are mixed. The desired green bodies are formed for instance by granulation and dry pressing, plastification and extrusion. Sometimes the green body requires an additional drying step.

A stable glass body is finally formed by sintering. The temperature used for this process has to be in the range of the softening point of the glass but must be lower than the melting point of the salt. In this temperature range the glass can undergo viscous flow while the salt particles remain solid. During this sintering process the glass fuses with glass and salt contacts with salt, which results in a reticulate skeletal structure of the glass body. The lower sintering temperatures required for glasses as compared to a ceramic powder are beneficial for the process so that inorganic salts can be used as template material for the porous network. High melting salts with a high solubility, such as halides, sulfates, carbonates, phosphates and nitrates, are commonly used as pore-forming agents. After cooling the salt is simply leached out of the sintered glass body leaving an open porous glass body.

If an open-porous sintered glassceramic has to be manufactured a crystallisation step has to be included. Normally a partial crystallisation of the glass takes place simultaneously to the sintering prior to the dissolution of the salt in order to prevent the deformation of the glass body during the sintering process. Depending on the ion exchange capability between the glass and inorganic salt additional crystal phases might form that will affect the final properties of the sintered glassceramic body [466].

The filler process typically results in open porous glass or glassceramic parts with an open pore volume of around 60 vol % and only 8 vol % of dead-end pores and 2 vol % of closed pores.

The filler process has been used for the preparation of open porous glass carrier balls, such as Siran® [452], and also to produce complex open porous glass and glassceramic carrier bodies [466]. They are used in biotechnology for storage, conduction and distribution of liquids and in filtration and separation processes and also as catalyst support material.

Sol–Gel Principle

Marques et al. [346] described the manufacturing of sol–gel derived porous scaffolds for bone regeneration, exhibiting a nano/micro bimodal pore size distribution. The interconnected micropores have dimensions between 10 and 200 μm and the nanopores in the gel skeleton between 5 and 40 nm. The chosen sol compositions allow for bioactive glasses in the CaO-SiO_2 and $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$ systems. The procedure for micropores combines the metal–organic sol–gel glass route with the spinodal phase separation, which occurs simultaneously with the sol–gel transition when a water-soluble polymer

or a triblock copolymer was added to the sol. The nanopores are generated by solvent exchange procedures.

The optical properties of nanoporous silica-based materials can be of interest for photonic applications. The doping of these systems with rare earth ions or semiconducting nanoparticles can lead to the development of improved optical amplifiers or displays. The sol-gel glass technique presents advantages for the preparation of such nanoporous vitreous oxides [421].

6.2.2 Electrochemical Discharge Machining

Electrochemical is a special form of electrical discharge (or ‘spark’) machining, which is primarily used for the machining of complex contours or fragile cavities that would be otherwise difficult to produce into conductive materials such as metals or conductive ceramics, e.g. $\text{Al}_2\text{O}_3/\text{TiN}$ ceramic [565]. Material is removed from the workpiece by an electrical discharge generated in a continuously flowing non-conducting fluid [531]. In the special case an insulating material, such as glasses [465, 528] or non-conducting ceramics [90, 519], in an electrically conducting electrolyte is used.

The working principle of electrochemical discharge machining is illustrated in Fig. 6.6. The glass workpiece is positioned on an xyz -table in a bath containing the electrolyte. The bath also contains a needle-like tool and a reference electrode. The movement of the workpiece in the z -axis brings the workpiece in contact with the tool and so controls the depth during the machining process. The contours of any geometric structure are created by moving the workpiece in the x - and y -axis relative to the tool. During the electrochemical discharge machining the geometry of the tool is etched into the workpiece. Cavities in a glass substrate with a minimum diameter of about $100\text{ }\mu\text{m}$ and a depth of $300\text{ }\mu\text{m}$ can be realised [465]. Electrical discharges between the electrode tool and the workpiece are created by applying DC voltages between 30 and 100 V. Alkaline solutions as NaOH, KOH, NaNO_3 or KNO_3 in water are favourable electrolytes. The most commonly used reference electrode is platinum and the tool needle electrode is made from metals, such as platinum, tungsten, steel or nickel.

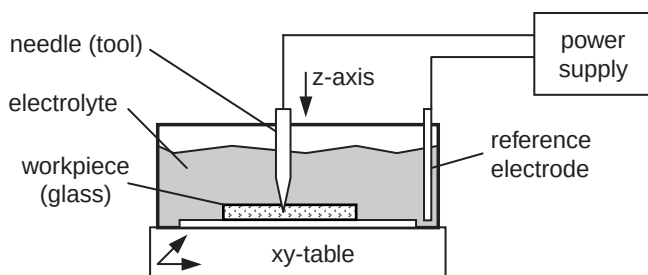


Fig. 6.6. Principle of electrochemical discharge machining

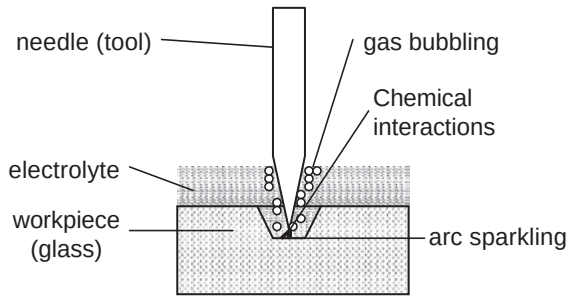


Fig. 6.7. Processes occurring at the tip of the needle electrode tool during electrochemical discharge machining

It is necessary in electrochemical discharge machining that the needle tool electrode is in contact with the insulating workpiece. It is not necessary to apply a high load on the needle. As soon as a voltage is applied to the system an electric discharge is created, which generates gases and induces chemical reactions that cause the removal of material. If the needle is removed from the surface the machining process, i.e. materials removal, stops.

The effects occurring at the tip of the needle are shown in Fig. 6.7. During the machining most of the needle surface is insulated by the formation of a gas stream during the electrolysis. The electrical field concentrates at the tip of the needle electrode, which supplies the electrons required for the electrochemical processes. The region surrounding the needle is locally heated by electron impact.

The complex processes occurring during the electrochemical discharge are still not completely understood. The material removal is mainly attributed to the chemical reactions occurring between the electrolyte and workpiece, which are assisted by the high local heating and electron impact. The heating is initiated by the electrical discharge at the tip of the needle. The poling of the voltage is important for the process. Higher material removal rates were found if the tool was the negative pole and the reference electrode the positive pole. An increase in the applied voltage results in a higher material removal rate. A lower voltage limit, which depends on the electrolyte composition, must be overcome to create an electrical discharge. The most commonly used electrolytes are concentrated solutions of NaOH and KOH. The useful concentration range is between 20 and 40 mass %. The material removal rate increases also with an increase of the concentration of the electrolyte.

The material removal process depends on the composition of the workpiece. In particular, the ion conductivity of the material and its chemical resistance are of importance. The observed material removal rates for ceramics are on average 20 times smaller than those of glasses [528]. However, the material removal rate of fused silica is significantly smaller as compared to that of soda-lime silicate or borosilicate glass.

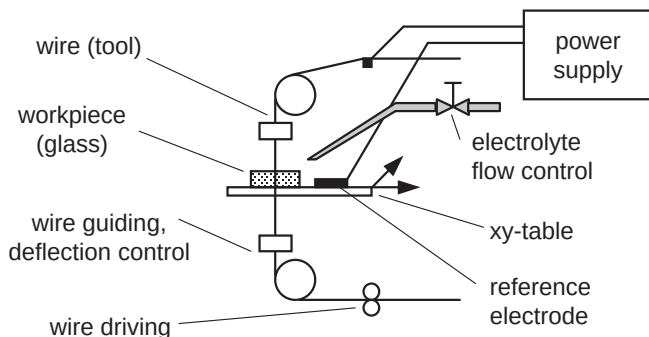


Fig. 6.8. Illustration of wire electrochemical discharge machining

Wire electrochemical discharge machining for cutting glass is a form of electrochemical discharge machining [528]. The principle of the process is shown in Fig. 6.8. In this case the tool electrode consists of a thin wire. These wires are typically made of brass and have diameters around $200\text{ }\mu\text{m}$. The wire is driven with a speed in the range of 60 cm s^{-1} . The workpiece is fixed on an *xy*-table. The movement of the table is controlled using the wire deflection. The electrolyte is sprayed on the surface of the workpiece so that both electrodes, wire and platinum reference electrode, are completely immersed in the electrolyte. The voltage effects occurring at the wire electrode are the same as those described earlier for the standard electrochemical discharge machining process. However, if high voltages are applied during the machining through an electrolyte with a high ion concentration the wire might melt, causing it to fail.

Wire electrochemical discharge machining allows for the cutting of two-dimensional geometrical structures. The cutting rates for various glasses are in the range of $2.5\text{--}4\text{ mm min}^{-1}$ but only of $0.12\text{--}0.14\text{ mm min}^{-1}$ for ceramics. The minimum kerf width is in the range of 300 and $400\text{ }\mu\text{m}$ for a wire with diameter of $200\text{ }\mu\text{m}$. The cutting rates increase with increasing kerf width.

Thermal and Thermomechanical Structuring Processes

7.1 Sintering

Sintering is a very useful method to produce open porous glass or glass ceramic bodies with a controlled porosity in the micrometre range. Sintering processes are used for the preparation of carrier material for biotechnological applications and applications in pharmaceutical industry [166, 369, 466]. Furthermore, porous glasses and glass ceramics are used as filters in chemical processing [425] and as sound absorbers [177]. Sintering processes are also used to produce glass coatings with various properties [98].

The raw materials for sintering processes are fine glass particles, which can be glass beads or powders. For powder processing, a grinding process guarantees the required fine particle sizes. The ground material is fractionated and mixed in defined proportions. Various thermal sintering processes are used:

- Thermal sintering without additives
- Assisted sintering using sintering additives coated onto the glass (Fig. 7.1)
- Sintering with supplementary crystallisation

Pure thermal sintering without additives is the most challenging process. The pore form, volume and diameter can only be controlled by the temperature, processing time and applied external pressure. The major advantage of this process is the purity of the material. The chemical resistance and/or thermal stability of the resulting glass body are not affected by additives or additional phases which might form. Pore sizes between 1 and 500 μm can be reproducibly produced in a glass body made from borosilicate glass 3.3 (“3.3” is a trademark and signalizes a thermal expansion coefficient of $3.3 \times 10^{-6} \text{ K}^{-1}$). It is a very interesting material, because of its high chemical resistance, low thermal expansion coefficient and its ability to be joined to conventional laboratory glass ware [425].

The sintering process can be assisted by sintering additives, which are usually coated onto the particles to be sintered [177]. The activated surface of the

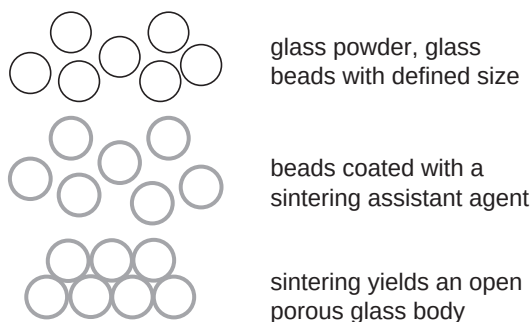


Fig. 7.1. Glass sintering process

glass particles melts during the sintering process. This liquid phase coexists with the solid beads at the sintering temperature and causes a point contact between them. The capillary action exerted by the liquid phase rearranges the particles during the early stages of sintering. The interaction between the liquid and the solid results in rapid densification because of the higher diffusivity and mass transport in the melt. An open porous glass body results because the temperature–time regime is chosen such that the particle core remains solid and, therefore, guarantees the stability of the body during the sintering. This process can be controlled much easier than the pure thermal sintering. The main disadvantage of liquid-assisted sintering is the presence of the additional phase which reduces the chemical and thermal stability of the porous glass at the contact points and at the surface of glass particles.

Another variation of glass sintering is the sintering with supplementary crystallisation of the powder. It obstructs the viscous flow and therefore reduces the shrinkage of the green body by crystallisation. The effect is called *sinter blockade*. The crystallisation of high quartz at cordierite-containing glass particles was investigated [369]. Müller has studied the nucleation influence (see Sect. 2.3) on the combined sintering and crystallisation process. It was controlled by shrinkage measurements.

The sintering and crystallisation of glass powders of cordierite stoichiometry were also used for the manufacture of open porous carrier material for applications in biotechnology [166]. Geleil et al. [165] published a production method for hollow glass microspheres. They used an irregular glass frit made from a glass doped with foaming agents. The particles were spheroidized in a propane/oxygen torch.

7.2 Embossing and Press Forming

Embossing and press forming are thermomechanical glass forming methods. They are especially important because the viscosity of glasses continuously changes as function of temperature (see Fig. 1.11). Commonly a glass is

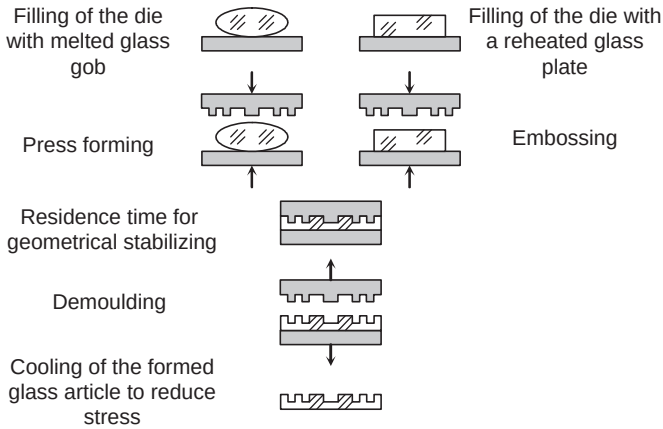


Fig. 7.2. Press forming and embossing

melted, the melt press formed and the formed article cooled, or a semi-finished glass part is reheated, formed by embossing and finally cooled. Both variants of the process are illustrated in Fig. 7.2.

The direct press forming of a glass melt (see also Sect. 3.3.2) is commonly used for the forming of optical elements, such as lenses. A review of the historical development and a comparison of the processes used to produce traditional glass articles can be found in [409]. The following press forming and embossing processes to produce precise optical lenses are used:

- *Glass blank moulding* is the near to net shape moulding of glass melts to a preform shape to minimise the effort to be spent for grinding and polishing to the final shape.
- *Moulding fire polishing process* is the net shape moulding of at least one optical surface of a lens.
- *Precision lens moulding* is a method for precise net shape moulding of optical lenses.
- *Thermal replication* is the thermal reshaping of pre-polished preforms by heating until they sag into the final mould.
- *Thermal reforming* is the heating of the surface of a polished preform which is then reformed by a heated tool to generate the net shape.

However, direct pressing processes have also been used to produce glass titre plates from borosilicate glass [182]. The microgeometry was created by pressing the melted glass into a die using a structured stamp. Direct pressing was also used to produce a structured glass channel plate for a Zeus panel, which is a special kind of a flat and slim display [331]. A special borosilicate glass with a thermal expansion coefficient adapted to AF45-glass was used to produce these channel plate. Four inch (10.16 cm) channel plates with a pitch between the channels of 3 mm and a channel depth of 4.8 mm were

produced. Initially the glass is melted, then the gob is definedly placed into the mould, which is followed by pressing the article, cooling and demoulding. The good forming results were obtained when the temperature of the glass before forming was kept in between 1430 and 1450°C and during forming between 980 and 1035°C. The glass product could be demoulded at temperatures between 780 and 870°C. The pressure during forming was 12 bar and the pressing speed was 0.3 m s^{-1} . The glass article was pressed for about 2 s. A main problem was that the mould had to be completely filled with the gob before the pressing starts. Using this process it was, however, impossible to produce glass articles with nearly rectangular side walls. The angle of inclination was typically 7°.

Embossing techniques used in microtechnology enable for mass production and, therefore, have found many applications. Hot embossing is often used to structure polymers. Hot embossing of polymers as a process for the generation of optical elements, such as optical waveguides, has been described [19, 308]. Nano-imprint lithography or hot embossing has been used to transfer geometrical features. The embossing die was produced by an UV-curing process to create an array of structures in thermosetting and thermoplastic polymers, such as lines and cylinders. The patterns created have been used as embossing die to transfer the structures [456, 579]. The polymers developed exhibit excellent dry etch resistance and good imprintability in a hot embossing process. This process allows for the replication of geometrical structures down to the 50 nm scale [441].

Embossing processes of metallic parts are described in the literature [57, 381, 454]. Metallic embossing is divided into cold embossing and super-elastic embossing. Embossing experiments were carried out using silicon dies. Contrary to the embossing of polymers and glasses, which undergo viscous flowing at elevated temperatures, the ductile behaviour of metals causes the forming.

Another example of embossing techniques is the use for inorganic–organic composite layers to structure them [54, 458]. A range of substrates can be coated with such a surface layer using sol-gel processes which is followed by the actual embossing process during which a stamp is printed (pressed) or rolled into the surface layer. UV exposure is used to cure the structured layer. Such a process is suitable for the modification of large surface areas for optical applications, i.e. for the production of gratings, arrays of lenses or of anti-reflection coatings.

A similar sol-gel layer process utilising only inorganic components was developed for the generation of glass-like microstructured surfaces allowing for significantly shorter process times but without any structure relaxation [172]. The surface is coated by a sol-gel layer, which is embossed using silicone stamp after a pre-drying. The structure is fixed using an initial curing set for 10 min at 50°C which is followed by final curing for 1 h at 500°C. This curing protocol reduces the shrinkage by 25%. The process allows us to produce features with heights up to 30 μm [171].

An additive technology for the generation of topographic structures on the surface of glass sheets as well as of the tool used to create such structures was developed by Ostendarp [394]. The structures in the tool were filled with a paste-like material. The tool was heated up to the melting temperature of the paste-like material when it is in contact with the glass sheet. Then the melted paste is transferred onto the glass sheet, and a sintering or melting process follows to finalise the microgeometry on the glass surface. The tool can be used for stamping and rolling processes to structure surfaces.

Contrary to the direct pressing of a glass melt, in embossing a reheated glass preform is used in final forming process. This process has been used to manufacture precise optical components [31]. Various optical-grade glasses with different viscosity–temperature profiles were formed using various embossing materials. During the embossing process, the glass is reheated to a viscosity of $\log \eta = 8.2\text{--}9.2$ (η in Pa s). The temperature required to reach the desired viscosity depends of course on the glass composition and varies from 500 to 675°C. If the pre-defined geometry is achieved during the embossing, the pressure and temperature are reduced. After a defined pressure–temperature–time regime for structure stabilizing the final part can be demoulded.

Various patents have been disclosed describing different methods and technical concepts for the press moulding of optical glass components [316, 444]. Embossing techniques are particularly well suited for microstructuring of glasses [243, 326, 327, 344]. An embossing process has been used for the generation of optical diffraction elements with microscopic surface features and gratings [344]. The process used was a non-isothermal embossing process with short cycle times. The embossing tool was PVD coated to reduce the adhesion between the tool and the workpiece [344].

The advantages of the embossing process of reheated samples compared to the direct pressing of glass melts have been discussed in the literature [326, 327]. Hot embossing processes can be performed in closed process chambers with controlled atmospheric conditions and a simpler temperature and position control. Silicon and steel dies with TiN and TiAlN coatings seem to be the preferred tools. Lehnicke et al. [326] demonstrated the embossing of V-grooves into low melting fluoride phosphate glass with a transformation temperature of $T_g = 440^\circ\text{C}$. The experiments were performed in a nitrogen atmosphere but the embossing pressure and time were varied. If the glass viscosity was less than 10^8 dPa s, V-grooves could be embossed with a pitch of 200 μm using a force of 50 N and an embossing time of 40 s.

The microstructuring of different glasses by embossing was investigated by Schubert et al. [455]. Using complex-structured tools such as etched silicon tools complex geometries were also made.

The fine embossing of chalcogenide glasses for photonic integrated circuits was demonstrated by Seddon et al. [457] and Pan et al. [396]. Glasses can also be structured by embossing in an open process chamber using ceramic dies [252]. Cylindrical groove structures (Fig. 7.3) were embossed into a

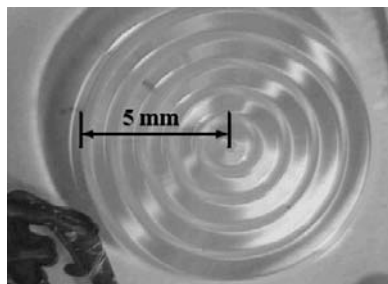


Fig. 7.3. A micrograph of an embossed borosilicate glass sample

borosilicate glass which was most successful at temperatures ranging from 630 to 770°C.

A major problem of all embossing processes is that perfectly microstructured tools have to be used and produced. A review of various techniques to produce such tools can be found in the literature [515]. (Wire) Microelectrical discharge machining can be used to produce such tools. Frequently wires with diameters as small as 30 μm are used. Depending on the discharge distance grooves with widths of 40 μm can be machined. However, only linear structures can be produced using this technique. Micropath and microsink erosion can be used to create various surface features. A tip electrode is moved along the surface during micropath erosion. Microchannels of about 100 μm width, a two-dimensional free shape and a surface roughness down to $R_a = 0.3 \mu\text{m}$ can be created. Microsink erosion allows producing features with diameters down to 0.05 mm. In this case, a shaped electrode is eroded into the workpiece. However, it is rather challenging to produce the fine structures of the complex electrodes. The materials used for the electrodes are usually tungsten, tungsten-copper, cemented carbides or special steels. The use of multi-layer machining processes for tools making and the reduction of the discharge energy help to achieve thermally influenced surface layers of less than 1 μm .

Mechanical shaping processes have also been used to produce the embossing tools. However, ultra precision machining of embossing tools using single crystal diamonds (see Sect. 5.2) is problematic because of the high chemical wear-out during the structuring of materials with high iron content. Alternatively profiled boron nitride grinding tools can be used. The geometric features that can be produced using ultra precision machining have tolerances of about 1 μm and surface roughness of $R_a < 0.5 \mu\text{m}$. A physical vapour deposition (PVD) process through a mask has been used to fabricate embossing tools with sub- μm surface topography [83]. After a pre-defined thickness of the structured layer is achieved, the deposition is continued without a mask.

The surface layer of the tool which will be in contact with the glass provides major challenges for all pressing and embossing techniques. This layer must be of perfect surface quality because its surface topography is replicated into the formed glass part. The tool surface has to be of sufficient wear and chemical

resistance as it is repeatedly in contact with a hot glass melt. Furthermore, the tool must not stick to the hot glass during the forming process. The tendency of the tool to stick to the glass increases with increasing temperature of the melt. Considering the aforementioned requirements of the tool materials which will be in contact with the glass, they are much more stringent for the direct forming of a glass melt as compared to tools used for embossing of a reheated glass plate.

Investigations on the suitability of different tooling materials for the contact with a hot glass preform show that oxide ceramics, quartz glass and materials with a low oxidation resistance have a tendency to sticking. Whereas metals and alloys with higher oxidation resistance, such as stainless steel, allow for an increase of the working cycles. However, the best contact behaviour between the tool and hot glass was found for carbides and nitrides [31].

The use of various metals and alloys as contact tooling material to a glass melt was investigated in detail [106,141]. Nickel and tungsten were found to be the most suitable metals offering the highest initial adherence temperatures to a soda-lime-silicate glass and have the highest durability in contact to a glass. It was also found that the smoother the metal tool surface, the higher the initial adherence temperature. The authors also found that a higher carbon content in iron causes the permissible initial adherence temperature to decrease.

Hülseberg et al. [252] studied the use of tools made from ceramics. Nitrides in general have good contact behaviour to hot borosilicate glasses. In particular, a mixed sintered boron nitride and silicon nitride have very good contact behaviour to the glass. Furthermore this material is suitable for mechanical structuring by turning or milling techniques (see Sect. 5.2.6).

However, the contact problems between a tool and the glass to be formed can be reduced by using the levitation principle. This principle has been routinely used in glass blowing. A glass article is blown in a water-soaked wood mould, which causes the water to vaporise giving rise to a thin gas film between the mould and the glass article. This principle was adapted by using a compressed gas film [18,321]. A gas flow between the mould and the glass gob is achieved by forcing gas through a porous plate at the contact surface of the mould. This technique allows for the production of glass parts with very good surface qualities enabling to reduce any post-processing such grinding and polishing to a minimum.

Another route to minimise the contact problems and to improve the surface quality is the use of functional contact layers coated onto the surface of the embossing die [56,231,278,280,343]. Of particular importance, because of the very good contact behaviour with the glass, are aluminium nitride coatings. The PVD of AlN and TiN coatings on steel, glass and silicon substrates and the effect of the process parameters, such as total pressure, partial pressures of nitrogen and argon, substrate temperature and distance between target and substrate on the stresses and the mechanical properties of the coating were investigated [277,280]. The use of TiAlN and boron nitride coatings for the

hot forming of glass by pressing and embossing was tested in detail [56, 278, 279]. Such coatings can be deposited onto the surfaces of tools in a variety of ways. However, RF-magnetron sputtering seems to produce coatings with the best surface quality, lowest internal stress and best wear, thermal, oxidation and chemical resistance as compared to coatings deposited using ion beam sputtering and energetic cluster impact processing. Depending on the coating parameters, the properties of the surface layers vary widely. Sticking tests have been performed using the deposited coatings in contact with various molten glasses in the temperature range 550–610°C, which produced generally good results.

TiAlN/ZrN super-lattice coatings deposited on the die by reactive RF-magnetron sputtering have been used to emboss a variety of commercial optical glasses [280]. The TiAlN/ZrN coated tools did not stick to the glasses. Furthermore, the coatings were not damaged during the processing.

The mechanical properties of Ti/AlN coatings exposed to elevated temperatures in an oxidative environment were investigated [438]. It was found that coatings with initial compressive stresses offer a better resistance against microcracking in contrast to coatings with initial tensile stresses.

Manns et al. [343] tested various contact layers, such as Cr, Si₃N₄, SiC, BN, AlN, TiN and TiAlN, deposited on various substrates by dipping them into a soda-lime-silicate glass melt at a temperature of 1,050°C. The adhesion behaviour between the coating and the melt was investigated by measuring the separation forces. An exponential increase of the separation forces up to permanent adhesion was found with increasing temperature. Only a boron nitride coating still performs at higher temperatures.

7.3 Drawing of Preformed Glass

7.3.1 Redrawing Methods

Drawing of glass half-products or preforms after reheating is a frequently used forming method to produce materials used in microtechnology. These redrawing methods are for the forming of sheet glass, rods, tubes, profiles and fibres [122, 123]. The redrawing process starts with a semi-finished preform. It is fixed in a driving probe holder which moves the glass downwards passing it through a heater. The viscosity decreases corresponding to the viscosity–temperature behaviour. The speed of the pull-off drive is much higher compared with that of the probe holder what allows for elongation the glass preforms. The redrawn glass is finally cut off.

Figure 7.4 illustrates the process for redrawing of silica glass tubes. During this process, the preform is deformed in a geometrically similar manner forming a drawing onion (described in Sect. 3.3.2 for the float process). The geometry of the preform determines the final shape of the redrawn element. The ratio of preform feed speed to the pull-off speed of the final article

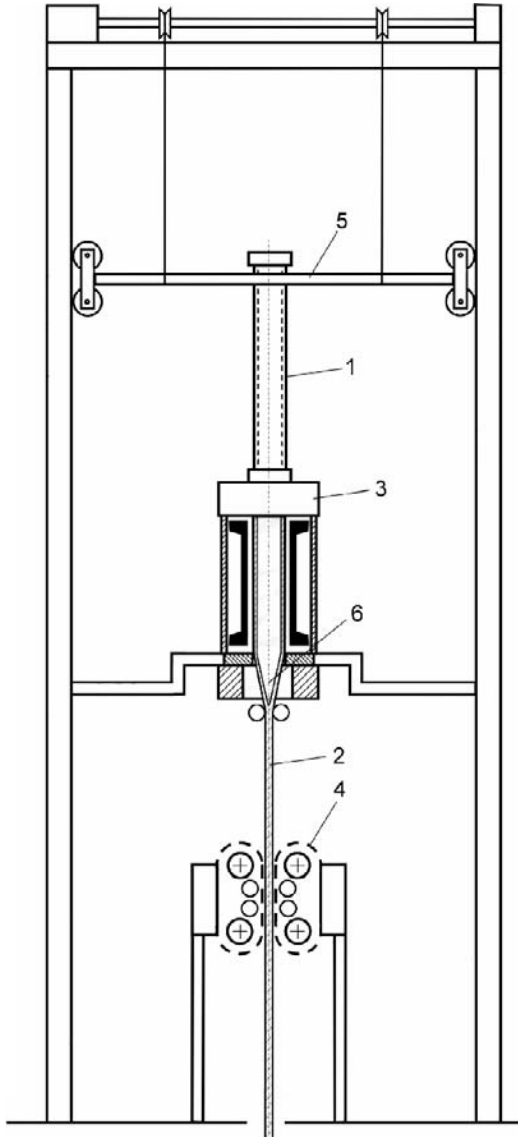


Fig. 7.4. Drawing equipment for the contact-free production of clear silica glass tubes, where *1* is the silica glass ingot (preform), *2* the drawn tube, *3* the furnace (graphite resistance-heated), *4* the drawing machine, *5* the supporting assembly and *6* the onion

determines the draw-down ratio. To guarantee a stable process, a constant temperature profile during the drawing process is required. Normally the glass should have viscosity in the range between 10^5 and 10^8 dPa s for the redrawing process.

Preforms can be manufactured by all forming processes usual for glass melts. If necessary the preforms can be polished or otherwise mechanically treated [122].

It is also possible to use joined preforms which are produced using different glass sheets, tubes or rods. However, in this case, it is necessary that thermal expansion coefficients and viscosity–temperature profile match. Multi-layer structures consisting of individual layers with an absolute thickness of less than 100 nm were generated by redrawing [123]. Such drawn elements are frequently used in optics as interference structures.

A special drawing process is the low-temperature tensile drawing of metal particle-containing flat glasses to generate dichroism [58]. This drawing process takes place at temperatures only slightly above the glass transformation temperature. High tensile stresses up to 200 N mm^{-2} and low rates of deformation are required. This drawing process results in a deformation of the randomly orientated metal particles to elongated spheroids which are orientated parallel to the tensile axis. The glass elements are used for colour-selective polarisers.

7.3.2 Processing of Optical Fibres

Principle

Optical fibres commonly consist of a core through which the light is guided by total internal reflection surrounded by a cladding having different optical properties. The refractive index of the cladding should be lower than that of the core. Depending on the optical fibre type, whether they are single-mode or multi-mode having a step or gradient index profile, the differences in refractive index profiles vary and different methods for production are required. The various manufacturing methods for optical fibres are reviewed [1, 181, 569]. In the following sections, we briefly introduce the most important manufacturing processes.

Rod–Tube Method

In the rod–tube method to produce optical fibres, a rod – made from a high refractive index glass which will form the core – is inserted into a tube made from a glass with a lower refractive index, which will later form the cladding. This loosely joined compound is then continuously fed through an oven and heated up to the glass softening. By drawing down the loosely joined glass rod and tube, an onion develops in the hottest zone of the rod–tube compound. Caused by the surface tension, at this point the two different glasses join, allowing us to draw a stable core–cladding fibre. The fibre is continuously drawn, coated with a polymeric coating and wound onto a spill tube [181]. Previous polishing and cleaning processes of rod and tube prevent the creation of defects in the contact zone between cladding and core.

Chemical Vapour Deposition (CVD) Process

In the CVD process, the preform of the optical fibres is produced by depositing the cladding onto the core using chemical vapour reactions. The substrate is selectively heated up in a plasma or a detonating gas burner. A mixture of silicon tetra chloride (SiCl_4) and oxygen is injected into this heated zone causing the transformation of the silicon halogenide to SiO_2 . The produced silicon oxide is deposited as fine particles forming porous material on the substrate surface. An additional thermal treatment guarantees the complete sintering and the removal of the pores in the deposited silica layer. Adding doping agents into the heated zone allows tailoring the refractive index of the deposited layers [181, 569]. Two kinds of CVD processes are commonly used: the outside and inside process.

The outside process uses a cylindrical high-temperature resistant substrate, such as Al_2O_3 , graphite or most commonly SiO_2 . The pure or doped SiO_2 layers are deposited on the outside of the substrate. If required, the substrate is removed, for instance by drilling, after the deposition procedure. It is also possible to use the substrate, especially if it is pure SiO_2 , as core material [350]. However, the final product is only of low to medium grade quality.

The inside process is similar to the outside process, however the substrate is now a tube and pure or doped SiO_2 is deposited in the interior of the tube [181]. It is also possible to use plasma-enhanced CVD [315]. In this case, the quality of the final product is much better than compared to those obtained using the outside process.

The processing steps that follow to produce an optical fibre are the collapse of the preform to close the inner opening (if present) and the drawing of the fibres.

Vapour Axial Deposition (VAD) Process

This method combines the rod generation by vapour axial deposition with the cladding generation by radial vapour deposition in a continuous process to make a porous ingot. The process is similar to the much older Verneuil process, in which a finely powdered material is melt fused in an oxyhydrogen flame to produce synthetic gemstones [181, 259]. Figure 7.5 shows a schematic of the flame fusion process to produce silica glass or the preforms for doped optical fibres. The process consists of three parts: synthesis of the oxides forming a porous OH^- - and H_2O -containing ingot which is then dehydrated by reacting with SOCl_2 . In the final step, porous glass is densified by the action of pressure and heat. The resulting preform is completely dense and water-free. A collapsing step as described before for the CVD process is not required. The preform can be drawn down immediately (see Fig. 7.4).

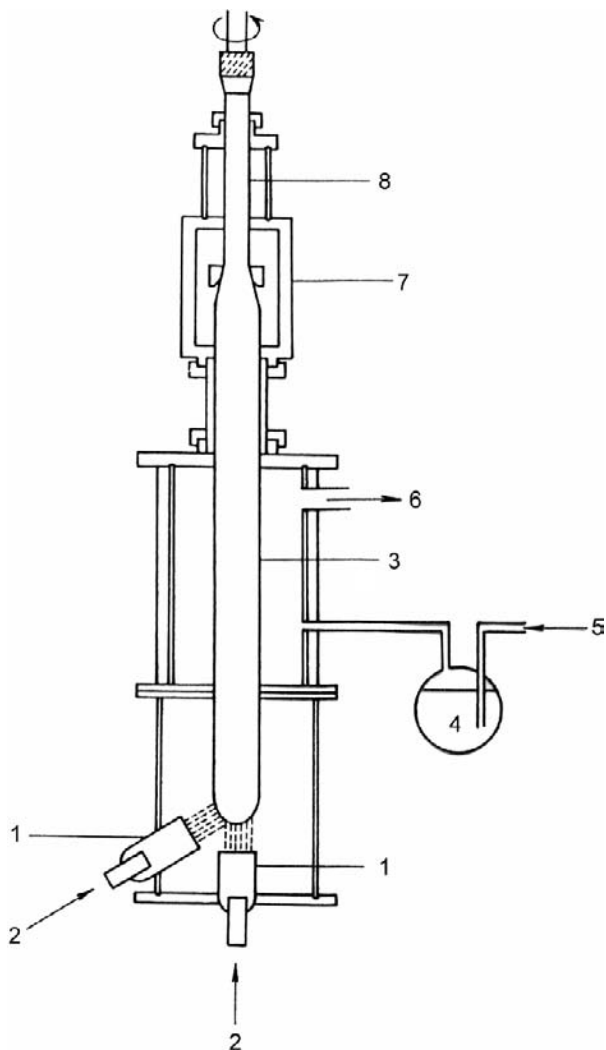


Fig. 7.5. Device used for the manufacturing of silica glass or preforms for optical fibres by flame hydrolysis (VAD method by Nippon Electric Glass), where 1 are the burners, 2 the inlet of SiCl_4 and $\text{H}_2 + \text{O}_2$ gases (which could also contain the doping agents such as GeCl_4), 3 the fused-on porous ingot (preform), 4 the liquid SOCl_2 , 5 the supply of gaseous O_2 , 6 the exhaust, 7 the graphite resistance furnace (preform sintering) and 8 the final clear silica glass product

Double Crucible Method

The double crucible method to draw optical fibres uses two crucibles positioned into each other. The inner crucible contains the glass material from which the core is drawn whereas the outer crucible holds the melt for the

cladding. The glasses are pre-melted rods. Commonly the crucibles are made from pure platinum or high purity fused silica. The axes of the nozzles, which are in the bottom of the crucibles, are aligned and stacked together. The hot glass melts flow from of the nozzles. The melt forming the core is cladded by the melt from the outer crucible. Both glasses join while they are drawn off together [10,11,26,276]. The relationships between crucible and fibre geometry were investigated and modelled [459].

This method also allows for the formation of multi-filaments which are drawn from crucibles with many nozzles. Geometrical arrangements up to 100 fibres are quite common [181]. If three crucibles are stacked into each other, it is possible to produce multi-layer fibres [10,276].

A modified crucible technique allows the preparation of gradient index optical fibres [276,301]. In this technique, a larger distance between the nozzles of inside and outside crucible is used, so that the glass leaving the inner crucible flows through the melt of the outer crucible. During this time, ion diffusion occurs to form a parabolic index profile. An ion diffusion process can also be initiated during an additional thermal treatment step.

Other Methods

Special optical fibres can also be produced by a modified jacketing method [270]. A tapered glass preform is produced by suction casting of the core material into a tube made of the cladding material. This initial preform is then drawn off and loosely joined to circular positioned outer tube glasses to form a secondary preform, which is used for the fibre drawing process. This method allows the production of multi-layer fibres with large refractive index steps.

Glass fibres with fine electrically conducting cores can be produced by either melting a metal (powder or wire) within a glass capillary followed by drawing a fibre from the soft glass, or drawing a fibre from a tube containing a metal glass powder mix [15].

Glasses Used for the Production of Optical Fibres

A variety of glass materials are of interest for fibre drawing. The following glasses have been used:

- Silica glass [180,219,315,400,467,569]
- Multi-component glasses [10,11,26,276]
- Chalkogenide glasses [293,518]
- Fluoride glasses [270]
- Fluoro-gallate glasses [510]

The refractive index of the basic glass compositions is often modified by the addition of rare earth dopants [219,518]. To modify the mechanical and optical properties, occasionally the fibres are crystallised before use [510].

The damping behaviour of fibres is often critical for many applications. It is particularly affected by water and polyvalent element content. Several authors investigated the optical losses of fibres and developed fibres with reduced losses [10, 11, 26, 150, 180, 219, 271, 379, 400].

Modelling of Fibre Drawing

In this section, it is impossible to give a sufficient view of the modelling results. Therefore it is only mentioned what problems are modelled. Modelling of the fibre drawing process helps in determining the variables affecting the process parameters and to the production of fibres with uniform fibre diameters [97, 401, 428]. A physical model predicting the neck (onion) shape and temperature distribution within the neck-down zone during the drawing of a fibre from a high silica rod was developed by Peak and Runk [401]. The model is based on the equations of momentum and energy for given fibre drawing conditions.

The convective and radiation heat transfer involving heating as well as cooling along the drawing path was considered in the model presented by Geyling and Homsy [168].

Models allow for the determination of the maximum draw-down speed at which a fibre can be drawn without rupturing. This speed depends on furnace temperature and fibre radius [97].

The neck-down profile and the speed during fibre drawing process have been modelled and examined by solving the mass and momentum conservation equations of a two-dimensional axial-symmetric cylinder with varying the radius. This model includes gravitational effects in a vertically drawn fibre [428].

Gospodinov and Yarin [178] used an one-dimensional model to describe the drawing of microcapillaries based on hollow cylindrical preforms. Fitt et al. [149] used a model based on an asymptotic analysis of the Navier–Stokes equations to model the drawing process of hollow fibres.

7.3.3 Drawing of Complex (Definedly Designed) Glass Components

Complex glass components with pre-determined microstructures can be drawn, but modified drawing methods have to be used [40, 468, 547]. Such complex geometries are commonly drawn starting from a bundle of semi-finished elements (Fig. 7.6), such as rods, profiles or hollow elements, i.e. tubes, capillaries and hollow profiles.

These semi-finished glass elements can be combined in any variety of ways. In the first processing step, the single semi-finished elements are bundled. This bundle is fixed and is called the preform for the drawing process. The cross-sectional geometry and arrangement of the bundle represent in principle the structure of the cross section of the final drawn part. The bundle is gripped and mounted onto the linear z -axis of a moving system. The bottom end of

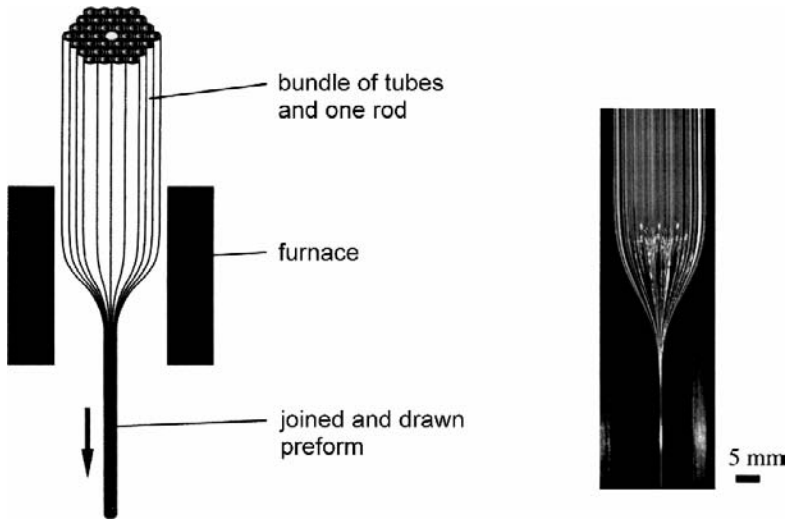


Fig. 7.6. Drawing process of complex designed components [32]

the preform is positioned in a furnace operating at a temperature enabling the softening of the glass. The heated preform is drawn down from below and tapered into a smaller bundle, in extremum a fibre. For doing so, a second moving system, usually a pair of rolls, is arranged below the furnace. It draws down the glass element with a higher speed as the upper system. During the tapering process in the furnace, the individual glass elements making up the bundle is joined. The draw-down ratio (i.e. the ratio between feed and pull-off speed) determines the degree of tapering and the final size of drawn element. The drawn component is now a mechanically stable and compact body.

This process can also be repeated using an assemblage of the firstly produced drawn components as new preform, which allows for the preparation of glass components containing structural details of less than 100 nm. Now, the surface tension plays an important part and overlaps the geometrically similar drawing process. The produced geometry depends on design (rods, tubes, etc.) and make-up of the bundles forming the preform, the wall thickness of the individual elements and the presence of “holes” in the geometry caused by missing rods but also on the following process parameters, such as the drawing temperature, the number of drawing repetitions and whether additional air blowing or vacuum is used. This process allows for the production of glass components with a variety of geometrical patterns (Figs. 7.7–7.9).

The drawn structured glass components are further processed by cutting, grinding and polishing [335] and sometimes thermal processes to manipulate the geometry of the cross section of the part. This can be done by blowing up the pre-packed glass elements during the heating, see Belau et al. [33] and Hülsenberg et al. [254].

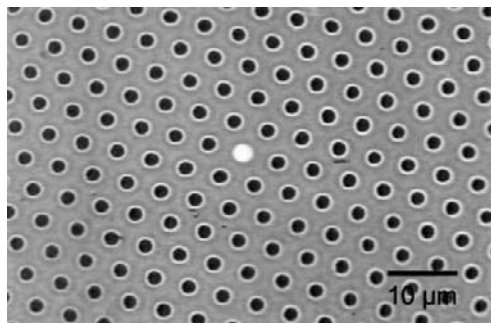


Fig. 7.7. SEM of a part of a complex designed glass component with a drawn rod in the centre made by TEGS (science production society) Saratov/Russia [442]

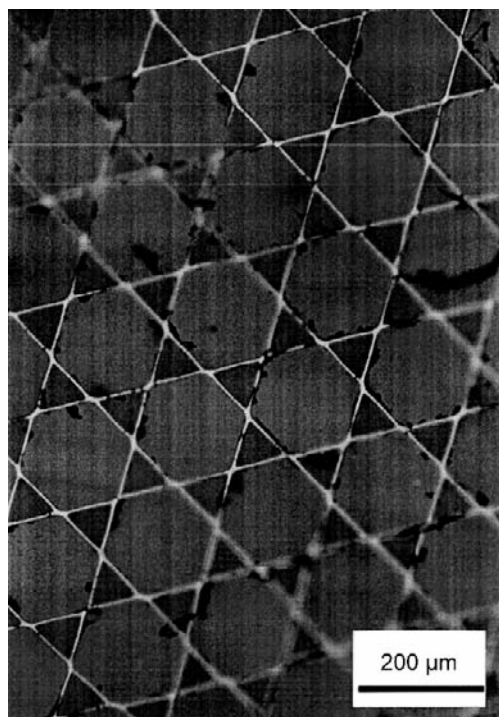


Fig. 7.8. SEM of a photonic crystal structure consisting of very thin glass walls and triangular and hexagonal holes made by TEGS (science production society) Saratov/Russia [442]

Drawn microcapillary elements were used in X-ray optics. Such elements have been applied in X-ray analytics and for the focusing of X-rays [553], for distance compensation and partial monochromatisation [370] and optics

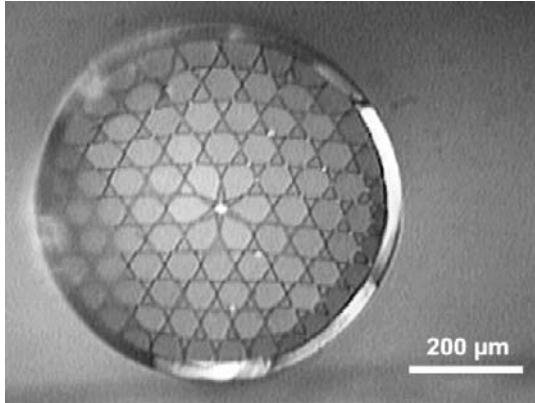


Fig. 7.9. A two times drawn and simultaneously air blown glass component with a drawn rod in the centre [222] (The used glass is I-860 commonly used for capillary production by the Technische Glaswerke Ilmenau.)

for X-ray stress analysis [169]. Moenster et al. [358] reported the use of a structured fibre in a fibre laser.

This technique can also be used for the production of photonic crystal fibres [33]. *Photonic crystals* are periodical optical structures affecting the motion of photons. They must not be a crystallised material but may also consist of a glass with definedly positioned holes in it. Photonic crystal fibres are a new class of optical fibres with a glass core in a defined geometrically microstructured glass. Such fibres can be produced by alternating fine capillaries with a glass core in the centre of the component (Fig. 7.7). These structures act as light guide by corralling it along the fibre axis [432]. The optical elements are divided into those that are operating by total internal reflection (see Sect. 7.3.2) and those operating by utilising photonic band gap effects [66]. The fabrication of such fibres by drawing methods and geometry optimisation as well as their application as two-dimensional photonic band gap structures is described in the literature [51–53, 64, 65, 91, 100, 221, 292, 416, 429, 432, 543]. Haas et al. [187] calculated the omni-directional photonic bands in a two-dimensional photonic crystal.

A process enabling the production of microscopic elements having high precision surface structures by shaping a body of glass or glass ceramic consisting of elongated structures applied to the surface is described by Büllesfeld et al. [80]. These structures are created for instance by a mechanical treatment of the half-product, such as grinding. A thermal process to draw out this body follows.

The production of triangular silica glass fibres with flat sides (Fig. 7.10) was attempted by Heiber [207] and Wegmann et al. [554]. The triangular preform used was a cut, ground and polished silica glass rod. This preform was drawn down at 1750°C at a drawing rate of 4.2 m min^{-1} .

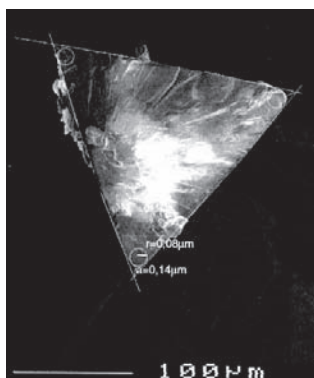


Fig. 7.10. Cross section of a triangular, broken glass fibre [207]

The other way to produce triangular and rectangular fibres is a thermoplastic extrusion process [208, 554]. SiO_2 powders were mixed with a binder system and extruded. After debinding a final sinter process follows.

Kirchhof et al. [274] described the viscous behaviour of silica tubes during collapsing and hollow fibre drawing. Integrating the surface tension in their elementary model, the authors found very good agreement between the calculations and the measured values of fibre dimensions.

Channel plates have been manufactured from a preform consisting of a bundle of tubes [547]. Channel plates with various geometries were produced using a multi-step drawing process combined with various confectioning steps.

A modified process based on the idea described above uses elements of differently composed glasses. The glasses used have different chemical stabilities; for instance, acid inert and acid leachable glasses with high content of boron oxide are commonly used [41, 265, 547]. However, the used different glasses should have similar thermal expansion coefficients and viscosity–temperature behaviour, which is required for the thermal drawing process to fabricate stable structured multi-glass elements. After the drawing process, the produced elements are cut. A treatment in an acid solution follows to dissolve the acid-soluble glass. This process enables the production of a fine-structured acid resistant glass element. The main advantage of this process over a process involving the drawing of bundles containing capillary, which can collapse during the drawing processes, is the high mechanical stability of the bundle preforms. Furthermore, the handling of pre-structured elements during further processing, i.e. cutting, grinding or polishing, is non-problematic. This process can also be used to manufacture etching masks for further processing in microelectronics [402, 522, 523] and microchannel plate detectors [566].

A similar process can also be used to produce multi-fibre optical elements. In this case, glasses with similar thermal but different optical properties, i.e. different refractive index, have to be used for the process.

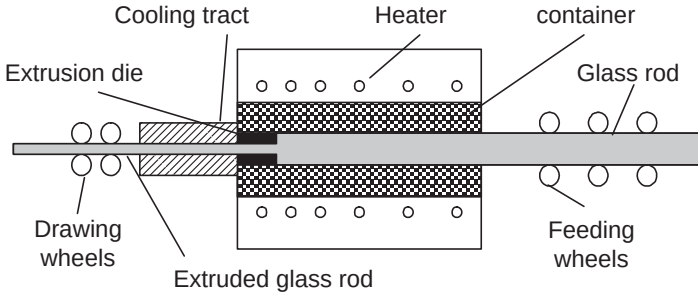


Fig. 7.11. Principle of continuous pull extrusion of glasses

7.4 Pull Extrusion

Continuous pull extrusion offers a possibility to form simultaneously arbitrary interior and exterior glass profiles [419]. The process is well suited for the preparation of profiles with very precise interior and exterior geometries which is guaranteed by the high viscosity of the softened glass ($\eta = 10^7\text{--}10^8$ dPa s) during the forming process compared with the viscosity during drawing or blowing. This process allows for the production of sharply edged profiles. An illustration of the process is shown in Fig. 7.11.

A long cylindrical unfinished glass rod is continuously fed into a container in which the glass is heated up to the forming temperature, which corresponds to a viscosity of $10^{7.6}$ dPa s. Finally the glass is pressed through a die at pressures of about 400 bar. The die has the negative cross-sectional profile of the desired glass contour. To reduce the wall friction between the glass and the container commonly made of nickel-base alloy, the container is lined with a non-wettable material, such as electric graphite, offering anti-friction properties. The extrusion die is made from heat-resisting steel or electric graphite.

After forming, the semi-finished glass profile is passed through a cooling tract to equalise the temperature in the cross section. The temperature remains as high as necessary for further forming. The final cross section of the glass profile is produced by a “cold” drawing process, i.e. the glass is not more reheated. This process allows producing glass profiles with maximum tolerances of the diameter of about $\pm 2\%$. This process is particularly useful for the manufacturing of circular rods with millimetre dimensions containing various holes or cross-bars as inner contours.

7.5 Printing Processes

Besides lithographic methods, printing processes are very often used to produce arrays [342]. These processes can be used to deposit polymer coatings, but can also be used to print a range of glasses using sol-gel processes or

glass suspensions. The printing processes used are jet printing, microspotting, screen printing, microcontact printing using a stamp, laser-induced material transfer [375] and nowadays also gravure printing, see also Sect. 11.2 and [70].

Jet printing, like commercial ink jet printing, uses a jet nozzle which is connected with a reservoir chamber filled with the printing medium. Electrical impulses to an actuator generate a pressure in the chamber which ejects drops through the nozzle. The substrate to be coated is placed onto a computer-controlled x – y stage. To be able to print, the printing medium should have an appropriate viscosity and surface tension [544]. By depositing droplets on top of each other complex geometries can in principle be created. Printing has been used to deposit solder bumps in microelectronics, to produce various lenses on planar surfaces, on the end of optical fibres to create spacer elements and to shape biomaterials for diagnostics and testing [544].

In microspotting a pin containing a capillary, which is loaded with a small amount of the printing medium, is used to transfer it to a solid surface to which the printing medium is stuck by a physical contact. Using computer-controlled x – y stages, this technique also allows us to create structures and pattern on surfaces.

Screen printing uses a patterned partially blocked sieve. The blocked part is the negative of the pattern to be printed. A paste of the printing medium placed into the sieve is pressed through the sieve openings using a rubber tool (blade). Through the permeable part of the sieve, the paste is deposited onto the substrate. The principle can be used to print onto planar substrates.

Stamp printing utilises a soft stamp which is coated, for instance by screen printing, and the pattern is eventually transferred onto a substrate by physical contact. This technique is particularly useful for the patterning not planar substrates, such as ceramic dishes.

Microstructuring Glasses Using Lasers

8.1 Introductory Remarks about Laser Processing

The interaction between a laser beam and a material is determined by the wavelength emitted by the laser, its fluence or energy density ε_L and whether or not the laser emits continuous (cw) or pulsed beams, the pulse duration, repetition rate and pulse energy and also of course by the material's properties, such as its absorption characteristics, which is governed by the physical material parameters and structure (bindings) of the material. The lasers tabulated in Table 8.1 are most commonly used to process glasses.

CO₂ and excimer lasers are the preferred lasers used for glass processing. The Nd:YAG lasers are used only for special cases, because of the low absorption of the emitted wavelength by common trade glasses [76]. Frequency converted Nd:YAG lasers emitting at wavelengths of 532 and 266 nm are also used in glass processing [241, 576]. In recent years short pulse lasers emitting laser pulses in the range of femtoseconds found applications in glass processing [384, 504, 534, 568].

Lasers are used to polish, cut, etch, inscribe, decorate and engrave glasses, and also to find applications in microstructuring of glasses. In the context of the book the application of lasers for microstructuring of glasses is of most interest and, therefore, the other processes will only be briefly discussed.

During laser polishing thin layers are ablated to smooth a glass surface. Lasers are often used to polish fused silica glass parts [494] and to cut glasses [290].

Two principles are discussed for cutting. The one possibility is partially heating the glass without causing it to melt or evaporate. The induced thermal stress will result in the formation of a crack in the glass along the laser path. This principle is particularly useful for glasses with high thermal expansion coefficients, such as soda-lime-silicate glass. Glasses can also be cut using lasers by melting and evaporating the glass. The laser beam partially heats up the glass to the melting and evaporating temperature. This method is used for glasses with low thermal expansion coefficients.

Table 8.1. Lasers used for glass processing

Laser	Wavelength (nm)	Photon energy (eV)	Characteristic
F ₂ excimer laser	157	7.9	Pulsed
ArF excimer laser	193	6.4	Pulsed
KrF excimer laser	248	5.0	Pulsed
Frequency quadrupled Nd:YAG laser	266	4.7	
XeCl excimer laser	308	4.0	Pulsed
Frequency trebled Nd:YAG laser	355	3.5	
Frequency doubled Nd:YAG laser	532	2.3	
Ti:sapphire laser	680–1,100	1.8–1.13	Ultra short pulses
Nd:YAG laser	1,064	1.17	
CO ₂ laser	10,600	0.117	Cw or pulsed

Marking, inscribing, engraving and decorating are important for technical products as well as for processing of artistic glasses. The reader is referred for detailed descriptions to the literature [164, 269, 417, 480]. Laser-assisted processing of photosensitive glasses will be discussed in detail in Sect. 9.3.

Lasers are frequently used in order to modify the material in a localised, narrow interaction zone, for instance to change the refractive index. For instance, the densification of silica and binary silica glasses can be initiated by exposure to an excimer laser emitting a wavelength of 248 and 193 nm [60]. Optical waveguides can be produced in silica glass by changing the refractive index using a Ti:sapphire laser emitting pulses for a duration of 130 fs at wavelength of 800 nm [568]. The refractive index of fused silica and borosilicate glass was also modified using a Ti:sapphire laser but emitting pulses for a duration of only 25–30 fs at a wavelength of 800 nm [504]. A review of the used lasers and methods for the fabrication of glass photonic devices using ultra short laser pulse treatments can be found in reference [228].

8.2 Microstructuring Glasses by Laser Processing

8.2.1 Interactions Between Laser Beam and Glass

A detailed discussing of the interactions occurring between laser irradiation and glass can be found in the literature [76, 261]. Glass is optically transparent over a wide spectral range, which means that until a few years ago glasses could only be processed using special lasers emitting in IR- or UV-range. Depending on the laser wavelength glasses interact differently with the emitted laser radiation. Figure 8.1 shows the transmission spectra of various glasses in the UV range. The optical transmission is determined by the binding state of the

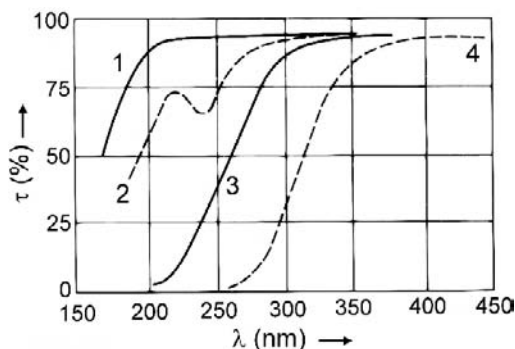


Fig. 8.1. UV-transmission spectra of very pure quartz glass (1) common quartz glass (2) very pure $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass (3) and common $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ (4) glass with thickness 1 mm [449]

oxygen anions and an interaction of the beam with the outer electrons of the oxygen (see also Sect. 1.2.1). However, the oxidation state of the polyvalent ions ($\text{Fe}^{2+}/\text{Fe}^{3+}$ or $\text{Sn}^{2+}/\text{Sn}^{4+}$) that might be present in the glass also affects the transmission spectra of the glass (Ehrt et al., [129]). In fused silica all the oxygen is bridging oxygen and in a hybrid state. Only high energy radiation will be absorbed by fused silica. To encourage the absorption in this glass the photoenergy of the laser beam must be very high and the wavelength of the laser beam should be short. The absorption edge is shifted further in to the UV range as compared to all other silicate glasses.

The addition of network modifiers (see Sect. 1.1.3), such as alkali ions, results in the formation of non-bridging oxygen, which causes a shift of the absorption edge to higher wavelengths. The higher the amount of alkali oxides in a particular glass, the further the shift of the absorption edge to higher wavelengths. Already a very small content of network modifiers, stemming for instance from contaminations of the raw materials, significantly influences the transmission behaviour as can be seen in Fig. 8.1 comparing very pure and common glasses. Transition metal ions, such as the ions of Fe, Co, Cr, Cu, Mn, etc., present in glasses cause absorption bands in the visible range and, therefore, cause the colouring of a glass. The characteristic of absorption band varies depending on the valency of the ions. Silicate glasses are not transparent in the IR range above a wavelength of $4\text{ }\mu\text{m}$ because of the absorption caused by the vibration of the Si–O–Si bindings.

The wavelength of the CO_2 laser ($10.6\text{ }\mu\text{m}$) is absorbed very strongly because of the absorption behaviour of silicate glasses, whereas the absorption of the radiation of the Nd:YAG laser ($1.06\text{ }\mu\text{m}$) is rather low. However, the absorption can be increased by doping the glass, for instance, by the addition of FeO and TiO_2 [503]. Such modified glasses can be easily structured using Nd:YAG lasers (see Sect. 1.2.3 and Fig. 1.38) in the normal mode. But lasers

emitting in the normal mode operation in IR range could also be used for VIS and UV treatment if frequency doubling, trebling and quadrupling is possible.

To understand why laser radiation of the visible wavelength range is also used nowadays for absorption by transparent glass, non-linear optical effects and multi photon absorption need to be considered.

The propagation of light in a medium is characterised by the optical constants as refraction index n and absorption coefficient β_E of the material. These values are independent on the intensity I at low intensities of the light. Reflection, refraction, the speed of light and debilitation of the light are constants of the medium the light passes through. Light waves can be superimposed without mutual interaction. The frequency of the light remains constant even if the light interacts with the material. The polarisation P_E is proportional to the field strength F_E (8.1):

$$P_E = \varepsilon_0 \chi F_E, \quad (8.1)$$

where ε_0 is the electrical field constant and χ is the susceptibility. The refractive index of a material and susceptibility are linked by (8.2):

$$n = \sqrt{1 + \chi}. \quad (8.2)$$

However, for real absorbing materials the polarisation does not respond instantaneously to an applied field, which causes dielectric loss. This is expressed by a permittivity that is both complex and frequency dependent. Taking these aspects into consideration a complex index of refraction n can be defined, see (8.3):

$$n = n_1 + in_2, \quad (8.3)$$

where n_1 is the refraction index indicating the phase velocity and n_2 is the absorption constant called the extinction coefficient. i is the imaginary unit. n_1 and n_2 are a function of the wavelength of light λ . The absorption coefficient is defined by (8.4):

$$\beta_E = 2\omega \frac{n_2}{c} = 4\pi \frac{n_2}{\lambda}, \quad (8.4)$$

where ω is the angular frequency and c is the speed of light in vacuum.

The interaction between laser beam and glass during the light exposure is characterised by the absorption of light by the material and the depth of penetration of the laser beam into the material. The sum of reflection R_E , absorption A_E and transmission τ is equal to 1. The reflection for a perpendicular incidence of light can be calculated by the Fresnel equilibrium, which is valid in vacuum and almost in air, see (8.5):

$$R_E = \frac{(n_1 - 1)^2 + n_2^2}{(n_1 + 1)^2 + n_2^2}. \quad (8.5)$$

In a transparent medium such as glass n_2 is almost 0. In absorbing materials, however, the intensity of the transmitted light I decreases with increase in penetration depth, which is described by the Lambert Beer law, see (8.6):

Table 8.2. Effective band gap for various glasses [261]

Glass type	Effective band gap E_B (eV)
Soda-lime-silicate glass	3.9
Borosilicate glass	4.4
Fused silica	7.5

$$I = I_0 (1 - R_E) \exp(-\beta_E z), \quad (8.6)$$

where I_0 is the initial intensity of the light and z is the penetration depth of the light in the glass.

The thermally caused ablation behaviour of a material was explained by Krüger [313]. Generally the laser beam is absorbed by the material because of the interaction of the electromagnetic radiation with the electrons in the solid. The highly excited electrons interact with the crystalline lattice or the amorphous network of the solid, which causes it to heat up. The thermal equilibrium between the electrons and the solid is established again after a few picoseconds. The first step of the absorption of a photon entails the transition of an electron between energy bands. If the energy of the hitting laser beam is larger than the gap between the two different energy bands, a band to band absorption takes place. However, if the energy of the laser beam is lower than the band gap, excitons can be generated or light absorption at impurities such as foreign ions or network defects can take place. The effective band gap of various glasses (see Table 8.2) was determined from the wavelength position of the absorption edge [261].

However, at high intensities of the laser radiation ($I \gg 10^{10} \text{ W cm}^{-2}$) (8.1) is not valid anymore and becomes, see (8.7):

$$P_E = \varepsilon_0 \chi(F_E) F_E. \quad (8.7)$$

The amplitude of the electron oscillation increases so it is not able anymore to follow the oscillation of the electrical field. This oscillation of the electrons can be described by a series development, see (8.8):

$$P_E = \varepsilon_0 (\chi_1 F_E + \chi_2 F_E^2 + \chi_3 F_E^3 + \dots). \quad (8.8)$$

In this series the first term describes the linear optical effects, i.e. the refractive index n and absorption coefficient β_E , whereas the second term describes the optical losses in isotropic materials and the third term the non-linear effects, such as non-linear refractive index n' and non-linear absorption coefficient β'_E .

Multiphoton absorption is a process in which more than one photon is absorbed simultaneously. This process is highly dependent on the density of defect structures within a material. If the density of defect structures decreases in a glass the interaction between the material and the light is reduced, which means that the intensity of a laser pulse has to be very high to result in multiphoton absorption. In case of VIS lasers only a combination of high laser

pulse intensity (fs-pulses) and multiphoton absorption enable to create effects in transparent glasses. A non-stoichiometric composition, which causes local defects in the glass structure, and electron hole centres, which are initiated by the radiation itself, can cause multiphoton absorption. Both of these effects lead to many not compensated states, which either come from the manufacturing of the material itself or directly from the interaction of the material with the radiation. Two-photon absorption is described by the following equation:

$$\frac{dI}{dz} = -(\beta_E I + \beta'_E I^2), \quad (8.9)$$

where β_E is the linear absorption coefficient in one-photon absorption and β'_E is the non-linear absorption coefficient in two-photon absorption.

Defects in glass can result in new resonance frequencies or absorption bands, which facilitate two-photon absorption. Defects resulting in absorption bands in the VIS or UV spectrum are called colour centres. Such colour centres can also be generated by exposing glasses to X-ray or electron radiation, which results in the formation of a bonded electron-hole-couple (exciton) ($e^- + h^+$). The generation of various colour centres in fused silica is described in the literature [138].

Self-focusing is another important non-linear effect. It describes the change of refraction behaviour of the glass by the interaction with very intense laser beams. For isotropic materials and linearly polarised light the refraction index is n_0 and can be described by (8.10):

$$n_0 = n + n' I \quad (8.10)$$

A Kerr non-linearity leads to an increase of the intensity in the centre of a laser beam, which results in an effectively increased refraction index in this zone causing the laser beam to be focused. The volume of the modified refraction index acts as focusing lens, which can cause damage in the material. This effect allows for glass ablation or modification of the glass properties by a fs-laser emitting in the visible wavelength range (see Table 8.1).

Photothermal and photochemical process are distinguished depending on the actual effect a laser beam produces in a glass [24, 261, 521].

In photothermal processing the photons interact with the components of the glass network especially with the electrons. The energy of the photons (Table 8.1) is low compared to the effective band gap energy ($E_{Ph} < E_B$) of the material (Table 8.2). Oscillations of the network are excited if the photon energy is transformed into oscillatory energy respectively into thermal energy. If the fluence of the laser beam is higher than the threshold energy for ablation $\varepsilon_L > \varepsilon_{Ab}$, the heating is very intense causing the material to melt and evaporate. The process takes place as one-photon absorption at short wavelength (e.g. $\lambda = 157$ nm, $E_{Ph} = 7.9$ eV) or as two-photon absorption at ultra-short pulsed laser radiation (e.g. $\lambda = 700$ nm) [313, 406, 534]. If the fluence drops to $\varepsilon_L < \varepsilon_{Ab}$, only a relaxation process takes place in the material.

In this process the absorbed optical energy is also transformed into thermal oscillations causing the temperature rise in the material.

In photochemical processing, the energy of the photons is high compared to the effective band gap ($E_{Ph} > E_B$). In this case bonds are directly broken by the interaction with the photons [258].

If the photon energy and the effective band gap energy are in the same order of magnitude, mixed effects of photothermal and photochemical interactions take place, which is the case for glass processing using excimer laser radiation. Brokmann [67] provides a more detailed summary of the effects described earlier.

8.2.2 Photothermal Processes for Microstructuring

Photothermal microstructuring of glasses using lasers induces the melting and evaporation of the material by a selective heating of the material by a focused laser beam. The interactions occurring between a laser pulse and the glass are reviewed in the literature [407] and schematically shown in Fig. 8.2. The first step occurring in the photothermal process is the absorption of the energy by the material, which causes the material to heat up selectively. This heating causes the glass to melt and evaporate. The heating front propagates into the material generating a plasma. This plasma further interacts with the laser beam. The photothermal process generates by-products during the geometrical structuring (Fig. 8.3) [407].

During the laser microstructuring a roll of solidified melt forms at the edge of the ablated structure, which is called *recast* (Fig. 8.3). The formation of the recast is due to the material melted and ejected out of the structure by action of the laser pulse. The recast formation can be minimised by reducing the volume of the melted material generated by the pulse [407, 488]. The recast is commonly removed by mechanical processes, such as grinding and polishing.

The precipitation of vaporised material on the surface of the structured glass causes the deposition of *debris* around the structure formed. The debris formation can be significantly reduced when the laser microstructuring is performed in a suitable environment [261]. Normally, the debris layer does not

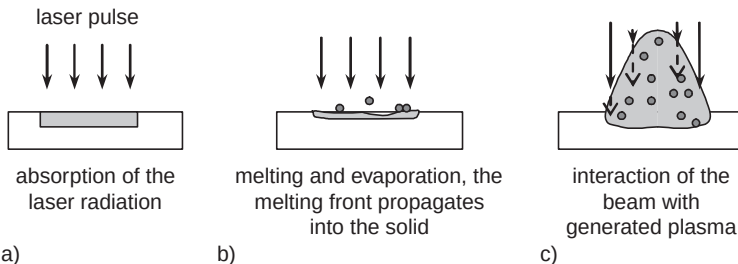


Fig. 8.2. Schematic of the physical interactions between glass and a laser pulse

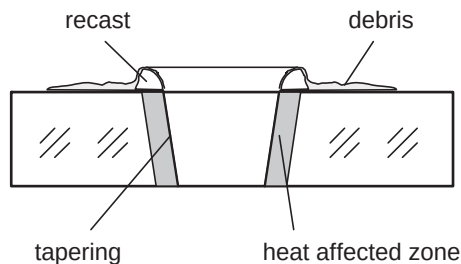


Fig. 8.3. Cross-section of a laser microstructured glass sheet and by-products

adhere strongly to the materials surface and can therefore easily be removed by solvent cleaning in an ultrasound bath. However, commonly protective layers are used to cover the glass surface. This layer can be removed together with the deposited debris after the processing.

Laser microstructuring causes the formation of a *heat-affected zone* surrounding the structure. This heat-affected zone is a zone in which the material was thermally modified by the heat generated during the laser processing. The size of the heat-affected zone is mainly determined by the duration of the laser pulse. If a metallic powder is injected simultaneously with the laser beam into the as generated holes or trenches, then their walls are able to transform into a metal-glass-composite. Baldus and Rohde [17] described the modification of the electrical and thermal properties of the trench faces by adding tungsten powder during CO_2 laser treatment. The tungsten powder combines with the molten soda-lime-silicate or silica glass in the heat-affected zone and produces current conducting lines.

The structures produced during laser microstructuring are *tapered*, which is due to optical diffraction, the numerical aperture of the optic used, the divergence of the laser beam and shadowing effects. The tapering effect can be minimised if a laser with a high fluence ϵ_L and large numerical aperture is used, which can sometimes even result in a negative tapering [407].

Various authors [392,572] investigated the drilling of holes into glass substrates using a CO_2 laser. Synthetic quartz, Pyrex glass and soda-lime-silicate glass were used as materials. Similar drilling rates were found for all glasses for single-pulse exposure experiments. The team also showed that synthetic quartz glass is suitable for laser processing. The depth of a hole can be controlled, because up to a depth of $600\text{ }\mu\text{m}$ it is a linear function of the pulse duration. As shown by scanning electron micrographs of the produced holes a larger recast zone was observed for the laser drilling of Pyrex and soda-lime-silicate glass. Most debris was found when structuring soda-lime-silicate glass. The tapering of the side walls in microstructured synthetic quartz glass can be controlled by laser drilling using a multiple-pulse mode in contrast to the single-pulse process.

The geometrical microstructuring using CO₂ and Nd:YAG lasers is a thermal process, in particular if holes are drilled into borosilicate and quartz glass using CO₂ lasers [55].

The elementary volume ablation process, also called EVA process, is a special structuring process using a pulsed CO₂ laser. For this process the pulses of the CO₂ laser are modified and stabilised using a modulator. Only the material that has to be removed is melted by a pulse and is also completely removed from the materials surface [487–489]. This process minimises the amount of material to be melted and solidified and thereby reducing thermal stresses and the tendency for crack formation. The optical constants of the material are very important for this process.

Mathematical models of laser processing have been developed and the results were compared with the experimental data obtained for the processing of fused silica and soda-lime-silicate glass using various (CO₂, Nd:YAG) lasers by Buerhop et al. [77]. A model was developed describing the interaction of the laser beam with the glass and temperature distributions. In case of a CO₂ laser the absorption depth was determined to be only a few micrometres, resulting in local surface heating. Temperatures exceeding T_g should result at medium laser power densities, which would cause the material to flow smooth of the surface. The authors found that the calculated temperature distributions agreed well with the experimental results obtained using SEM and profilometry of processed glass samples.

Silicate glass was textured using a CO₂ laser [330]. The texturing is used to fabricate computer discs of high specific information density made from glass substrates. Laser pulses create a nanotexture on a surface of a glass disc. The process is based on rapid thermal cycles to manipulate the transformation temperature and finally the microstructure of the glass in the zone affected by the heat.

A permanent modification of a BaO-B₂O₃-TiO₂ glass by CO₂ laser irradiation is reported by Avasi et al. [12]. Hirose et al. [230] described the generation of structures showing a changed refractive index in sputtered silica films by CO₂ laser irradiation. Depending on the annealing time the refractive index of the sputtered layer decreases. The effect is used to form 20 wave guides.

Fused quartz and Pyrex glass were processed by plasma-assisted ablation using Nd:YAG and frequency converted Nd:YAG lasers [576]. High quality surface structuring is possible at all wavelengths (266, 532 and 1,064 nm) investigated beyond an ablation threshold of 0.7 J cm⁻² for the 266 nm laser, 1.5 J cm⁻² for the 532 nm laser and 3.7 J cm⁻² for the 1,064 nm laser. A surface machining of gratings with a period of 14 μm for the 266 nm laser, 20 μm for the 532 nm laser and 30 μm for the 1,064 nm laser was possible. The ablation rate using the 266 nm wavelength laser is much larger than that observed for the lasers operating at a longer wavelength.

High quality holes could be drilled into fused silica and BK7 glass substrates using a copper vapour laser [406]. In particular, it was possible to create

geometrical structures with a high aspect ratio. The following phenomena were observed when working with a copper vapour laser [307]:

- *Spalling.* This is only possible for brittle materials. In this case the energy required to ablate an unit of volume is much smaller than the binding enthalpy between the ions (see Sect. 2.1) or the latent heat of melting.
- *Ablation by evaporation near its threshold.* In this case the homogeneity of the laser beam (distribution of the specific energy density) and material composition are most important for the process. Local deviations in the absorbed fluence at the ablation threshold cause an inhomogeneity of the structural depth.
- *Ablation by stationary evaporation.* The vapour pressure of the glass is not high enough to remove the molten material. Deep and narrow holes form because of multiple reflections.
- *Ablation by stationary melt displacement and ejection.* At high fluences ε_L the melted material removes with a low viscosity. The geometry of the holes created is circular and structures with large aspect ratios can be produced.

A Nd:YAG laser has been used for the damage free marking of glass [329]. Commonly glass is very transparent for the $1.06\ \mu\text{m}$ wavelength of the Nd:YAG laser. In the case of high power densities ($>10^{10}\ \text{W cm}^{-2}$), however, absorption takes place, which is caused by the non-linear effects described above (Sect. 8.2). The refractive index of the glass changes if the power density of the laser exceeds $10^{10}\ \text{W cm}^{-2}$ generating a refractive index distribution acting as a focusing lens so that multi-photon absorption becomes more effective. Also the free electrons generated by multi-photon absorption interact with the laser causing the absorption of energy. The authors show various samples of glass marking.

A new $\text{Fe}^{2+}/\text{Ti}^{4+}$ -doped borosilicate glass was developed, which can be ablated using an Nd:YAG laser operating at a wavelength of $\lambda = 1,064\ \text{nm}$ [503]. The $\text{Fe}^{2+}/\text{Ti}^{4+}$ -doped borosilicate glass absorbs this wavelength. This glass is described in Sect. 1.2.3 (for the glass composition see Table 1.4, and Fig. 1.38 shows its transmission spectrum). The thermal expansion coefficient of this glass matches that of silicon at the temperature used for anodic bonding. The exchange of sodium oxide (Pyrex glass) against lithium oxide lowers the temperature for anodic bonding. The glass is also suitable for the encapsulation of silicon sensors. Holes in the glass are required to provide electrical contacts for the silicon chip.

The geometry of the holes depends on the displacement of the focus of the laser beam relative to the surface of the glass sheet. Various focus positions and their effect on the resulting structural geometries produced has been investigated. The path of laser beams as a function of focus position and the resulting hole geometry is shown in Fig. 8.4. Holes with a diameter of less than $100\ \mu\text{m}$ in an $800\ \mu\text{m}$ thick, 4 in. sheet can be produced (Fig. 8.5). Figure 8.6 illustrates the reproducibility with which sack holes cavities can be produced.

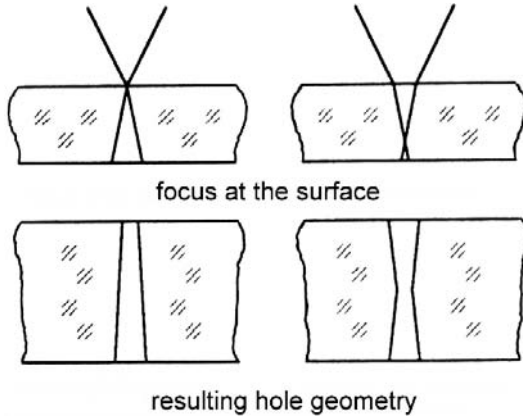


Fig. 8.4. Different focus positions of the laser beam (*above*) and the resulting hole geometry (*below*) [351]

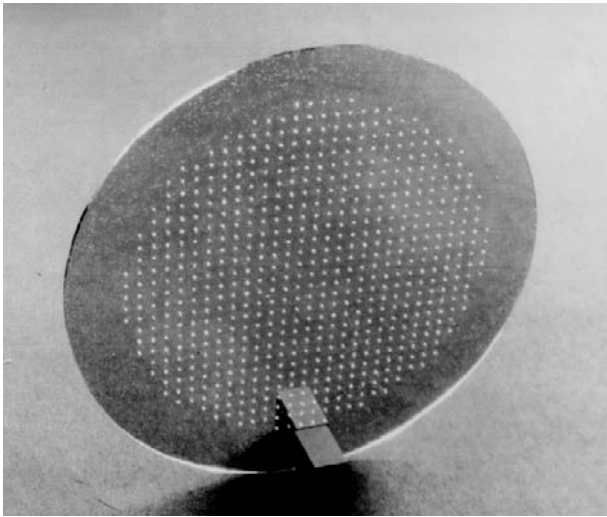


Fig. 8.5. 4 in. glass sheet with holes for covering a silicon wafer [503]

The drilling of anodically bondable Pyrex glass is demonstrated by Keiper et al. [272]. An excimer laser mask processing technique (248 and 193 nm wavelength, 10 ns pulse duration) was used. The average ablation depth per laser pulse between 150 and 260 nm depends on the laser fluence, the repetition rate and the diameter of the drilled holes ranging between 30 and 100 μm .

A modified Nd:YAG laser and a Nd:YVO₄ laser were applied for the ablation of optical glass [119, 120, 577]. To geometrically structure the glass, the laser beam was coupled into the glass starting from the backside (Fig. 8.7). The focus is stepwise moved from the backside into the interior of the glass

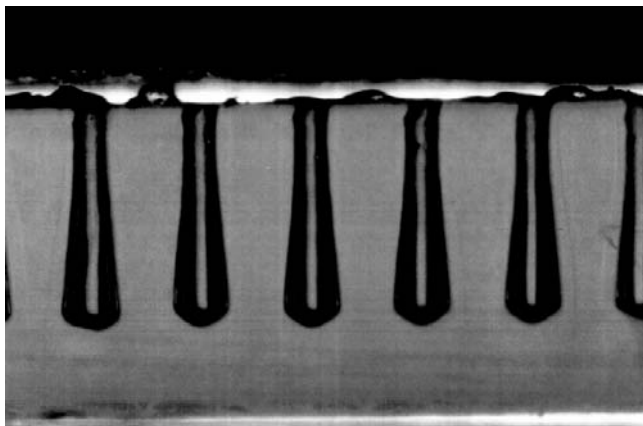


Fig. 8.6. Sack holes in an 800 μm thick glass sheet [351]. For the glass composition see Table 1.4.

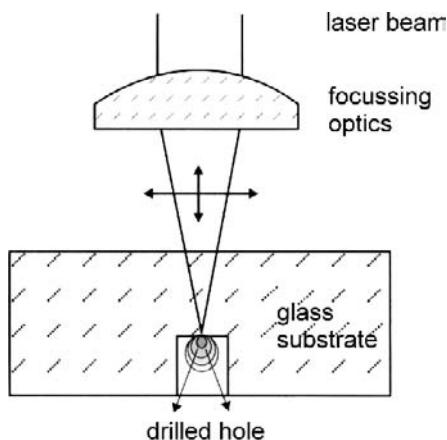


Fig. 8.7. Precision drilling of glass: Holes in a glass body can be produced by starting the ablation from the backside [120]

sheet. The ablation occurs because of the increase of the refraction index by the enhanced beam intensity in the focus plane (8.10). The advantage is that there is no interaction between the vaporized material and the beam. It is possible to generate deep holes with a different cross section and high quality.

Furthermore, it is possible to place the focus also directly at a given position within the glass body right from the start of the laser treatment. This causes the absorption coefficient β'_E to increase abruptly by several 10% causing the laser energy to be mainly absorbed at this point [120]. The glass wants to melt and evaporate. However, because of the surrounding solid material both processes are suppressed. The glass overheats at this particular position. The thermal expansion coefficient of the glass results in very large stresses

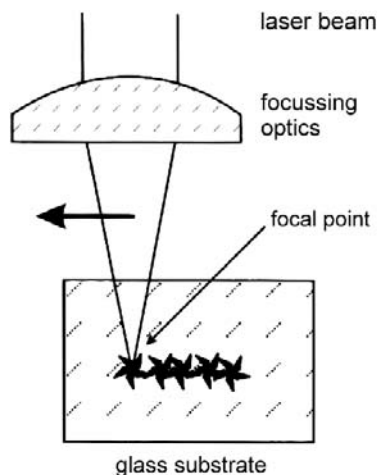


Fig. 8.8. Nonlinear absorption of very intensive laser radiation in transparent glass causing the formation of cracks [120]

during fast cooling so that cracks form as illustrated in Fig. 8.8. The crack formation can be used to decorate and to mark glass pieces in the bulk.

Glasses can also be processed using the third harmonic of an Nd:YAG laser, which results in a reduction of the heat-affected zone and no other damage occurs in the glass [241]. Caused by the wavelength of this frequency converted 355 nm Nd:YAG laser operating at a photon energy of 3.5 eV, it is possible to induce not only a thermal processes but also partially photochemical processes. This laser can be focused to a spot size of 1–2 μm .

Lan et al. [319] used the principle of pocket scanning by a low-energy Nd:YAG laser (355 nm, 30 ns) for the preparation of high quality structures in glass. Pocket scanning involves the scanning by a laser beam along parallel overlapped paths and significantly reduces cracks formed around the edges of structures compared to conventionally direct scanning.

Jacquorie [261] investigated the threshold energy for ablation and the ablation rates of different glasses using an 193 nm ArF excimer laser (Table 8.3). The ablation rate of glasses strongly depends on the fluence ε_L of the laser. It increases with increase in fluence. For smaller fluences the ablation rate increases more than that for higher ones. The ablation rate depends also on the glass composition. It also increases with increase in the number of laser pulses. However, the ablation rate levels off if the number of pulses exceeds 10 pulses. The accumulated value of ablation rate depends also on the fluence of the laser. An accumulated ablation rate of 130 nm pulse^{-1} was found for fused silica glass for a laser fluence of $\varepsilon_L = 6 \text{ J cm}^{-2}$. The ablation rate of soda-lime-silicate glass is influenced particularly for higher numbers of pulses by the formation of by-products forming during the process, i.e. recast and debris. In general, the 193 nm ArF excimer laser is better suited for glass

Table 8.3. Ablation threshold and ablation rates of different glasses processed using an ArF excimer laser [261]

	Threshold energy for ablation (J cm^{-2})	Ablation rate ($\epsilon_L = 4 \text{ J cm}^{-2}$, $N = 10$) (nm pulse^{-1})
Soda lime silicate glass	0.42	120
Borosilicate glass	1.05	165
Fused silica	4.05	105

structuring as compared to the 248 nm KrF excimer laser. If the laser structuring is performed in F_2/He atmosphere the debris and recast is modified in such a way that a simple cleaning of the processed samples is possible.

Amorphous SiO_2 synthesized by liquid-phase-deposition at room temperature needs a much lower threshold fluence (below 200 mJ cm^{-2}) for ablation with an ArF excimer laser compared with SiO_2 glass fabricated by thermal processes [4].

A single pulse treatment using a 308 nm XeCl excimer laser does not result in an increase of the low absorption coefficient [77]. However, ablation takes place for further laser pulses because of an improved coupling of the laser beam due to a reduction of the bond energy by the photochemically modified surface. A surface energy source is assumed for calculations. Ablation effects are included in the calculations by removing volume elements. The development of the structure shape and also of the temperature at the edges of the hole was shown. Ablation rates ranging from $3 \mu\text{m pulse}^{-1}$ for fused silica glass and borosilicate glass and $0.4 \mu\text{m pulse}^{-1}$ for lead silicate glass were reported [78]. The ablation rates of ceramics are one order of magnitude lower than those of glasses. Depending on the number of pulses used different surface roughness and topographies can be generated [78].

The suitability of excimer lasers operating at wavelengths of 248 and 308 nm for the machining of different types of fused silica was investigated [238]. The reported results show that the ablation behaviour of silica glass is a function of the wavelength and the intensity of the laser radiation and also of the surface quality and the degree of purity of the glass. An ablation rate up to $4 \mu\text{m pulse}^{-1}$ was found for all types of fused silica glass for a 308 nm excimer laser at a fluence of 5 J cm^{-2} . Smaller ablation rates were achieved when using a 248 nm excimer laser. However, the quality of the fabricated pattern was higher. The ablation threshold of polished glasses was generally higher than the ablation threshold of rough glasses.

The suitability of excimer lasers for the micromachining of glasses remains limited even though high ablation rates were obtained, because of the rough surface topography and poorly defined edges of the fabricated structures.

Frequently the opposite effect as just described is the object of interest. Not the micromachining of glass is desired, but the resistance of high pure

silica glass against the damage caused by ArF-laser radiation of lithographic equipment. Burkert et al. [82] have intensively investigated this effect and found that already fluences as small as 10 mJ cm^{-2} may cause microchannel-like damages in silica glass pieces if the number of laser pulses increases. The reasons are cumulative or multipulse effects. Compaction as well as absorption induced refraction index changes contribute to the intensity enhancement in ArF-laser hot spots at the beam exit surfaces of the glass.

8.2.3 Photochemical Processes for Microstructuring

Photochemical processes are mainly used for the fabrication of planar waveguides in thin glass layers, or at the surface of absorbing glass devices, or in the bulk of transparent glass pieces and also for the fabrication of Bragg gratings in fibres (Ebendorff - Heidepriem [124]). Another application is the inside colouring for marking glass articles [309, 310].

Laser induced photochemical processes are not used for geometrical microstructuring by material removal but used indeed to modify the local optical properties, such as refractive index and absorption, in a glass. The interaction of the photons of the laser radiation with the different components of the glass network results in the formation of colour centres, local densification of the glass due to photoelastic effect as well as structural rearrangements in glasses having a more dense structure (Ebendorff - Heidepriem [124]). The creation of locally defined colour centres is the most commonly exploited effect. The actual quantity of the colour change and mechanism of the formation of colour centres depends on the interaction between the glass and the wavelength of the laser beam used to 'write' the structures. Figure 8.9 illustrated the three extreme cases of the interaction between the glass and the laser.

In the first case I, the energy of the laser photons, i.e. at short wavelengths λ_L , is larger than the effective band gap. This corresponds with the absorption edge of the glass, which results in a strong laser beam absorption. In

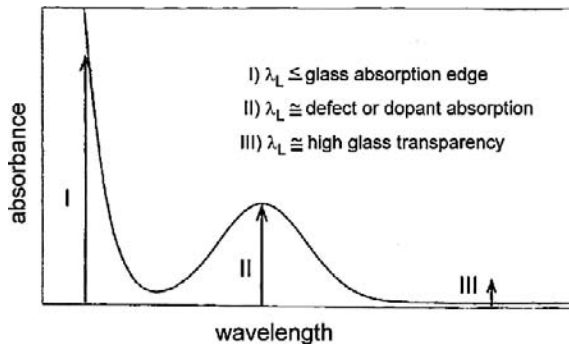


Fig. 8.9. Schematic illustration of the relationship between absorption spectrum of a glass and laser wavelength λ_L used for writing (Ebendorff - Heidepriem [124])

this case one-photon-processes are prevailing and the laser-induced effects are confined to a thin surface layer of the exposed sample. This phenomenon was observed for Ge-doped silica waveguides exposed to a F_2 -excimer laser, PbO-containing silicate glasses and also for fluoride and sulphide glasses, which are not explained in this book. In the second case II, the absorption is due to dopants or localised defects in the glass network. If the emitted laser radiation has approximately the same wavelength as the maximum of the absorption band the localised defects or dopants will be excited and absorb these photons. Commonly for waveguides dopants used to induce absorption are Eu^{2+} and Ce^{3+} . In the third case III, the wavelength of the laser radiation is in the range in which glass is transparent. In order for these wavelengths to be absorbed a high power density laser beam is required so that non-linear optical effects and two-photon-interaction are produced. Very short (fs), high intensity, very well focused laser pulses (see Sect. 8.2.4) can produce colour centres in various transparent glasses not only at the surface of glass sheets but also in the interior of bulk glass.

The photon absorption is caused by different effects in glasses and is still not fully understood. Nevertheless, three main possibilities for the absorption are considered and explained for OH-group free and OH-group containing silica glass [138]. Deep UV (DUV) absorption can take place at defect centres, such as the E' -centre, the non-bridging oxygen hole centre (NBOHC) and on peroxy radicals.

The optical band gap for pure crystalline silica is 8.7 eV (142 nm), whereas the band gap of a very pure silica glass is only 8.3 eV (149 nm). The reduction in the band gap is due to the weaker and varying Si–O–Si bonds (see Sect. 1.1.4). If this fact is superimposed by localised non-stoichiometric compositions and strained bonds, a weak absorption band ranging from 160 to 200 nm appears.

E' -centres are the result of radiation damage and connected with electron–hole pairs, so called exciton. NBOHC-centres are generated in ‘dry’ silica glass by the cleavage of Si–O–Si bonds or in ‘wet’ silica glass by the dissociation of OH^- groups. In the latter case the resulting defect consists of a hole trap on a dangling non-bridging oxygen (see Sect. 1.1.3) and a free hydrogen ion in the glass matrix. The NBOHC defect causes maximum absorption at $\lambda = 248$ nm. Because of the high mobility of free H^+ -ions in the glass at room temperature this effect disappears rapidly at room temperature in ‘wet’ silica glass. However, this NBOHC-defect is stable for an extended period of time in ‘dry’ silica glass, causing it to be sensitive for radiation at the appropriate wavelength. Peroxy radicals (O_2^*) are primarily created by the interaction of an interstitial oxygen molecule with an E' -defect [138]. The absorption band at $\lambda = 163$ nm of peroxy radicals is close to the radiation of the F_2 -excimer laser ($\lambda = 157$ nm), which gives rise to considerable damage in laser optic systems operating at this wavelength. However, this effect allows for optical microstructuring of silica glass devices.

The influence of iron or tin dopants or impurities in boron–silicate glasses (Duran-type, composition without dopants (mass %): $82\text{SiO}_2 \cdot 12\text{B}_2\text{O}_3 \cdot 1\text{Al}_2\text{O}_3 \cdot 5\text{Na}_2\text{O}/\text{K}_2\text{O}$) on the absorption of various excimer laser radiation was investigated by Ehrhart et al. [129]. Iron and tin are polyvalent elements ($\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Sn}^{2+}/\text{Sn}^{4+}$). The interaction between the ions and laser radiation at the absorption maximum (see case II described earlier) results in the valency change and the formation of colour centres. As a consequence, absorption of lights occurs now at other wavelengths with other intensities. Duran glass tubes would only be suitable for the disinfection of drinking water if UV-B radiation (280–320 nm) is not absorbed by the glass itself (Natura and Ehrhart, [380]). The authors found that the melting conditions (oxidising or reducing) affect the valency of iron and tin ions, which in turn could influence photochemical processes during UV-B exposure. Ehrhart et al. [129] aimed on the one hand to eliminate any laser-induced photochemical reactions with the glass components. However, on the other hand this effect could be exploited to create light absorbing lines in glass devices. Pictures can be created in glasses using this method, because the absorption takes place not only in UV range but also in VIS spectrum. Writing silver or gold ruby lines is possible by combination of the photochemical with the photothermal effect.

Also the UV-light induced photoreduction in doped phosphate and fluoride-phosphate glasses [359] and the phase separation in highly tin-doped fibres and preforms during UV-exposure [63] were investigated.

Using the just described effect, Nalin et al. [377] were able to store holographic 3D data in glasses of the $(1 - x)\text{SbPO}_4 \cdot x\text{WO}_3$ -composition. The valence of the antimony ion had changed during irradiation with a tuneable Ar-laser (visible wavelength range). At the exposed lines and areas the colour of the glass changed from first yellow to now blue. Simultaneously, the refractive index was influenced. The intensity of the effects depends on the time of irradiation at given beam intensity. The valence change is a reversible process and can be annealed by heat treating at 200°C. The effects were measured using a holographic setup.

The use of excimer lasers offers the following advantages over CO_2 and Nd:YAG lasers for the production of waveguides and Bragg gratings [404]. Excimer lasers operate at shorter laser wavelength, which can vary from 157 to 351 nm depending on the gas used in excimer lasers. These lasers enable short pulse duration in the range from 10 to 50 ns and have high pulse peak powers, which are typically in the range from 1 to 50 MW. The high output power in combination with these features make excimer lasers to an effective UV-light source for microstructuring and marking applications [404]. The use of excimer lasers for structuring allows simultaneously modifying the refractive index locally. Such glass devices can be used as microoptical elements. The writing of optical fibre gratings is of major interest. Optical fibre gratings can be written by focusing two laser beams at a single spot (Fig. 8.10). The refractive index is modified locally by the cleavage of Si–O–Si bonds caused by the action of the high energy intensity of the lasers.

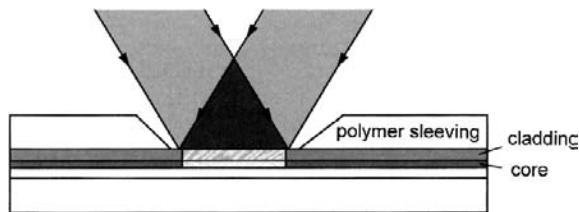


Fig. 8.10. Schematic of excimer laser writing of optical fibre gratings [404]

8.2.4 Microstructuring using Short-Pulse Lasers

Because of the increased importance of short-pulse lasers, their application for microstructuring of glasses is discussed separately. Short-pulse lasers offer three major advantages over ordinary lasers. The very short pulse duration in the order of 3–300 fs allows for an extremely high pulse power intensity $>10^{10} \text{ W cm}^{-2}$. The very high beam intensity enables to create the desired effect in the glass before the energy is dissipated in the surrounding of the exposed glass volume by heat conduction. The very high laser intensity gives rise to non-linear optical effects (see Sect. 8.2.1). Self focusing of the beam is caused by the increased refraction index with increased radiation intensity causing a further increase of the beam intensity. Because of this nonlinear effect the emitted pulse energy of $280 \mu\text{J}$ in the visible wavelength spectrum is enough to induce photochemical and photothermal reactions in transparent glasses. The use of short-pulse lasers allows to minimise the thermal damage (cracks and recast) in glass because the total energy coupled into the glass is relatively small and is almost exclusively used for structuring, see Nolte [384].

Well-defined and highly reproducible micrometre sized channels of a lengths of over 1 mm (Fig. 8.11) have been produced in silica glass using Ti:sapphire laser pulses of 790 nm wavelength and pulse lengths of 100–200 fs [534]. The experiments were carried out in N_2 (1 bar) and under vacuum conditions (1 mbar and $<10^{-4}$ mbar). The pulses frequency was varied between 10 Hz and 1 kHz. The holes produced had a diameter varying between 200 and $300 \mu\text{m}$, which widened near the glass surface. The depths of the holes could be controlled by the number of laser pulses and increased almost linearly up to 2,500 pulses. The formation of cracks near the surface of the glass sheet surrounding the holes was observed. This damage disappears as soon as the narrow part of the holes was formed (Fig. 8.11). The laser pulse duration had to be sufficiently short in order to produce multiphoton excitation of electrons into the conduction band during the rise time of the laser pulse.

Hiromatsu et al. [229] produced channels with diameters on the order of tens of microns, high aspect ratios and good wall-surface quality. Furthermore, they manufactured high quality waveguides by high repetition rate femtosecond laser, combined with the channel. Fibre Bragg gratings were written in large diameter ($350\text{--}400 \mu\text{m}$) air cladded optical fibres using an amplified

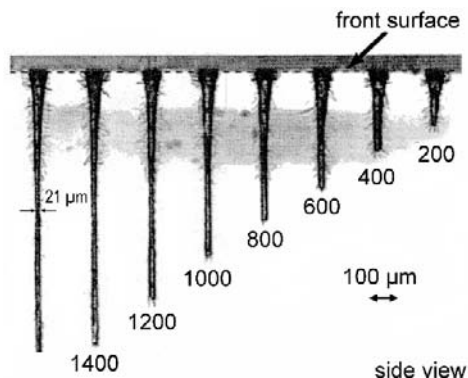


Fig. 8.11. Channels produced in silica glass in a vacuum of $<10^{-4}$ mbar using 120 fs laser pulses at 790 nm, 16 Hz, $\varepsilon = 42 \text{ J cm}^{-2}$ for different numbers of laser pulses [534]

fs Ti:Sapphire laser (800 nm, 100 fs, $0.3 \mu\text{J pulse}^{-1}$) with a point-by-point method. Multi-photon absorption occurred [183].

The ablation behaviour of various glasses, a silica glass (SQ 1 produced by Schott Glas Jena), a sodium–calcium-silicate glass (substrates for microscopy produced by Menzel-Glas) and a barium–boro-silicate glass (Corning Code 7059), during laser processing was compared [313]. The band gap was 4 eV for the sodium–calcium- and the barium–boro-silicate glass and 9 eV for the silica glass. The glasses have a similar transmission behaviour in the VIS spectral range. A dye-CPM ring laser emitting a wavelength of 610–625 nm with a single pulse energy of 100 pJ and a pulse duration between 70 and 130 fs was used for the study. After a certain number of incubation pulses of a given fluence ε_L the ablation depth increases almost linearly with the number of pulses. Incubation in this case means that for a constant fluence ε_L a certain number of pulses are required for the ablation to start. These initial incubation pulses result only in photochemical reactions, leading to the formation of colour centres and a roughening of the surface and thereby creating the conditions required for an increased absorption of the pulses that follow, which then causes ablation. Krüger [313] observed the formation of periodical ripple pattern in the wall and on the bottom of the cavities created by the laser ablation (Fig. 8.12). It was found that the ripple pattern varies during the laser ablation process using a constant fluency for a Na–Ca- and Ba–B-silicate glass with increasing depth of cavity. A possible explanation for the formation of these substructures could be the relaxation of stress occurring during laser exposure and rapid cooling that follows [314]. Similar substructures were found after the laser machining of silica glass.

Photonic glass devices can be produced by femtosecond lasers exposure [228]. To produce such devices ablation should be avoided but photochemical effects are desired to modify the refractive index. Femtosecond laser

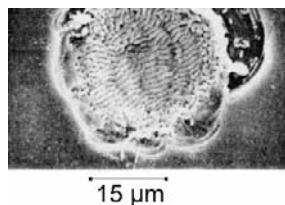


Fig. 8.12. Ablation of a barium-boro-silicate glass caused by $N = 20$ laser-pulses of a wavelength of $\lambda = 620$ nm for a pulse duration of $t = 300$ fs and a fluence of $\varepsilon_L = 2.5 \text{ J cm}^{-2}$ [313]

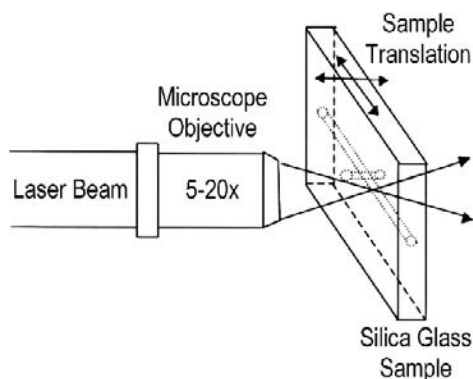


Fig. 8.13. Schematic illustration of the production of an optical waveguide by femtosecond laser pulse machining [228]

processing could be used to fabricate photostructured optical waveguides, photo induced refractive-index gratings and optical storage devices [376]. Figure 8.13 shows schematically the writing of an optical waveguide using laser machining.

An amplified 810 nm Ti:sapphire laser emitting mode-coupled 120 fs pulses with a frequency of 200 kHz and an average power of 975 mW was used to fabricate waveguides in Ge-doped silica glass, borate, soda-lime-silicate and fluorozirconate glasses. The focus of the laser beam must be moved away from the glass surface in the bulk of the glass in order to produce flaws-free regions with a higher refractive index. Using the described laser, processing a change in the refractive index of about $\Delta n \approx 0.035$ can be achieved, which is sufficient for the intended application.

Both, the change of valency of dopants, e.g. Ag^+ in doped glasses, and also the generation of optical images are described by Shimotsuna et al. [464]. They used a pulsed femtosecond Ti:Sapphire laser and different silicate and tellurite glass.

The photo-induced microcrystallisation in photosensitive glasses was also investigated [304]. The crystallisation is induced by multi-photon absorption of a fs-laser beam operating in the non-resonant wavelength range.

Kaempfe et al. [269] used a fs-pulse-laser to produce glasses containing anisotropic silver nanoparticles. A silver-rich glass surface layer was produced by diffusion. After a sophisticated thermal treatment silver particles with an average diameter of approximately 17 nm (varying between 10 and 28 nm) were detected up to a depth of around 35 μm . The concentration of the silver particles varied between 10^{-3} and 10^{-4} . The presence of silver particles in the glass produces an absorption band with a maximum at 427 nm (2.9 eV). The exposure of the glass to a single, linear polarised, frequency-doubled <200 fs pulse with an energy of 100 μJ and almost Gaussian intensity profile from an amplified Ti:sapphire laser operating at a wavelength of 400 nm with a spectral width of <3 nm induced colour change. The glass showed dichroic behaviour. The axis of dichroism was parallel to the polarisation direction of the laser beam. This remarkable effect was caused by changing the spherical geometry of the silver nanoparticles to an anisotropic ellipsoidal shape with a preferred direction. The interaction of the initially spherical nanoparticles with the high power laser pulse heated up the particles and the surrounding glass causing the particle shape to change. The colour change depends on the aspect ratio of the particles.

8.2.5 Laser-Assisted and Laser-Activated Etching

Laser-assisted and activated etching relies on different chemical processes. These processes are based on the one hand on the fact that bonds in the glass can be broken or that the valency of ions can be changed creating vacancies or voids. On the other hand especially during chemical etching, laser exposure can assist chemical reactions between etching gases and the glass.

Laser-induced structuring of photosensitive glasses is a particular kind of photostructuring and will be discussed in detail in Sect. 9.3.

The lasers assisted chemical processing of various materials is discussed in the literature [23]. ArF- and KrF-excimer laser-assisted etching of silica glass in CF_2Cl_2 and CF_2Br_2 enables etching rates ranging from 0.02 to 0.05 nm pulse $^{-1}$. It was found that CF_2 radicals etch glasses more effectively than CF_3 radicals. Etching of silica glass in an ArF excimer laser-activated mixture of NF_3 and H_2 was also investigated. Increasing the H_2 partial pressure results in an increased etching rate. Silica glass can also be etched in a Cl_2 atmosphere activated by Ar^+ laser radiation. An etching rate of 0.3 nm s $^{-1}$ was observed when using a 457.9 nm radiation. However, when using a 514.5 nm radiation the etching rate decreases. It was observed that the lateral dimensions of the geometrical structures created are much larger than the spot size of the laser beam because of the random diffusion of Cl^* radicals produced within the gas phase.

Laser induced etching is also described by Rytz-Froidevaux et al. [434]. Laser induced etching processes are mainly used in microelectronics.

Marcinkevicius et al. [345] and Juodkazis et al. [268] developed a process for the fabrication of a three-dimensional network of microchannels in silica.

Table 8.4. Etching behaviour of silica glass depending on used solvents, Juodkazis et al. [268]

	Etching rate of the unmodified glass (nm min ⁻¹)	Etching rate of the modified glass (μm min ⁻¹)	Etching ratio
HF/HNO ₃ mixture	12–17.3	1.1	60
Diluted HF (5%)	72–79	>3	40
Buffered HF	88	1.7	20

A two step process was used. In the first step a damage of the glass structure is induced by the exposure to a 120 fs Ti:sapphire laser pulse of a wavelength of 795 nm. The laser beam was focused into the silica glass sample using an objective to a spot size of 0.78 μm. The laser fluence ε_L was varied between 5 and 50 J cm⁻². In the second step damaged areas are selectively etched away in a solution of hydrofluoric acid. Solutions of HF, buffered HF and a mixture of HF and HNO₃ were used as etching media. During the etching process the etching solution was mixed using a mechanical shaker. The etching times varied between 20 and 480 min. The etching rates of laser beam modified and unmodified areas of the glass sample were different but were a function of the etching medium used (Table 8.4). The lowest etching rate of the unmodified glass was during the etching in a HF/HNO₃ mixture, which results in the highest selectivity in the removal of the modified areas and overall moderate etching rates. Using this technique, channels with a width down to 10 μm at arbitrary angle of interconnection and an aspect ratio of 10 can be produced. The process allows the fabrication of three-dimensional structures. Juodkazis et al. [268] produced a spiral inside the glass using this process.

193, 248 and 308 nm radiation excimer laser-activated etching of optical glasses was investigated [386]. Fluences up to 5 J cm⁻² and different inert and reactive gases were used. A threshold energy of around 1 J cm⁻² to induce etching was found when using a 193 nm laser. If the laser energy was lower etching took place only in reactive gases. Above this threshold energy the etching rate increases rapidly and almost in a linear manner with the laser energy. The highest etching rates were found in vacuum and at H₂ atmosphere. In the ablation region the etching depth increases in linear fashion with the number of pulses applied to the sample. The etching rate of 130 nm pulse⁻¹ did not depend on the frequency of the laser pulses at a fluence of $\varepsilon = 3.6$ J cm⁻² of an 193 nm laser.

Huang et al. [242] reported the selective etching of quartz glass substrates by laser induced backside wet etching. The technique does not require the laser energy to be absorbed by the glass, but it is the liquid that absorbs the laser energy to induce etching. The process allows the fabrication of crack free structures and reduces the effort of pre-processing. The used laser was a frequency trebled Nd:YAG laser, and the absorbing liquid was a mixture of toluene and pyrene.

Geometrical Photostructuring

9.1 Basics

9.1.1 Process Steps

Stookey [497, 498] was the first to publish the complete photostructuring process under the name *Chemical Machining* or *Sculpturing* describing a suitable glass composition, the principle of the process and optimum processing conditions as well as first applications. This process was further developed over the years ([227, 399]). A new description of the photostructuring process and new results can be found in the literature [190, 446].

Geometrical photostructuring requires special, photostructurable glasses of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system containing several dopants. These glass compositions and photochemically induced compositional changes are described in detail in Sect. 1.2.4.

The standard structuring process is based on photolithography and consists of three main steps UV exposure, thermal treatment and acid etching. A schematic of the process is shown in Fig. 9.1. The following discussion focuses on the photostructurable glass FS21 developed at the Technische Universität Ilmenau.

The correct valence of the dopands, Ce^{3+} and Ag^+ , which are required for the photochemical process, has to be guaranteed during the melting process. This, however, is problematic because under normal circumstances Ce^{3+} has to be reduced from Ce^{4+} while Ag needs to be oxidized making the melting process very sophisticated. The valency changes again from Ce^{3+} to Ce^{4+} during the exposure to UV light. During a thermal treatment that follows, the areas exposed to UV light will crystallise partially. Atomic silver clusters form the nuclei, around which lithium metasilicate crystallises. This crystalline phase is very easily soluble in hydrofluoric acid. The crystalline areas can now be removed in an etching process in a hydrofluoric acid solution.

Figure 9.2 shows an example of a photostructured FS21 glass. The structure was designed to test the minimum width of beams that can be fabricated

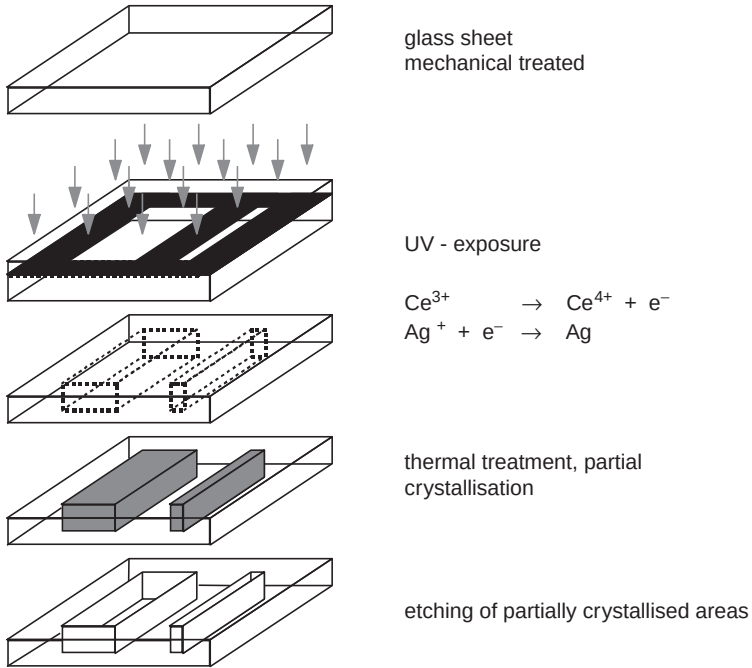


Fig. 9.1. Main steps of the standard structuring process

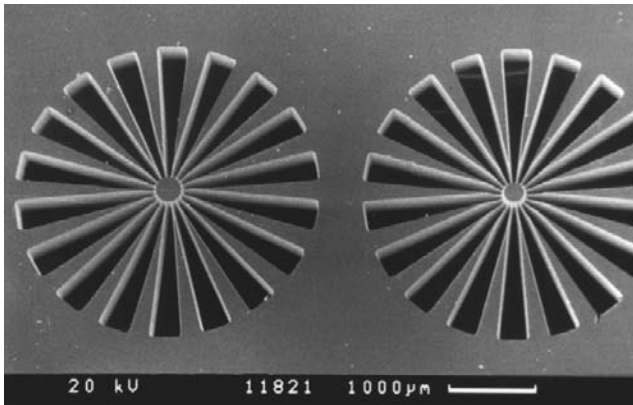


Fig. 9.2. Example of a photostructured FS21 glass using a standard structuring process to generate slits and bars [190]

using a given mask geometry. The photostructuring process and process parameters are described in detail in the following sections.

For photostructuring, a polished sheet of a photostructurable glass is required. The substrates are prepared by grinding and polishing processes

similar to those used in production of optical components. The surface quality of the glass has to be excellent, i.e. the surface roughness should be smaller than $R_a = 10\text{ nm}$, which is important to guarantee a high-quality optical transfer of the mask structure into the glass sheet but also to reduce any surface crystallisation of the glass during the thermal treatment. Commonly the structures created have widths exceeding $10\text{ }\mu\text{m}$ and the glasses to be structured have a limited thickness which means that small deformations of the sheets, e.g. $3\text{ }\mu\text{m}$ over a length of 50 mm , can be tolerated. The sheet thickness varies between 200 and $3,000\text{ }\mu\text{m}$. The lower limit is defined by the handling and deformation during the thermal process. The upper limit results from the decrease of the energy density of the UV light through the thickness of the sheet as well as the mass transport limitations encountered during the etching step, which affects the accuracy of the patterns that can be created.

9.1.2 UV Exposure

Introductory Remarks

Standard mask aligners, such as those used in the silicon microtechnology, are commonly used for the UV exposure of photostructurable glasses. These devices have vacuum chucks to fix the substrate and the mask. Mask aligners enable to adjust the relative position between substrate and mask as well as to correct the contact angle between both. The mask can be in direct contact with the substrate, or a proximity space of a few micrometres can be realised. For the exposure of photostructurable glasses, close contact between the mask and the substrate is preferred. The mask openings must be transparent for the wavelength of the radiation used but non-transparent in the covered areas. Furthermore the entire mobile mask must cover the glass sheet and wavelength of the light used has to be absorbed by the glass in the exposed areas.

UV-Light Sensitivity Range of the Photostructurable Glasses

Stookey [496] investigated the spectral sensitivity of a Ce^{3+} containing photosensitive glass. The glass was found to be sensitive to UV light in the wavelength range between 240 and 360 nm with a maximum at 310 nm . Later, Stookey and Schuler [502] investigated a wavelength region between 300 and 350 nm for photostructuring, but found no significant effect on transmission of the glass after exposure to UV light with these wavelengths. However, exposing a photosensitive glass to a wider spectrum of wavelength (in particular to light with wavelengths lower than 300 nm) causes a reduction in the transmission of the exposed glass. This effect was explained by the formation of colour centres. Various authors claim that different wavelength ranges (310 , 312 , the spectrum between 310 and 320 nm or simply short wavelength UV light) are effective for the UV exposure of the photostructurable glass [110, 111, 246, 446, 481]. Brunsch [75] used edge-type glass filters of varying edge positions and a

wide band mercury lamp for the UV exposure of several Ce^{3+} containing photosensitive glasses. The exposed glasses were found to crystallise partially during the thermal treating when exposed through a 50% transmission filter at $\lambda \leq 325$ nm. Filters with a 50% transmission at $\lambda \geq 325$ nm did not induce any photochemical reaction and, therefore, no crystallisation during thermal treatment. Schmidt [446] calculated that the minimum energy density of UV light of wavelengths between 300 and 320 nm was required for the complete exposure of a glass sheet with a thickness of 500 μm . She found that an energy density of 480 mJ cm^{-2} is required for complete exposure.

The effective wavelength range is significantly wider if laser radiation is used for the photostructuring. The effective range to induce photochemical changes in photosensitive glasses was found to be between 270 and 335 nm, if a laser was used [303]. Differences between the UV exposure using lasers with an effective wavelength range from 150 to 400 nm and a mask aligner with an effective wavelength range from 240 to 360 nm were investigated by Yabe et al. [567].

Kondo et al. [304] investigated the crystallisation induced by exposure to three different UV-light sources followed by a heat treatment in a glass containing sodium, fluor, Ag^+ and Ce^{3+} . They used a femtosecond optical parametric amplifier pumped Ti-sapphire laser with a wavelength of 630 nm, a nanosecond, YAG-laser pumped dye laser of 630 nm as well as a high-pressure wide-band mercury lamp. Using a femtosecond laser and the mercury lamp sodium fluoride crystallisation occurred in the glass, whereas no crystallisation was found if the glass was exposed to UV light generated by the nanosecond laser. The mechanism for the generation of photoelectrons varies. On the one hand, it was found that the wavelength of the mercury lamp is resonant with the absorption maximum of Ce^{3+} . The oxidation of Ce^{3+} provided the electrons for the reduction of silver. However, on the other hand a photochemical reduction of Ag^+ can also be achieved by an exposure with very short pulses of laser radiation of non-resonant wavelength.

The UV exposure of photosensitive glass using excimer laser was also investigated. The wavelength range from 193 to 355 nm was found to be effective in inducing photochemical changes [68].

Harnisch [190] determined the effective UV-wavelength range for the exposure of photosensitive glass using a high-pressure mercury lamp. The wavelength range 300–320 nm corresponding to the maximum absorption of Ce^{3+} ions was found to be most effective. However, other wavelength ranges, smaller and larger, are also suitable to induce photochemical changes, but the required energy density is significantly larger as compared to the optimal range.

High-pressure mercury¹ and UV-fluorescent lamps as well as XeCl excimer beamer and UV lasers are UV-light sources suitable for the photostructuring of glasses [366, 367]. However, the preferred UV-light sources are wide

¹ They are the most commonly used light source in mask aligners.

band high-pressure mercury lamps. The other light sources have significant disadvantages, such as the very high cost of XeCl excimer beamers or the unsuitable emission characteristics of UV-fluorescent lamps. All the mentioned light sources also require an optical system, which has to have high transmission in the most sensitive wavelength range of the photostructurable glass and which guarantees the homogenisation and parallelisation of the light. Commonly it is a system made from quartz glass.

The exposure of photosensitive glass is also possible using a focused beam of protons (proton beam writing). Microfluidic channels with integrated waveguides and optical diffraction gratings are made using this technique [45].

Masks Used for the UV Exposure

In order to create photochemical changes in photosensitive glasses during the UV-exposure masks have to be used. Besides the requirements already mentioned above the masks have to have a very high precision of the openings. They must be mechanically stable and wear resistant. Furthermore, the masks should be easily integrated into the technological process and be low cost. The advantages and disadvantages of various masking materials with respect to the most important process parameters are summarised in Table 9.1. The suitability of various masking materials was investigated by Mrotzek et al. [366,367]. The precision of the geometrical structure itself and the relative position of several structures with respect to each other are determined by the kind of machining of the non-transparent part (absorber structure) of the mask.

The standard masks used to manufacture microstructured glass components are chromium layers deposited on quartz glass or soda lime silicate glass. The thickness of the glass blank varies between 2 and 4 mm, whereas

Table 9.1. Comparison of various mask materials

Material	Precision	Process effort	Multiple use	Structure variation	Transmission	Costs
Chromium/fused silica	++	+	+	++	++	--
Chromium/soda lime silicate glass	++	+	+	++	--	-
Stainless steal foils	0	0	0	-	++	0
Thin brass sheets	-	+	++	--	++	+
Structured aluminium surface layers	+	--	--	++	++	-

+ favourable, 0 neutral, - unfavourable

the thickness of the chromium layer is about 300 nm. The chromium layer is structured using electron beam writers. The structures created have a precision of about 100 nm. Fused silica glass is better suited for the manufacturing of blanks because of its high transmission (>90%) in the wavelength range 300–320 nm. In this range, soda lime silicate glass absorbs more than 80%, which therefore would require significantly longer exposure time.

Alternatively laser-structured stainless steel foils or even machined thin brass sheets can be used to photostructure glasses. However, such masks offer lower precision. The precision of structures in laser-structured stainless steel foils is around 20 μm , whereas that of machined thin brass sheets is not better than 50 μm . Such masks offer only a limited variety of structures. No freely standing structures are possible, because these masks do not possess a mask blank. However, the main advantage of these masks is their low cost. These masks are therefore a cost effective alternative to manufacture simple structures.

Structured thin aluminium layers, which are directly deposited onto the surface of the glass substrate, are used for prototyping and in science because they can only be used once. An aluminium layer is deposited directly on the surface of the substrate and structured by conventional microtechnical methods. The glass is exposed through the structured aluminium mask, after which the aluminium mask layer is removed.

Concluding it can be said that the standard masks, i.e. a structured chromium layer on fused silica, are the most suitable masks for the UV exposure of glass.

Minimum Energy Density Necessary for the Photochemical Effect

The energy density D , which is relevant for the exposure of the glass, equals the power density P times the exposure time t_L (9.1):

$$D = P \times t_L. \quad (9.1)$$

The power density P of a beam with a given spectral range can be measured using standard light measurement equipment. Figure 9.3 shows how the depth of structures created depends on the energy density and etching time [190]. The glass FS21 was exposed to UV light with a mask aligner, thermally treated at 590°C for 1 h and etched in 10% hydrofluoric acid. A minimum energy density $D_{\min}$ ² of the light used is required in order to modify the glass so that structures can be etched after the thermal treatment. A selective etching of the exposed areas is impossible if the energy density of the light

² The *minimum energy density* $D_{\min}$ is defined as the energy density required for a local glass modification after a thermal treatment, allowing for selective etching of a structure with a depth of 20 μm in an etching time of 15 min of a given glass exposed to UV light using the available conditions, which depends on equipment and given glass material.

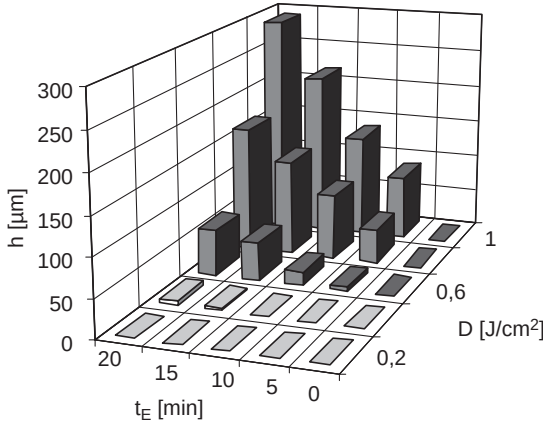


Fig. 9.3. Etching depth (h) as function of the energy density (D) and etching time (t_e) [190]

used is too low. For the investigated case (equipment and glass) the minimum energy density was found to be $D_{\min} = 0.5 \text{ J cm}^{-2}$ [190].

The equipment used for the structuring of photosensitive glasses as well as the glass itself (for various producers see Sect. 1.2.4) vary, which all affect the structuring efficiency. This includes the light source, the specific optical system used in the UV-exposure device, the homogeneity of the light beam, the spectral sensitivity of the power measuring system, etc. To compare various experimental setups, it is necessary to normalise the energy density. The normalised respective relative energy density D_S is defined as, see (9.2):

$$D_S = D/D_{\min}. \quad (9.2)$$

Conclusions

- The effect of the UV exposure on a photosensitive glass is a function of the wavelength of the light used and its energy density. Photoelectrons can be generated in a wide range of UV wavelengths. Photoelectrons can also be generated for instance by using ultra short laser pulses or protons.
- Using of wide band light sources, such as high-pressure mercury lamps, does not affect the precision of the structured glass.
- The wavelength range from 300 to 320 nm is most effective, i.e. energy density required for the generation of photoelectrons is the lowest in this wavelength range.
- A minimum free electron density is necessary to generate a sufficient number of silver nuclei (see Fig. 1.40) and, therefore, of LMS crystals (see Fig. 1.41) to enable selective etching.
- In principle all light sources can be used, provided they emit the light required by the photosensitive wavelength range of the glass. The required energy density depends on the used wavelength of the light emitted.

- A range of masking materials and technologies is available, but the required precision and the cost of the mask will in the end determine which mask will be used.
- A user has to select from a range of exposure light sources, measuring techniques and photosensitive glasses. The final outcome of the structuring is determined by the equipment used for given glass.

9.1.3 Thermal Treatment

Introductory Remarks

In the standard photostructuring process (Fig. 9.1) a thermal treatment induces crystallisation on the nuclei of silver atoms generated in the areas exposed to UV light. No crystallisation should take place in the areas that have not been exposed to the UV light, which is important to create areas with large differences in etching rates for the following etching step. The fundamentals of the partial crystallisation process are described in Sects. 1.2.4 and 2.3. In the following section we will discuss the parameters and process conditions affecting the thermally induced partial crystallisation.

To achieve large differences in the etching rates of the exposed and unexposed areas, allowing for the removal of selective materials, a high degree of crystallisation consisting of a high number of small crystals in the exposed areas is required. The crystals should be interlacing, i.e. the crystals should be in contact with each other (left-hand side Fig. 9.10). The exposed area should very regularly and consistently crystallise whereas no crystals should grow in the unexposed areas.

The nucleation and crystal growth in the exposed areas is caused by a thermal treatment using two residence steps. The agglomerates of silver atoms created during the UV exposure act as heteroseeds or -nuclei. The nucleation temperature is less above the transformation temperature T_g (see Sect. 1.2.4), whereas the crystal growth occurs above temperatures of 550°C. The crystallisation temperatures should be below 600°C to avoid homogeneous, undesired nucleation in the not exposed areas.

Thermal Treatment Process

Thermal processes can be studied by differential thermo analysis (DTA). Figure 9.4 shows a DTA-curve of an unexposed and an UV-exposed photostructurable glass FS21. The DTA-curve of the unexposed glass has one exothermic peak with maximum at 665°C, which corresponds to the crystallisation of one crystal phase. The shoulder of the peak at lower temperatures, around 600°C, is due to the homogeneous nucleation. The endothermic peak at 450°C signifies the transformation temperature of the glass (see Table 1.7). The DTA-curve of the UV-exposed glass also shows one exothermic effect occurring at a maximum temperature of only 653°C which corresponds to the

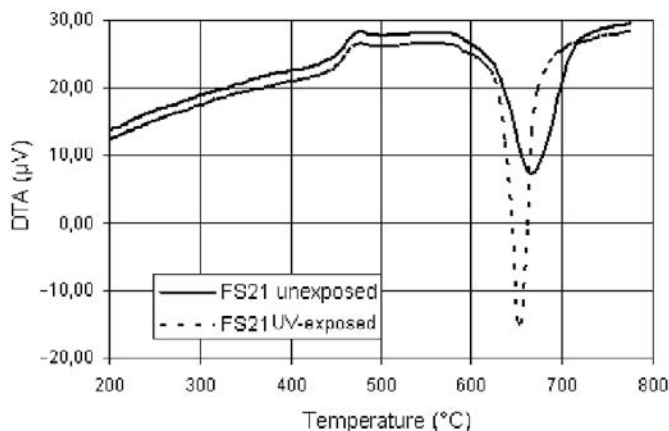


Fig. 9.4. DTA of an unexposed and UV-exposed photostructurable glass FS21

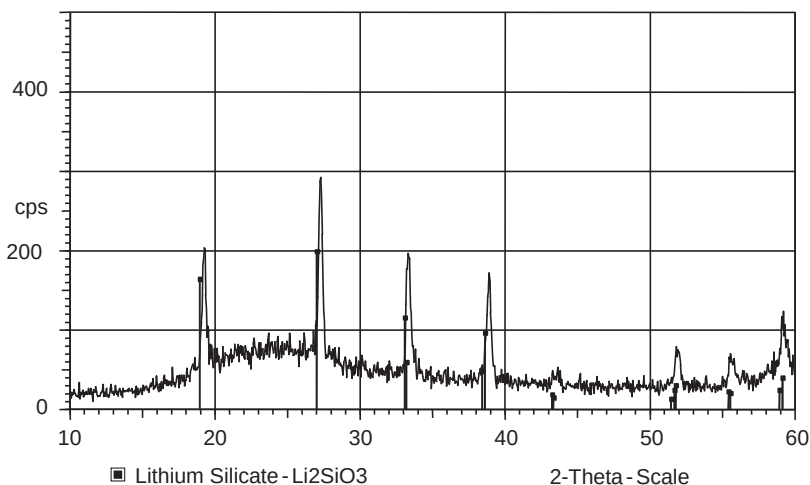


Fig. 9.5. X-ray diffractogram of an UV-exposed and thermally treated photostructurable FS21 glass (thermal treatment: 1 h, 590 $^{\circ}\text{C}$) [128]

crystallisation of the same crystal phase. However, in this case the exothermic effect occurs at a lower temperature and with a much higher but smaller peak.

X-ray diffraction (Fig. 9.5) was used to confirm that the crystal phase in both cases is lithium metasilicate ($\text{Li}_2\text{O} \cdot \text{SiO}_2$). Normally this crystal phase is white, however, because of the presence of agglomerates of silver atoms acting as nuclei, these crystals have brown colour. The intensity of the colour as well as colour shifts from yellow to brown and green depend not only on the number of nuclei but also the size and shape of the LMS crystals.

Crystallisation at a temperature of 600 $^{\circ}\text{C}$ (10 K higher than 590 $^{\circ}\text{C}$!) would also lead only to the formation of the lithium metasilicate crystal phase,

however, this also occurs in the part of the glass that was not exposed to the UV irradiation. During the thermal treatment of the FS21 glass, an amorphous phase also remains (Fig. 9.5, basis line of the curve), which can be explained by the matrix glass phase and the difference in the chemical composition of the droplets in the photostructurable glass and the stoichiometric composition of lithium metasilicate, see also Sect. 1.2.4. The ratio between the crystal phase and the remaining amorphous glass phase is very important for the etching process that follows.

Calculations and Measurements of the Amount of Crystal Phase in FS21

The maximum amount of lithium metasilicate that can possibly form in the original glass composition of FS21 ([mass%] 74.29 SiO₂, 7.2 Al₂O₃, 11.61 Li₂O, 2.74 Na₂O, 4.16 K₂O, see Table 1.7), neglecting the presence of dopants, was calculated [190]. A maximum transition of Li₂O into lithium metasilicate is required. If all Li₂O is incorporated in to the crystal phase, a maximum 35 mass% LMS could form. The remaining amorphous glass phase then has a composition of [mass%] 78.3 SiO₂, 11.1 Al₂O₃, 4.2 Na₂O and 6.4 K₂O.

Quantitative X-ray diffractometry allows the determination of the real amount of LMS crystals that formed within the glass [128]. It requires a calibration of the XRD-curve. This was performed using mixtures of synthetic lithium metasilicate and the exactly composed glass phase as described above [128]. Ehrhardt estimated that only 15 mass% lithium metasilicate crystals form, which is significantly lower than the theoretically possible crystalline phase. This discrepancy is due to the diffusion limitation of the lithium ions in the glass matrix.

The LMS crystals (Fig. 9.10) are anisotropic having a columnar/dendritic structure. The crystal phase is rhombic-pseudo-hexagonal. Lithium metasilicate melts congruently at a temperature of 1201°C [226]. The coefficient of thermal expansion (CTE) depends on the crystal axis. In the direction of the columnar axis the CTE is $\alpha_{20-400^\circ\text{C}} = 9.31 \times 10^{-6} \text{ K}^{-1}$, however perpendicular to this direction the CTE is $\alpha_{20-400^\circ\text{C}} = 14.82 \times 10^{-6} \text{ K}^{-1}$. A sintered body with randomly oriented single crystals has a CTE of $\alpha_{20-400^\circ\text{C}} = 10.34 \times 10^{-6} \text{ K}^{-1}$ [128].

The difference between CTE of the crystalline phase in the *c*- and *a*-resp. *b*-axis and of the glass ($\alpha_{20-400^\circ\text{C}} = 10.6 \times 10^{-6} \text{ K}^{-1}$) results in the formation of mechanical stresses during the heat treatment but especially during the cooling. The arising mechanical stresses are shown in the stress optical photograph in Fig. 9.6. The dark areas are the partially crystallised regions of the glass and the grey areas are the glassy phase. The stress is shown by the light areas at the corners of the partially crystallised geometrical structures.

The structural order is higher in partially crystallised areas of the material as compared to the amorphous regions. This means that the volume of the partially crystallised part is smaller, i.e. of a higher density, than the volume

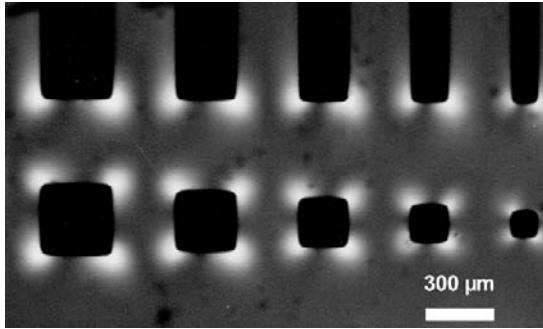


Fig. 9.6. Stress optical photograph of partially crystallised structures in a FS21 glass matrix

of the same but still amorphous part. The photostructurable glass FS21 has a density of 2.376 g cm^{-3} [190] whereas the density of the lithium metasilicate crystal phase is 2.519 g cm^{-3} [128]. The actual density difference between the partially crystallised area and the glassy area depends on the content of the crystal phase and the real density of the remaining glass phase. Whereas in the horizontal direction of the partially crystallized glass sheet only stress occurs, see once more Fig. 9.6, in the vertical direction of crystallised areas stress are detected in the surface (Fig. 9.7).

Technological Features

The thermal treatment of the UV-exposed glass wafers takes place in conventional or circulating air furnaces. During this process the glass sheets must be supported mechanically, because the highest temperature is about 100 K above the transformation temperature of the glass and it is able to flow. Commonly the glass sheets are placed on a ground plate and covered by a second plate, which provides a homogeneous heating of the glass sheets. During the thermal treatment, the surface tension, the diminishing viscosity and the difference in CTE between crystal and glass phase cause the substrate to deform. A small space ($<100 \mu\text{m}$) between the wafer and the covering plate reduces the compression and an additional deformation of the glass sheet. During tempering the substrates should be horizontally oriented to avoid any deformation under the action of gravity. Normally no mechanical treatment of the thermally treated wafer has to follow, but for applications which demand an excellent surface finish additional mechanical processing might be necessary.

The thermal treatment is also possible between two plates and with application of an additional pressure. This kind of thermal treatment reduces the deformation of the wafers by surface tension, but an additional mechanical treatment after the thermal process is absolutely necessary.

An air atmosphere during the thermal treatment was found to be best, because reducing conditions or inert gas or vacuum will result in the reduction

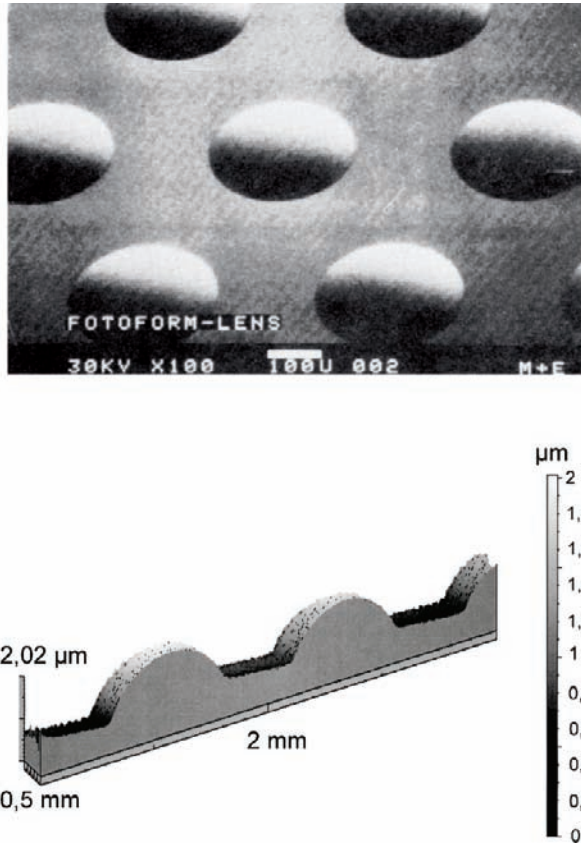


Fig. 9.7. A step profile between partially crystallised and glassy areas of thermally treated samples of the photostructurable glass Fotoform®; the matrix is crystallised. The hills are rounded because of the surface tension causing the formation of glass lenses [477]

of the silver ions at the substrate surface. The undesired formation of silver agglomerates results in a darkening of the glass and consequently to the partial crystallisation of the glass sheet near the surface.

The material used to make the ground support plate and the cover plate have to be chemically inert to avoid chemical reaction between glass sheet and supporting plates. Furthermore, thermal reactions could cause the glass to stick or even fuse with the support. The plates have to be perfectly flat with a low surface roughness. Nevertheless, the material to make the plates should be low cost. The following materials have been explored as supporting plates: stainless steel with a surface coating, silica glass, Macor which is a machinable glass ceramic, Ceran which is a low expansion glass ceramic, alumina, silicon, boron nitride, silicon nitride, combinations of silicon carbide and boron nitride and graphite. It was found that the glass sample stuck to

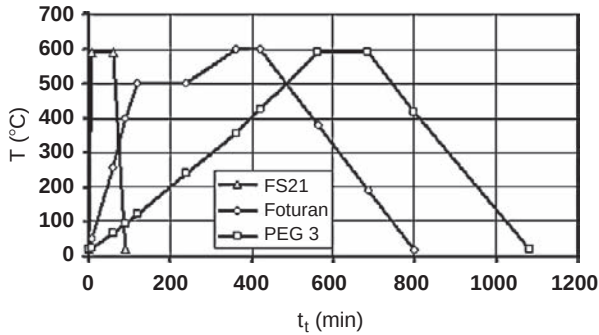


Fig. 9.8. Comparison of the temperature-time regimes for the thermal treatment of various photostructurable glasses [366]

silica, Ceran and ground silicon plates, whereas all the other materials did not cause any sticking. Graphite is a reducing material causing problems with the stability of the glass. A brown colour of the glass in contact with the graphite was observed indicating the reduction of silver ions to atomic silver. Silver agglomerates will then form silver nuclei and induce the crystallisation of the lithium metasilicate. Stainless steel plates do require an anti-sticking but thermally stable surface coating. Various ceramic materials, such as silicon carbide/boron nitride, alumina or silicon nitride can be used. However, the disadvantage of these materials is that it is rather difficult to machine them.

Temperature–Time Regimes

The recommended temperature–time regimes (Fig. 9.8) vary for the various available photostructurable glasses FS21 (see Table 1.7), Foturan and PEG 3 (see Table 1.6). Additional to the residence times at the tempering temperatures defined heating and cooling rates have to be used. A defined heating rate is necessary for a consistent warm up of the glass wafers and to avoid mechanical stresses during the heating process. Defined cooling rates are necessary to avoid the formation of mechanical stresses and cracks in the glass. In some cases for PEG 3 a two residence-time regime similar to that used for the thermal treatment of Foturan is recommended. The temperature-time regime has to be adapted to the actual composition of the photostructurable glass and the special requirements, for instance, to minimise deformation or the process time. For instance two different thermal treatment regimes (1 h at 570°C or 16 h at 510°C) for the glass FS21 have been identified which both result in the same etching rates, however, the observed glass wafer deformation after the thermal treatment at 510°C for 16 h was lower.

Additional Crystallisation Processes

Various applications of structured glass components frequently require certain properties. The properties of the etched glass structure can be modified by

additional crystallisation steps. Different additional thermal treatments can generate quite different crystal phases in the present glassy components. Three variants are described as follows:

A microstructured photostructurable glass can again be exposed to a second, unmasked UV treatment. The partial crystallisation of lithium metasilicate takes place during the second thermal treatment similarly to the first one ([247], [481]).

Another possibility consists of a heat treatment at higher temperature after a second UV exposure. This process generates the crystallisation of the lithium disilicate phase by a reaction of lithium metasilicate which formed during heating with silica from the residual glass which results in a harder and stronger material. This material is highly crystalline and more ceramic-like than glass-like [476, 481, 500].

A third option to modify the glass properties is to induce the precipitation of spodumene during a thermal treatment of the device at about 750°C [247]. This precipitation of spodumene results in a significantly lower thermal expansion coefficient. For example, a thermal treatment of an alumina enriched photostructurable glass (FS23, mass.-%, 70.95 SiO₂, 13.08 Al₂O₃, 10.01 Li₂O, 2.36 Na₂O, 3.59 K₂O; dopants like FS21) for 12 h at 780°C results in a CTE of $6.9 \times 10^{-6} \text{ K}^{-1}$.

Ehrhardt [128] investigated the thermal expansion behaviour of photostructurable glasses and glass ceramics in detail. An additional thermal treatment causes the crystallisation of lithium metasilicate and virgilite in photostructurable glasses with an increased Al₂O₃ content as compared to the glass FS21 (see also Sect. 1.2.4). The CTE of the glass decreases depending on the amount of virgilite crystals in the glass. The CTE could be tuned to be in the range from $\alpha_{20-400^\circ\text{C}} = 9.91 \times 10^{-6} \text{ K}^{-1}$ to $\alpha_{20-400^\circ\text{C}} = 4.5 \times 10^{-6} \text{ K}^{-1}$.

Hesse [220] investigated the influence of the crystallisation conditions on the amount and shape of the LMS crystals. As expected different crystallisation conditions are required to generate partial crystallisation of a glass in order to enable etching or to increase its strength. Etching processes require the formation of dendritic LMS crystals that touch each other. However, such crystals act as flaws and stress concentrations (see Fig. 1.34) during loading and lead to a reduction of the strength of the devices. Therefore, such crystals are undesired in a finished microstructured glass device. To increase the strength of devices, the thermal post-treatment has to allow for energy dissipation under load which requires spherulitic (round) crystals. Droplets, remaining from the phase separation, also assist in the dissipation of energy. Spherulitic crystals form during tempering of the glass at the nucleation temperature for long periods of time. As shown in Fig. 2.4, nucleation and crystal growth overlap in a small temperature range which enables a single crystallisation step, i.e. by tempering near the optimal nucleation temperature, nucleation and, simultaneously, slow growth of spherulitic LMS crystals occur. The more spherulitic crystals (see Fig. 9.9) are present in a glass the higher its strength. This explains the positive effect of an increasing

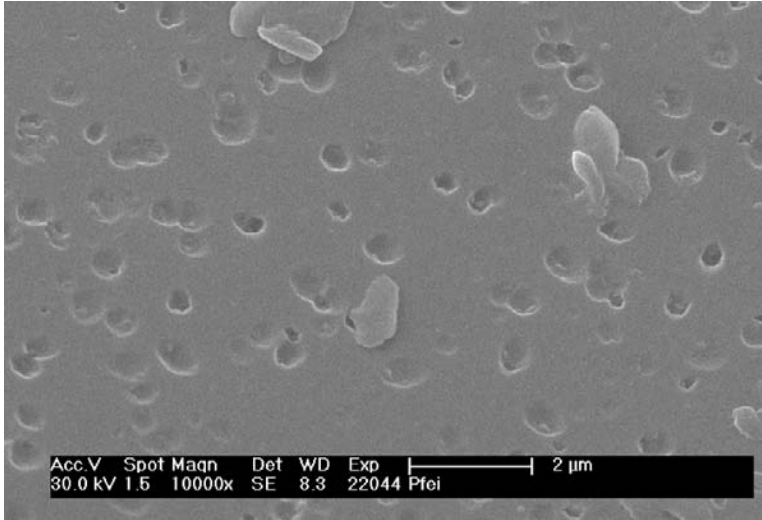


Fig. 9.9. Scanning electron micrograph of a post-crystallised microstructured FS21 glass sample (UV fluency = 360 J cm^{-2} (mask aligner), $T = 500^\circ\text{C}$, $t = 6 \text{ h}$). Crystals are etched away by probes preparation [220]

UV-exposure density which additionally causes an increasing nuclei number. Hesse [220] measured a three-point-bending strength of $\sigma_b = 572 \pm 50 \text{ MPa}$ for samples prepared by microstructuring and post-processing treatment as compared to $\sigma_b = 348 \pm 30 \text{ MPa}$ for microstructured glass bars which did not undergo the post-treatment. The post-treatment conditions used were: UV fluency = 360 J cm^{-2} (mask aligner, complete wavelength band), tempering temperature $T = 500^\circ\text{C}$ and time $t = 6 \text{ h}$.

The three-point-bending strength measured for the not post-treated, microstructured FS21 glass bars is already high compared to window sheet glass. The relatively high strength is due to the action of hydrofluoric acid during etching process causing the removal of flaws. The post-crystallisation causes the bending strength to increase by nearly 65%, see Hesse et al. [220].

The crystallisation processes in photostructurable glasses are affected by the amount of silver and cerium dopants present. The composition of FS21 most commonly used in laboratory tests is summarised in Table 1.7. The melting conditions in lab-scale tests, i.e. the redox conditions, in small crucible sizes are well established. However, any scale-up affects the melting conditions. A greater amount of dopants favours the growth of many more but smaller LMS crystals that are in contact with each other. This result can be used to optimise the etching behaviour. The raw materials used influence the redox behaviour dramatically. The ratio of carbonates to nitrates has to be controlled precisely [365]. Because phase separation also occurs during forming and cooling the heat content of a produced glass device further affects the crystallisation behaviour.

Conclusions

- Only lithium metasilicate crystallises in the areas of a FS21 glass sample that has previously exposed to UV light during the thermal treatment. The presence of silver nuclei is the precondition. 500°C is a suitable nucleation temperature.
- The recommended regimes of thermal treatment vary dependent on the specific glass composition and the specific demands of the users.
- The temperature used during the thermal treatment exceeds the transformation temperature of the glass, therefore, it is necessary to support the sample during the thermal processing step.
- Because the thermal expansion coefficients of glass and crystal phase are different stresses arise during thermal treatment and can be observed in the samples afterwards.
- The mechanical properties of devices made from photostructured glasses can be improved in a second crystallisation process following the one after the photostructuring process. The crystal phases formed may be lithium metasilicate, lithium disilicate, virgilite or spodumene. The properties of the samples depend on the crystal phase that forms, the shape of the crystals and their amount present in the glass.

9.1.4 Etching

Equipment

The geometrical structuring of the glass in the narrower sense follows the heat treatment and uses an etching process. The etching process of the partially crystallised photostructured glass takes place in a hydrofluoric acid solution. During this process the partially crystallised areas of the glass are dissolved selectively. Two etching methods are commonly used for the selective etching of photostructurable glasses; conventional etching in an etching bath or spray etching. The etching in conventional etching baths is the most commonly used process. The same simple baths as in wet etching processes in the microtechnique are often used. The materials for the bath and the elements for fluid handling have to be stable against hydrofluoric acid attack. The etching process can be assisted by ultrasound or megasound.

Usually the UV-exposed and thermally treated glass sheets are positioned in a carrier which is then placed in the etching solution for a certain amount of time. After the etching various washing steps follow. Finally, the samples are dried in a spin dryer or in an air stream.

Spray etching requires a special spray etcher. A spray etcher consists of fluid chambers, a pressure system, an array of nozzles and a sample holder. The complete system is encased to avoid the vaporisation of the etching solution.

In spray etching the samples are positioned on the sample holder while the etching medium is sprayed by the pressure system through the nozzles on the

samples. The etching process is assisted by a relative movement between sample holder and spraying system. After etching the samples are washed and dried again. The spray-etching technology enables improved etching rates compared to the conventional bath etching because fresh reactive etching fluid is sprayed into the structures allowing for a good transport of the used fluid out of the structures causing the effective removal of materials from the geometrical structures.

Processes During Etching

The solubility of LMS crystals in HF is significantly higher than that of the glass, which can be shown by a simple etching test. To prepare the sample shown in Fig. 9.10 a rather gentle etching procedure was used, but the crystals were dissolved. The sample was exposed for 5 min to 0.5% HF solution. Table 9.2 shows a comparison of the etching rates obtained from an etching test of 10 min in 10% HF of various materials of interest. The samples used were FS21 glass with and without partially crystallised areas and several other especially synthesized crystal phases [128]. The etching rate of pure lithium metasilicate is the highest. Consequently it was desired that after the UV exposure and thermal treatment the amount of lithium metasilicate crystals should be as high as possible whereas the formation of other crystal phases, such as lithium disilicate or virgillite, during the first tempering is not desired (but commonly also not observed). The formation of lithium metasilicate in the areas of the glass that have not been exposed to UV light should be avoided because of the required high selectivity in the etching rates causing the removal of materials from the structures. A ratio of the etching rates of lithium metasilicate to lithium disilicate of 3.56 was found by Ehrhardt [128]

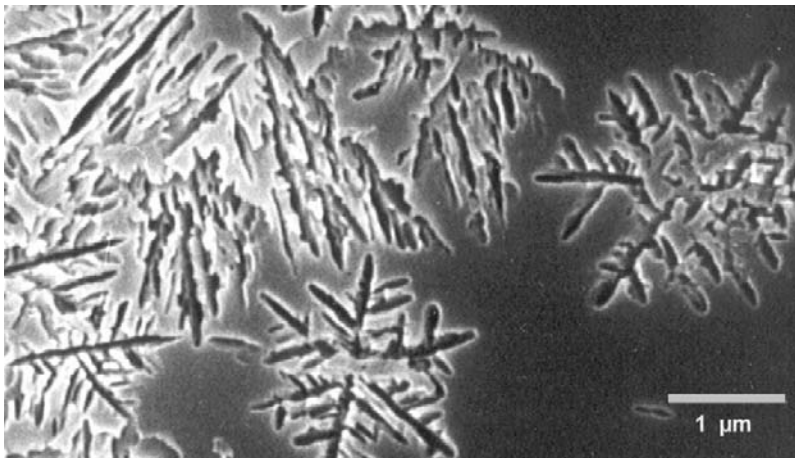


Fig. 9.10. Scanning electron micrograph of a HF-etched FS21 glass surface. During the etching process the LMS crystals were dissolved

Table 9.2. Comparison of the etching rate of various substrates [128, 190]

	Etching rate ($\text{mg cm}^{-2} \text{ min}^{-1}$)	Etching ratio relative to the FS21 glass areas
FS21 glass	0.3	1
Partially crystallised areas in FS21	5.4	18
Lithium metasilicate	15.3	51
Lithium disilicate	4.3	14.3
Virgilite	4.4	14.7

whereas Hinz [224] published a ratio of 3.1 and Vogel [537] of 3.6 for the etching of ground material.

During the etching step that shall form the geometrical structures, the LMS crystals dissolve which results at the beginning in a spongy remaining glass layer. This layer of the residual glass phase at the etched device surface is only temporarily stable. With progressing etching time the residual glass material also will dissolve or simply break off. The removal of such residual glass particles out of the geometrical structure is of importance to achieve high etching speeds. If, however, residual glass particles accumulate in the geometrical structure the etching process will slow down considerably.

The material that is removed during the etching process results in the formation of a muddy residue on the bottom of the etching pot. This mud contains silver, silver fluoride, silicon fluoride, lithium fluoride, lithium aluminium fluoride, lithium sodium aluminium fluoride amongst others as shown by XRD analysis. These crystalline materials are from the residual silver nuclei, i.e. those that induced the crystallisation of the glass, but also insoluble reaction products of the HF attack on the glass and the lithium metasilicate. If only pure lithium metasilicate would have been dissolved only XRD peaks for lithium fluoride would have been found.

Longer etching times are required especially for deep etching of geometrical structures. They lead to an increased roughness of the interaction layer between the etching solution and the partially crystallised areas causing the spongy structure (Fig. 9.11). The spongy, residual glassy phase hinders the further etching of the lithium metasilicate crystals. The thickness of the interaction layer is normally in the range of $20 \mu\text{m}$. The overlapping removal of pure lithium metasilicate crystals and the glass phase affects the etching speed. The average etching rate of the partially crystallised areas is only $5.4 \text{ mg cm}^{-2} \text{ min}^{-1}$. The etching rate strongly depends on the amount of crystal phase, the size of the crystals and the contact points of the crystals.

The interaction layer can be removed also via a treatment in hot, very concentrated alkaline solutions (for example in NaOH).

Influence of the Glass Composition on Etching

The influence of the composition of a photostructurable glass in the partially crystallised state on the etching behaviour was investigated by Hinz

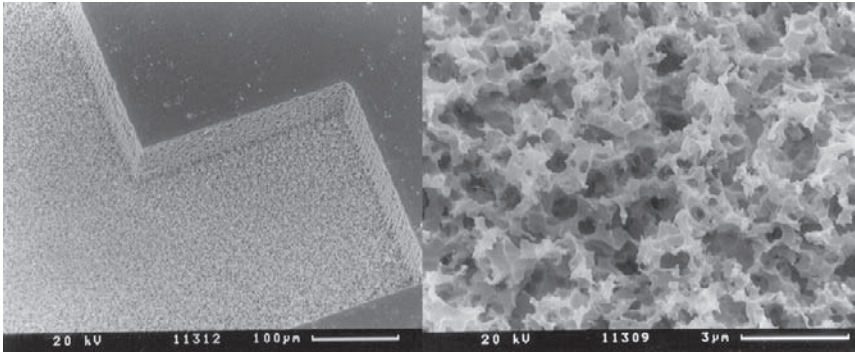


Fig. 9.11. Scanning electron micrograph of the residual glass layer after an etch stop of an etched partially crystallised FS21 structure (*left*: etched geometrical structure; *right*: etched bottom of this structure)

[224]. Two, three and four component glasses with the following compositions [mass%] 75–91 SiO_2 , 9–17 Li_2O , 0–8 K_2O and 0–16 Al_2O_3 were tested.

It was found that the etching rate strongly depends on the K_2O content. Glasses that do not contain any K_2O have a very low etching rate, which is caused by the high content of lithium disilicate in these glasses after partially crystallisation. A dependence of the etching rate on the Li_2O content was not found in this case. The etching rate of glasses containing 4% K_2O was two to four times higher, which is due to the crystalline structure which now varies with the Li_2O content. The amount of lithium disilicate in the partially crystallised glass decreases with an increasing content of lithium metasilicate as the result of more Li_2O . However, lithium metasilicate is the desired phase in the system because it is most susceptible to etching. Increasing the amount of K_2O in the glass to 8% causes a further increase of the lithium metasilicate content in the partially crystallised glass, which also leads to an increased etching rate. The content of lithium disilicate decreases in the partially crystallised glass with increasing K_2O content. The optimal $\text{K}_2\text{O} : \text{Li}_2\text{O} = 1:2$. A Li_2O content of 14 mass% in the glass was found to be optimal for yield a high selectivity of the etching process. Decreasing the Li_2O content causes the etching rate of the partially crystallised areas to decrease progressively.

Increasing the Al_2O_3 content up to 6% also leads to an increased amount of lithium metasilicate, which again results in an increased etching rate. However, increasing the content of Al_2O_3 in the glass further requires increased crystallisation temperatures, which also causes partial crystallisation in those areas of the glass that have not been exposed to UV light.

Process Parameters

The results of the etching process are very dependent on the process conditions used and the specific geometrical structures that shall be produced.

The influence of the hydrofluoric acid concentration on the etching rate was analysed [446]. 5% and 10% HF solutions were used for the tests. The ratio of the etching rates between partially crystallised areas and glass areas was found to be 6% higher if a 5% HF solution was used. It was found that the etching ratio improved when the process was ultrasound assisted. The effect of the ultrasound power (from 45 to 450 W) on the etching selectivity was investigated. It increased with increasing ultrasound power [446].

Detailed investigations of the etching process are reported in the literature [366,367]. The hydrofluoric acid concentration of the etching solution was varied between 2.5 and 20%. The results can be summarised as follows:

- The etching of both, the glassy and crystalline phase increases with increasing HF concentration. However, to achieve a high selectivity in the etching rates between glassy and crystalline phase a very high etching rate is desired for the crystallised areas and a very low one for the glassy phase.
- The etching rate of the partially crystallised areas was too low if only a 2.5% HF solution was used.
- If 15 or 20% HF solutions were used the etching rate of the glassy areas were also very high, resulting in a bad etching ratio.
- The best etching ratio between partially crystallised and glassy areas was found when HF solutions with concentrations between 5 and 10% were used. The etching ratio was not remarkably different when HF solutions in this concentration range were used.
- The etching time required to remove a partially crystallised glass structure with a given thickness decreases with increasing HF concentration. Therefore, commonly a 10% HF solution is used because of the notably shorter etching times.

The influence of the temperature of the etching solution on the etching rate of the crystallised areas was examined in the range from 20 to 50°C. An increase in temperature results in a reduction of etching time. However, the etching rate of the glass phase also increases with increasing temperature. Consequently the width of the remaining glass walls also depends on the temperature of the etching solution (Fig. 9.12). The widest walls were found at a temperature of 30°C, which means that at this temperature the etching ratio is at a maximum. On the one hand, lower temperatures (i.e. 20°C) of the etching solution require longer etching times, which also provide more time for the chemical attack on the glass phase. Higher temperatures (40 and 50°C) on the other hand generally lead to an increased solubility of the glass phase.

To guarantee an effective and constant etching process macro- and micro-flow of the etching agent is necessary. Macrostreaming on the one hand compensates for any temperature or concentration gradients. It is also required for the removal of particles and reaction products of the etching process. Microstreaming on the other hand supports the removal of materials from the geometrical structures. It assists in the transport of substances from the active

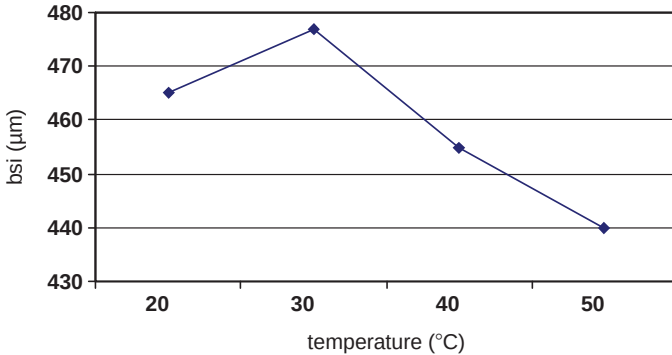


Fig. 9.12. Width bs_i of remaining glass walls in depending on the etching temperature (mask structure $500\text{ }\mu\text{m}$) after UV exposure, thermal treatment and etching (bs_i see Fig. 4.5)

surface at the bottom of the geometrical structure to the surrounding etching fluid. It helps for instance to remove particles consisting of residual glass or insoluble reaction products, also gas bubbles from the geometrical structures, but also to exchange used up etching liquid with fresh reactive etching fluid in the geometrical structures.

Commonly two types of process assistances are used for macro- and microflow of the etching agent; ultrasound or megasound based. The equipments used to assist the process differ in the frequency and the absolute power used. Ultrasound equipment usually operates at a frequency of 20 kHz and a power of up to 450 W whereas megasound operates at 1 MHz and 250 W. Megasound is more intensive, and the structures in the glass are handled more carefully. However, the costs of a megasonic module including the generator are significantly higher than those of an ultrasonic module. An increase of the intensity of mega- and ultrasound was found to lead to a reduction of etching time. The effect was more pronounced for megasound.

The real width of a trench pattern (bg_i) after thermal treatment and etching compared with the opening in the mask for UV exposure is a very important value for the characterisation of the etching processes [190]. To generate small trenches the ratio of etching between the crystalline phase and the glass should be as high as possible. The effect of power of a megasonic or ultrasonic system on the trench width after etching is shown in Fig. 9.13. It was found that the higher the intensity of process assistance the smaller the trench width. This can be explained by the fact that the transport of substances within the geometrical structures is more effective leading to shorter etching times.

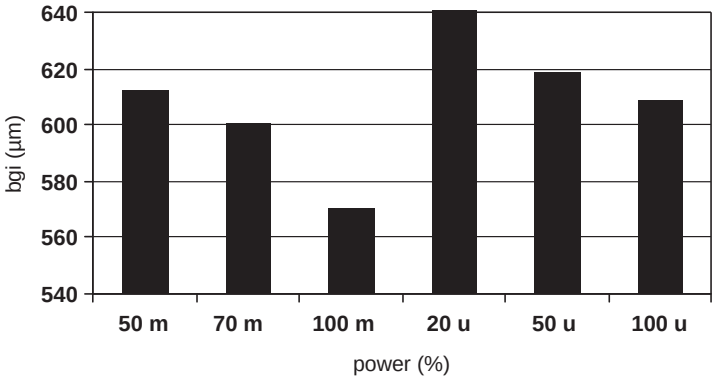


Fig. 9.13. Trench width b_{gi} after UV exposure, thermal treatment and etching as a function of the intensity of megasonic and ultrasonic power. The numbers stand for the used portion of the maximum possible power of the equipment (m = mega, u = ultra, b_{gi} see Fig. 4.5)

Conclusions

- During the etching process the partially crystallised areas should be dissolved whereas the glass areas should remain intact, i.e. a high selectivity of the etching is required.
- A high content of lithium metasilicate in the partially crystallised areas is desired, because of the high rate of etching of this phase. The LMS crystals should be in contact with each other.
- The best etching solution is 10% hydrofluoric acid at a temperature of 30°C.
- To achieve the desired etching rates and selectivity a process assistance is necessary. Commonly used are macroflow for guaranteeing homogeneity of HF concentration and temperature, and a microflow for an effective exchange of substances in the geometric structures using ultra- or megasound.

9.2 Technical Variations of the Photostructuring Process

9.2.1 Fabrication of Holes and Trenches

Process

A schematic flowchart of the standard photostructuring process is shown in Fig. 9.1. An example of a microstructured glass is shown in Fig. 9.2. Using the standard photostructuring process it is possible to create high aspect ratio structures. The final depth of a structure to be created is limited by

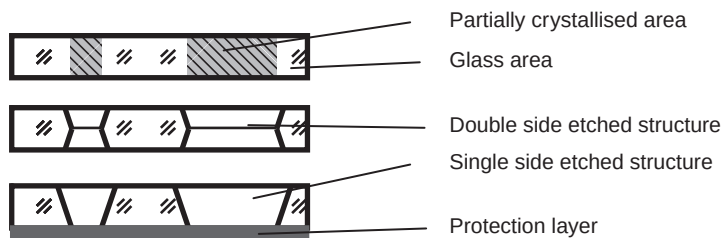


Fig. 9.14. Variants of etching of partially crystallised structures

the substrate thickness and varies between $20\text{ }\mu\text{m}$ and 2 mm . The geometry of structures is in x - and y -direction determined by the openings in the masks and in z -direction by some modifications of the standard method. Consequently a three dimensional (3D) nearly unlimited structuring is possible. The structures to be created within the glass do not depend on the orientation of crystal axis, as is the case in silicon. Structures with a very small angle of inclination can be created. The angle can definitely vary in the range of some degrees. A photostructured glass can be etched from just one side (single-side etching) or from both sides (double-side etching) (Fig. 9.14).

Double-side etching does not require any protection of the samples, which results in a two sides tapered geometry of structure. The etching process starts simultaneously at the top and the bottom of the glass sheet. If the energy density of the process assisting sound equipment is equal throughout the reaction vessel, the rate of etching on either side of the sample will also be the same. Single-side etching, however, requires the protection of one surface, which results in a single-side tapered geometry of structures. The protection layer is crucial because of the limited stability of many materials in the hydrofluoric acid etching fluid. Protection materials that are commonly used are various resists, silicone, metals or even optical sealing cement and special tapes. The materials used to make the protection layers should be chemically stable in the etching fluid but also adhere well to the glass surface. After the etching the protection layer has to be removed.

Geometry of the Etched Structures

As already described above it is possible to generate free-standing structures using a structured chromium layer on fused silica glass mask blank. This continuous blank as substrate for the chromium structures guarantees the holding together. However, this is not possible if a low cost mask, such as a structured metal foil or a machined brass sheet, is used.

The absolute geometry of final structures in glass is strongly limited by minimum width of trenches/holes or width of walls/bars/beams in the mask. The minimum width of holes that can be produced depends on the thickness of the substrate and the nominal width of holes in the mask (Table 9.3).

Table 9.3. Minimum width of holes that can be produced at the top side. The widening of holes depends on their nominal width and the thickness of the substrate (double-side etching) [446] (for explanations of bg_s , bg_i , Δbg see Fig. 4.5)

Substrate thickness/ μm	Nominal width of holes $bg_s/\mu\text{m}$	Minimum real width of holes $bg_i/\mu\text{m}$	Widening of holes $2\Delta bg/\mu\text{m}$
160	100	106	6
	10	17	7
	5	12	7
450	100	116	16
	50	68	18
	10	30	20
1000	100	154	54
	50	106	56

The minimum real width of a structure at the bottom side is around $5\mu\text{m}$ smaller than the minimum diameter at the top side on a glass sheet of a thickness of $500\mu\text{m}$. The substrate thickness restricts the possible diameter of holes because of optical scattering during the UV exposure. Therefore, very small holes with a nominal diameter of $5\mu\text{m}$ can only be created in thin substrates.

It is impossible to generate holes equal to the nominal diameter of the mask structure because not only is the UV-exposed and partially crystallised material etched off but also (in a smaller amount) the surrounding not exposed glass. Therefore the minimum width of geometrical structures in the glass sheet that can be produced depends also on the time of etching, which also affects the glassy phase and therefore the widening of any structures. A thinner substrate requires shorter etching times, which results in smaller widening of the holes so that the real holes width is relatively smaller as of compared holes produced in thicker substrates. The widening of holes also depends on the absolute hole diameter. The observed widening of structures with smaller nominal diameters is larger than of structures with bigger diameters if the same substrate and identical etching parameters are used. This later observation can be explained by the better fluid exchange during the etching in structures with bigger diameter.

The real width of bars/walls and the etching depth as function of the etching time and the relative energy density as obtained during the single side etching is shown in Figs. 9.15 and 9.16, respectively. The nominal width of the bars was $100\mu\text{m}$. The real width of bars decreases with the increase of the etching time for all energy densities used. It results from the longer time of chemical attack on the glass bars. The selectivity of etching is rather low at low UV-energy densities. The depth of structures remains small also after long etching times. The depth of etching increases if the UV-energy density exceeds a minimum. However, if the used relative energy densities exceed 3.2

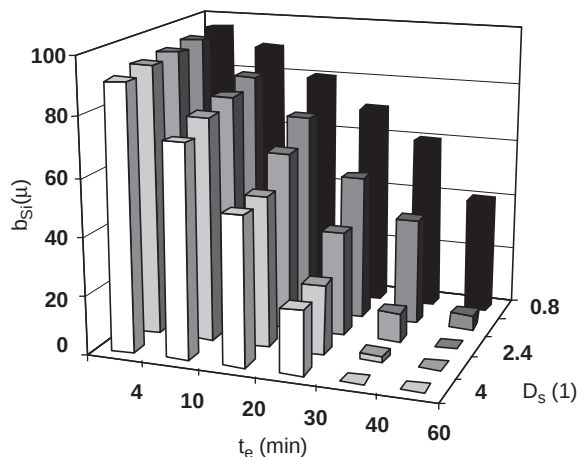


Fig. 9.15. Real width of bars b_{si} as function of etching time t_e and the relative energy density D_s . The nominal width of the bars was $b_{s0} = 100\mu\text{m}$

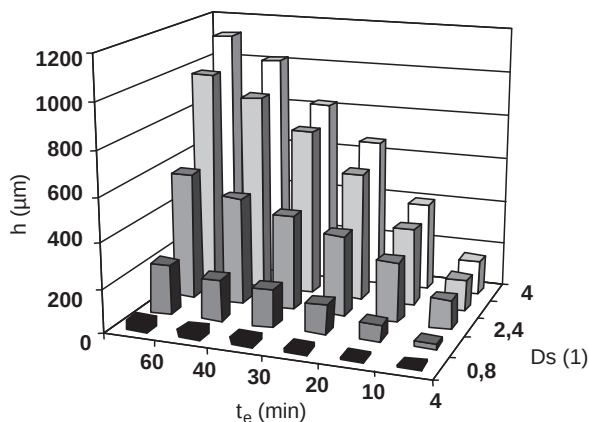


Fig. 9.16. Depth h of structures as function of etching time t_e and the relative energy density D_s (pay attention that the D_s axis is turned compared with Fig. 9.15)

no further effect on the etching depths is observed. The width of bars is equal to $0\mu\text{m}$ if the structure was completely removed during the etching process. This happens if the etching time exceeds 60 min and at a relative energy density exceeding 2.4.

An extreme structuring test was performed on almost 5-mm thick FS21-sheets using one-sided etching. It was not possible to create holes at the top side with a real diameter of less than 2 mm. The problems encountered were the not uniform UV exposure through the full depth, the materials transport in very deep holes as well as the stability of the protection layer over the duration of etching. The required processing times for the UV exposure

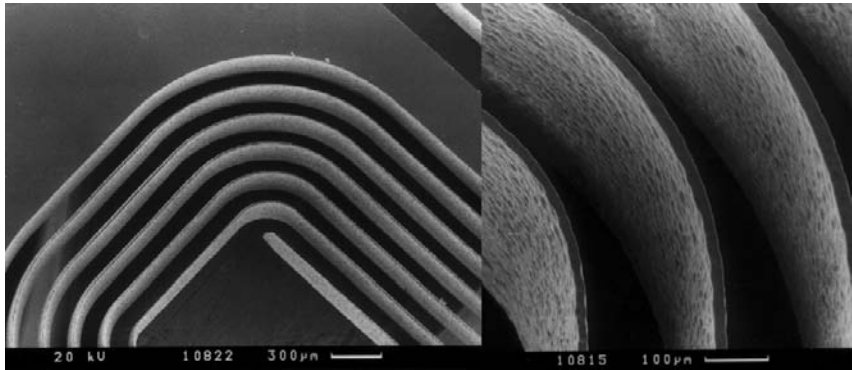


Fig. 9.17. Scanning electron micrographs at lower (*left*) and higher (*right*) magnification of a structured glass coil with a minimum width of bars of $30\text{ }\mu\text{m}$ [190]

and etching are very long which makes it impossible to structure such thick substrates by photostructuring.

A glass coil made by photostructuring with a minimum width of bars of $30\text{ }\mu\text{m}$ is shown in Fig. 9.17 (left). The structure created has an excellent surface quality (Fig. 9.17 right). Furthermore, the shell structure of the side walls and the homogeneity of the structuring process can be seen in Fig. 9.17 (right).

Roughness of the Generated Structure Surfaces

The surface roughness of the side walls of the etched structures is mainly determined by the conditions of the etching process. The roughness of the side walls of Foturan varies between 1 and $3\text{ }\mu\text{m}$ [453]. Salim [435] used this effect for the production of contact surfaces of a microgripper with definite roughness and so for a control of the static friction of the gripper made in Foturan.

The highest surface roughness was found in the middle of a double-sided etched structure of FG21 glass etched using normal conditions (10% HF assisted by ultrasound) [446]. The surface roughness of the etched hole walls decreased towards both surfaces of the glass substrate, which is explained by the longer exposure time to the chemical attack on the top and bottom ends of the hole wall after all the lithium metasilicate crystals were dissolved. The extended exposure time to the HF solution leads to surface polishing. However, as soon as the crystalline phase is removed from the middle of the structure the process was stopped so no further acid polishing took place here.

Harnisch [190] has found for microstructured FS21 glass an average roughness of the side walls $R_a = 0.38\text{ }\mu\text{m}$. This relatively low surface roughness value was due to the long etching time (1 h) which resulted in considerable surface smoothing.

However, beside the etching process parameters the surface roughness of the side walls to be created depends also on the conditions used for the UV exposure and the thermal treatment. The size of the LMS crystals is decisive for the surface roughness. LMS-crystal size depends strongly on the UV-light energy density used during the exposure, because the UV-energy density is responsible for the number of nuclei. The surface roughness is also influenced by the degree of connectivity of the crystals formed during tempering.

A strong dependence of the surface roughness of the side walls on the energy density during UV exposure was found [337]. High-pressure mercury-vapour lamps were used for the UV exposure. Figures 9.18 and 9.19 illustrate the impact of the energy density used during the UV exposure on the roughness of the produced surfaces. Only a few nuclei form on the one hand, if the

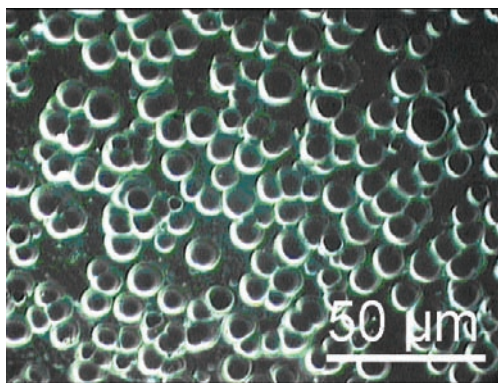


Fig. 9.18. Scanning electron micrograph of an etched FS21 surface, exposed to UV light with an energy density of 5.8 J cm^{-2} , tempered for 60 min at 570°C and finally etched in 10% HF [337]

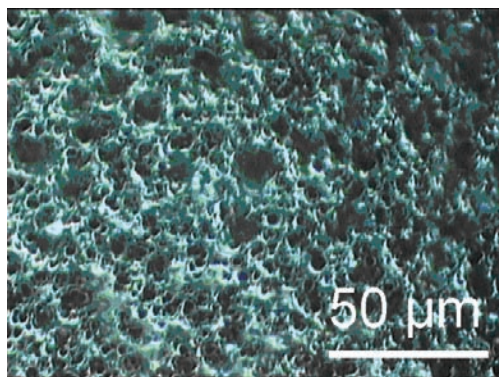


Fig. 9.19. Scanning electron micrograph of an etched FS21 surface, exposed to UV light with an energy density of 15 J cm^{-2} , tempered for 60 min at 570°C and finally etched in 10% HF [337]

energy density of the UV light used during exposure with the broad band lamp is only 5.8 J cm^{-2} , which have room to grow resulting in large crystals. If the crystals are finally dissolved during etching a remarkable surface roughness remains. On the other hand if a high energy density is used during UV exposure, many nuclei are generated which will hinder their growth. The crystals will be soon in contact and remain small. The etching will progress rapidly and a relatively low roughness is formed. This effect and the absorption of the UV light in the glass sheet from the surface to the inner part (9.3) explain additionally, why the roughness of the side walls in distance to the UV-exposed surface is higher.

9.2.2 The Etch-Stop Process

It is often required to produce not holes or trenches but channels or sack holes respectively depressions, i.e. to etch a desired geometric structure only to a definite depth. This is particularly the case for microfluidic devices containing channels and cavities or for structures used in the bio or medicine technique.

Geometrical structuring to a defined depth is possible by using the etch-stop process. Figure 9.20 shows a schematic illustration of this process. It is rather similar to the standard photostructuring process. The first two process steps, i.e. UV exposure and thermal treatment, are identical. However, a modified etching process is used. The one-side etching process can in principal be stopped any time after a certain depth of the structure is realised. Examples of structures created using the etch-stop process are shown in Fig. 9.21.

The surface roughness at the bottom of a structure is significantly higher than at the side walls, which is caused by the etching attack on the crystals and the reduced chemical attack on the residual glass phase which results in the formation of a porous layer of the residual glassy phase. An example is shown in Fig. 9.11 (right).

The etch-stop process can be used to produce narrow geometrical features up to a depth of a half of the sample thickness. However, the process is not suitable to produce foils with a thickness of less than $200 \mu\text{m}$. The major advantages of the etch-stop process are the low technical effort, short process-

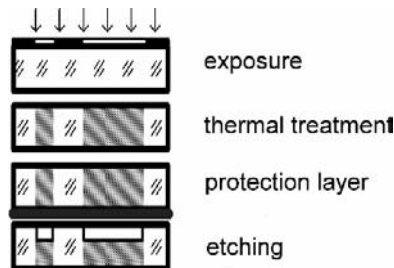


Fig. 9.20. The etch-stop process

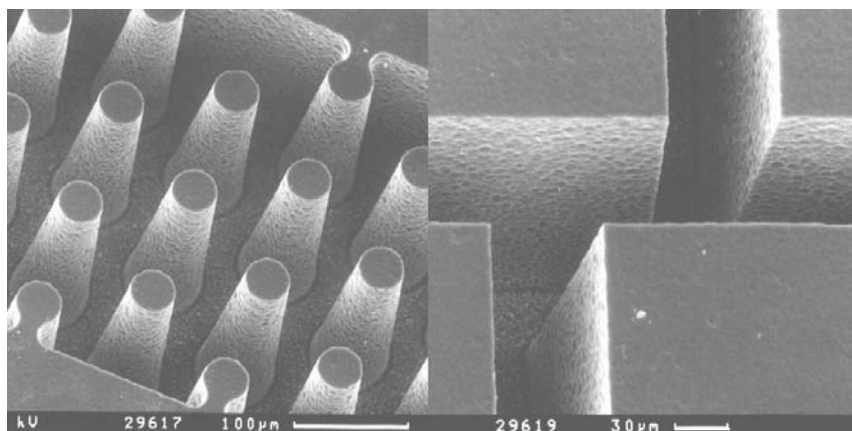


Fig. 9.21. Two examples of structures produced by the etch-top process [28]

ing times, good control over the depth of the structures to be created and the possibility to fabricate structures with very small bars. The disadvantages of the process are that a residual crystalline phase, which has different properties, remains below the etched off geometrical structures. The presence of crystals beneath the geometric structure results in a different thermal expansion coefficient and a brown coloured non transparent layer. The bottom of the structured channels consists of a porous interaction layer which gives rise to a large surface roughness on the bottom of the geometrical structure. Furthermore, the process is not very flexible. For instance, it is not possible to create holes and trenches simultaneously with channels of various depths. However, a possible solution for this problem would be if the glass crystallises only in regions up to the required depth of the structures that shall be fabricated. The following section explains the corresponding ideas.

9.2.3 Structuring up to a Defined Depth

Effects of Different Energy Densities and Structure Dimensions

To create structures with varying, defined depth it is aimed to let crystals only grow up to a depth that is similar to the desired depth of the structure to be eventually created during the etching process. The requirements for very selective etching are a sufficient UV-exposure depth and a sufficient depth of crystallisation only in the areas exposed to UV light. The depth to which the glass was exposed to UV light cannot be measured because no measurable changes occurred during the UV exposure. The measurable effect that occurs during the thermal treatment is the darkening of the exposed areas caused by the formation of nuclei of silver atoms and crystallisation of lithium metasilicate that follows. The depth of exposure and, therefore, the depth to which the glass will crystallise depends on the energy density of the UV light used

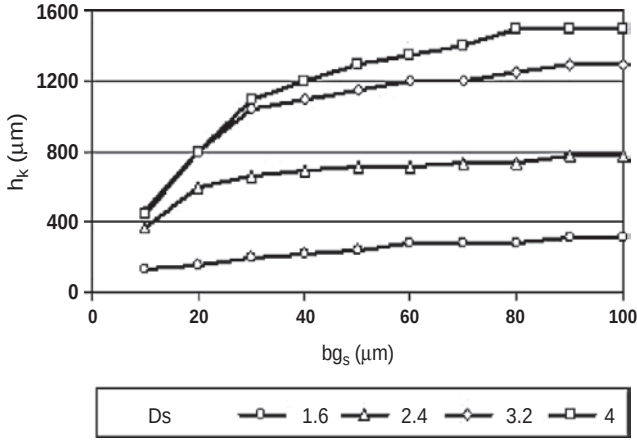


Fig. 9.22. Depth of crystallisation h_k as function of the relative UV-energy density D_S and the nominal width of trenches b_{g_s}

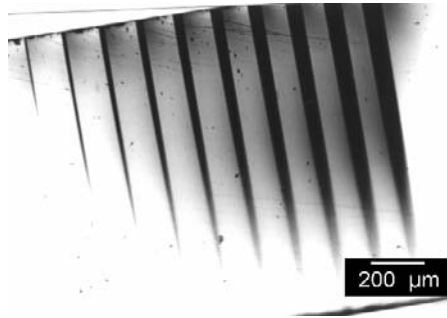


Fig. 9.23. Optical micrograph of a cross section of a partially crystallised FS21 sample with the nominal width b_{g_s} of trenches ranging between 10 and 100 μm (dark areas), relative UV-energy density $D_S = 4$ [190]

and the geometry of the structures to be created (Fig. 9.22). Figure 9.23 shows a cross-section of a sample with structures of nominal widths ranging from 10 to 100 μm which were created by exposure to UV light with a relative energy density $D_S = 4$ followed by crystallisation and etching.

A strong correlation between the energy density used during UV exposure and the depth to which the glass crystallises was found [190]. Low UV-energy densities, i.e. $D_S < 2$, will lead to the formation of short structures after crystallisation and etching. The influence of the diameter of the features to be created on their depth is rather small and becomes only evident if high UV-energy densities are used. The effect is due to the generally small depth of interaction of UV beam with the material. If a low energy density UV-light source is used only a small number of photons penetrate into the glass, which induces the reaction of Ce^{3+} to Ce^{4+} only in the volume near the surface

but not deeper in the bulk. A further interaction with the other Ce^{3+} ions positioned deeper in the glass is not possible.

With increasing energy density of the UV light the thickness of the partially crystallised material increases and, therefore, the depth of the structures; i.e. the higher the number of photons, the larger the probability that photons interact with Ce^{3+} ions deeper in the bulk material. Extending the exposure time has the same effect.

Figure 9.22 shows the depth of the crystallisation which corresponds to the depth of UV exposure. This effect can be explained also by the Lambert–Beer law (9.3), see also (8.6):

$$\frac{I}{I_0} = e^{-\beta_E \cdot d}. \quad (9.3)$$

Thus the rate of etching decreases continuously with increasing depth of the structures to be created. In this case the etch process does not stop abruptly at a given depth, and distinguishes consequently from the etch stop during the anisotropic etching of silicon at the (111)-layer.

The depth of geometrical structures is also influenced by diffraction effects and the quality of the beam used for UV exposure. This is especially important for small structures, Fig. 9.23. The influence of the nominal diameter of the geometrical structures on their depth increases additionally because diffraction effects increase. In the range of energy densities ($D = 0.4\text{--}3\text{ J cm}^{-2}$) investigated it was impossible to fabricate structures with nominal diameters smaller than $10\text{ }\mu\text{m}$ and a depth exceeding $500\text{ }\mu\text{m}$.

Figure 9.24 shows the depth of etching as a function of the relative energy density D_s and the nominal width of trenches bg_s after an etching time of 60 min. The achieved etching depth corresponds to the depth to which the glass partially crystallised (Fig. 9.22). An increasing etching time will lead to the complete removal of the crystallised material. The best way to control

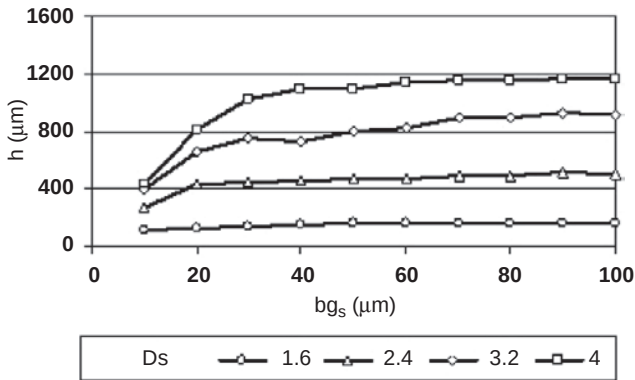


Fig. 9.24. Depth h of etching as function of the relative energy density D_s and the nominal width bg_s of trenches (time of etching 60 min)

the depth of a geometrical structure is the combination of an optimum energy density during the UV exposure to crystallise during tempering the structures only up to the required depth with an etch stop as soon as the desired depth was achieved. However, this method does not allow for the fabrication of geometrical structures with variable nominal widths and a constant depth in the same substrate.

Inclination of Walls and Etching Ratio

The wall inclination of the fabricated geometrical structures depends strongly on the kind of glass and the process conditions used as well as the thickness of the substrate.

The glass material itself affects the inclination of the walls fabricated doubly. At first it affects the etching ratio between glass and crystallised areas. The etching ratio is affected by the chemical resistance of the glass, which depends on the content of alkali oxides. The higher the content of alkali oxides the lower the chemical resistance of the glass (see also Sect. 1.2.2). A lower chemical resistance of the glass will result in a larger wall inclination, because the longer exposure time to the etching solution will lead to an increased removal of the surrounding glassy materials. Vice versa, the lower content of alkali oxides, i.e. the higher the chemical resistance of the glass, the smaller is the angle of wall inclination of the structures fabricated. This connection is especially important for the development of photostructurable glasses with a high CTE [128] (see also Sect. 1.2.4). Second the glass composition also determines which crystalline phase forms, which determines the chemical solubility of the crystallised areas. The formation of lithium metasilicate is desired as it allows for the highest etching rates and ratios compared to the glass phase (see Sect. 9.1.4).

However, the wall inclination also depends on the processing conditions used, i.e. the concentration of the etching acid, the etching temperature and the flow of the etching fluid in the macro- and microrange (determined by the use of ultra- or megasound). All these parameters influence the etching time, which also limits the time for the exposition of the remaining glass areas to the chemical attack and, therefore, results in the angle of wall inclination. The effect of the variation of the process parameters on the etching process was discussed in detail in Sect. 9.1.4.

The depth of structures to be created also influences of the angle of wall inclination. This is because of materials transport problems in small and deep structures, which causes the etching rate to decrease with increasing depth of structures.

Figures 9.25 and 9.26 show the angle of wall inclination β and the etching ratio Q of FS21 glass as function of the etching time and the relative energy density, respectively. Both, the angle of wall inclination and the etching ratio, depend on the etchability of the glassy phase. Neither a small angle of inclination nor a high ratio of etching can be realized if a low relative energy density

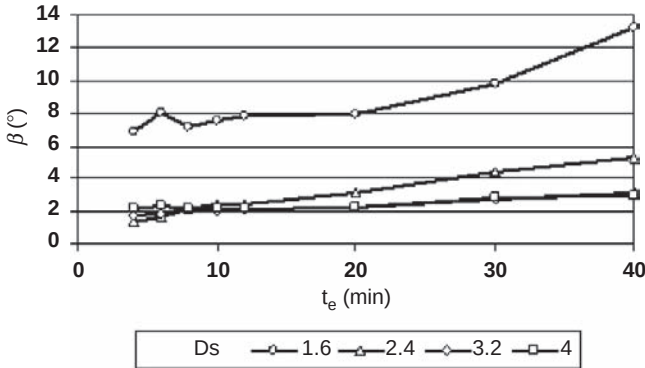


Fig. 9.25. Angle of wall inclination β as function of the etching time t_e and the relative energy density D_S

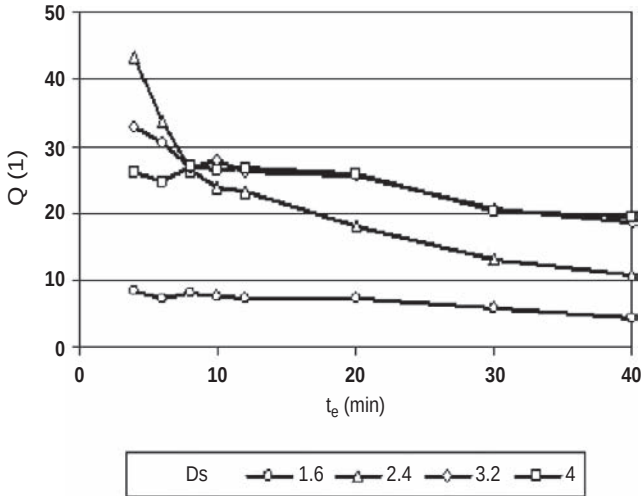


Fig. 9.26. Etching ratio Q as function of the etching time t_e and the relative energy density D_S [190]

of $D_S = 1.6$ is used. The angle of inclination decreases with an increase of density of energy if the relative energy density exceeds 2.4. For short etching times below 10 min no reliable correlation between the angle of inclination and the relative energy density in the range between 2.4 and 4 was found [190]. An etching time of 12 min and more is changing the behaviour. This has two reasons. At first can be explained that an optimum UV-energy density exists which only creates nuclei in the exposed areas inducing later the crystallisation only in those areas but not in the glass material in the immediate vicinity of the exposed structure. This will result in the highest etching ratio. This effect is important for structures of small depths or short etching times. But

a higher UV-energy density causes also the partial formation of nuclei near the surface in areas of the glass in the immediate vicinity of the exposed structure, which later cause partial crystallisation. Consequently an increased etching rate results in the surrounding glass areas to a decrease of etching ratio. Secondly the reduced depths of interaction between the FS21 glass and the UV light at low UV-energy densities results in a decrease of the rate of etching of the partially crystallised glass area with increasing etching depths. This effect is of importance for the fabrication of deeper structures or longer etching times.

9.2.4 Structuring of Diffusion-Modified Glass

Defined, localised diffusion-modification of glasses could be used to structure photosensitive glasses. The following three methods could be possible. (1) If a glass does not contain any silver but otherwise all other dopants of FS21, silver ions can be added by diffusion into a thin surface layer of the glass in such a concentration that the generation of structures is possible using standard photostructuring procedures (i.e. UV exposure, thermal treatment and etching, see Fig. 9.1) [25]. (2) It is also possible to let the silver ions diffuse selectively through a mask into a thin glass surface layer. The glass is structured using the three-step structuring process which now does not require UV exposure through a mask. The main challenge of this technology is the selective masking of the glass for the silver diffusion process. The generation of complex and geometrically precise structures using this process is impossible. (3) Another possibility to structure a silver containing (FS21) glass would be the partial but selective removal of silver ions from the glass or the selective fixing of the silver ions within the glass in order to block photostructuring process in these areas. However, this was found to be technically impossible [25].

Only the first method is really useful for geometrical microstructuring applications [25]. A schematic representation of the process is shown in Fig. 9.27. A glass of a similar composition as FS21 (see Table 1.7) is used for this process. The glass contains the same amount of CeO_2 , Sb_2O_3 and SnO as in the FS21 composition but does not contain any Ag_2O . A diffusion process was used to dope the surface layer to a defined depth with silver ions. A detailed description of the process can be found in the literature [25]. A $\text{LiNO}_3\text{--AgNO}_3$ melt was used for the diffusion experiments following a published protocol [532]. The melt consisted of 99.75 mass% LiNO_3 and of 0.25 mass% AgNO_3 .

A variation of the composition of the salt melt did not prove successful. The optimal temperature for the diffusion process was 405°C. Temperatures below 405°C resulted in the formation of microcracks in the modified surface layer because of big differences of the CTE between the bulk glass and the silver ion exchanged glass layer. If the temperatures exceeded 405°C visible

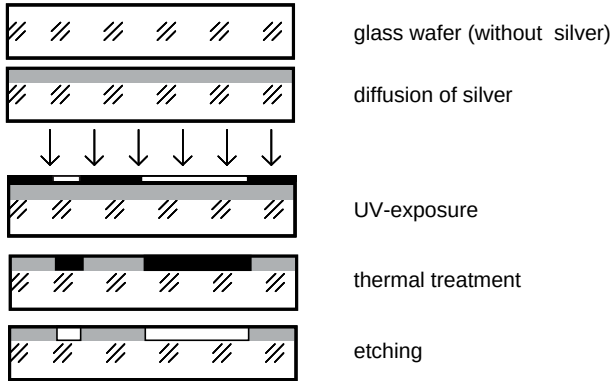


Fig. 9.27. Geometrical structuring of diffusion modified glasses

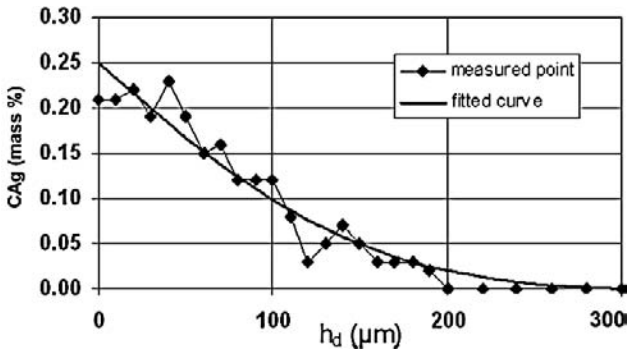


Fig. 9.28. Concentration of silver ions c_{Ag} as function of the diffusion depth h_d (the process time was 20 h and the temperature 405°C) [25]

crystallisation occurred near the surface. The crystal phase formed was lithium metasilicate.

The surface layer modified by ion exchange was indeed photosensitive. Baumgart [25] measured the concentration profiles of various ions and calculated the threshold value of the silver concentration required for photostructuring of the modified surface layer. It was found that Si^{4+} , Al^{3+} and K^+ ions do not take a part in the diffusion process, but Na^+ ions diffuse out of the glass whereas Ag^+ and Li^+ ions diffuse into the glass.

The measured concentration profile and a fitted curve of the silver ions near the surface of the ion exchanged glass are shown in Fig. 9.28. A maximum concentration of about 0.23 mass% silver was found directly at the surface of the sheet. The concentration of silver ions decreases with increasing distance from the surface. The calculated diffusion constants basing on the measured concentration profiles of various ions are given in Table 9.4.

Table 9.4. Diffusion coefficients based on the measured concentration profiles of the participating ions at 405°C after 20 h [25]

Ion	Diffusion coefficient, D ($10^{-10} \text{ cm}^2 \text{ s}^{-1}$)
Li^+	20.1
Na^+	20.7
Ag^+	9.87

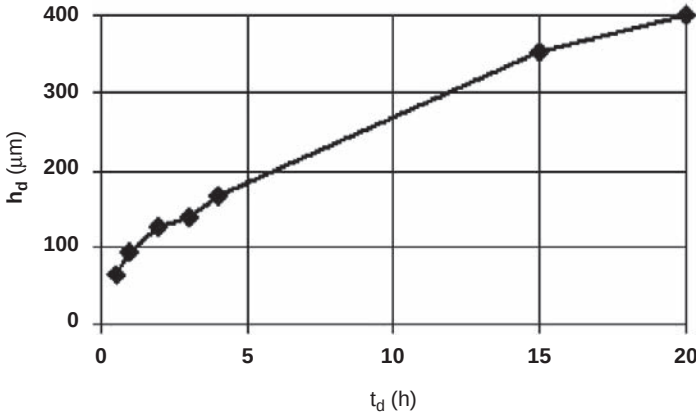


Fig. 9.29. Depth h_d of etching as function of the diffusion time t_d (the process temperature was 405°C) [25]

Additionally the influence of the diffusion time on the concentration of silver ions in the surface layer is evident [25]. Sufficient removal of materials during etching occurs only if the glass contains a sufficiently high amount of crystals which is only possible if enough silver diffused into the glass which requires time. The measured etching depth h_d , therefore, depends on the diffusion time t_d , which is shown in Fig. 9.29. The crystallisation process requires a certain minimum number of nucleation possibilities consisting of nuclei of silver atoms, which should be above the threshold value. Baumgart [25] also calculated this threshold value for silver nuclei based on the measured Ag^+ concentration and the depth of geometrical structures produced by the etching process. According to Baumgart [25] a concentration of 0.00025 ± 0.00005 mass% silver is at least required to initiate the crystallisation of LMS in a technically feasible manner.

A comparison of the value of the threshold silver concentration as determined by Baumgart with the silver concentration c_{Ag} in other photostructurable glasses (FS21 $c_{\text{Ag}} = 0.083$ mass%, Foturan $c_{\text{Ag}} = 0.05$ mass% and PEG3 $c_{\text{Ag}} = 0.009$ mass%) shows huge variations in the used amount of silver. This leads to the conclusion that most silver ions present in photostructurable glasses are not active to induce nucleation and, therefore, do not take part

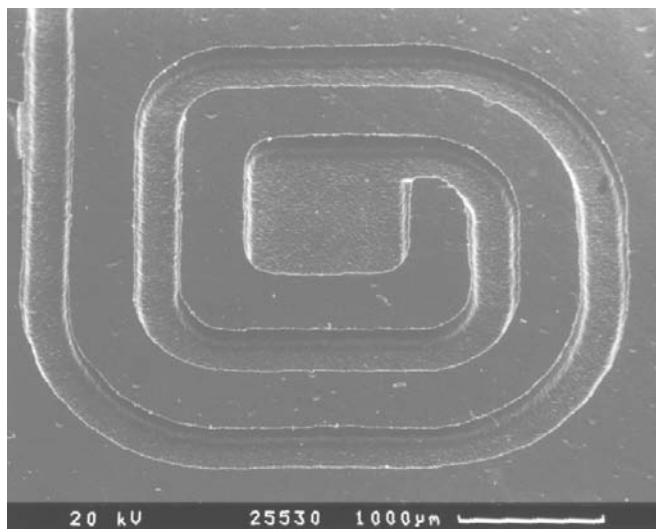


Fig. 9.30. Scanning electron micrograph of photostructured diffusion modified glass [25]

in the structuring process, which was confirmed by other investigations [365]. Only Ag^+ actually present in the phase separated droplets (see Fig. 1.39), act as nuclei for LMS growth. Most of the Ag^+ is accumulated in the surrounding glassy phase. Also these silver ions may form small Ag clusters [365], but the glass composition surrounding these clusters does not allow for the formation of LMS and, therefore, these clusters in the glassy phase do not act as nuclei. Only the smallest amount of silver really participates in the nucleation.

A geometrically ion exchange structured sample is shown in Fig. 9.30.

The main advantage of diffusion modification method to structure glasses is the relatively precise etch stop at the position of the threshold value of the silver concentration. The maximum permitted diffusion time is 20 h which allows for a maximum depth of structures of $400\text{ }\mu\text{m}$. This limit of diffusion time is due to the onset of undesired LMS crystallisation at the glass surface during the crystallisation process. The reason is the presence of too much silver in the glass surface which will be reduced also without special UV exposure and forms nuclei during thermal treatment. If diffusion times in excess of 10 h are required a surface treatment should follow the diffusion process.

The photostructuring of diffusion-modified FS21 glasses is limited with a depth of $400\text{ }\mu\text{m}$ because of the long diffusion time required, the onset of surface crystallisation and additionally an angle of wall inclination that exceeds 10° . Using this method it is impossible to fabricate holes, trenches and structures of a definedly varying depth in the same substrate.

9.2.5 Protection Layer Method

The simplest method is the protection of the back side of a glass substrate for single-sided etching as described in Sect. 9.1.4. It is of particular importance for the production of nozzles for filling in or pushing out fluids in microfluidic systems. The diameter of the underside of the nozzles (outlet) is, caused by the protection layer, see once more Fig. 9.14, smaller than the diameter at the top side (inlet).

The requirement specification for a material used as protection layer is high. Such layers have to have good chemical resistance in hydrofluoric acid, they must adhere well to the substrate surfaces but should also be easily removable after the structuring and should be structureable by lithographic methods. For this technology it is absolutely crucial that the protection layer is stable in hydrofluoric acid. The protection layer has to withstand extremely harsh condition during processing without significant dissolution in the etching solution. The process temperature is about 30°C and the exposure time can exceed 1 h. The process also is ultrasound assisted. During the processing the protection layer must stick to the substrate to avoid underetching which would lead to a noticeable reduction of the precision of geometrical structures.

To allow for the selective glass sheet protection (protection of defined glass areas and acid treatment of the not protected parts), the protection layer itself has to be structured. Photoresists can only be used as structured protection layers if the etching time is going to be short, because of their limited chemical stability and adhesion problems with the glass substrate [110]. Protection layers made from photoresists will be destroyed during long etching periods.

Thin metal layers, such as chromium layers, can also be used as protection layers. They can be deposited covering the entire sample using vapour deposition techniques. Additional lithographic structuring of the metal layer is required for the selective protection of the substrate.

The production of geometrical structures with various defined depths using the protection layer technology involves the following sequence of machining processes:

1. *Mechanical treatment of the substrate material* using grinding and polishing to create high quality sheets with flat and parallel surface of optical quality.
2. *Exposure of the photosensitive glass* using UV light of a wavelength of 310 nm with an energy density optimised for the structuring of the deepest part of the structure through a special mask, which could be for instance a fused silica glass blank with structured chromium layer.
3. *Thermal treatment of the photosensitive glass* that was exposed to UV irradiation to induce the partial crystallisation of these exposed areas.
4. *Mechanical treatment* of the complete glass sheets by grinding and polishing to remove any deformations which might have formed during the crystallisation process, which is necessary to produce flat and high quality surface prior to the next processing step.

5. *Deposition of a metal layer* to mask the wafer during the etching process in hydrofluoric acid.
6. *Deposition of a photoresist layer* by spin coating. This layer is required as an etch mask to structure the metal layer.
7. *Structuring of the photoresist layer* using standard UV-lithography and a standard mask. Heat treatment and development of the photoresist.
8. *Etching of the resist covered metal layer* opens it at this areas where in the following the first etching of the photostructurable glass will start.
9. *First etching* of the selectively by the metal layer protected photostructurable glass in hydrofluoric acid to the first predetermined level of depth of the geometric structures.
10. *Removal of the protection metal layer* from the top side of the glass sheet in order to lay open the areas of the photostructured glass that should be etched during the second etching step.
11. *Second etching* of the photostructured glass sheets to fabricate the second level of the geometrical structure depth. Please note that all the other structures produced in the initial etching step are etched again. The combined etching time determines not only the depth but also the width of the structures produced in the first etching step, whereas the depth and width of the structures produced during the second etching step are determined only by the time of the second etching.
12. *Removal of the protection layer* from bottom side and cleaning of the glass sheet.

The main advantages of the protection layer technology are the possibilities to create geometrical structures with various defined depths and the control and precision of the depth of structures. The major disadvantages are that the process is rather laborious, requiring many process steps. The main technical challenge is the stability of the protection layer during the etching step in hydrofluoric acid. Furthermore, a porous layer of the residual glass phase remains on the bottom of the not completely through etched structures, such as sack holes and trenches, produced in the second etching step. This might in some cases, for instance microfluidic devices, limit their applicability.

9.2.6 Multi-step Structuring Method

Various references in the literature describe a process enabling the fabrication of structures, such as deep trenches and sack holes, with various levels of depth in a photostructurable glass using multiple UV-exposure steps [110, 144, 145, 190, 194, 195]. A schematic of the process is shown in Fig. 9.31.

A polished glass substrate is exposed to a UV source in a first step using an optimised energy density to produce the nuclei for the following crystallisation to initiate the deepest geometrical structures (or for through structured holes and slits). Additionally during this first UV-exposure step special marks for the adjustment of the glass sheet and the second mask in the second treatment

steps have to be realised. The geometry of these marks and their position in the substrate depend on the kind of mask aligner used and the substrate diameter. After the UV-exposure step the thermal treatment of the sample follows to induce the partial crystallisation in the exposed areas. During the thermal treatment it is necessary to minimise any deformation of the glass sheet, as any surface roughness and reduced flatness will result in problems during the second UV-exposure step of the substrate. An additional grinding and polishing step might follow if perfect quality and precision is required. Prior to the second UV-exposure step the initial geometrical structure has to be produced in the first etching step. This initial etching process can be stopped after a few minutes if the maximum desired depth is etched. This depth should be deeper than the structures to be produced in the second etching step. However, it is also possible to etch completely through the thickness of the substrate during the first etching step as shown in Fig. 9.31.

Further features are produced during the second UV exposure, thermal treatment and etching step. The UV-source energy density should be optimised to produce structures of the required depth. The second etching process will affect the depth and width of all structures which is important for the design of masks and the residual structure shape at all levels. An example of microstructured glass device produced using this technology is shown in Fig. 9.32.

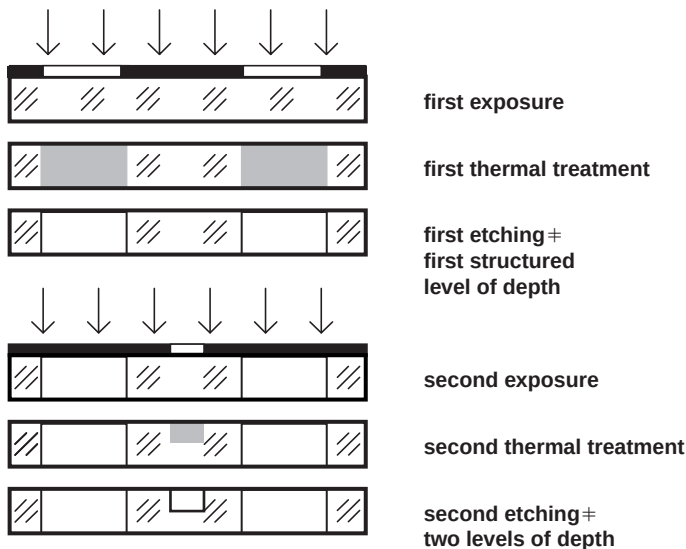


Fig. 9.31. The multi-step technology to produce geometrical structures

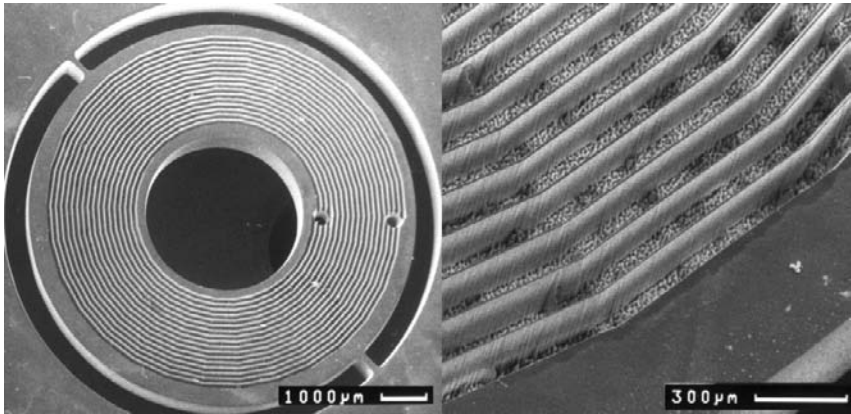


Fig. 9.32. Scanning electron micrographs of a glass sample structured using the multi step technology (*left*: bed for an electromagnet coil; *right*: detail at higher magnification) [190]

The multi-step technology is very versatile. However one should be aware that

- The first step determines the entire geometry (holes and trenches) and the level of depth to which structures and adjusting marks are going to be produced.
- The number of exposure steps should be minimised to reduce the costs of the process. Also the dimensional precision of the structures initially created will be reduced if many more thermal treatment and etching steps follow.
- All exposure steps that follow can only produce shallower structures.
- UV exposure from the top and bottom sides is possible. However, the substrate has to be of sufficient thickness. If the substrate is not thick enough the double-sided exposure will lead to a double exposure in the middle of the substrate resulting in exceeding the energy density threshold value. The double exposure will prevent the etch stop so that it will be impossible to fabricate structures with predetermined depth levels.

A glass element for an electrodynamic actuator produced by double sided photostructuring is shown in Fig. 9.33 (right). The multi-step technology allows for the production of glass elements with a certain outside contour and defined interior structures with various depth levels. Another advantage of the multi-step technology is the possibility to fabricate structures, such as trenches, that are separated by very thin walls (see Fig. 9.33, left). However, the disadvantages are the high production costs of any devices and the restrictions of positional control of the structures because of the adjustment marks that are necessary prior the any subsequent UV-exposure steps. Furthermore, residual partially crystallised areas remain at the bottom of deep structures.

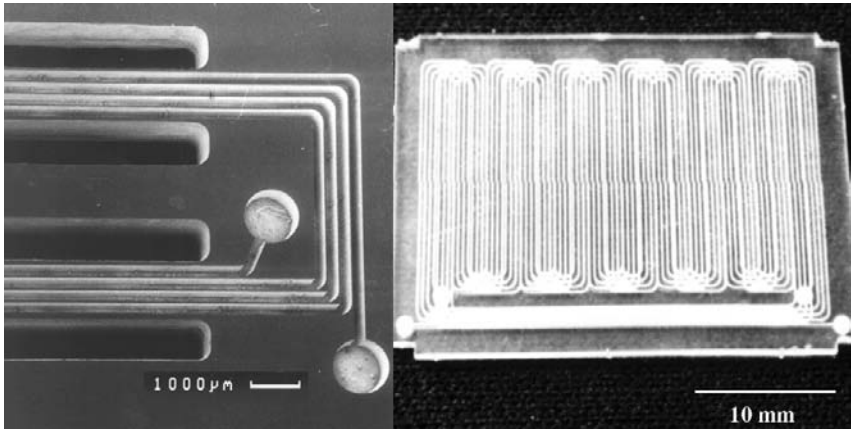


Fig. 9.33. Scanning electron micrograph of a glass element used as wire bed for a reluctance stepping actuator (*left*) and an example of a double-sided exposed glass element (*right*) [190]

9.2.7 Photostructuring Using the Modified Mask Method

Principle

The control over the depth of structures created in thick photoresists by varying the transmission of the mask used during the exposure has been used for the structuring of silicon for a few years [474]. This method was transferred to the photostructuring of UV-sensitive glass.

A correlation between the diameter of openings in the mask and the resulting exposure depth for photostructurable glasses was found by Schmidt [446]. She has found that it is impossible to completely expose geometrical structures in a 500-μm thick glass sheet with a nominal diameter of 5 μm, which was explained by the diffraction of light at the walls of the mask openings. This result corresponds with the observations shown in Figs. 9.22 and 9.23. Diffraction effects are particularly important for production of structures with nominal diameters below 50 μm. The smaller the nominal diameters of a structure the more important become diffraction effects. Considering these results it should be possible to control the depth of structures to be created by the nominal diameter of the openings in the masks. The depth of big trenches or sack holes can be controlled by a modification of the transmission of normally transparent openings by perforations of the masking layer (see Fig. 9.34) [145, 190]. The absorbing Cr layer is not removed completely but instead precisely microstructured. By using such microstructured masks it is possible to exposure the complete wafer of photosensitive glass through the mask using one and the same UV-energy density to produce structures with varying depth profiles. The UV-energy density is instead optimised by the local variation of the mask transmission. The areas of the glass that should not be structured, i.e. no etching should occur, are protected as before by the

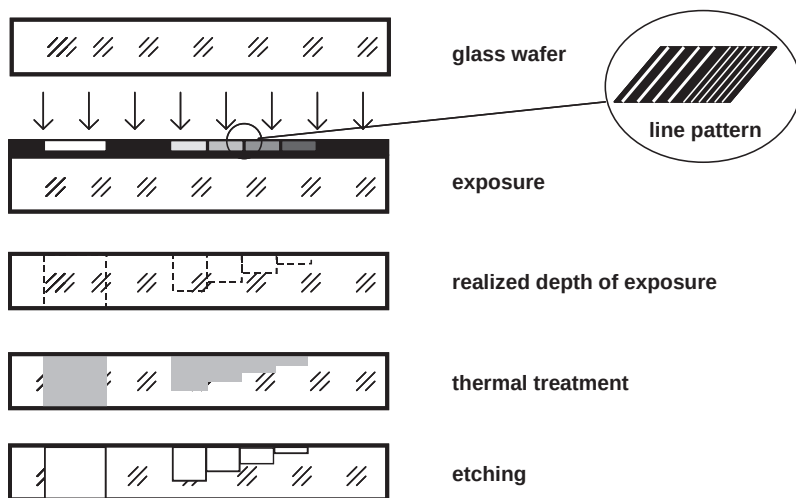


Fig. 9.34. The structuring process using the modified mask technology

standard chromium layer on the mask blank. To create through structured holes or slits the mask is open, as before. However, the mask has a reduced transmission in those areas where a structuring to a shallow depth is desired.

The optical transmission of the mask can be controlled either by controlling the thickness of the absorption layer of the mask or by using a geometrical substructure or perforation in the mask areas which should be optically controlled. The absorption of the mask can be controlled by either using additive or subtractive techniques. The thickness of the absorption layer of the mask can be tuned by using an additional sputtering mask and controlling the sputtering time. Subtractive technologies utilise etching processes after lithographic structuring of the masking layer. However, the technical realization of these masks is difficult and therefore rather expensive. The mentioned substructures can be easily produced for instance during the electron beam writing of the mask. Electron beam writers that are commonly used for the production of masks have a resolution of 100 nm. This resolution is two orders of magnitude higher than the diameter of geometrical structures that are realised in photostructurable glasses. The depth of the geometrical structures to be created in the glass sheet can be controlled by reducing the free area in the openings for the UV transmission (transmission control) or by producing diffraction effect substructures in the openings of the mask (diffraction control).

The method is demonstrated using patterns of orthogonally crossed stripes or parallel stripes. Examples of successful structures in glasses are shown in Fig. 9.35. The parallel stripes pattern allows for better control of the structure because the depth of structures can be varied by enhancing the resolution of the stripes pattern. Therefore the parallel stripe design was used to examine the process parameters and for calculations. This will be described later in this section.

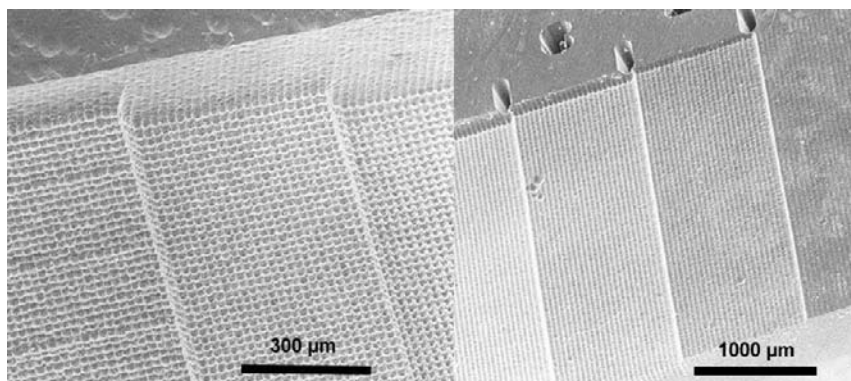


Fig. 9.35. Scanning electron micrographs of structured glasses having various substructures using the modified mask technology (*left*: orthogonally crossed stripes; *right*: parallel stripes) [190]

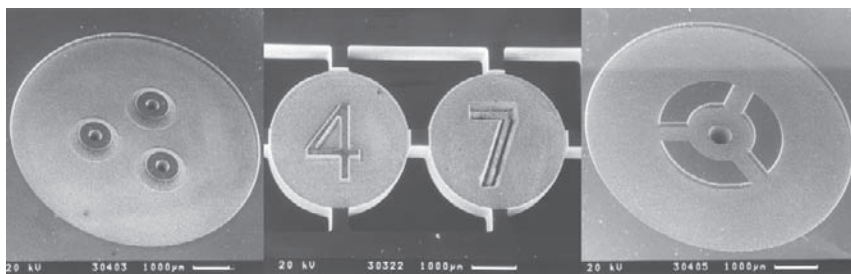


Fig. 9.36. Micrographs of examples of three-dimensional structures produced using the modified mask technology

The modification of the transmission of a mask allows for the production of three-dimensional structures in glass samples without undercuts. Some examples are shown in Fig. 9.36.

Variation of Parameters Controlling the Structuring Using Modified Masks

For the discussion of the processes occurring during the geometrical structuring using modified masks we will define the parameters that are of importance. The macroscopic geometrical structure of a mask is consisting of a raster of a period i formed by microscopic absorber stripes of a width g and transmission stripes (perforation) of a width o (see Fig. 9.37). The ratio between o and g is defined as the line ratio o/g . The ratio of transmission of the mask TA is the ratio of the transparent area, i.e. the area of all perforations, to the total area of the structure in the mask. TA is a characteristic value of a geometrical pattern. The same ratio of the width of the perforations o to the period i for various periods causes the same ratio of transmission TA .

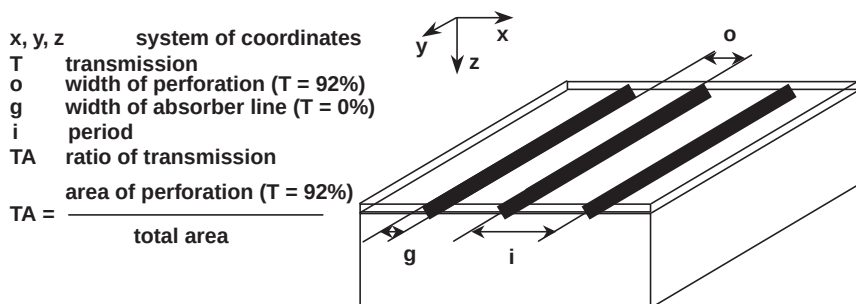
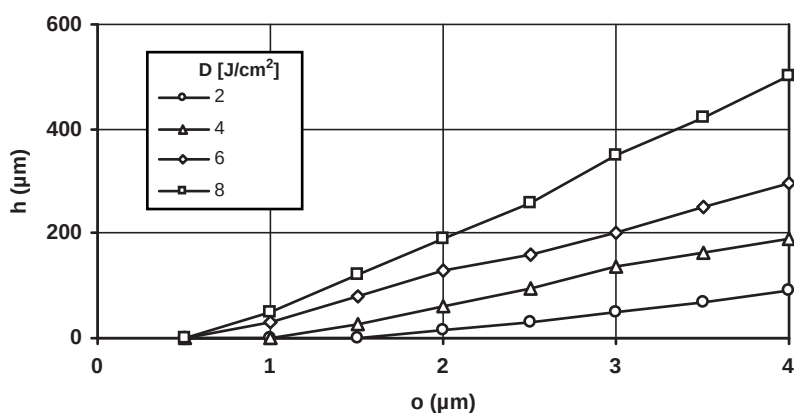


Fig. 9.37. Parameters of modified masks

Fig. 9.38. Depth h of structures as function of the width o of perforations and the energy density D at fixed $t_e = 40$ min and $i = 40 \mu\text{m}$ [190]

As described in Sect. 9.2.3 the crystallisation depth decreases with decreasing energy density used during the UV exposure, which simultaneously affects the etching depth that can be achieved. In other words the depth of a structure is influenced by the energy density used during the UV exposure. If the UV-energy density is reduced below the threshold value no measurable structuring will occur.

The etching depth (which is equal to the final depth of a structure) as function of the energy density D used during the UV exposure and the width o of perforations in the mask structure of a constant period i of $40 \mu\text{m}$ after etching for 40 min is shown in Fig. 9.38. As can be seen it is possible to control the depth of geometrical structures by controlling the UV-energy density or by varying the pattern geometry of the mask.

The control of the depth of structures by variation of the UV-energy density can only be used for controlling the depth of the deepest geometrical structures. The depth of all structures with a shallower depth can only be adjusted by varying the geometry of the mask pattern. The dependence of the depth of structures on the width of the mask perforations and on the

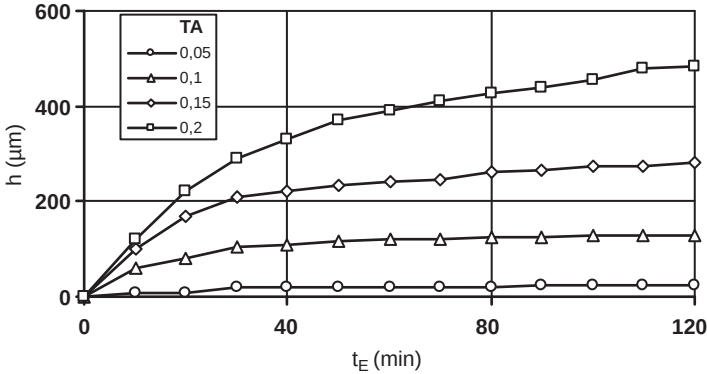


Fig. 9.39. Depth h of structures as function of the etching time t_e and the transmission ratio TA at fixed $i = 20\ \mu\text{m}$ and $D_S = 10$ [190]

UV-energy density is nearly linear in the investigated range (Fig. 9.38). A threshold value for the width of mask perforation was found below which etching was impossible to produce any structures. The threshold value ranging from $o = 0.5$ to $1.5\ \mu\text{m}$ was found. This value depends on the energy density of the UV source used for the exposure.

As previously described the depth of geometrical structures depends at a given transmission ratio TA on the time of etching. The correlation between etching time for various TA at a relative UV-energy density $D_S = 10$ and a constant period of $i = 20\ \mu\text{m}$ is given in Fig. 9.39. The depth of produced structures approaches asymptotically a limiting value with increasing etching times. This limiting value is determined by the transmission ratio TA and corresponds with the maximum exposure depth using a given energy density. The etching time required to achieve this limiting, maximum structural depth thus depends on TA and ranges between 20 and 100 min for the process parameters used.

The etching rate as function of the transmission ratio and the etching time is shown in Fig. 9.40. The etching rate decreases (i.e. etch stop) with increasing etching time.

The highest etching rate of $13.1\ \mu\text{m}\ \text{min}^{-1}$ was measured if the photosensitive glass was exposed to UV light through a mask without substructures ($TA = 1$) and, therefore, the highest possible crystallisation occurred. On the other hand the average etching rate of the glassy phase, i.e. of the areas that were not exposed to UV, was $0.94\ \mu\text{m}\ \text{min}^{-1}$. Therefore, the maximum possible etching ratio is 14. This etching ratio was measured on FS21 glass which was exposed to a relative UV-energy density $D_S = 10$ and etched for 80 min.

However, the initial etching rate, i.e. the rate at the start of the etching process, never approaches the highest etching rate which was observed for the areas containing the maximum possible amount of crystals ($TA = 1$). An etching rate of $12\ \mu\text{m}\ \text{min}^{-1}$ was measured if a transmission ratio of 0.2 was

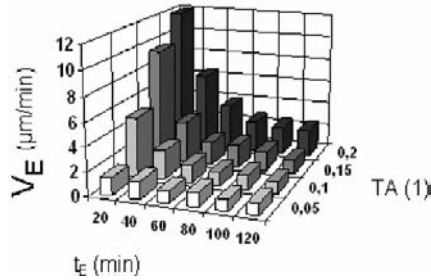


Fig. 9.40. Etching rate v_E as function of the transmission ratio TA and the etching time t_e at fixed $i = 20\mu\text{m}$ and $D_S = 10$ [190]

used, which is not very different from the maximum possible etching rate of $13.1\mu\text{m min}^{-1}$. It can be concluded from this observation that a transmission ratio exceeding 0.2 (which corresponds to perforations width o of $4\mu\text{m}$ and a period i of $20\mu\text{m}$) does not lead to a significant increase in the etching rate and, therefore, not to a larger depth of the produced structures. However, a reduction of the transmission ratio TA below 0.2 results in a significant decrease of the observed etching rate. The etching rate also decreases with increase in etching time irrespective of transmission ratio used. This effect is more dramatic for larger transmission ratios.

The etching rate is generally low for small transmission ratios around $TA = 0.05$ approaching that of the pure glassy phase. All crystallised material is etched away after an etching time of around 30 min. Very shallow structures result and no dependence of the depth of structures occurs if the etching time exceeds 30 min.

The etching rate starts with $6\mu\text{m min}^{-1}$ for a transmission ratio of $TA = 0.1$, however, with increasing etching time up to about 60 min the etching rate decreases significantly until the etching rate of the non-exposed glassy areas is reached. After this time, depth of the structures created does not increase any further. If transmission ratio is $TA = 0.15$ the etching process stops at a time of about 100 min.

Again, the etching rate decreases with increasing etching time if a transmission ratio of $TA = 0.2$ is used, but in this case etching rate for the pure glassy phase will not be approached within the time scale of the experiment. This also means that the maximum possible depth of the structure, i.e. that to which the glass is crystallised, will not be achieved and no complete and abrupt etch stop occurs for larger structures. This is in contrast to the hard etch stop for the anisotropic etching of silicon. It can be concluded that the depth of shallower structures can be more precisely controlled without relying on the actual etching conditions as compared to the realisation of deeper structures.

Figure 9.41 shows the etching depth h as function of the transmission ratio TA and the raster period i . It is apparent that deeper structures can be created

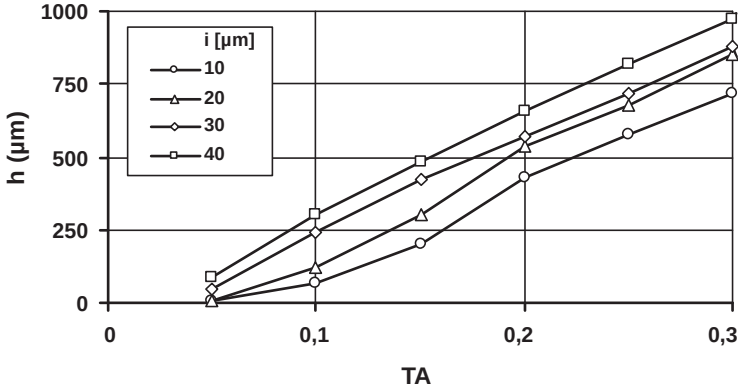


Fig. 9.41. Depth h of structures as function of the transmission ratio TA and the period i at fixed $D_S = 12$ and $t_e = 140$ min [190]

with increasing raster period if transmission ratios between 0.15 and 0.3 are used. This behaviour was expected because according to the definition of the transmission ratio a constant transmission ratio is equivalent to a constant UV-energy density that the volume of the glass was exposed to. For raster periods of 10 and 20 μm at transmission ratios below $TA < 0.15$ the curve $h = f(TA)$ deviates from linearity. This depends on the period used. It is larger for smaller raster periods and cannot be explained by transmission effects. It seems that even though the UV-energy density is constant the energy distribution in the bulk is not. The energy distribution in the bulk seems to be affected by diffraction effects. This can be explained by the occurrence of diffraction effects in smaller structures which will be described in detail further on.

Continuous Change of the Structures Depth

Structures with inclined side walls at predefined angles can be generated by varying the width of perforations of the structures in the mask used. An example is shown in Fig. 9.42. These structures were produced using a mask with a raster period of $i = 20 \mu\text{m}$ but the width of perforations o of the mask was varied from 0.5 to 5 μm . The five different geometrical structures shown in Fig. 9.42 were produced by varying the number of transparent lines (perforations) of the same width. Structure 1 (left) contains a single line of each width and structure 5 always five lines of the same width, because of that the integral angle of the walls varies.

Another possibility to create side walls with defined wall angles is the variation of the period between groups of lines.

Interesting from an application point of view would be the possibility to produce geometrical structures with continuously inclined walls rather than creating inclined walls using a series of steps (Fig. 9.42). Such structures with

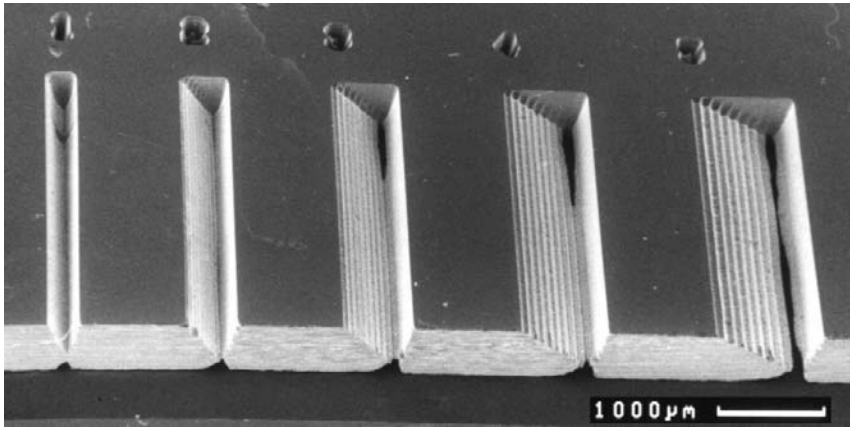


Fig. 9.42. Scanning electron micrograph of a glass structure with staircase-like inclined walls [190]

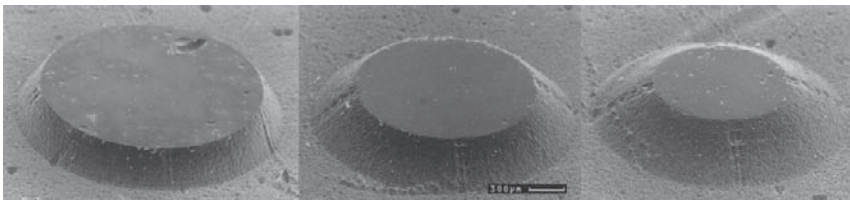


Fig. 9.43. Scanning electron micrographs of glass structures with almost continuously inclined walls. The angle of inclination decreases from the left to the right

continuously inclined walls can be created by using a mask with a minimum difference of the width between two neighbouring perforations. If a standard electron beam writer can be used for the perforation of the masks, then a minimum difference of width between two neighbouring perforations of 100 nm could be achieved. This resolution is high enough for the realisation of quasi-continuously inclined side walls as shown in Fig. 9.43. Etching in a hydrofluoric acid solution smoothes the resulting extremely small steps of the walls. This helps to produce almost continuous wall inclinations.

Crossing of Mask Structures

It is frequently required to create masks to produce geometrical structures with crossing structural lines. An important problem of the modified mask method is that a certain distance on the mask between two structural lines crossing orthogonally later in the glass is necessary to guarantee that the structures to be eventually created in the glass joint at the same depth level at the crossing point. This issue is highlighted in Fig. 9.44.

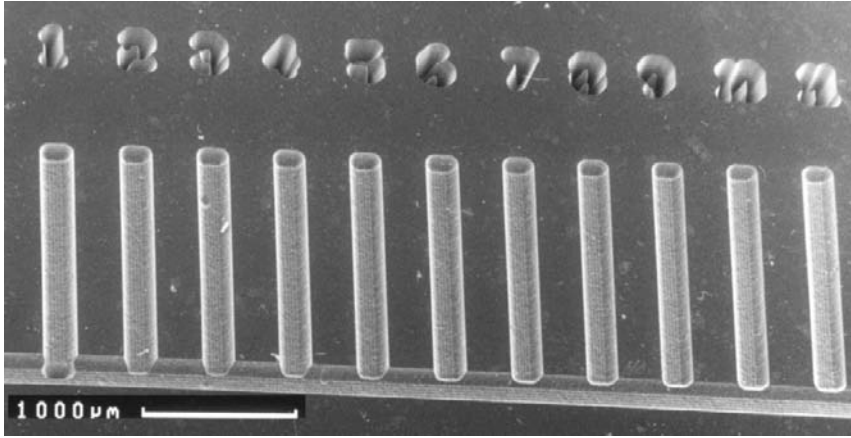


Fig. 9.44. Scanning electron micrograph of trenches crossing (one trench is horizontal, 1–11 are perpendicular) which is the result of different distances of the mask perforations varied from 0 to 100 μm) [190]

If the distance between two structures arranged orthogonally in the mask is too small, a hole will be formed in the glass device where both structures have a contact with each other as shown in position 1 in Fig. 9.44. The formation of the hole is due to the fact that the transmission through the mask is higher at the point where both structures cross. The glass bulk below this area of the mask is therefore exposed to more UV light (the light through both crossing perforated lines adds). But if the distance between two structures arranged orthogonally in the mask is too large, the resulting geometrical structures in the glass are separated by walls which will be produced as shown in position 6–11 in Fig. 9.44. Both cases cause problems if the glass device to be manufactured is to be used as microfluidic device. In the first case a leak in the channel may occur and in the second one a not useful impediment of the fluid results.

This incorrect part of structure depth h_f describes direction and size of a defect that is caused by wrongly designed masks as just mentioned. A negative value of h_f describes the formation of a hole whereas positive values, the presence of a bar separating the two structures. $h_f = 0$ means that both geometrical structures join perfectly at the same level. As can be seen in Fig. 9.45 the incorrect part of structure depth increases at shorter distances b_s with decreasing distance between the mask perforations, but also increases with increasing distances between the mask perforations as longer distances b_s . However, as can also be seen, a range of distances between mask perforations exists where all curves cross the abscissa of the diagram. For this distance between crossing perforations b_s of around 30 μm, incorrect part of structures seems to be independent on all the other structuring parameters which means that in all cases where a modified mask is used for structuring

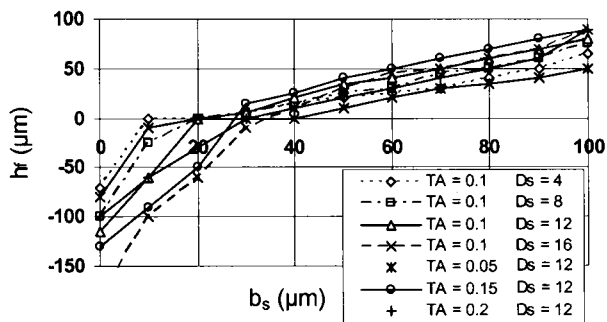


Fig. 9.45. Depth of incorrect part of structure h_f as function of the distance between crossing perforations b_s , the transmission ratio TA and the relative energy density D_s [190]

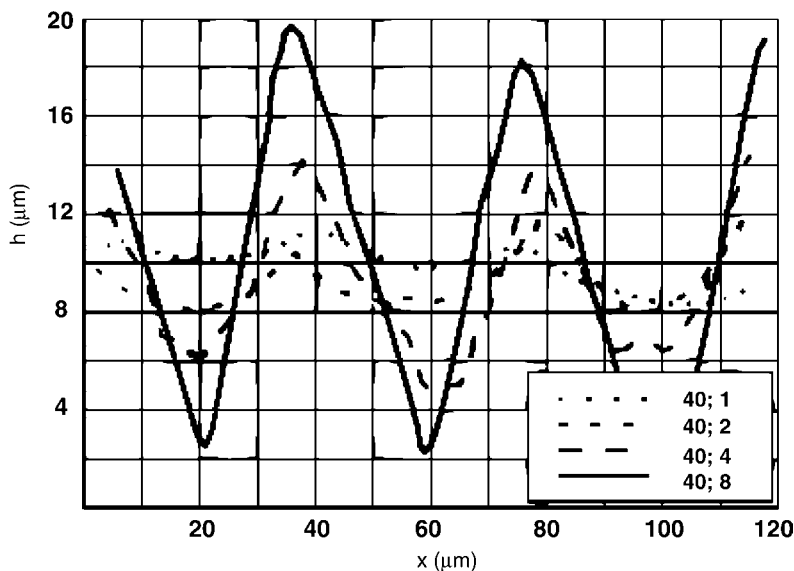


Fig. 9.46. Measured topography h on the bottom of geometrical structures as function of the position x and the width o of the perforation of the modified masks used to produce the structure. o was varied from 1 to $8\text{ }\mu\text{m}$ at a constant raster period $i = 40\text{ }\mu\text{m}$ [190]

glass the distance between crossing perforations of $30\text{ }\mu\text{m}$ is useful to fabricate geometrical structures that join up at even depth.

Topography of Depth Structured Channel Bottoms

Commonly in defined depth structuring a porous layer consisting of the residual glass phase remains at the bottom of the produced structure (see Figs. 9.11 (right) and 9.32 (right)). Figure 9.46 shows the topography of the bottom of

such a geometrical structure after etching as function of the lateral position and the width of the perforations in the mask substructures at a constant period i of $40\text{ }\mu\text{m}$. The topography of the structured glass reflects the raster period of $40\text{ }\mu\text{m}$, i.e. the distance between the perforations. The roughness of the bottom is determined by the width of the perforations o ; the wider the perforations the more rough the resulting structures. An enlargement of perforations width o results in deep structures as well as in an enhanced roughness of their bottom. Perforations of $8\text{ }\mu\text{m}$ in a mask with a period of $40\text{ }\mu\text{m}$ and a transmission ratio of $TA = 0.2$ produce an absolute roughness of about $18\text{ }\mu\text{m}$. This value decreases to about $2\text{ }\mu\text{m}$ if perforations of $1\text{ }\mu\text{m}$ at the same period of $40\text{ }\mu\text{m}$ and a transmission ratio of $TA = 0.025$ are used, see once more the SEM picture of the bottom of a structure made by the modified mask method, Fig. 9.35.

The surface roughness on the bottom of a geometrical structure differs remarkably depending on whether the structure was produced using the etch stop process or the modified mask method. The modified mask method results in smoother bottoms of the produced structures, as no porous layer of the residual glass phase remains. Instead the bottom still consists of the original glass phase with a small amount of lithium metasilicate crystals in it. The presence of the crystals makes the glass translucent.

Intensity Distribution During the UV Exposure

Light is considered as a wave for the simulation of diffraction effects on the mask structures. Both absorption and diffraction occur if the extension of a wave is disturbed by an obstacle, e.g. a geometric object. The diffraction effect is dominant if many of very small objects block the path of light. Diffraction is the bending of the light wave front as it passes around the edge of an obstacle. The diffraction depends on the ratio of the wavelength of light to the distance between the obstacles. The not absorbed, diffracted parts of the light wave front will interfere behind the geometric objects which will result in a local intensity distribution. The Fresnel and Huygens principle, namely that all uncovered points of an advancing wave front are in fact centres of fresh spherical elemental waves and the source of new trains of waves, will be used for calculating the intensity distribution in the exposed volume of glass sample behind a mask. We briefly review the basics of the calculation [190]. The geometry used for calculation is shown in Fig. 9.47.

For the determination of the intensity distribution in two-dimensions, i.e. in the x and z -directions, a modified mask with a stripe substructure as shown in Fig. 9.37 is used. The z -coordinate, representing the depth into the glass sample, starts at the mask plane. The x -coordinate is orthogonal to the z -direction, and the y -coordinate runs parallel to the stripes of the mask. Edge effects in x and y -directions are not included into the calculation; i.e. the extension is infinite but the calculation is locally restricted. 10,000 elemental waves start at a distance of $x = 200\text{ }\mu\text{m}$ at the absorber structure of the

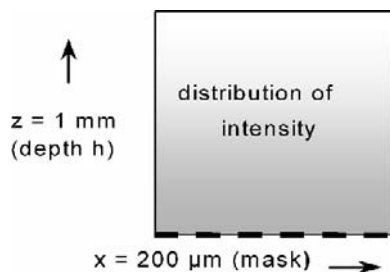


Fig. 9.47. Layout used for calculation of the intensity distribution (z -direction corresponds to the thickness of the glass sheet, the gray field after the mask is the UV-exposed region)

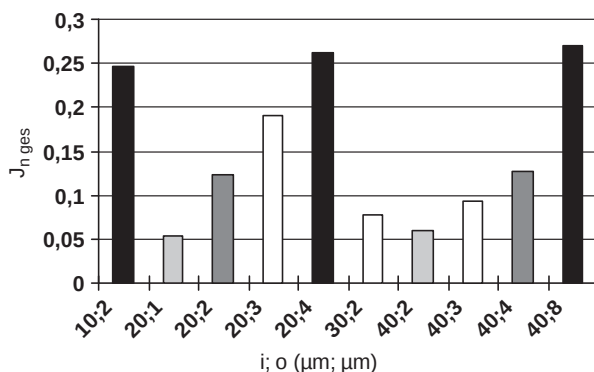


Fig. 9.48. Relative total intensity $J_{n\text{ ges}}$ as function of raster geometry of the mask (period i ; width o of perforations) [190]

mask. Only the waves not absorbed by the mask for various mask designs, i.e. varying width o of perforations, were used for the calculation. The intensity is calculated by summation of the influence of all elemental waves passing through the mask openings with their amplitude and phase. This calculation allows approximating the real intensity distribution in the bulk of glass sample. The relative intensity J_n of the light at all points $P_n(x, z)$ (pattern: $x = 1 \mu\text{m}$; $z = 10 \mu\text{m}$) up to a depth $z = 1 \text{ mm}$ behind the mask was calculated. The relative total intensity $J_{n\text{ ges}}$ is the sum of all values of J_n within the selected area ($x = 200 \mu\text{m}$; $z = 1 \text{ mm}$) considering the relative initial parameters of each pattern. The calculated intensity pattern is defined by the raster period i and the width o of perforation of the mask substructure. $J_{n, h=1}$, the relative depth intensity, is the sum of the relative intensities over the entire depth of $h = 1 \text{ mm}$ normalised over a width in the x -direction of $x = 1 \mu\text{m}$. The ratio of the relative total intensity $J_{n\text{ ges}}$ to the structural depth h gives the depth related relative total intensity.

Figure 9.48 shows the relative total intensity as function of the raster geometry of the mask. The relative total intensity increases with increasing

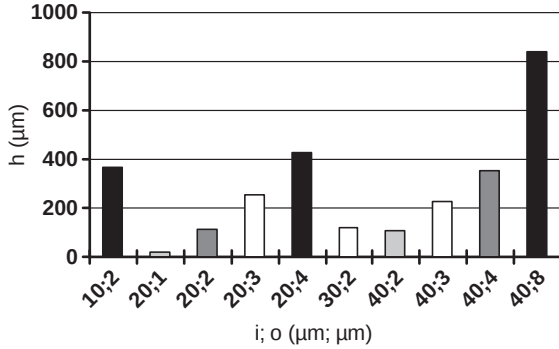


Fig. 9.49. Structural depth h as function of the raster geometry of the mask (period i ; width o of perforations) [190]

width o of perforations at a constant period i . The increase of J_{nges} is nearly linear. The relative total intensity is almost unaffected when the period i is varied at a constant transmission ratio TA , i.e. the ratio o/i is constant. This behaviour is expected because definition of the transmission ratio.

We will compare the relative total intensity with the depth of real geometrical structures. Figure 9.49 shows the observed depth as function of the raster geometry of the mask. The observed depth of a geometrical structure increases progressively with increased width of perforations, if the period i is constant. The structural depth decreases noticeably at small widths of perforation. However, the observed depth does not remain constant if the period i varies at a constant transmission ratio (i.e. $o/i = \text{const.}$). The area dependent definition of the ratio of transmission does not allow it. If only the transmission controls the UV-penetration depth, it would be expected that the observed structural depth is constant for a constant ratio of transmission which corresponds to a constant relative total intensity.

The depth related relative total intensity J_{nges}/h depends on the raster geometry of the mask as shown in Fig. 9.50. Decreasing the width o of transparent perforations at a constant period i leads to a significant increase of the depth related relative total intensity, which cannot be explained by the transmission control of the depth.

The relative depth intensity $J_{n,h=1}$ for a depth h of 1 mm as function of position in x -direction increases with increasing width o of perforations which is independent on the period i between the perforations (Figs. 9.51 and 9.52).

Two types of maxima are visible in Fig. 9.51. Local maxima of the relative depth intensity $J_{n,h=1}$ of higher order can be found between the main maxima at 53, 73 and 93 μm. The main maxima are higher and narrower as compared to the different local maxima around 63 and 83 μm. The main maxima can be assigned to the transparent perforations of the mask. The appearance of the local maxima is due to diffraction effects. They are smaller if a larger period $i = 40$ μm is used (see Fig. 9.52) as compared to relative depth intensity $J_{n,h=1}$

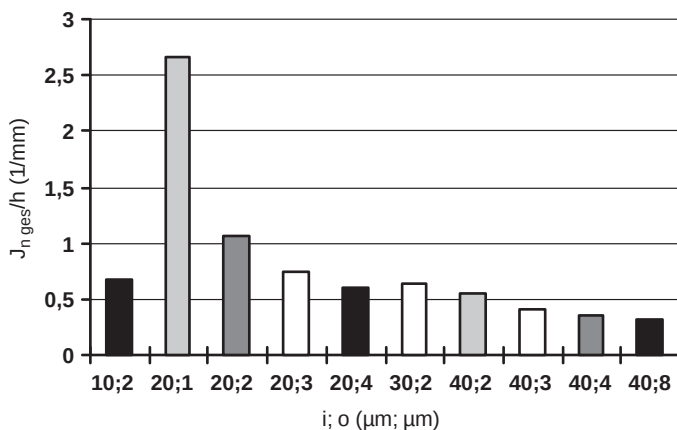


Fig. 9.50. Depth related relative total intensity $J_{n\ ges}/h$ as function of the raster geometry of mask (period i ; width o of the perforations) [190]

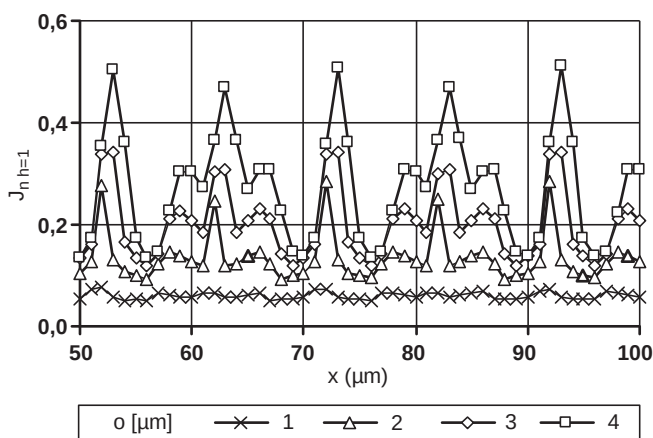


Fig. 9.51. Relative depth intensity $J_{n,h=1}$ for width o of perforations as function of the distance along the x -coordinate at a constant period $i = 20\ \mu\text{m}$ [190]

profile for a smaller period $i = 20\ \mu\text{m}$ (see Fig. 9.51). In case of the same ratio of transmission and various periods of the perforations a significantly higher main maximum and a low basic intensity result with increasing periods. In this later case each perforation of the mask generates a precise image in the glass. The characterisation of the real, open structures in the glass after the etching process confirms this observation.

An almost continuous basic intensity of UV exposure is the result of a decreasing width of the perforations, which makes it impossible to distinguish the main maxima which would correspond to the individual mask perforations. The effect of single structures on the light distribution profile decreases and that of the constant basic intensity increases, however, the total intensity

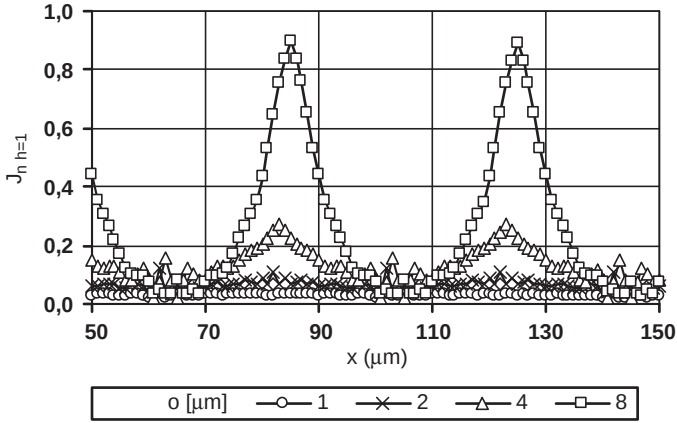


Fig. 9.52. Relative depth intensity $J_{n,h=1}$ for width o of perforations as function of the distance along the x -coordinate at a constant period $i = 40 \mu\text{m}$ [190]

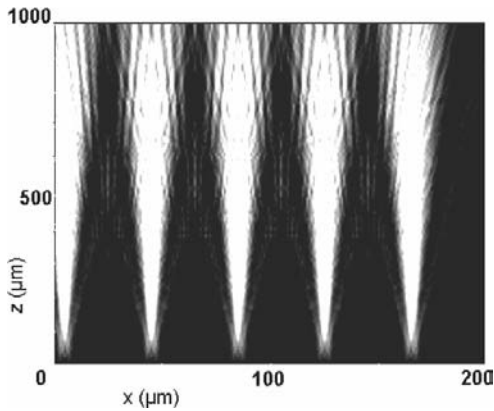


Fig. 9.53. Calculated intensity distribution of the glass area under a mask with a raster period $i = 40 \mu\text{m}$ and a perforation width $o = 8 \mu\text{m}$ [190]

(area below the curve) is significantly lower which will eventually result in a shallower structural depth (see Fig. 9.52 compared with Fig. 9.51 taking into consideration the different scales).

Simulations of the concrete distributions of the UV-light intensity in the glass behind the mask permit further conclusions and explanations. Figures 9.53 and 9.54 show the calculated actual intensity distribution in the volume of glass directly behind the mask. In these figures the white areas represent areas of high UV-light intensity whereas the black areas correspond to areas with low intensity. The figures highlight the influence of the mask geometry on the UV-light intensity distribution within the glass.

Diffraction effects are not observed if a mask with a raster period $i = 40 \mu\text{m}$ and a perforation width $o = 8 \mu\text{m}$ is used (Fig. 9.53). Channels of high

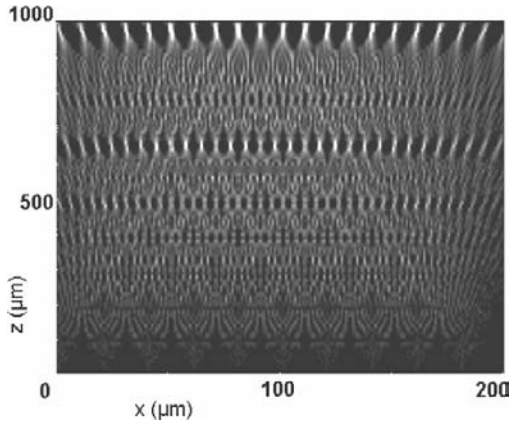


Fig. 9.54. Calculated intensity distribution of the area under a mask with a raster period $i = 20\ \mu\text{m}$ and a perforation width $o = 1\ \mu\text{m}$ [190]

UV-intensity start directly behind the perforations of mask, which are spaced $40\ \mu\text{m}$ apart (which corresponds to the raster period $i = 40\ \mu\text{m}$). The areas of high intensity widen up with increasing depth in to bulk of the glass. This effect is reflected in the measured actual roughness at the bottom of structures that have been created by exposure through such a mask after etching (Fig. 9.46). The increase of structural roughness is caused by a widening of the high-intensity channels.

Figure 9.54 shows the intensity distribution in the bulk of glass behind a mask with a raster period $i = 20\ \mu\text{m}$ and a perforation width $o = 1\ \mu\text{m}$. As can be seen for this mask diffraction effects dominate so that the light intensity is low down to a depth of $200\ \mu\text{m}$. However, throughout the bulk exists a number of local intensity maxima, which however do not depend on the distance in z -direction. Therefore, the structural depth of a particular structure is mainly controlled by diffraction effects.

The two cases discussed above represent the two extremes. A decrease of the raster period of a mask as well as decrease of the perforation width leads to an increase of diffraction effects on the intensity distribution.

From the above the following conclusions can be drawn:

- The transition from transmission control to diffraction control of the depth of geometrical structures in a glass sheet is smooth.
- A decreasing perforation width results in a higher influence of diffraction effects for a constant period between perforations.
- It is possible to control the depth of geometrical structures in a glass sheet using a fine pattern (substructure) of mask openings which allows fabrication of three-dimensional structures (without undercut).

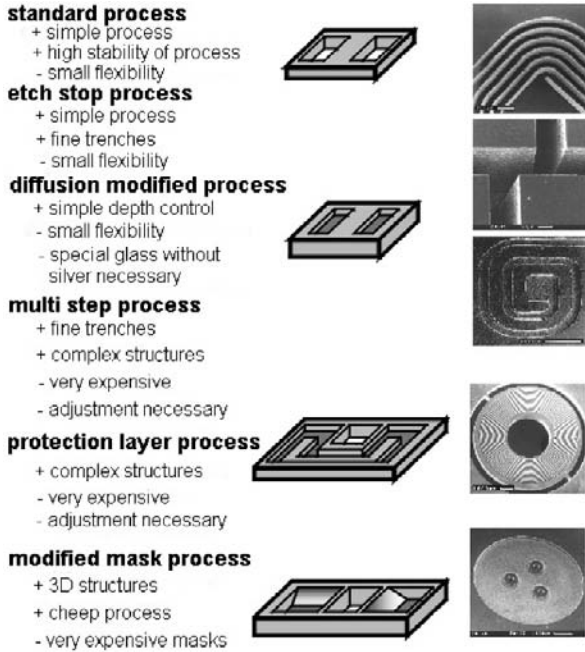


Fig. 9.55. Comparison of various photostructuring methods

9.2.8 Comparison of the Different Photostructuring Methods

The advantages and disadvantages of various photostructuring methods described above as well as examples of geometrical structures created using these methods are shown in Fig. 9.55. The standard photostructuring process is the best option for the fabrication of holes and slits. Structures that can be created using this method are springs, sieves and coils. But it is possible to modify this standard photostructuring process in a variety of ways. Geometrical structures of a defined depth can be easily produced using the etch-stop process. In this process the actual depth of a structure is controlled by controlling the etching time. The process is not very flexible; i.e. only structures with the same depth can be produced. Moreover, after the etching process a residual rough layer always remains at the bottom of the produced structures. The devices that are produced using this method are commonly used in microfluidics.

Photostructuring of glasses whose composition has been modified by diffusion provides excellent depth control. However, special glasses without silver are required and only geometrical structures with a small aspect ratio can be fabricated.

The modified mask method and the protection layer technology enable the simultaneous fabrication of geometrical structures of different depth, such as holes or slits and sack holes or trenches with predefined depths, in a single

glass device. Such structures are of major interest for microfluidic systems and for the production of coils. However, the main disadvantage of the protection layer technology is that the process is very laborious which makes the devices very costly.

The best photostructuring technology for the fabrication of complicated and complex structures is the modified mask method. This process enables the production of three dimensional geometrical structures (without undercut) in single processing step. Unfortunately the masks are very expensive. The produced devices are suitable for many microtechnology applications.

9.3 Laser-Initiated Structuring of Photosensitive Glasses

9.3.1 Threshold Energy Densities to Generate Photoelectrons

In contrast to the laser ablation of glasses (see Sect. 8.2.2) or laser-assisted etching processes (see Sect. 8.2.5) laser-assisted processing of photosensitive glasses requires just these special glasses. The fabrication of geometrical structures in this photosensitive glasses using laser-assisted processing also requires the previously described thermal treatment and etching steps (Fig. 9.1).

The energy density required to change the valency of cerium ions during UV-exposure process is significantly smaller than the energy density required for any ablation process. For single-photon processes, see Jacquorie [261], the wavelength of the UV light should be in the range of the maximum sensitivity of the photosensitive glass used, which is the case for various UV lasers, in particular the XeCl excimer laser (see Table 8.1). For multi-photon processes, see once more Jacquorie [261], also other lasers, such as the frequency trebled Nd-YAG laser, can be used.

One advantage of lasers for the UV-exposure process of photosensitive glasses is their flexibility in designing geometrical structures. Focused laser beams allow for the serial writing of points but also for the exposure through flexible masks. Furthermore, lasers allow for the fabrication of quite different patterns because various wavelength and various beam characteristics can be used. However, the disadvantage of the serial generation of structures is the time required for the generation of complex structures. Laser exposure of photosensitive glasses is therefore a valuable option for rapid prototyping but not for mass production.

To determine the appropriate energy density for the UV exposure its upper and lower limits were investigated.

The upper limit of the energy density ε_{Ab} is determined by the onset of glass melting and evaporation, which corresponds to the ablation threshold (Sect. 8.2.2), which has to be avoided. The precise value of ε_{Ab} varies and depends on the type of interactions between glass and the radiation which in turn depends on laser wavelength [67]. She determined the upper limits of the

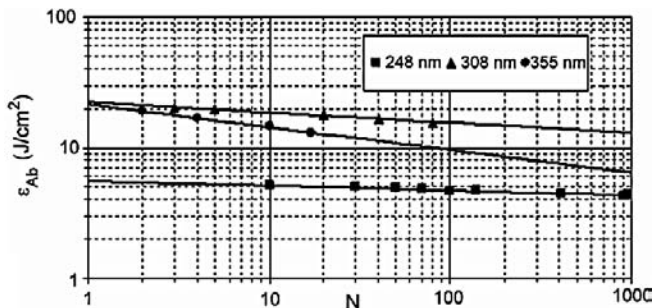


Fig. 9.56. Upper threshold energy densities ε_{Ab} as function of the number N of pulses per area and wavelength of the laser used $\lambda = 248, 308$ and 355 nm [67]

energy density ε_{Ab} for FS21 glass using KrF ($\lambda = 248$ nm), XeCl ($\lambda = 308$ nm) and frequency trebled Nd-YAG ($\lambda = 355$ nm) lasers (Table 8.1). FS21 is not transparent at $\lambda = 248$ nm but is partially transparent as shown in Fig. 1.42 for $\lambda = 308$ nm and very well transparent for $\lambda = 355$ nm. Consequently the KrF-laser irradiation is expected to be absorbed directly by the glass surface.

Structures are written using single laser pulses, which frequently overlap in the laser path. To determine the actual energy density the energy of the single pulses has to be added up simultaneously considering the heat conduction. The overlap of several laser pulses can be described from a geometrical point of view by an effective number of pulses N_{eff} per area [65], which has to be considered to determine ε_{Ab} . The results are shown in Fig. 9.56. The upper threshold energy density is also defined as the energy density which is just not able to produce microscopic defects on the surface of the sample. As can be seen in Fig. 9.56 the higher N_{eff} the lower is ε_{Ab} . The effect is very distinct for $\lambda = 355$ nm (remember, the glass is very well transparent). ε_{Ab} is significantly lower at $\lambda = 248$ nm, which is absorbed at the glass surface.

The under energy density limit ε_S is defined as the lowest possible energy density to still cause photochemical effects, e.g. the separation of photoelectrons. ε_S is determined practically by measuring the energy density that still initiates the transfer of Ce^{3+} to Ce^{3++} and consequently still allows for nucleation and crystal growth. It is rather difficult to determine ε_S because the laser must be strongly throttled. ε_S for FS21 was determined by Brokmann [67] to be 0.115 J cm^{-2} at $\lambda = 355$ nm and 0.038 J cm^{-2} at $\lambda = 248$ nm but could not be determined at $\lambda = 308$ nm. Two-photon absorption occurs at $\lambda = 355$ nm which leads to a larger ε_S as compared to $\lambda = 248$ nm. At $\lambda = 308$ nm one-photon absorption is prevalent.

All the energy densities in the range $\varepsilon_S < \varepsilon < \varepsilon_{Ab}$ for a given wavelength are suitable to initiate photostructuring. The energy density ε that is eventually used during the photostructuring is determining how many photoelectrons are generated, which affects how many silver atoms form nuclei affecting the amount of LMS crystals produced.

9.3.2 Interactions

The UV-exposure parameters affects compositional changes in glass, i.e. the breakage of chemical bonds, change of valency of sensitive polyvalent cations but also the generation of vacancies in the oxygen part of the network. The following exposure parameters are important:

- the emitted wavelength λ_L of the laser
- its energy density
- the effective number of pulses per area as well as
- the writing rate

The influence of the emitted wavelength on the optical transmission τ of FS21 was determined at a constant energy density $\varepsilon_L = 2 \text{ J cm}^{-2}$ using a single pulse per area (Fig. 9.57) [67]. These parameters allow to make plain the influence of the photon energy, see Table 8.1. The absorption edges in the UV range of the transmission spectra shift from the position for unexposed glass towards to higher wavelength for the glasses that were exposed to increasing photon energy.

Moreover an adsorption band exists, visible as shoulder from $300 \text{ nm} < \lambda < 320 \text{ nm}$. The transmission in this wavelength range decreases in general with increasing energy of the UV radiation used during the exposure process. It was identified as the absorption band of Ce^{3+} with a maximum at $\lambda = 310 \text{ nm}$ [75,496,505]. The maximum of the absorption band is almost identical to the emitted wavelength of the XeCl-excimer laser. This fact enlarges the absorption after exposure just to this excimer laser. The light at this wavelength excites the $4f \rightarrow 5d$ transition of Ce^{3+} ions causing the emission

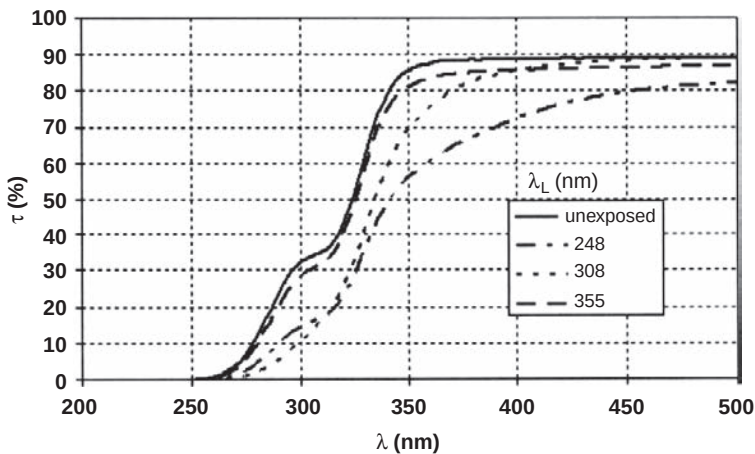


Fig. 9.57. Transmission spectra τ of unexposed and UV-exposed FS21 glass sheets of 1 mm thickness. FS21 was exposed to various wavelength λ_L at $\varepsilon_L = 2 \text{ J cm}^{-2}$; $N_{\text{eff}} = 1$ [67]

of a photoelectron. The emitted photoelectron remains in the vicinity of the cation it originated from. For this reason the symbol Ce^{3++} is used instead of Ce^{4+} .

The degree to which the absorption shoulder disappears after the laser treatment provides a measure to the extent the photochemical reaction progressed. The adsorption spectra of the unexposed glass and the glass that was exposed to 355 nm light are not very different. The glass is almost transparent to this radiation so that almost not any interaction between the light and the material occurs. The absorption band disappeared completely after exposing the glass to a laser beam of 308 nm, which indicates that all Ce^{3+} ions were converted into Ce^{3++} . Ce^{3++} absorbs at $\lambda = 270$ nm as shown by various investigators [8, 305, 505] which is not visible in Fig. 9.57. Exposing FS21 to a 248 nm laser leads only to a significant reduction of the absorption band, indicating that not all Ce^{3+} was converted which is due to the fact that most light is directly absorbed at the glass surface.

The optical densities of the glass sheets exposed to UV light were calculated as function of the laser wavelength the glass was exposed. Using the transmission spectra Brokmann [67] could confirm the $\text{Ce}^{3+}/\text{Ce}^{3++}$ transition in dependence on the applied laser energy density. Figure 9.58 shows the results of the differences in the optical density ΔOD of FS21 after exposure to 308 nm. ΔOD is the difference of the optical density of the material that was exposed to UV light and the unexposed material expressed by the logarithm of the reciprocal transmission quotient, see (9.4):

$$\Delta\text{OD} = \log \frac{\tau_{\text{nexp}}}{\tau_{\text{exp}}}, \quad (9.4)$$

where τ_{nexp} is the transmission of the unexposed sheet at λ and τ_{exp} the transmission of the exposed sheet at λ .

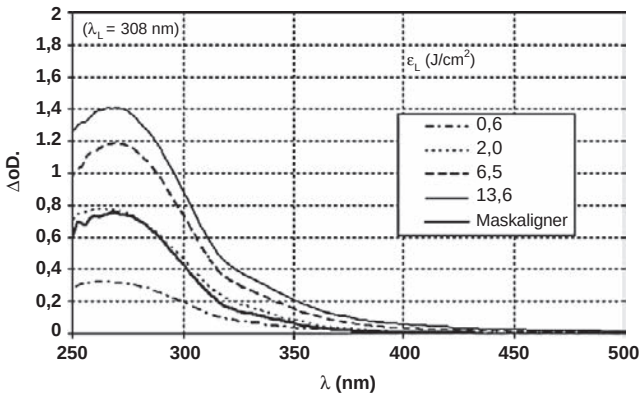


Fig. 9.58. Difference of the optical densities ΔOD as function of the wavelength and the energy density ε_L after exposure to a 308 nm laser [67]

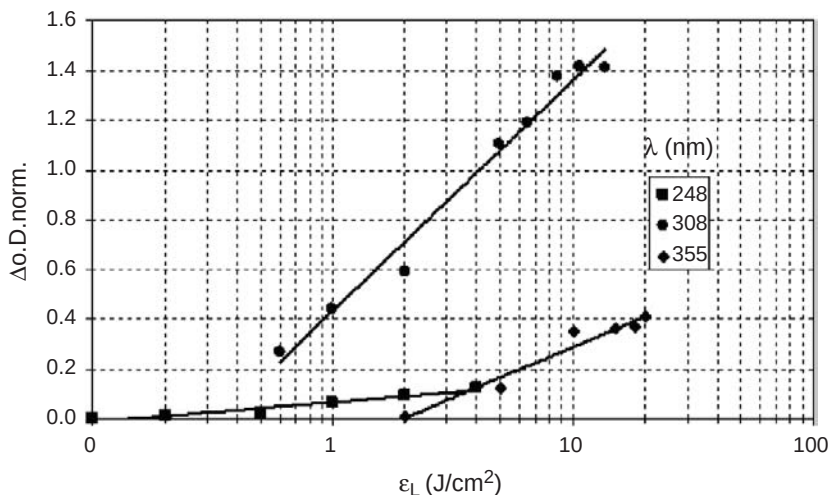


Fig. 9.59. Difference of the optical densities at $\lambda = 270$ nm after laser exposure [67]

The adsorption maximum at 270 nm, as an indicator of the $\text{Ce}^{3+}/\text{Ce}^{3++}$ transition, increases with increasing intensity of the 308 nm laser. Figure 9.58 also shows the difference of the optical densities as function of the wavelength of FS21 after exposure by a mask aligner, which emits a broad band radiation. The intensity in the 308 nm range corresponds to an energy density of 2 J cm^{-2} of the excimer laser.

Figure 9.59 summarises all results of the optical density difference at $\lambda = 270$ nm normalised to unexposed FS21. As can be seen the XeCl-excimer-laser generates most photoelectrons resulting in an increase of the absorption and optical densities. The generated photoelectrons are initially in the vicinity of the Ce ions, but with increasing temperature, i.e. increasing mobility, they migrate to reduce Ag^+ to $\text{Ag}^{\pm 0}$.

9.3.3 UV-Laser Assisted Photostructuring

UV-laser assisted photostructuring also requires a thermal treatment and an etching to open the geometrical structures (Fig. 9.1). However, UV-laser assisted photostructuring enables to generate quite other shaped geometrical structures, because different amounts of photoelectrons are generated depending on the laser wavelength used. Furthermore, the absorption behaviour of the glass depends on the laser wavelength which affects the penetration depth of the beam into the glass, which controls the structural depth of the features created [67, 69, 212]. Laser light causes scattering which affects the dimensional precision of the structures created. UV-laser assisted photostructuring allows writing of structures point by point. These points can either overlap or not. Furthermore, a defocused laser beam and a mask can be used. However,

the complete glass sheet is not exposed simultaneously as compared to a continuous mask aligner radiation, see Brokmann et al. [69].

Because the UV wavelength of $\lambda = 308$ nm is in resonance with the Ce^{3+} absorption band, it generates most photoelectrons and consequently the most nuclei that will eventually be able to grow. However, the more the nuclei are generated the smaller the crystals are. An exposure using a wavelength of $\lambda = 355$ nm generates less photoelectrons and even fewer ones are produced at a wavelength of $\lambda = 248$ nm, which results in the growth of larger crystals as shown in Fig. 9.60.

The crystal size as function of ε_L and λ_L is shown in Fig. 9.61. The surface roughness of the walls of the features after the etching away of the LMS

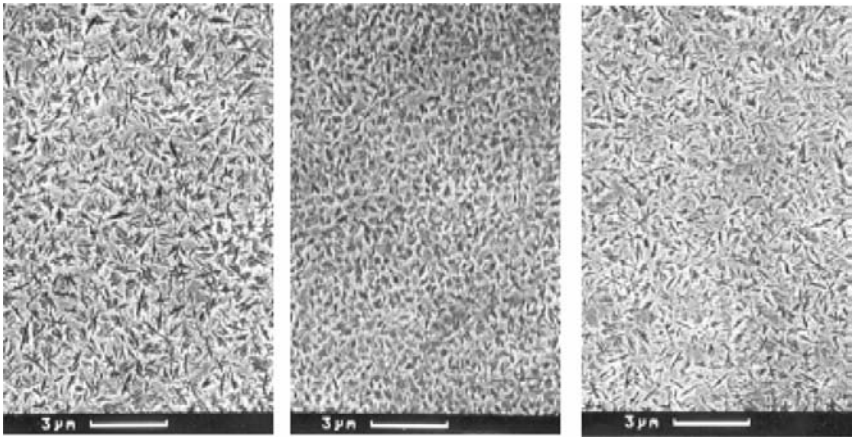


Fig. 9.60. Scanning electron micrographs of FS21 after exposure to UV light ($\varepsilon_L = 5 \text{ J cm}^{-2}$), tempered for 60 min at 570°C and 5 min etched in 0.5% HF (*left* $\lambda_L = 248$ nm, *middle* $\lambda_L = 308$ nm, *right* $\lambda_L = 355$ nm) [67]

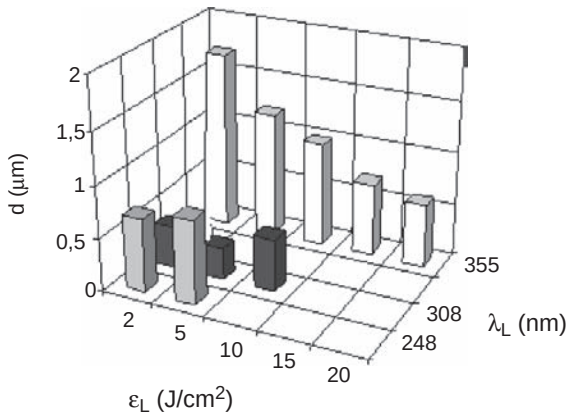


Fig. 9.61. Resulting crystal size as function of ε_L and λ_L [67]

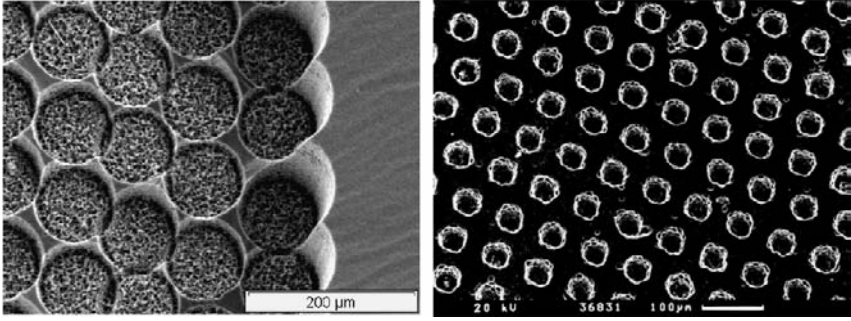


Fig. 9.62. Scanning electron micrographs of sack holes after exposure ($\varepsilon_L = 1 \text{ J cm}^{-2}$, $N_{\text{eff}} = 1$), tempered 60 min at 570°C and etched 10 min at 30°C in 10% HF (*left* $\lambda_L = 308 \text{ nm}$, *right* $\lambda_L = 355 \text{ nm}$) [67]

crystals is proportional to the crystal size. The precision of the structural contours is strongly affected by scattering effects. The dimensional precision is best when using 308 nm laser.

Because of the bad absorption of the 355 nm radiation and the not even distribution of the energy density over the pulse cross section (maximum in the centre) despite the same diameter of the laser-beam focus, the crystallised and etched away structures do not exhibit the same areas compared with $\lambda = 308 \text{ nm}$, which is seen in Fig. 9.62.

Complex structures e.g. free-standing meander springs and microfluidic elements are generated by Helvajian [212]. Controlling the intensity and the focus of the laser beam in relation to the critical dose it is also possible to create embedded structures [154, 212, 507].

Joining Methods for Glass Based Microdevices

10.1 Adhesive Bonding of Glass Parts

Adhesive bonding of glass parts is a very fast, simple and inexpensive joining technique. It can be used to join glasses to all materials and is very flexible [341]. However, the disadvantage of adhesive bonding is the necessity of an additional material, i.e. the adhesive which often results in a low thermal and chemical stability of the bond. Furthermore, adhesive joints tend to have limited long term stability.

Three main types of adhesives commonly used for the joining of glass devices in the microtechnology are UV-curable adhesives, epoxy-based adhesives and cyanoacrylates. UV-curable adhesives are the most widely used adhesives for glass joining. Because of their low viscosity these adhesives can simply be spread over the surfaces. The parts to be joined can be easily positioned and fixed because the adhesives cure only if exposed to UV light. However, UV-curing requires that the material is sufficiently transparent for UV light, which is the case for glasses.

The curing of epoxy-based adhesives is either induced thermally or chemically or occurs as a result of combined action. Epoxy-based adhesives can be one- or more-component systems. The viscosity of epoxy-based adhesives is rather high, which causes problems if structured surfaces are to be bonded. The curing of the adhesives starts either directly after the mixing of the components or during thermal heating.

Cyanoacrylate adhesives (such as Superglue or Krazy Glue) are also known as instant adhesives because of the short curing times. Cyanoacrylates are an acrylic resin that rapidly polymerises in the presence of humidity (water) forming long polymer chains, thereby joining the bonded surfaces together. The disadvantage of cyanoacrylate-based adhesives is the very short time window available for positioning of the parts to be joined.

The properties of the adhesives can be modified by the addition of metal or other powder fillers. Electrically and thermally conductive adhesives

are of particular importance, because they integrate two functions simultaneously, i.e. mechanical joining and stabilizing combined with electrical conductivity [16].

Under normal conditions glass surfaces are hydrolysed because of the humidity in the surrounding atmosphere. OH^- groups and also H^+ -bridge-bindings occur. Because of the hydrophilic nature of glasses, complete H_2O molecules are also present on glass surfaces, which often result in poor adhesion. The resulting adhesion is not primarily the adhesion between the glue and the glass surface, but the interaction between the hydroxyl groups at the surface and the adhesive [440]. The surface hydroxyl groups can be removed, but it is rather expensive. An intimate contact between the adhesive and the glass surface is a prerequisite for good adhesion, which requires a small contact angle between the glass and adhesive. For good adhesion the adhesive should wet the parts to be joined completely.

The successful application of the adhesives is a major problem in the microtechnique [22]. The amount of the adhesive used and its viscosity should be optimised with respect to surface area and the shape of the surface. Often a pulsating pressurised capillary system is used to apply tiny amounts of adhesives [22]. Overflow trenches allow for the removal of adhesive that is not required to bond the surfaces. These trenches help to protect the geometrical fine structures against unintentional filling by the adhesive.

The application of adhesives can also be assisted by various other means. For instance, it is possible to use spaces with a predefined depth to dose exactly the amount of glue required. An adhesive with a low viscosity will penetrate these spaces under capillary action. This technique is called capillary space adhesive technique and is very often used in the microtechnique for example to join microvalve systems by adhesive bonding [341]. The fabrication of a micropump and the optimisation of microstructures for the adhesive bonding process are described in the literature [339, 340].

Adhesive bonding is very often used for microoptics applications [125, 126]. The most commonly used adhesives for microoptics applications are UV-curable adhesives with low shrinkage and low thermal expansion coefficient. To minimise the shrinkage and to optimise the adhesion and positioning, only very small volumes of adhesives can be used. For instance, the joining of fibre end faces requires 0.5–1 nl and the joining of a planar surface to a cylinder lens requires between 5 and 30 nl. The precise dosage of such volumes is extremely difficult using conventional techniques, such as piston pumps. Alternatively, stamp-transfer-methods are used for such applications. The adhesive volume depends on the size of the stamp, the viscosity and surface tension of the adhesive as well as on the immersion depth of the stamp into the adhesive reservoir. This technique enables the volume transfer down to 0.1 nl.

10.2 Joining Using Glass Solders

Glass soldering is of major importance in the microtechnique. The method is used to join glass to glass, glass to other materials and also to join other materials to each other. Glass solders are special glasses with low softening temperatures. The joints produced using glass solders are hermetically dense and electrically isolating. If glass solders are used the thermal expansion coefficient of the parts to be joined and of the glass solder as well as the necessary temperature for joining have to be considered. The joining takes place at temperatures above the transformation temperature of the glass solder used. The joined materials contract during cooling. The dimensional change is governed by the thermal expansion coefficient of the joining partners as well as the glass solder. At temperatures below the transformation range the glass becomes brittle-elastic (see Sect. 3.3.3) so that viscous flow is prevented. Any difference in thermal expansion behaviour of the joining partners and the solder will result in thermal stresses in the joining zone. A small compression stress in the joining space is desired. Therefore, the thermal expansion coefficient of the glass solder may be by $0.5\text{--}1 \cdot 10^{-6} \text{ K}^{-1}$ smaller than those of the joining parts as reported [105]. For the joining of glasses the residual stresses should be in principle minimised, which makes it necessary that the thermal expansion coefficients of glass solder and joining parts are matched.

The maximum joining temperature is given by the material of the parts to be joined and the actual use conditions of the joined device. It is advised to use the lowest possible joining temperature. In praxis the thermal expansion coefficient of the glass solder is linked reciprocally to the joining temperature [397]. A lower thermal expansion coefficient of the glass requires that the joining temperature increases frequently.

Three types of glass solders can be distinguished: stable glass, crystallising and composite glass solders. Stable glass solders require comparatively high soldering temperatures and have thermal expansion coefficients between 3 and $6 \times 10^{-6} \text{ K}^{-1}$. After soldering and cooling these solders remain glasses. If the temperature is increased above the soldering temperature the solder starts to soften again, which allows to dismantle the join parts or to rebond the surfaces.

Crystallizing glass solders are used in the amorphous state. These solders have a lower soldering temperature compared with stable glass solders. During the thermal soldering, in the range of soldering temperatures, the solder additionally crystallises into a polycrystalline, ceramic-like material. These joints can withstand significantly higher temperatures compared with stable glass solders.

Composite glass solders consist of a glass phase and a crystalline phase with a low thermal expansion coefficient. The crystals are inert and dispersed in the glass phase. The thermal expansion coefficient of the composite is given by the rule of mixture of the thermal expansion coefficient of the glass phase and the inert crystalline phase. The addition of the crystalline phase allows to tailor the thermal expansion coefficient of the solder at given soldering

temperature or to reduce the soldering temperature at a constant thermal expansion coefficient of the solder.

Glass solders are used as powders or as geometrically pre-pressed and pre-sintered bodies. The powders are dispersed in water or alcohol or mixed with a binder into a paste. Glass solders are applied by painting, spraying, screen printing or as sintered body. Before soldering the binder must be evaporated or burned off in order to prevent boiling and therefore seed formation. Paschke [397] reviewed various applications of different glass solders.

A very detailed investigation into the joining of silicon using glass solders as well as for the joining of low expansion glasses, such as Pyrex-type glasses, was performed by [536]. Of major interest is the minimisation of stresses in the joining zone in order to minimise any detrimental effect on the fabricated devices, for instance the deformation of a membrane by the resulting stress induced by the soldering seam. Reactions of the solder glass with silicon can affect the composition of the soldering zone, which affects the functioning of piezo-resistive pressure and acceleration sensors [372]. In the case of sensor applications the maximum admissible soldering temperature is often limited by additional components present, such as metal layers.

In cathode ray tubes and plasma display panels frit glasses are commonly used to join parts. For these applications low sealing temperatures are required and environmentally harmful components have to be avoided. Because of this new frit glasses were developed [84]. The sealing temperature used for the former standard sealing frit with a lead oxide content of more than 70 mass % was reduced from 450°C to 390°C by modification of the chemical composition of the glass solder. This was possible by reducing the PbO content while increasing the ZnO content and by the addition of Bi₂O₃ and TiO₂ as well as small amounts of other components. However, the low softening temperature of the glass was paid with a high thermal expansion coefficient. But it could be tailored by the addition of low-expansion ceramic fillers. Furthermore, a lead oxide-free sealing frit with a sealing temperature of 450°C was developed [84].

He and Day [200] reported the development of low-temperature phosphate sealing glasses. The P₂O₅-PbO-ZnO system with various amounts of lithium or other oxides was demonstrated to be a useful solder glass with a thermal expansion coefficient in the range between 8 and $9 \times 10^{-6} \text{ K}^{-1}$ and a dilatometric softening temperature of 370°C. The chemical stability of the solder glass in water was similar to that of conventional window glass.

10.3 Diffusion Welding

Diffusion welding is a solid state high temperature welding process to join surfaces using the simultaneous action of pressure and heat. Diffusion welding is of particular interest for the joining of metals and ceramics often with additional interlayers [3, 103]. A discussion of the theoretical basis and the principle of bonding by diffusion welding can be found in the literature [352].

The diffusion welding processes are also used to join glasses [297, 299, 447]. They can be joined when heated up to the transformation range in which viscous flow starts (see Fig. 1.11) and diffusion processes become appreciable. Very smooth glass pieces can be joined by diffusion welding simply by heating the materials under pressure. The surfaces to be joined are pressed against each other at room temperature, which causes the surface layers up to a depth of some nanometre to break so that centres of physical contact form. Another possibility is to press glass parts of a sufficient surface quality against each other so that attractive interaction forces between the gel layers, formed due to the absorption of water, are created. This interaction forms the initial physical contact between the surfaces. Heating is required to induce the formation of chemical bonds. Chemisorption starts between the physically activated centres transforming the physical contact into a chemical contact. Upon further heating this contact area grows by diffusion processes, which will eventually join the glass pieces. This process does not require any additional materials for joining and is therefore commonly used to join optical devices. However, this process is suitable only to bond materials with very similar thermal expansion coefficients [580].

In microtechnological applications often very small glass parts have to be joined, which causes problems. The major requirement of the diffusion welding process is the quality of the original surfaces to be joined, i.e. the surfaces have to be planar and very smooth, and the second problem is the chemical behaviour [355].

10.4 Laser Beam Welding

Laser beam welding is a highly flexible joining technique. The laser beam is used as a concentrated heat source that allows for narrow, deep welds and high welding rates. The laser beam is used to soften and melt the glass selectively. Laser soldering, laser brazing and laser welding are distinguished depending on the temperatures used and the materials that can be joined [325]. In laser soldering and laser brazing often metals and metal alloys are joined. These techniques are mainly used in the field of microelectronics and contacting techniques. However, laser welding is a flexible method that can be used to join many other materials. The main advantages of laser welding are that the energy is supplied contactless and can be directly coupled in the joining zone. Very narrow joining zones are possible because the laser beam can be focused exactly, which enables excellent controlled positions of heated spots in time and place. Most materials can be joined by selecting the wavelength of the laser beam.

Glasses can be easily joined with non-transparent materials using Nd:YAG-lasers emitting a wavelength of 1,060 nm. Most glasses are transparent for this wavelength and, therefore, it is possible to couple the laser beam directly into the joining zone through the glass part [173]. If the surface of the other joining

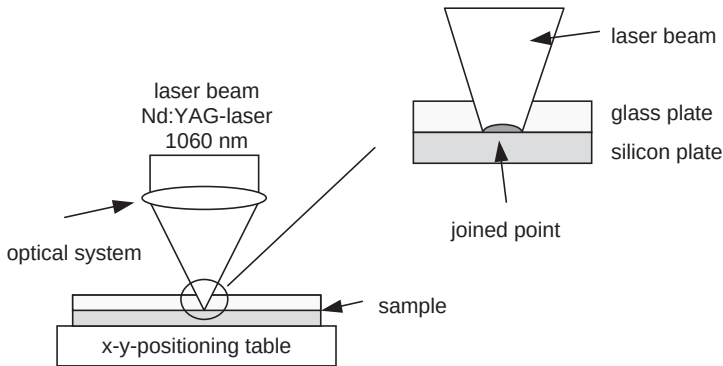


Fig. 10.1. Laser welding. The laser beam is coupled directly in the joining zone through the volume of one of the joining partners

part is not transparent to this wavelength, absorption of the beam results in heating up of the contact zone but only in the focus of the laser. This localised heating causes the formation of a melting zone and the joining of the materials. A schematic of this process is shown in Fig. 10.1. However, this process can only be used if at least one of the parts to be joined is transparent. For instance silicon can be directly bonded to glass using a laser. It is also possible to place a polymer film between the two parts to be joined. The polymer film is melted forming a glass–polymer–silicon join.

A method (the principle of joining, the effects during the laser treatment and differences between various materials) to join quartz glass using a CO₂-laser was demonstrated [370]. The advantage of quartz glass for joining is its very low thermal expansion coefficient ($5 \times 10^{-7} \text{ K}^{-1}$), which means that it can be welded without significant temporary stresses. However, quartz glass starts to evaporate far below its melting temperature, which makes it necessary to compensate for the volume lost. The material loss can be compensated by feeding a filler material also quartz glass into the melting zone.

10.5 Ultrasonic Welding

Ultrasonic welding is not normally considered to be a microjoining technique. However, the process can be used to join glasses and could be miniaturised. The principle of ultrasonic welding is illustrated in Fig. 10.2.

Ultrasonic welding uses high-frequency ultrasonic acoustic vibrations to bond surfaces together. The ultrasonic frequency is commonly in the range of 20–40 kHz. The ultrasound is generated by an ultrasonic generator, and a piezoelectric converter transforms the ultrasound frequency into a mechanical oscillation. The booster–sonotrode unit intensifies the oscillation up to amplitudes of 10–20 μm . This amplitude of the horizontal oscillation is coupled

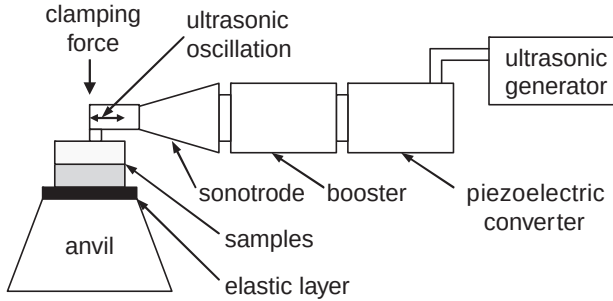


Fig. 10.2. Ultrasonic welding

into the stack of workpieces to be joined by a vertical clamping force. The workpieces are placed on an anvil, which is protected by an elastic interlayer.

The main welding parameters, i.e. force, amplitude, time and energy, can be controlled in this arrangement. Often the sample temperature is monitored and controlled using a heating system [426]. One advantage of ultrasonic welding is that the process does not require any surface treatment before joining. Furthermore, the joining can actually be performed in normal atmosphere and at joining temperatures below 400°C. Ultrasonic joining is very fast. The joining time is in the range of 1 s. However, in ultrasonic welding the booster-sonotrode unit needs to be tuned to the frequency required to join a certain material. Furthermore, ultrasonic welding exerts a relatively high load on to the material during the joining process.

Ultrasonic welding was used already in 1968 for the joining of glasses to aluminium [493]. It was possible to join glass directly to aluminium; however, it could not be joined to copper. The very hard aluminium oxide layer combined with the ductile behaviour of the underlying metal was found to enable the welding process. In the initial phase of the process the aluminium oxide layer grinds into the glass surface providing a very good point contact between the materials. The joining starts during the ultrasonic activation if the maximum force is applied. The bonding front moves from this point to the margins of the contact zone.

Reuter [423] investigated the ultrasonic joining of glasses and glass ceramics to metals in detail. The welding of the workpieces to be joined takes place only when the lower piece is fixed to the anvil so that a relative movement between the joining parts is possible. This relative movement creates a ramp in the continuous gradient of oscillation amplitude during joining the pieces. The high mass of the anvil compared to the joining partners prevents its oscillation. The following observations were made during the joining of Tempax-glass to aluminium. It was found that the necessary joining time decreases with increasing joining force. An increasing joining time and oscillation amplitude leads to an increase in the joined surface area. However, the increased joining time and oscillation amplitude result in a decrease of the joint strength.

A direct joining of glasses by ultrasonic welding is impossible. Glasses can be joined only by using an aluminium interlayer.

Roll seam welding enables for continuous ultrasonic welding [130]. The principle is similar to ultrasonic spot welding but the anvil is replaced by a two-axis transport system. The sonotrode now has a wheel at its end. The continuous movement of the table with the joining pieces relative to the sonotrode allows for the formation of a continuous joined seam. This method was found useful for the joining of various glasses using an aluminium interlayer and for the joining of glasses to steels and aluminium.

It is commonly assumed that the thermal activation of the ions near the surface by ultrasound during the welding process causes the materials to bond together. The application of a static force during the welding process affects changes of place in the atomic distance, and by diffusion new chemical bonds form between the parts to be bonded. It was shown by high resolution transmission microscopy that the bonded layers for aluminium/alumina compounds are in the order of 5–20 nm. In the case of glass/metal bonds using aluminium interlayers the oxygen near the surface form a bridge between the ions of the glass and the aluminium ions in the interlayer. Interdiffusion processes between the aluminium interlayer and the metal part are also important, which occur often in combination with microscopic melting between joining components [130].

10.6 Thermal Bonding

Thermal bonding is a joining method that does not require any additional bonding material. Thermal bonding falls in between diffusion welding, which causes no deformation of the joined parts, and melt welding in which the joining zone undergoes complete deformation [190, 193]. During thermal bonding the glass parts are heated up to temperatures above the transformation temperature of the glass (see Sect. 1.1.4). At this temperature the material can undergo a limited flow under pressure. The main advantage of this bonding method is the possibility to join parts with rough surfaces. In contrast to diffusion welding thermal bonding does not require any additional polishing processes. Polishing of glass sheets containing very fine structures is rather difficult. The polishing might cause damage or crack formation.¹ Thermal bonding enables to weld photostructured glass directly after the structuring process and, therefore, reduces the processing costs remarkably.

Prior to thermal bonding the glass pieces should be cleaned and have to be positioned relatively to each other. After positioning the entire stack

¹ A possibility to avoid damaging of the fine structures is to fill the structures with a polymer or a wax before the polishing operation. The filling material can later be dissolved.

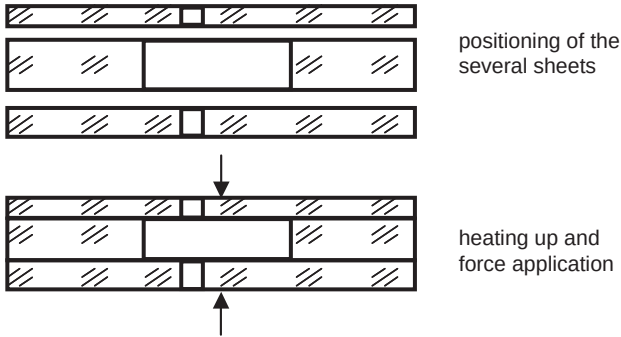


Fig. 10.3. The principle of thermal bonding

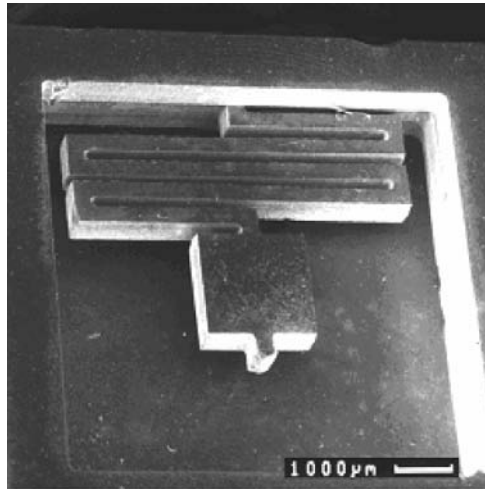


Fig. 10.4. A freely oscillating glass spring produced by thermal bonding [190]

is heated under pressure. An illustration of the thermal bonding process is shown in Fig. 10.3. The following ranges of process parameters for the joining of the photostructurable glass FS21 were investigated:

- Temperature: 450–550°C
- Pressure: 0.005–0.2 MPa
- Time: 30–1,000 min

A sample of a joined three sheets device is shown in Fig. 10.4. An increase of temperature and of joining time favours the bonding process and the stability of the joint. Simultaneously the precision of the contours deteriorates.

A partial joining of glass components is possible using thermal bonding by applying pressure selectively. The spring structure that is part of the middle sheet shown in Fig. 10.4 can oscillate freely. The structure was created

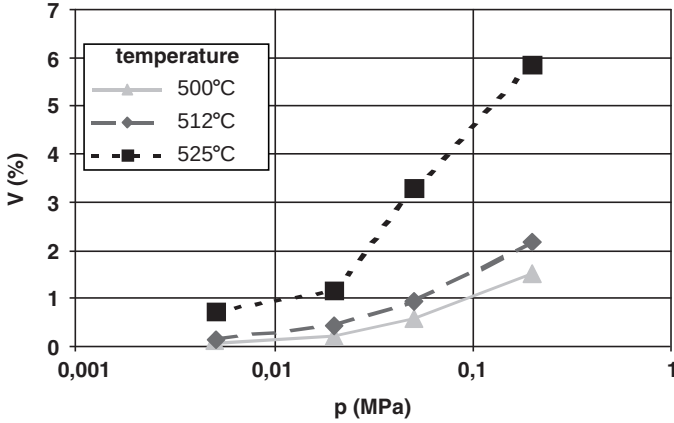


Fig. 10.5. Deformation V of glass samples as function of the joining temperature and pressure p after a joining time of 90 min [190]

by joining only at the outside frame structure. During the joining pressure was applied only to the frame structure. The spring structure was supported during joining to avoid any deformation of it.

A joining temperature of 525°C, a joining time of 120 min and a pressure of 0.05 MPa was found to be optimal for the joining of parts made of the photostructurable glass FS21. Under this conditions a stable joint forms and minimal deformation of the glass takes place. Figure 10.5 shows the observed deformation of a glass part as function of temperature and pressure for a joining time of 90 min.

At temperatures $\leq 512^\circ\text{C}$ no stable bond forms between the glass parts during the 90 min in the investigated pressure range. However, an increasing joining time for instance 1,020 min at 500°C leads to the formation of stable bond. For FS21 also a stable bond was found after bonding at a temperature of 525°C for only 60 min at a pressure of 0.02 MPa. These conditions allow minimisation of the total deformation V of the thickness of the stack to $<1\%$. An increase in joining pressure, however, results in an increase in deformation of the joined glass parts [190].

Stjernström and Roeraade [495] described a thermal bonding method for the fabrication of microfluidic elements. A sodium-lime silicate glass with a columnar structure was used to reduce the surface area of the bond. The columnar structures were made using isotropic etching while creating the fluid structure itself. When using the glass of columnar structures to assemble the device by thermal bonding, the quality of the bond formed was significantly better compared with a bonding without this columns.

A single chip combinatorial synthetic reactor was fabricated by thermal bonding three layers of Pyrex-glass for 5 h at 650°C under pressure [273]. The glass-to-glass bonding of Pyrex substrates was also investigated by [418]. The

thermal bonding was performed in a horizontal tube reactor at temperatures between 600°C and 800°C in nitrogen atmosphere using joining times of about 30 min. The quality of the glass–glass bond was found to improve with increase in joining temperature. However, even at temperatures as low as 600°C the glass sheets deformed. Therefore, a quartz–glass support was required.

10.7 Anodic Bonding

Anodic bonding is mainly used to bond glass to silicon or to metals. This technique is used for the manufacturing of sensors, microfluidic structures and microtechnical packaging in general [215]. The anodic bonding process is described for the packaging of sensors [102, 137, 215, 408] and also for the production of functional elements, such as inkjet printer heads [349]. Anodic bonding is also a cost effective process for the fabrication of silicon accelerometers using an one-mask process [256].

Anodic bonding was first reported in 1968 [410]. Figure 10.6 shows a schematic of the anodic bonding process. A detailed description of an apparatus for bonding at atmospheric pressure and in vacuum can be found in the literature [137].

The materials to be bonded, i.e. a silicon wafer and glass, are stacked up and heated up to temperatures that are typically in the range between 300°C and 500°C. A voltage of a few hundred volt up to some kilovolt is applied to the stack. The under electrode is commonly a surface electrode with integrated heater, whereas depending on the specific bonding apparatus, the upper electrode is a tip electrode or a surface electrode. The main process parameters are the voltage difference and current across the joining partners, the temperature and time for bonding as well as the roughness, flatness and cleanness of the glass sheets and silicon wafers. Furthermore, the thermal expansion behaviour of the different materials to be bonded has to be adapted.

Favoured by the increased temperature the alkali-ions in the glass, especially Na^+ in Pyrex-glass, become mobile and migrate under the action of the applied electrical field to the cathode (see Fig. 10.7), which eventually results in the formation of a depletion layer with high electric field strength in the contact area between the glass sheet and the silicon wafer. The resulting

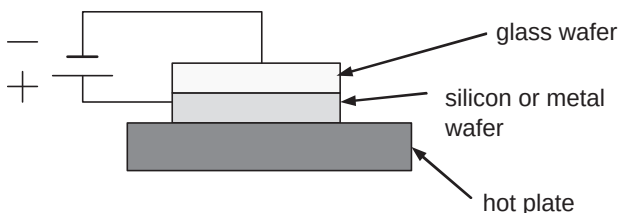


Fig. 10.6. The anodic bonding process

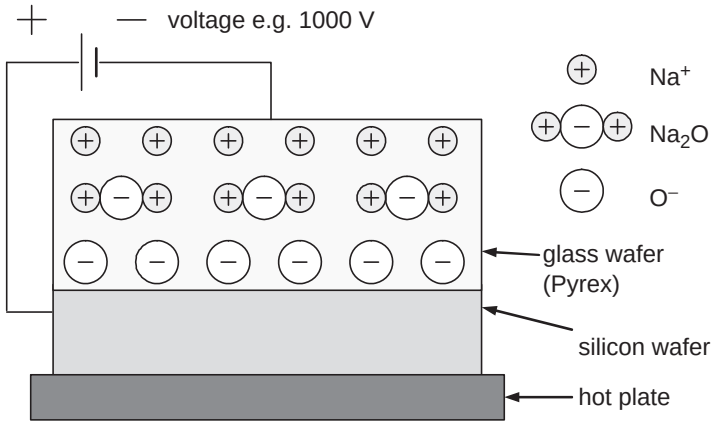


Fig. 10.7. An electrostatic field forms during the anodic bonding process caused by the migration of ions

electrostatic attraction forces the silicon and glass into intimate contact therefore promoting the joining process. The oxygen anions migrate in the opposite direction, from the glass to the silicon, which results in an anodic reaction at the interface causing the formation of permanent chemical bonds (Si–O–bindings) between the glass and the silicon at the contact surface.

The ion drift in borosilicate glasses during anodic bonding was examined by [320] using Elastic Recoil Detection Analysis. A significant drift of sodium and lithium ions was detected. The thickness of the depleted layer at technologically used temperatures and voltages was in the order of $1\text{ }\mu\text{m}$. The alkali drift rates level off at temperatures which are commonly used for anodic bonding.

The bonded sandwich is cooled after the joining process. To minimise any thermal stresses in the bond interface between the partners the thermal expansion coefficient of the glass sheet and silicon wafer should be very similar.

The glasses that are commonly used in anodic bonding processes are Pyrex type glasses, such as Tempax or Borofloat from Schott, SD2 from Hoya, 7740 from Corning or other specially composed glasses [244, 503]. Straube [503] developed glass that can not only be used for anodic bonding but can also be microstructured using a Nd:YAG-laser (see Sect. 8.2.2). The bonding behaviour of various glasses (Borofloat, Corning 7740, SD2, Corning FH-IZM) to silicon was investigated by [563]. All these glasses have matching thermal expansion coefficients to silicon and are therefore suitable for anodic bonding process.

Cozma and Puers [102] investigated the influence of anodic bonding process parameters on the bonding of borosilicate glass (Corning 7740) to silicon. They found that the temperature and voltage are the most critical parameters for the bonding process to control the residual stresses. For the investigated

combination, temperature of 360°C and potential differences between 750 and 1,000 V were found to be the optimal parameters.

Glass can also be joined to a partially metallised silicon wafer using anodic bonding [387, 388]. Anodic bonding is also suitable for the joining of two silicon wafers [189]. It requires, however, the deposition of a thermally adapted glass layer (borosilicate glass) on the surface of one silicon wafer, which can be performed by sputtering. This sputtered borosilicate glass layer can be structured and is used as the bonding material and also as spacer between the two silicon wafers. The anodic bonding of 3 in. wafers was performed at 400°C using a potential difference of 50–200 V for 10 min. The negative electrode is connected to the sputter-coated silicon wafer. Instead of sputtered borosilicate glass SiO₂ or Si₃N₄ layers are also suitable.

Glasses can also be bonded to metals via anodic bonding [341, 525, 545]. Corning 7740 glass can in principal be anodically bonded to copper, copper coated with electroplated gold layers, nickel and invar [341]. However, the mismatch of the thermal expansion coefficients of the materials results in cracking of the bonded samples during the cooling. However, this indicates that the bonding process was indeed successful. Other glasses with a higher thermal expansion coefficient, causing reduced stress, can in some cases successfully be bonded to metals.

A reduction of the temperature used for anodic bonding would be beneficial for obvious reasons. Choi et al. [95, 96] developed a method to bond silicon to silicon at low temperatures and low voltages using a vapour-deposited layer onto a silicon wafer. Corning 7740 glass was deposited by electron beam evaporation. The deposited layers were more than 1 µm thick and had almost the same composition as the bulk Corning 7740 glass. Anodic bonding could be performed at temperatures as low as 135°C and applied voltages as small as 35 V. Additionally the role of sodium ions during anodic bonding was studied.

Lengtenberg et al. [328] used an atmospheric pressure chemical vapour deposition to deposit boron oxide as an intermediate layer for anodic bonding.

Esashi et al. [136] developed an anodic bonding process for silicon wafers that works at room temperature. A low melting point glass was used as the intermediate layer. The glass used was code 7570 from Iwaki Glass Co. This glass with a strain point of 342°C was magnetron-sputtered on the surface of one silicon wafer. The glass layer had a thickness ranging from 0.5 to 4 µm. Bonding voltages in the range of 30–60 V and a pressure of 160 kPa were applied for 10 min. The process also allows for the bonding of materials with different thermal expansion coefficients.

Another anodic bonding process at room temperature was described by [161]. They developed sodium/lithium-niobate-phosphate glasses, which have a high electrical conductivity at room temperature. The electrical conductivity of these glasses is about two orders of magnitude higher than that of standard glasses commonly used for anodic bonding. The thermal expansion coefficient is in the order of $11\text{--}18 \times 10^{-6} \text{ K}^{-1}$. The mismatch of thermal expansion coefficient between the glass and silicon is not so important in this

case because the bonding process takes place at room temperature. These glasses can be anodically bonded to silicon at room temperature at voltages of 300 V. However, if the bonded sample is thermally loaded tensions in the joining zone arise. The bonds are stable in the temperature range from -40°C to $+40^{\circ}\text{C}$.

Thin layers of the glasses can also be deposited onto silicon surfaces by RF-sputtering.

10.8 Microelectroforming

Microelectroforming was studied in connection with the LIGA process [27,72, 185] and resist technique [133,134]. It enables to fill a microstructure of an insulating material, such as PMMA or an UV-resist, with a metal or an alloy. Microelectroforming is used in the LIGA process for the in situ formation of masks and also for filling of structured polymer parts with metals [336].

This method was first used by [192] for the fabrication of glass/metal structures. The process is schematically shown in Fig. 10.8. At the beginning the geometrically structured glass samples are made electrically contacting with copper foils or by vapour deposition of copper. Afterwards microelectroforming is followed and finally the structure is ground and polished to produce the finished glass/metal part.

The actual process of providing the electrical contact used for the microelectroforming process varies depending on the geometrical structures present in the glass, which can either have a defined depth or be through-thickness holes and slits, e.g. vias. On the one hand, vapour deposition is used to deposit a contacting layer in structures that have a defined depth, such as sack holes or trenches. If deep structures in the glass sheet are produced, a stripping of the vapour deposited metal layer at the top surface of the glass sheet is necessary to avoid the later uncontrolled metal deposition at the surface. All

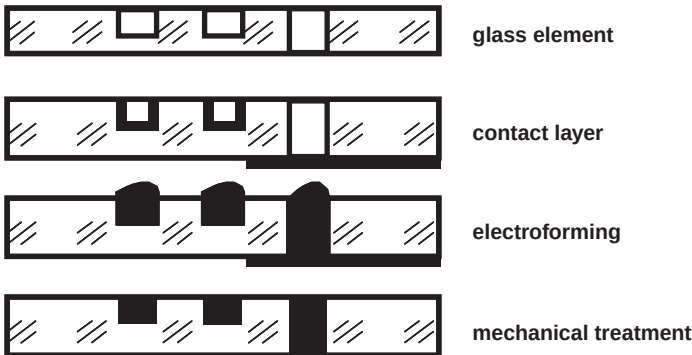


Fig. 10.8. Microelectroforming in structured glass parts [190]

metal-coated structures have to be contacted separately, or sacrificial structures must be to initiate the electrolytic metal deposition within the geometric structures. The sacrificial structures are removed after the microelectroforming by an additional mechanical grinding process. On the other hand, if metal is to be deposited in through-thickness holes and slits a metal foil can be used to provide electrical contact. This foil is simply pressed mechanically on the bottom of the structured glass sample. After the microelectroforming process the contact layer is removed.

The microelectroforming process starts at the contact layer and fills the structures in the insulator successively. Filling deep structures it is impossible to control the microelectroforming process so accurately that the metal electrodeposition stops exactly at the top of the geometrical structures in the glass insulator. Furthermore, the deposition rate varies from structure to structure so that an overgrowth of the metal has to be accepted. However, the overgrown metals can be easily removed in an additional grinding process.

The microelectroforming process differs from standard electroplating processes because the material transport in very fine and deep structures is mainly diffusion controlled. Therefore, the deposition rate of metals is often very low. Furthermore, the current density is very small which requires longer deposition times. Also, the wetting of the fine structures by the electrolyte can cause major problems. Therefore, electrolytes containing large amounts of wetting agents have to be used.

Frequently very different geometrical structures may be filled on a single sample, but the electroformed layer should have the same thickness. This requires that the macro and micro scattering capability of the electrolyte is high. Therefore, special additives are often added to the electrolyte and special arrangements of electrodes are used. If very fine geometrical structures have to be filled the electrolyte has to be filtered continuously to avoid blockages.

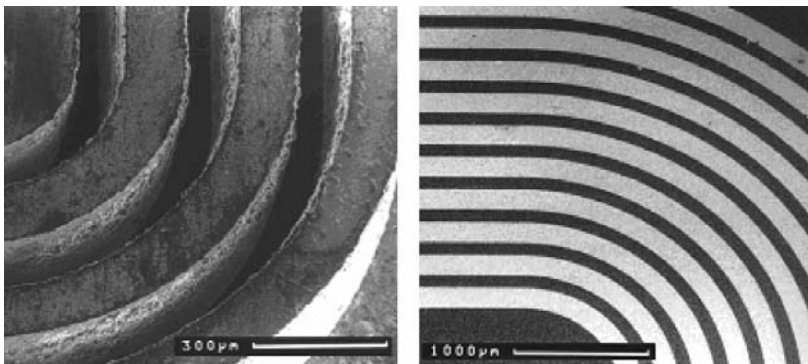


Fig. 10.9. Example of copper coil produced by microelectroforming using a microstructured glass template. (*left*) Copper coil after the removal of the glass template, (*right*) copper filled glass template

Furthermore, internal stresses in the electroformed structures can cause problems. The maximum stress should not exceed $10\text{--}20\text{ N mm}^{-2}$ to avoid damage of the glass structure [336].

Figure 10.9 (right) shows an example of a microelectroformed glass copper composite. The copper coil is part of an electrodynamic microactuator. The microstructured glass acts as a template (glass mould) for the production of the copper coil. Figure 10.9 (left) shows the copper coil after the removal of the glass in a solution of hydrofluoric acid. The depth of the structure is considerable. The surface roughness of the copper coil is due to the roughness of the glass template (substructures in the glass side walls, see also Fig. 9.11).

Properties and Selected Applications of Microstructured Glass Devices

11.1 Properties and Applications of Photostructured Glasses

11.1.1 Special Properties of Photostructured Glasses

The chemical stability of glasses is decisive for microfluidic, medicine and biological applications. It is characterised by the class of resistance against acids, water and lyes. The industrial standards DIN 12116, DIN 12111 and DIN 52322 provide a classification of the glasses. The chemical stability classes of the photostructurable glass FS21 are shown in Table 1.7.

The durability of polished or grinded surfaces of FS21 glass sheets was further studied by eluting tests in various fluids [196]. Glass samples were removed in intervals from the fluids and dried, and the mass loss was measured.

The results of the eluting tests of polished samples of some square centimetres are shown in Fig. 11.1. No significant mass loss of FS21 immersed into acidic solutions, organic solutions and water was detected. However, the mass loss in alkaline solutions, such as NaOH, Tiutol, is measurable but sufficiently small, which is still acceptable for cleaning purposes. The mass loss of the glass in alkaline solutions increases with the duration of the immersion. The chemical attack on the ground glass samples follows the same principle; however, the mass loss is nearly twice as big as that of the polished samples. This behaviour is expected because an increase of the real surface area leads to an increase in the area for chemical interactions.

It is possible to maximise the chemical stability in acidic and alkaline solutions by an additional surface coating. For instance, protective silicon nitride and silicon oxide coating are deposited using CVD-deposition [246]. These layers lead to a significantly increased durability of the glass. In particular, the silicon nitride layer leads to a much improved durability in alkaline solutions whereas the silicon dioxide layer enhances the durability against acids.

The mechanical properties of photostructured FS21 glass are relevant for all applications. A three-point bending test was used to determine them. Glass

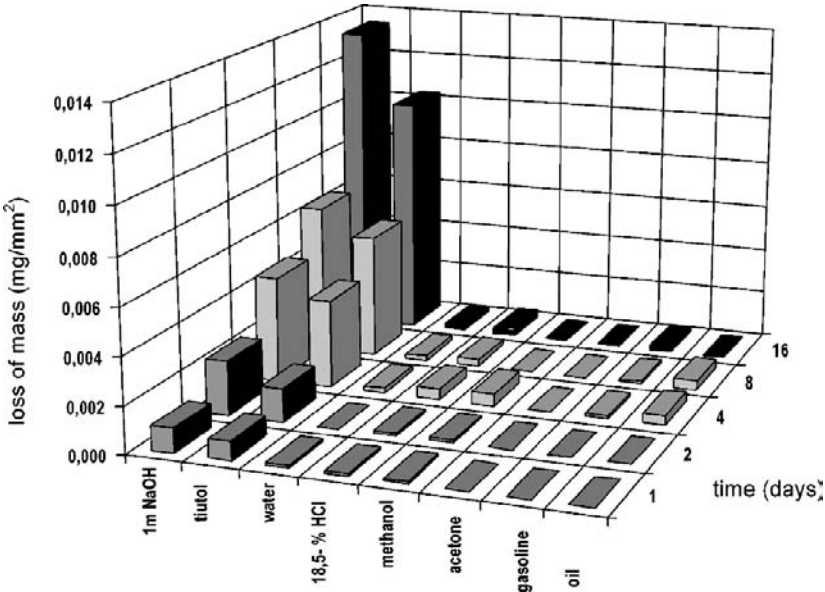


Fig. 11.1. Mass loss of polished FS21 glass during the eluation in various solutions (Tiutol is an alkaline cleaning fluid used to clean medical devices) [196]

Table 11.1. Results of a three-point bending test of variously structured FS21 glass bars

Treatment	Photostructurable glass	
	Microsawed	Photostructured
Maximum force (F)	5.33 ± 0.33	7.44 ± 1.22
Maximum deflection (mm)	0.17 ± 0.02	0.42 ± 0.07
Young's modulus (GPa)	82.1 ± 0.4	78.1 ± 1.2
Bending strength (MPa)	194 ± 20	385 ± 61

beams with a cross-sectional area of $1 \times 0.9 \text{ mm}^2$ were tested. The bearing distance used was 20 mm. The samples were loaded at a cross-head speed of 0.1 mm min^{-1} . At least 20 samples were tested and the values reported are averages and the error is the standard deviation [190,191]. The bars were made using a mechanical microsaw equipped with a diamond wheel at a commercial wafer cutting facility and also the photostructuring process as described in Sect. 9.1.1 and Fig. 9.1. Both processes yielded samples with a comparable roughness of the structured surfaces. The results of the three-point bending test are shown in Table 11.1. The measured bending strength is high compared with the bending strength of commercially available glass products, which is typically in the range of 50–80 MPa. The increased bending strength is due to the small cross-sectional area of the tested beams. A reduction in the cross-sectional area leads to a reduction of the absolute amount of defects

in the very small products and consequently to reduction in the probability of fracture. This effect is very well known for glass fibres. Moreover, the photostructured test bars had a significantly higher bending strength as compared to the microsawed glasses composed in the same way, which can be explained by the differences in the structuring processes. Microsawing using a diamond wheel causes the formation of microcracks on the surface, which is caused by the impact of the grains of the cutting wheel on the glass material. During the bending test, tensile stresses arise at the under side of the bar which causes these cracks to open and grow, finally leading to the early fracture of the sample. The bending strength of the glass elements structured using the microsawing process can be increased using an additional acid polishing step. The last step of photostructuring process is really an etching process comparable with an acid polishing. Photostructuring does not require mechanical tools and, therefore, no cracks are initiated during the structuring process. Instead of this, a rounding of the glass tips occurs after the removal of the LMS-crystals (see Sect. 9.1.4) leading to a reduction of the maximum stresses.

The high bending strength of the glass parts in combination with structuring in micrometre range is of particular interest. Photostructurable glasses could become a construction material in microtechnological devices. Possible applications are microsprings. Figure 11.2a shows glass microsprings with defined force–displacement characteristics to be loaded in the normal direction of the spring surface. The thickness of the glass parts is around 0.8 mm. The design dependence of the force–displacement behaviour can be clearly seen in Fig. 11.2b. It is possible to fabricate elastic glass structures of very different force–displacement behaviour by varying the design and thickness of the glass springs. The endpoints of the curves (Fig. 11.2b) are given by the measuring system used (displacement 1 mm and force 1 N) but not by the failure of the springs.

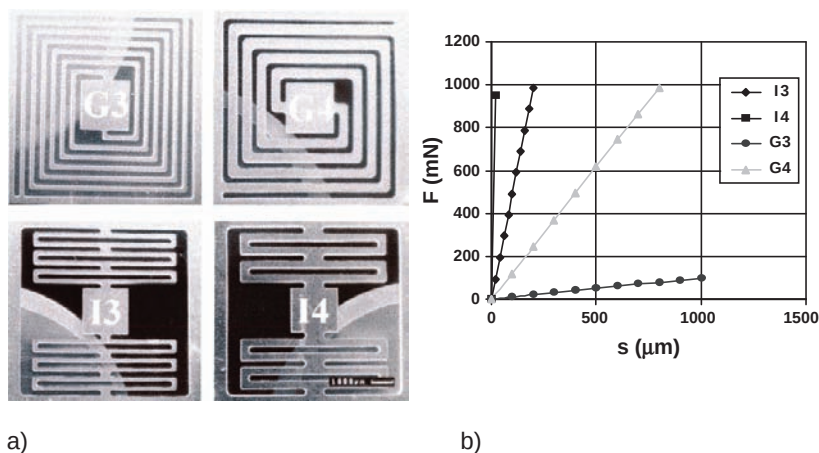


Fig. 11.2. Various FS21 glass springs (a) and their force–displacement behaviour (b)

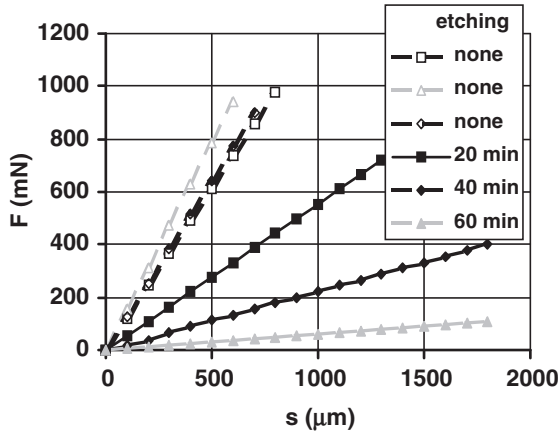


Fig. 11.3. Force–displacement behaviour of glass springs without or with an additional isotropic etching step [190]

The force–displacement behaviour can also be tailored using an additional isotropic etching of the produced samples, which is demonstrated in Fig. 11.3. Three G4-type springs (see Fig. 11.2a) were tested and the force–displacement behaviour was measured before and after etching for various etching times. During the isotropic etching process material is removed from the complete surface of the glass springs causing a reduction of the cross-sectional area of the spring. This in turn affects the constants of the spring.

The fatigue behaviour of microstructured glass parts is of major importance for any application of glass elements in various fields. The fatigue performance of the manufactured FS21 glass springs (type G4) was tested by cyclic loading between zero and maximum load (swelling load). The maximum displacement applied to the glass spring was $400\ \mu\text{m}$ in normal direction and the test frequency was 5 Hz. The force–displacement behaviour of the springs was characterised prior to the fatigue test and after several loading cycles (Fig. 11.4). An ideal elastic behaviour without relevant change in the force–displacement characteristic was observed for the springs even after 10^8 fatigue cycles. This result demonstrates that it is possible to use microstructured glass devices in measuring and gripping applications but also in the field of microactuators.

For applications in high precision measurement devices the elastic after-effects of the material is critical. These effects can be quantified using an interferometric system [6]. Special glass deformation elements utilising a parallel spring design were used for tests. The measuring facility was placed into a temperature controlled box. Different load was applied to the glass parts to be tested. The principle of the measuring system is shown in Fig. 11.5. After load removal and 30 min waiting at 20°C , further 34% elastic contraction relative to the entire contraction was measured. The value measured for FS21 is larger than that typically reported for other materials, such as fused silica

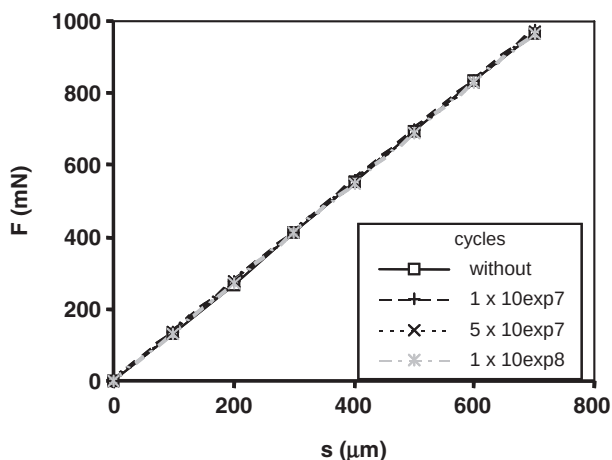


Fig. 11.4. Force–displacement characteristic of an FS21 glass spring (type G4) depending on a cyclic loading

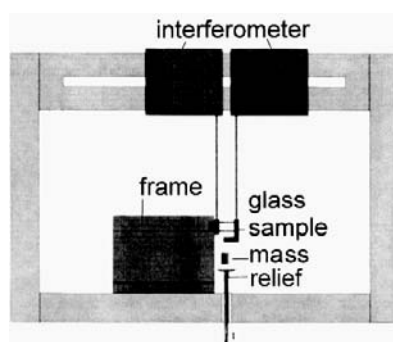


Fig. 11.5. Principle of an interferometer system for measuring the elastic after-effects

glass or aluminium alloys, used as deformation elements in precision measuring devices. However, the remaining deformation is expected to be minimised by inducing a partial crystallisation of the microstructured glass elements in an additional processing.

11.1.2 Applications of Microstructured Glasses in Medicine, Optics and in Microfluidic, Microreaction and Biotechnological Applications

Microstructured glasses are used in various areas, but to fully exploit all the possibilities offered by microstructured glasses new ideas are required and the materials properties and technical abilities must be fully understood.

In 1949 Stooky described the first application of photostructurable glass as photographic medium and in 1953 for geometrical structuring. Stooky demonstrated that various types of perforations, different patterns and sculptures could be created using this technology. He paved the way for many more technical applications for photostructurable glasses.

Photostructuring of glasses has been used for the fabrication of arrays of microlenses [20, 59]. The reported fabrication method does not rely on geometrical structuring by the last etching step but actually utilises only the thermally induced deformation of partially crystallised and glassy areas in the same sample (see Fig. 9.7b).

Photosensitive glasses have been used in the fabrication of dinnerware, in architectural applications and as artistic glass, and in technically more challenging applications, such as microlenses, alignment plates and cell sheets, which can be used to separate lighted pixels in displays [527].

Microstructured glass elements were already tested as deformations structures for medical applications. Figure 11.6 shows an example, a middle ear implant fabricated from photostructured glass [190]. This glass element was designed to transfer sound in the human middle ear [548]. This complex spring consists of two coupled elastic systems with different spring constants. An adjustment of the spring constants is possible by varying the thickness of the glass sheet and also by changing the conditions during the structuring process. In contrast to conventional middle ear implants, the frequency response of this microstructured glass element is adapted to the human cognition.

Figure 11.7 shows a scheme of a glass microvalve and its several parts [146]. This valve consists of a three-dimensional structured glass plate which was manufactured using the modified mask technique (see Sect. 9.2.7) and was combined using thermal bonding (see Sect. 10.6) to a glass membrane of the same photostructured glass. The membrane of a thickness of $100\mu\text{m}$ is mechanically produced by conventional grinding and polishing. During the thermal bonding a hermetically sealed bond between the base structure and membrane is formed. The valve actuator is a plunger coil. A tip closes and

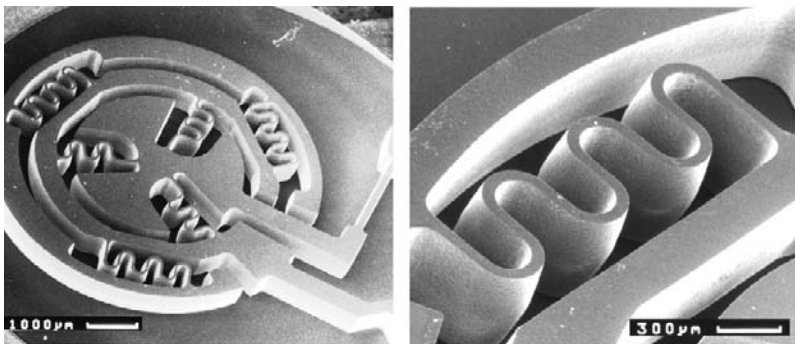


Fig. 11.6. Middle ear implant (Design: F. Wauro) made from microstructured glass [190]

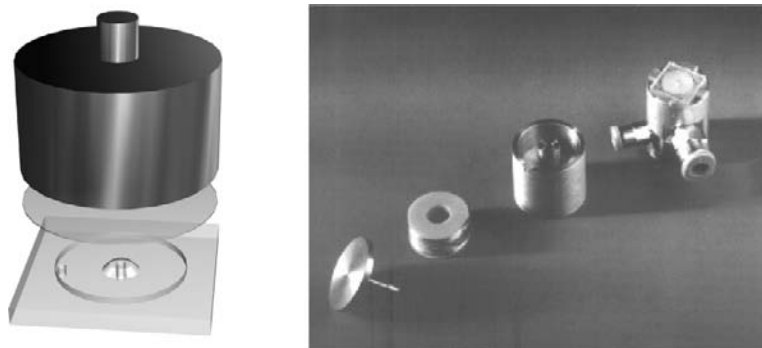


Fig. 11.7. Schematic of a glass microvalve (*left*) and its several parts (*right*)

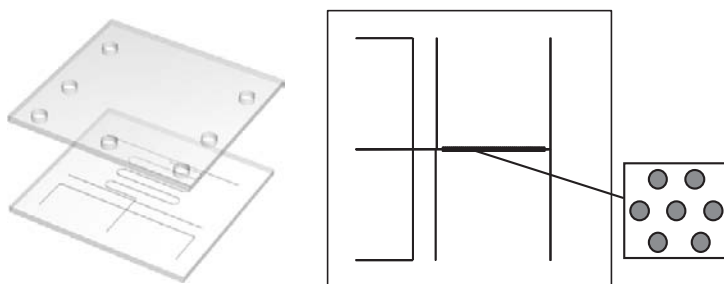


Fig. 11.8. Example of a chip: (*left*) a wavy trench in the base plate and holes in the covering plate and (*right*) a base plate with a channel with pillars [28], see also Fig. 9.21 (*left*)

opens the valve. Figure 11.7 also demonstrates a major problem in microfluidics, i.e. the fact that the connections and the appendant parts are often very much larger than the actual microelement.

Microstructured glasses are also used in biotechnology, for instance, in separation processes. For this purpose capillary systems are used in medical and biochips. Figure 11.8 shows typical elements and design features of a medical chip. The elements shown were successfully tested as capillary electrophoresis chip [28]. Using this microfabricated device the successful separation of amino acids was demonstrated. It can also be used to separate blood components.

One advantage of photostructuring of glasses is the possibility to fabricate high aspect ratio structures, that means deep channels up to several hundreds of micrometres. Such structures cannot be produced using conventional fabrication techniques as embossing of polymers. Figure 9.21 (*right*) shows very deep channel structures with a crossing of the channels. Furthermore, photostructuring allows for the fabrication of pillars within a channel (Fig. 9.21 (*left*)). The scanning electron micrographs in Fig. 9.21 show also the side walls roughness of the channels, which is in the range of $0.4\text{ }\mu\text{m}$ [190]. The surface roughness is caused (see also Sect. 9.2.1) by the removal of crystals

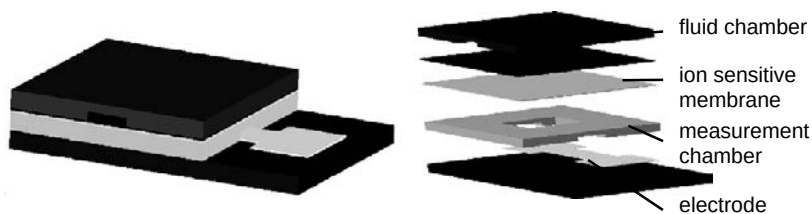


Fig. 11.9. A chemical sensor (*left*) and its layered design (*right*)

in the transition range between the partially crystallised and the glassy areas of sample during the etching process. The surface roughness at the bottom of the geometrical structures is commonly higher than that of the side walls, which is also caused by the etching of the partially crystallised part from the glass leaving a framework of the residual glass phase at the bottom surface (see Sect. 9.1.4).

Simultaneously ion-sensitive and photostructurable glasses with similar properties to the photostructurable glass FS21 (see Fig. 1.47) were developed and tested [198, 204]. Because of the similar property profile of these glasses, they can be joined to FS21 using thermal or adhesive bonding. Depending whether the glass is pH-, K^+ - or Na^+ -sensitive, it can find applications in various sensors. Figure 11.9 shows for example the schematic design of a pH-sensor.

The photostructurable glass Foturan (Table 1.6) has been used not only for the fabrication of microanalytic systems, static mixers, microreactors, printer heads, sensors, valves and pumps but also as parts of headphones [110, 111]. Jian-jun et al. [266] described the fabrication of substrates with high density holes array using the PEG3-glass, see also Table 1.6. Moreover, photostructured glasses were used to make cantilevers for atomic force microscopy [109] and microimpeller wheels [174].

Hessel et al. [223] described a lot of mixing principles and concrete micromixers. Many mixers used glasses as covermaterials. One important application is the use of microstructured silicon as mixing chamber with Pyrex glass cover plates.

Another possibility is the manufacturing of full glass mixers. Multi-plate stacks of structured Foturan glass e.g. for an interdigital micromixer or a cyclone laminating micromixer were fabricated.

11.1.3 Applications of Photostructured Glasses for Microactuators, Microhandling Devices and Microsensors

Microactuators often require reverse elements as in the case of an electrodynamic microlinear actuator [144]. This can be achieved, for instance, by using a microstructured glass/copper composite coil, which can be produced by microelectroforming (see Sect. 10.8). This coil was joined to the reverse element by adhesive bonding (sticking). Figure 11.10 shows two different designs

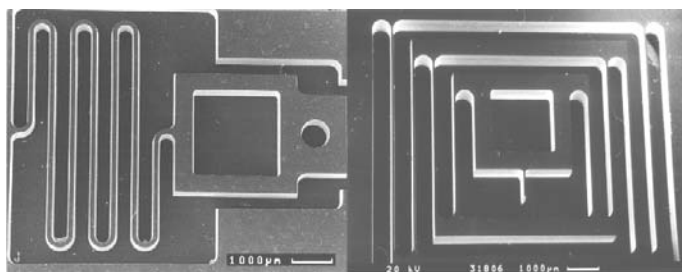


Fig. 11.10. Various glass spring designs as reverse elements used in microactuators

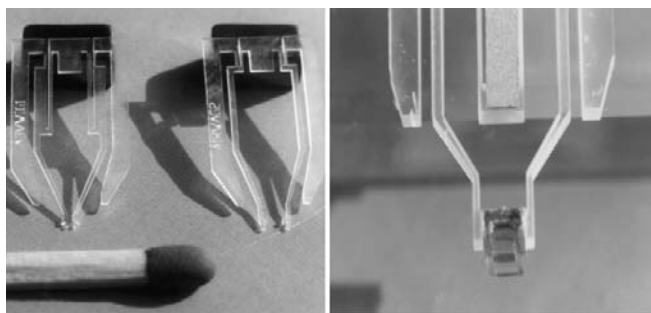


Fig. 11.11. (*Left*) Various microglass grippers (design: R. Salim) and (*right*) a gripper holding an object [190]

of the reversing glass device. A high energy permanent magnet is glued into the squared hole in the spring. If an electrical current is applied to the copper coil a magnetic field is generated, exerting a force to the magnet. The force equilibrium between the electrodynamic force and the elastic (reverse) force of the glass spring determines the actuator position. The spring design on the left in Fig. 11.10 does not enable precise linear motion, however, the parallel spring design (right) does.

Photostructurable glasses have also found applications in microgripping devices, especially for the fabrication of grippers for micropliers because of the good mechanical properties of the glass combined with the possibility of creating three-dimensional structures. Examples of micropliers are shown in Fig. 11.11 (left).

Figure 11.11 (right) shows a piezoelectric actuated gripping device made from photostructured glass holding an object. Piezoelectric actuators usually produce a small displacement but high forces. To use such an actuator for microgripping, a high ratio of gearing system is required. The microglass-gripper shown in Fig. 11.11 (right) works with gearing ratios of more than 100 [435].

The performance of microgrippers made from photostructurable glass or by anisotropic etching of silicon has been compared [435]. When using silicon

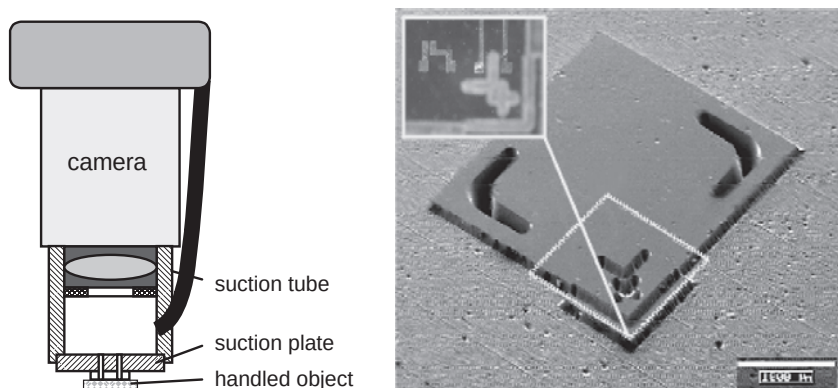


Fig. 11.12. A suction gripper (*left*) and an SEM image of a suction plate made from photostructured glass FS21 (*right*). The *inset* shows a detailed view through the suction plate at adjusting marks [190]

to fabricate grippers the inclination angles cause problems. These angles are defined by the crystal orientation within the silicon, which is about 55° for silicon (100). When using photostructurable glasses the angles of inclination that can be produced are around 3° , which is much better for a deformation in the sheet plane. Following photostructurable glass is the better material to make plier grippers [435].

Deformation elements for electrodynamic actuators produced using photostructured glass FS21 have also been made by Zöpping et al. [581]. Additionally, a copper coil fabricated by microelectroforming was embedded into microstructured glass channels of the gripping element. This copper coil is used for the electrodynamic actuation.

Suction grippers are another application area of microstructured glasses. This gripping system does not require any deforming structures. The principle of a suction gripper is illustrated in Fig. 11.12 (left). The key element of a suction gripper is the suction plate [581]. Figure 11.12 (right) shows such a suction plate made from photostructured glass and a view through the suction plate at adjusting marks. The advantages of suction plates fabricated from photostructured glasses are that they are optically transparent and therefore allow for adjustments of the grippers relative to the chip. Furthermore, the complete element can be made in one step using the modified mask method (see Sect. 9.2.7) with lithographic precision. Using this technique very fine suction nozzles and adjusting marks can be produced. The suction plate application utilises all advantages of the microstructuring process, which enables the production of several features with completely different designs in a single processing step and combines this fact with the excellent materials properties of the glass, such as optical transparency and good mechanical behaviour [145]. Photostructured glass parts have been used in the construction of suction grippers also by Nienhaus et al. [382].

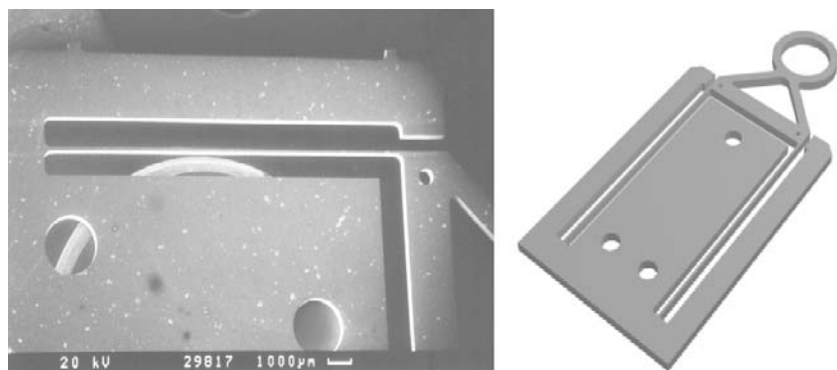


Fig. 11.13. Parallel glass spring for microforce measurements: scanning electron micrograph showing in detail a deformation bar (*left*) of a parallel spring, and the design of another parallel spring is shown on the *right*

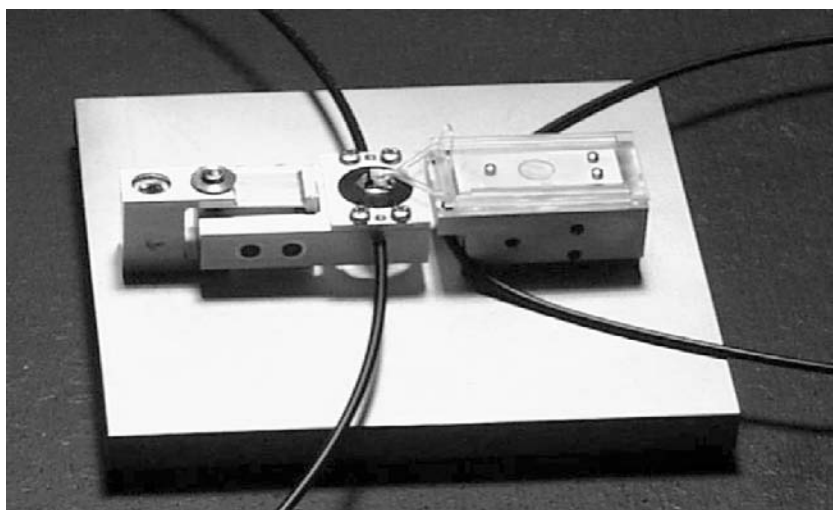


Fig. 11.14. Microtribometer (Tetra GmbH, Ilmenau, Germany)

The excellent mechanical properties of photostructured glass parts combined with the possibility to manufacture free, more dimensional structures make this processing route attractive for the production of precision measuring devices [205, 206]. Figure 11.13 (right) shows the design of a parallel glass spring and a scanning electron micrograph of a deformation bar (left) of a parallel spring. Especially the etching behaviour of the glass elements during the structuring process is of importance. The microstructuring process allows the fabrication of deformation bars with a high aspect ratio and absolute dimensions of less than $100\mu\text{m}$ in width and up to a thickness of more

than 1 mm. Parallel springs have the advantages of a small spring constant in lateral direction but a high spring constant in the vertical direction.

The produced glass elements have found applications as force–displacement modifiers to measure very low forces. Figure 11.14 shows a microtribometer using the photostructured glass parallel spring. The optical waveguides for position detection can be directly integrated into the structure by ion exchange (see also Fig. 1.51) [197, 198, 203, 205, 206].

11.2 More Microtechnological Glass Applications

Microstructured glass clichés for gravure printing of organic electronic circuits and other devices are a very surprising application of glass microstructuring. Brokmann et al. [70] have manufactured and tested the suitability of flat, microstructured clichés made from photosensitive FS21 glass and from borosilicate glass Borofloat (Schott, Jena). A very dense array of small deepening (cells) was produced on the surface of the clichés for at first collecting in and then – during printing – transferring picolitres of inks (electrically isolating, conducting or semiconducting) from each deepening onto the substrates. They may consist of plastic or even glass foils. In dependence on the used glass for the clichés and the microstructuring method it is possible to produce quite different geometries, dimensions and wall properties of the deepenings. The wall properties (chemical behaviour and geometrical substructures, see Fig. 9.11 for FS21 glass) influence to a great amount the adherence of the ink droplets in the deepenings. The borosilicate glass clichés, see Figs. 11.15 and 11.16, were microstructured by isotropic etching. The walls are relatively smooth and inclined, the depth of the deepenings does not exceed 2–5 μm .

The FS21 glass clichés, see Fig. 11.17, were structured as described in Chap. 9. The possibilities for varying the dimensions of the deepenings are much more pronounced compared with borosilicate glass. However, the wall roughness has to be considered, see Fig. 11.18.

Using this different clichés, it was possible to gravure print thin functioning layers of P3HT, PMMA, Ag-nanoparticle loaded ink and ITO.

Kirner et al. [275] presented a static micromixer based on a sandwich structure. The sandwich consists of a core chip made from Si and two cover chips made from glass. All three chips are structured microlithographically. Inside the generated channels, there are best conditions for optical measurements as a result of the smooth planes.

Microembossed glass parts will find many applications to produce V-groove structures and gratings for microoptics, in chemistry as mixers, reactors and separating devices and also in the life sciences [326]. All these applications rely on the good chemical and temperature stability of glasses, their optical properties (in particular the excellent surface quality that can be achieved using the embossing technique) and also its biocompatibility, steriliseability and the possibility to be cleaned easily. Manns et al. [344]

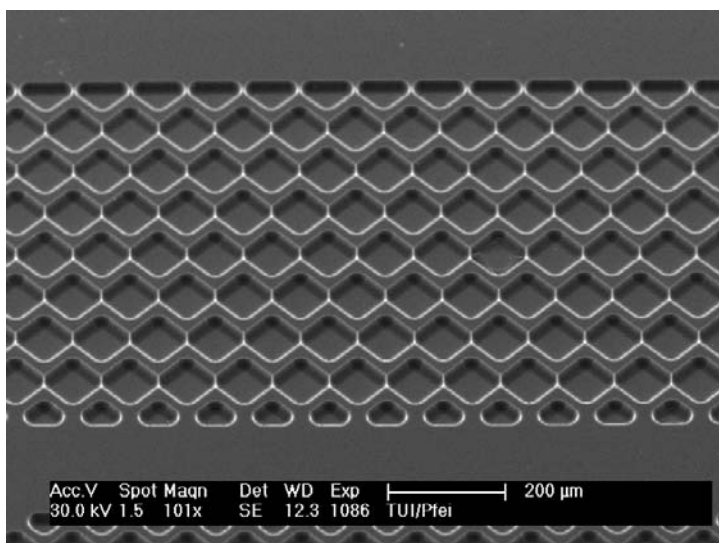


Fig. 11.15. Microstructured borosilicate glass (Borofloat[®]) cliché for gravure printing

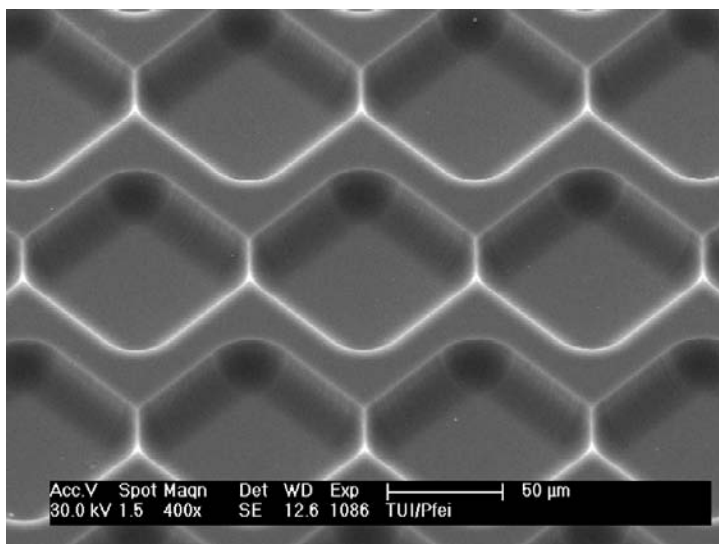


Fig. 11.16. Detail from Fig. 11.15

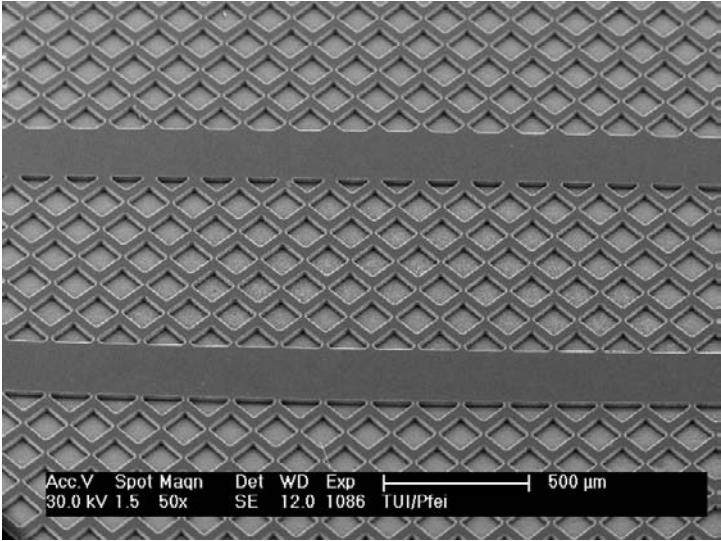


Fig. 11.17. Microstructured gravure pattern in the cliché made from photosensitive glass FS21

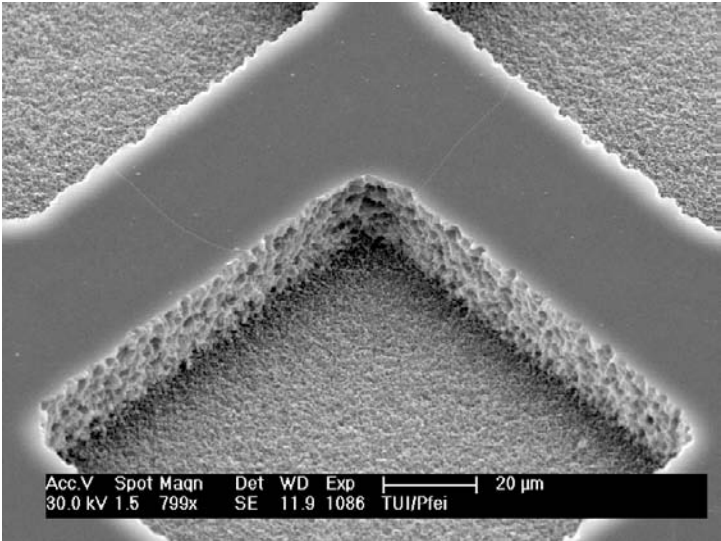


Fig. 11.18. A single deepening (cell) of the cliché shown in Fig. 11.17. In contrast to the smooth surface the cell walls are relatively rough

reported the embossing of very fine structures for optical applications. Grating structures for sensors and arrays for fibre-chip coupling and microfluidic components have been produced using embossing. However, complex microglass structures, such as channel plates for Zeus panels, have also been produced by pressing techniques [331].

Powder blasting is a very successful structuring process to generate structures in the range of millimetres down to a few hundred micrometres. The blasting process is very fast and the precision is often sufficient for a range of applications. In particular, microfluidic components are being successfully produced using blasting processes [36]. Commercial applications of powder blasting used for microstructured glasses in microfluidic devices have been reported by the companies micronit microfluidics and Little Things Factory. Channel plates for Zeus panels have also been produced by micropowder blasting [331]. Powder blasting of glass plates has been used to fabricate free standing mechanical elements for accelerometer bars for use in inertial sensors [34, 35, 39]. These elements have been produced using an oblique particle impact which allows for a defined underetching of the masked part of material. Using this technique, bars with structural features of less than 1 mm have been produced.

Microdrawing techniques of stacked capillaries are mainly used to manufacture optical elements. Nanochannel glass has been used to produce a mask, which was applied in massive parallel patterned lithography (Tonucci et al., [522, 523]). Multi-microcapillary systems are also used in optical applications, for instance, to focus X-ray beams [553]. Beloglazov et al. [41] described that apart in X-ray optics drawn stacked microcapillaries have found applications as parts of microactuators used in micromechanics, filters in bio and medicine technical applications, light guiding elements and photonic crystals and also for visualisation systems in electronics.

The use of multi-layer systems as a preform for microdrawing allows for the production of glass elements with new optical properties [122, 123] which may find applications in optical filters and interference devices. The most common application of drawn elements, however, is in fibre optics and photonic crystals [52, 292, 432].

Flat glasses are preferably used for the encapsulation of silicon sensors [465, 503] and as substrate material [148]. Encapsulating silicon sensors requires geometrically structured glass sheets, and metal microelectroforming glasses are necessary to produce connections through the glass wafers [192, 249, 250].

Because of serial generation of geometrical microstructures, laser microstructuring processes are not suitable for mass production of microstructured glass parts. However, these methods are of interest for prototyping and freeform applications and for the fabrication of small series of microfluidic and microoptical devices.

Mechanical processes for the surface treatment and geometrical structuring of glasses found many applications in the fabrication of optical parts. Vibration-assisted diamond turning of glasses is used to produce spherical and

aspherical lenses applied in CD-ROM drives and DVD players [287]. Micro-cutting processes allow for the fabrication of structures that can neither be manufactured by lithographic processes nor by macroscopic machining [235]. Pencil grinding is often used to produce microfluidic devices. Cutting in ductile regime allows for the direct fabrication of optically active surfaces [287, 364, 460].

Sintered glasses are commercially used as filters, carrier materials in bioprocessing, biomedical processes and also for thermal insulation, sound proofing and fire protection [166, 177, 466]. Porous glasses are used in separation processes, as supports for immobilised enzymes, as carriers for solid phase synthesis, for the immobilisation of biologically active materials and in membrane technology or for studying matter in confined spaces [263, 264].

The isotropic etching of glasses in hydrofluoric acid is used for contact holes in IC technologies [483] and for the production of microfluidic devices [495].

Sandwich structures of PEG3 and polysilicon were used to create microfluidic elements by a multi-step deposition and etch process [324]. The created channels had a cross-sectional area of $70 \times 4 \mu\text{m}^2$ and should be used for BioMEMS applications.

Microtitre plates made from the chemically resistant borosilicate glass Borofloat from Schott have been fabricated using ultrasonic-assisted structuring [262]. Initially, the glass was cut into wafers and various trenches and cavities (holes and trenches of various cross sections) of the titre plates have been produced using differently structured tools. The finished microtitre plates were cut from the structured glass wafer.

References

1. G.P. Agrawal, *Lightwave Technology, Components and Devices* (Wiley-VCH, Weinheim 2004)
2. K. Aiuchi, Y. Nishimura, M. Iwate, S. Aoki, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. E9, 2007
3. O.M. Akselsen, J. Mater. Sci. **27**, 5699 (1992)
4. Anon, *Hanauer Quarzglasoptik auf dem Mond* (Prospect of Heraeus, Hanau, Germany, 1969) (in German)
5. Anon (1990) Elektroschmelzen von Glas. Edn Hüttentechnische Vereinigung der Deutschen Glasindustrie, for developing one's knowledge (in German)
6. A. Aponyuk, Diploma Thesis, Technische Universität Ilmenau, 2000 (in German)
7. A.A. Appen, Proc. Acad. Sci. Sov. Union **69**, 841 (1949)
8. V.I. Arbuzov, M.N. Tolstoj, J. Non-Cryst. Solids **123**, 258 (1990)
9. W.H. Armistead, U.S. Patent 2,515,936, 8 Dec. 1943
10. H.A. Aulich, J.G. Grabmaier, K.H. Eisenrith, Appl. Opt. **17**(2), 170 (1978)
11. H.A. Aulich, J.G. Grabmaier, K.H. Eisenrith, G. Kinshofer, Siemens Forschungs- und Entwicklungsbericht **7**(5), 298 (1978)
12. W. Avasi, V.R. Mastelaro, M.R.B. Andreeta, J. Non-Cryst. Solids **352**, 3398 (2006)
13. I. Avramov, Eur. J. Glass Sci. Technol. B **48**(1), 61 (2007)
14. K. Awazu, J. Non-Cryst. Solids **353**, 215 (2007)
15. J.D. Ayers, J Mater. Sci. **28**, 2337 (1993)
16. R. Bähnisch, W. Groß, A. Menschig, in *Proceedings of 1st Euspen Conference*, Bremen, 1999, p. 506
17. K.J.O. Baldus, M. Rhode, Eur. J. Glass Sci. Technol. A **47**(4), 121 (2006)
18. P. Baniel, C. Belouet, J. Non-Cryst. Solids **161**, 1 (1993)
19. L.G. Baraldi, PhD Thesis, Eidgenössische Technische Hochschule Zürich, 1994 (in German)
20. D. Baranowski, L.G. Mann, R.H. Bellman, N.F. Borelli, Laser Focus World **25**(11), 139 (1989)
21. G.M. Bartenev, J. Non-Cryst. Solids **1**, 69 (1968)
22. Bauer, W. Kolbe, J. Köbel, R.P. Peters, in *Proceedings of 2nd International Conference on Adhesive Joining and Coating Technology in Electronics Manufacturing*, Stockholm, 1996, p. 108

23. D. Bäuerle, *Chemical Processing with Lasers* (Springer, Berlin Heidelberg New York, 1986)
24. D. Bäuerle, *Laser processing and Chemistry*, 2nd edn. (Springer, Berlin Heidelberg New York, 1996)
25. H. Baumgart, Doctor thesis, TU Ilmenau (ISBN 3-8265-4251-7), 1998 (in German)
26. K.J. Beales, S.F. Carter, P.W. France, S. Partington, J. Non-Cryst. Solids **70**, 253 (1985)
27. E.W. Becker, W. Ehrfeld, P. Hagmann, A. Maner, D. Münchmeyer, Microelectron. Eng. **4**, 35 (1986)
28. H. Becker, M. Arundell, A. Harnisch, D. Hülsenberg, Sens. Actuators B **86**, 271 (2002)
29. R. Beerkens, Glass Sci. Technol. **76**(4), 166 (2003)
30. R. Beerkens, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref H2, 2007
31. J. Beinert, J. Bormann, W. Döll, M. Doll, M. Gremmelspacher, G. Kleer, L. Könczöl, R. Kolloff, P. Manns, M.G. Schinker, *Material- und Verfahrensentwicklung für neue optische Abbildungssysteme*. IWM-Bericht V57/90, Fraunhofer-Institut für Werkstoffmechanik, Freiburg, Germany, 1990
32. S. Belau, Diploma Thesis. TU Ilmenau, 2003 (in German)
33. S. Belau, D. Hülsenberg, S. Mrotzek, A. Harnisch, in *Proceedings of 9th International Conference on New Actuators*, Bremen Germany, 2004, p. 506
34. E. Belloy, S. Thurre, E. Walckiers, A. Sayah, M.A.M. Gijs, in *Proceedings of 13th European Conference on Solid-State Transducers*, 1999, p. 827
35. E. Belloy, A. Sayah, M.A.M. Gijs, Sens. Actuators **86**, 231 (2000)
36. E. Belloy, S. Thurre, E. Walckiers, A. Sayah, M.A.M. Gijs, Sens. Actuators A **84**, 330 (2000)
37. E. Belloy, A. Sayah, M.A.M. Gijs, Sens. Actuators A **92**, 358 (2001)
38. E. Belloy, A.G. Pawlowskin, A. Sayah, M.A.M. Gijs, J. Microelectromech. Syst. **11**(5), 521 (2002)
39. E. Belloy, A. Sayah, M.A. Gijs, J. Microelectromech. Syst. **11**(1), 85 (2002)
40. V.I. Beloglazov, S.P. Suchovuev, N.V. Suetin, in *Three-Dimensional Micron and Submicron Structures Base*. Indo-Russian Workshop on Micro mechanical Systems. SPIE Proceedings Series, vol. 3903 (1999), p. 134
41. V.I. Beloglazov, S.P. Suchovuev, Russian Patent 2085523, 1995
42. Beltsios, E. Soterakou, N. Kanellopoulous, G. Tsangaris, Mater. Sci. Eng. C **15**, 257 (2001)
43. D. Benne, C. Rüssel, Glass Sci. Technol. **76**(3), 130 (2003)
44. P. Bergveld, IEEE Trans. Biomed. Eng. **19**, 340 (1972)
45. A.A. Bettiol, C.N.B. Udalagama, E.J. Teo, J.A. van Kan, F. Watt, Nucl. Instrum. Meth. Phys. Res. B **260**, 357 (2007)
46. P. Beyersdorfer (1964) Glashüttenkunde. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig (in German)
47. T.G. Bifano, T.A. Dow, R.O. Scattergood, *Advances in Fabrication and Metrology for Optics and Large Optics*. SPIE, vol. 966 (1988), p. 108
48. T.G. Bifano, T.A. Dow, R.O. Scattergood, Trans. ASME, **113**, 184 (1991)
49. T.G. Bifano, Y. Yi, Prec. Eng. **14**(4), 219 (1992)
50. Binnewies, E. Milke, *Thermo physical Data in Elements and Compounds* (Wiley-VHC, Weinheim, 1999)

51. T.A. Birks, J.C. Knight, P.S.t.J. Russell, *Opt. Lett.* **22**(13), 961 (1997)
52. T.A. Birks, J.C. Knight, P.S.t.J. Russell, World Patent: WO 99/00685, 1997
53. T.A. Birks, D. Mogilevtsev, J.C. Knight, P.S.t.J. Russell, *IEEE Photon. Technol. Lett.* **11**(6), 674 (1999)
54. B. Bläsi, V. Boerner, W. Döll, J. Dreibholz, A. Gombert, A. Heinzl, V. Kübler, P. Löbmann, P. Manns, K. Rose, D. Sporn, V. Wittwer, in *Proceedings of 1st International Conference and General Meeting of the European Society for Precision Engineering and Nanotechnology (EUSPEN)*, vol. 1, 1999, p. 522
55. J. Bliedtner, G. Köhler, H. Müller, A. Petrich, S. Wächter, *Glasbearbeitung mit Laser. Zukunft Glas – Von der Tradition zum High-Tech-Product*, Regensburg, Ostbayerisches Technologie Transfer Institute. V, 1997, p. 41 (in German)
56. Bodmann, PhD Thesis, Universität Karlsruhe/Germany, 1997
57. J. Böhm, A. Schubert, T. Otto, T. Burkhardt, *Microsys. Technol.* **7**, 191 (2001)
58. R. Borek, K.J. Berg, G. Berg, *Glass Sci Technol.* **71**(12), 352 (1998)
59. N.F. Borrelli, D.L. Morse, R.H. Bellman, W.L. Morgan, *Appl. Opt.* **24**(16), 2520 (1985)
60. N.F. Borrelli, C. Smith, D.C. Allan, *Laser Induced Densification in Silica and Binary Silica Systems. Bragg Gratings, Photosensitivity and Poling in Glass Waveguides*, Technical Digest, Optical Society of America, p. 249 (2000)
61. M. Bothen, in *Wissenschaftliche Schriftenreihe Prozessmodelle*, vol. 3, ed. by A. Nethe, H.D. Stahlmann (Verlag Dr. Köster, Berlin, 2000) (in German)
62. M. Bothen, L. Kieseewetter, in *Process Modelling*, ed. by B. Scholz-Reiter, H.D. Stahlmann, A. Nethe (Springer, Berlin, Heidelberg, New York, 1999), p. 407
63. G. Brambilla, P. Hua, J. Non-Cryst. Solids **352**, 2921 (2006)
64. J. Broeng, S.E. Barkou, A. Bjarklev, J.C. Knight, T.A. Birks, P.S.J. Russell, *Opt. Commun.* **156**, 240 (1998)
65. J. Broeng, T. Sondergaard, S.E. Barkou, P.M. Barbeito, A. Bjarklev, *J. Opt. A Pure Appl. Opt.* **1**, 477 (1999)
66. J. Broeng, S.E. Barkou, A. Bjarklev, T. Sondergaard, E. Knudsen, *Dan. Opt. Soc. News (DOPS-NYT)* **2**, 22 (2000)
67. U. Brokmann, Doctor Thesis, TU Ilmenau, Germany, 2005
68. U. Brokmann, A. Harnisch, D. Hülsenberg, M. Jacquorie, E.W. Kreutz, R. Poprawe, *Microsys. Technol.* **8**, 102 (2002)
69. U. Brokmann, W. Ertel-Ingrisch, A. Harnisch, D. Hülsenberg, *Glass Sci. Technol.* **77**(5), 249 (2004)
70. U. Brokmann, K. Sönnichsen, D. Hülsenberg, *J Microsys. Technol.* (2008) (in press)
71. J. Broukal, *Cire kremenne sklo. Informativni prehled SVUS. Hradec Kralove X. vol. 3* (1967) (in Czech)
72. R. Brück, N. Rizvi, A. Schmidt, *Angewandte Mikrotechnik, UGA-Laser-Feinwerktechnik* (Carl Hanser Verlag München Wien, 2001) (in German)
73. R. Brückner, G. Pähler, H. Stockhorst, *Glastechn. Ber.* **54**, 65 (1981) (in German)
74. R. Brückner, Y. Yue, J. Deubener, *Glastechn. Ber. Glass Sci. Technol.* **70**, (1997)
75. R. Bruntsch, PhD Thesis, Technische Universität Ilmenau, 1990
76. C. Buerhop, PhD Thesis, Universität Erlangen-Nürnberg/Germany, 1994
77. C. Buerhop, R. Weissmann, N. Lutz, *Appl. Surf. Sci.* **54**, 187 (1992)

78. C. Buerhop, L. Lutz, R. Weißmann, G. Tomandl, *Glastechn. Ber.* **66**, 61 (1993)
79. Buijs, J. *Am. Ceram. Soc.* **77**(6), 1676 (1994)
80. F. Büllersfeld, P. Kissl, S. Lehnice, M. Zimmermann, C. Kunert, B. Hoppe, V. Plapper, *World Patent WO 03/029156 A1*, 2002
81. A.J. Burggraaf, J. Cornelissen, W.J. Spoor, *Phys. Chem. Glasses* **5**, 123 (1964)
82. A. Burkert, W. Triebel, U. Nature, R. Martin, *Eur. J. Glass Sci. Technol. B*, **48**(3), 107 (2007)
83. F. Burmeister, W. Döll, G. Kleer, *Patent Application, DE 100 39 208 A1*, 2000
84. M. Busio, O. Steigelmann, *Glastechn. Ber. Glass Sci. Technol.* **73**(10), 319 (2000)
85. S. Büttgenbach, *Mikromechanik* (Teubner, Stuttgart, 1991) (in German)
86. R. Cadavid-Giraldo, Doctor Thesis, Technische Universität Kaiserslautern (ISBN-3-936890-46-3), 2004
87. F. Celarie, S. Prades, D. Bonamy, L. Ferrero, E. Bouchaud, C. Guillot, C. Marliere, *Phys. Rev. Lett.* **90**(7), 075504-1 (2003)
88. J.W. Chan, T.R. Huser, S.H. Risbud, D.M. Krol, *Appl. Phys. A* **76**, 367 (2003)
89. C.L. Chao, Ph.D. Thesis, College of Manufacturing, Cranfield Institute of Technology, 1991
90. K. Chicamori, *Int. J. Jpn. Soc. Prec. Eng.* **25**(2), 109 (1991)
91. E.F. Chillce, C.M.B. Cordeiro, L.C. Barbosa, C.H. Brito Cruz, *J Non-Cryst. Solids* **352**, 3423 (2006)
92. W.C. Chiu, M.D. Thouless, W.J. Endres, *Int. J. Fract.* **90**(4), 287 (1998)
93. W.C. Chiu, W.J. Endres, M.D. Thouless, *Mach. Sci. Technol.* **4**(2), 253 (2000)
94. J. Chladek, *Glass Sci. Technol.* **77**(1), 1-6 (2004)
95. W.B. Choi, B.K. Ju, Y.H. Lee, M.R. Haskard, S.J. Jeong, N.Y. Lee, M.Y. Sung, M.H. Oh, in *Material Research Society Symposium*, vol. 444, 1997, p. 173
96. W.B. Choi, B.K. Ju, Y.H. Lee, M.R. Haskard, M.Y. Sung, M.H. Oh, *J. Vac. Sci. Technol. B* **15**(2), 477 (1997)
97. S.R. Choudhury, Y. Jaluria, *J. Mater. Res.* **13**(2), 483 (1998)
98. R. Clasen, R. Blasig, S. Rosenbaum, in *Proceedings of the 5th ESG Conference*, Prag, 1999, p. C3-27
99. T. Corman, P. Enoksson, G. Stemme, *J. Micromech. Microeng.* **8**, 84 (1998)
100. F. Couny, H. Sabert, P.J. Roberts, D.P. Williams, A. Tomlinson, B.J. Mangan, L. Farr, J.C. Knight, T.A. Birks, P.S.t.J. Russel, *Opt. Exp.* **13**, 558 (2005)
101. J.A. Cox, R.M. Wilke, W.O. Patent 96/17266, 1994
102. A. Cozma, B. Puers, *J Micromech. Microeng.* **5**, 98 (1995)
103. T.H. Cross, M.J. Mayo, *Struct. Mater.* **3**, 163 (1993)
104. H.R. Dalton, U.S. Patent 2,326,012, 31 Mar. 1941
105. H.R. Dalton, *J. Am. Ceram. Soc.* **39**, 109 (1956)
106. R.C. Dartnell, H.V. Fairbanks, W.A. Koehler, *J. Am. Ceram. Soc.* **34**(11), 357 (1951)
107. De Bernardi, *J. Appl. Phys.* **63**, 234 (1988)
108. T. Diepold, E. Obermeier, *J. Micromech. Microeng.* **6**, 29 (1996)
109. T.R. Dietrich, M. Abraham, J. Diebel, M. Lacher, A. Ruf, *Micromechan. Microeng.* **3**, 187 (1993)
110. T.R. Dietrich, W. Ehrfeld, M. Lacher, M. Krämer, B. Speit, *Microelectron. Eng.* **30**, 497 (1996)
111. T.R. Dietrich, W. Ehrfeld, M. Lacher, B. Speit, *F & M* **104**, 520 (1996) (in German)

112. V. Dimpleby, W.E.S. Turner, J. Soc. Glass Technol. **10**, 304 (1926)
113. DIN 12 111, Prüfung von Glas; Gießverfahren zur Prüfung der Wasserbeständigkeit von Glas als Werkstoff bei 98°C und Einteilung der Gläser in hydrolytische Klassen (in German) (1976)
114. DIN 12 116, Prüfung von Glas; Bestimmung der Säurebeständigkeit (gravimetrisches Verfahren) und Einteilung der Gläser in Säureklassen (in German) (1976)
115. DIN 52 322, Bestimmung der Laugenbeständigkeit und Einteilung der Gläser in Laugenklassen (in German) (1971)
116. DIN 52 324, Prüfung von Glas; Bestimmung der Transformationstemperatur (in German) (1960)
117. J. Doyle, *Glass-making today*. (Portcullis, 1979)
118. C. Dresbach, A. Krombholz, M. Ebert, J. Bagdahn, Microsys. Technol. **12**, 473 (2006)
119. K. Du, D. Li, H. Zhang, P. Shi, X. Wie, R. Diart, Opt. Lett. **28**(2), 87 (2003)
120. K. Du, P. Shi, Glass Sci. Technol. **76**(2), 95 (2003)
121. W.H. Dumbaugh, P.L. Bocko, F.P. Fehlner, in *High-Performance Glasses*, ed. by M. Cable, J.M. Parker (Blackie and Son, 1992)
122. B. Durschang, M. Krauss, Wiederziehen von Glas. 74. Glastechnische Tagung, Ulm, 2000, p. 306 (in German)
123. B. Durschang, M. Krauss, Herstellung von Materialien mit speziellen Eigenschaften durch Ziehen von Glas-Glas-Verbunden. 75. Glastechnische Tagung, Wernigerode, 2001, p. 244 (in German)
124. H. Ebendorff-Heidepriem, *Progress in photosensitivity – Fundamentals and overview*. Glass Sci. Technol. 75c1, Proceedings of the first International Workshop on Glass and the Photonics Revolution, 28–29 May, Bad Soden (Germany), 131 (2002)
125. R. Eberhardt, G. Tittelbach, V. Guyenot, in *Proceedings of 1st International Congress on Adhesion Science & Technology*, Amsterdam, 1995, p. 98
126. R. Eberhardt, G. Tittelbach, V. Guyenot, in *New Results of Adhesion Technology for Assembly of Microoptical Components*. ed. by H. Reichel, A. Heuberger (Micro System Technologies 96, Berlin, VDI-Verlag, 1996), p. 525
127. K. Edinger, *Focused Ion Beams for Direct Writing*, ed. by A. Pique, D.B. Chrisey. Direct-write Technologies for Rapide Prototyping Applications: Sensors, Electronics and Integrated Power Sources (Academic, San Diego San Francisco, 2002)
128. A. Ehrhardt, Doctor Thesis, TU Ilmenau (ISBN 3-8265-6123-6) (1999) (in German)
129. D. Ehrhart, P. Ebeling, U. Natura, *Redox equilibria and Ultraviolet radiation induced defects in glasses*. Proc. Int. Congr. Glass, vol. 1, Edinburgh, Scotland, 1–6 July, 84 (2001)
130. D. Eifler, E. Roeder, U. Schicker, J. Wagner, Glastechn. Ber. Glass Sci. Technol. **69**(10), 326 (1996)
131. G. Eisenman, *Glass Electrodes for Hydrogen and other Cations* (Dekker, New York, 1967)
132. T.M.M. El Shamy, R.W. Douglas, J. Am. Ceram. Soc. **50**, 1 (1967)
133. G. Engelmann, O. Ehrmann, J. Simon, H. Reichl, in *Proceedings of Micro Electro Mechanical Systems 92*, Travemünde, 1992, p. 93
134. G. Engelmann, O. Ehrmann, R. Leutenbauer, H. Schmitz, H. Reichl, J. Micromech. Microeng. **3**, 152 (1993)

135. D. Enke, K. Otto, F. Janowski, W. Heyer, W. Schwieger, W. Gille, J. Mater. Sci. **36**, 2349 (2001)
136. M. Esashi, A. Nakano, S. Shoji, H. Hebiguchi, Sens. Actuators **A21–A23**, 931 (1990)
137. M. Esashi, N. Ura, Y. Matsumoto, in *Proceedings of Micro Electro Mechanical Systems 92*, Travemünde, 1992, p. 43
138. G.C. Escher, SPIE Proceedings, **998**, 30–37 (1988)
139. A.G. Evans, M.E. Gulden, M. Rosenblatt, Proc. R. Soc. London A, **A 361**, 343 (1978)
140. A.J. Faber, M. Rongen, R. Breeuwer, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. E3, 2007
141. H.V. Fairbanks, in *Symposium sur le contact du Verre Chaud avec le Metal*, Scheveningen, Union Scientifique Continentale du Verre, 1964, p. 575
142. J. Fanderlik, *Kremenne sklo a jeho vyuziti v praxi* (SNTL-Nakladatelství technické literatury, Praha, 1985) (in Czech)
143. F. Fasilow, B. Symoens, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. F15, 2007
144. K. Feindt, A. Harnisch, D. Hülsenberg, E. Kallenbach, in *Proceedings of Fourth International Conference on Ultra precision in Manufacturing Engineering*, Braunschweig, vol. 2, 1997, p. 714
145. K. Feindt, A. Harnisch, V. Zöppig, D. Hülsenberg, E. Kallenbach, 3D-Structuring of Photosensitive Glasses. *11th International Workshop on Micro Electro Mechanical Systems*, Heidelberg, (1998)
146. K. Feindt, A. Harnisch, D. Hülsenberg, E. Kallenbach, V. Zöpping, O. Mollenhauer, in *Proceedings on Applications of Microstructurable Glasses, Sensor 99*, Nürnberg, 1999, p. 351
147. Z. Feng, A. Ball, Wear 233–235, 674 (1999)
148. Fintel von S, T. Kloss, G. Lautenschläger, K. Schneider, Borofloat – genial um Welten zu erobern. Viertes Symposium Zukunft Glas – von der Tradition zum High-Tech-Produkt, Zwiesel, 2002, p. 64
149. A.D. Pitt, K. Furusawa, T.M. Monro, C.P. Please, J Lightwave Technol. **19**(12), 1924 (2001)
150. W.G. French, MacChesney, P.B. O'Connor, G.W. Tasker, Bell Sys. Techn. J. **53**(5), 951 (1974)
151. J. Frenkel, Zeitschrift Physik 35: 652 (1926) (in German)
152. G. Frischat, Glastechn. Ber. **52**, 143 (1979) (in German)
153. T. Fujita, Glass Int. **26**(3), 46 (2003)
154. Fuqua, D.P. Taylor, H. Helvajian, W.W. Hansen, M.H. Abraham, in *Materials Development for Direct-Write Technologies*, ed. by D.B. Chrisey, D.R. Gamota, H. Hevajian, D.P. Taylor. Material Research Society Proceedings, 2000, p. 624
155. J. Gaebler, H.W. Hofmeister, in *Micro System Technologies 96 - 5th International Conference on Micro-, Elec-tro- Opto-, Mechanical Systems and Components*, ed. by H. Reichel, A. Heuberger (VDI, 1996)
156. J. Gaebler, M. Fryda, T. Matthee, L. Schäfer, Entwicklung und Anwendungsbeispiele diamantbeschichteter Werkzeuge mit bestimmter und unbestimmter Schneide, in *Werkstoffwoche 98. vol. 5: Symposium 5: Werkstoffe für die Fertigungstechnik*, ed. by F. Klocke, B.R. Höhn (Wiley, Weinheim, 1999) (in German)

157. J. Gaebler, L. Schäfer, A. Wenda, H.W. Hoffmeister, in *Proceedings of the 1st International Conference and General Meeting of the European Society for Precision Engineering*, Bremen, Mai/Juni 1999, p. 434
158. J. Gaebler, L. Schäfer, H. Westermann, *Diam. Relat. Mater.* **9**, 921 (2000)
159. H. Gatzten, in *Proceedings of the 3rd International Micro Materials Conference, ddp goldenbogen, Dresden*, ed. by B. Michel, T. Winkler, M. Werner, H. Fecht, 2000, p. 141
160. H. Gatzten, M. Beck, J. Zeadan, in *Proceedings of 1st International Conference and General Meeting of the European Society for Precision Engineering and Nanotechnology (EUSPEN)*, vol. 1, 1999, p. 538
161. Gebhardt, V. Baier, in *Thüringer Werkstofftag 2002*, ed. by J.D. Schnapp, U. Glatzel, K.D. Jandt H. Knake (Verlag Dr. Köster, Berlin, 2002) p. 76 (in German)
162. A.E. Gee, R.C. Spragg, K.E. Puttick, M.R. Rudman, *SPIE Proc.*, **1573**, 39 (1991)
163. G. Gehlhoff, M. Thomas, *Z. Techn. Phys.* **7**, 105, 260 (1926) (in German)
164. S. Geiger, P. Urbanek, *Laser Optoelectron.* **21**(1), 43 (1989)
165. A.S. Geleil, M.M. Hall, J.E. Shelby, *J. Non-Cryst. Solids* **352**, 620 (2005)
166. M. Gemeinert, R. Müller, F.G. Whismann, *Glastechn. Ber. Glass Sci. Technol.* **70**(9), 278–282 (1997)
167. G. Gerlach, W. Dötzel, *Grundlagen der Mikrosystemtechnik* (Carl Hanser Verlag, München, 1997) (in German)
168. F.T. Geyling, G.M. Homsy, *Glass Technol.* **21**(2), 95 (1980)
169. J. Gibmeier, B. Scholtes, *Material. Werkstofftech.* **34**, 115 (2003)
170. W. Giegerich, W. Trier, *Glasmaschinen* (Springer, Berlin Heidelberg New York, 1964) (in German)
171. A. Gier, M. Mennig, H. Schmidt, Herstellung glasartiger Mikrostrukturen mit Strukturböhen bis 30µm über die Prägetechnik. 72. Glastechnische Tagung, Münster, 1998, p. 306 (in German)
172. A. Gier, H. Menning, H. Schmidt, Zur Herstellung optische Mikrostrukturen durch Prägen thixotroper Gelschichten. 74. Glastechnische Tagung, Ulm, 2000, p. 286 (in German)
173. A. Gillner, F. Legewie, R. Poprawe, M.J. Wild, in *Micro System Technologies 98*, ed. by O. Reichl (VDI, 1998), p. 159–163
174. C. Gimkiewicz, E. Gerhard, *Microsyst. Technol.* **4**, 40 (1997)
175. J.H. Giovannola, I. Finnie, *J. Matter. Sci.* **15**, 2508 (1980)
176. L.B. Glebov, *Eur. J. Glass Sci. Technol. B*, **48**(3), 123 (2007)
177. H. Gödeke, H.V. Fuchs, *Glastechn. Ber. Glass Sci. Technol.* **71**(9), 282 (1998)
178. P. Gospodinov, A.L. Yarin, *Int. J. Multiphase Flow* **23**(5), 967 (1997)
179. A. Goyal, V. Hood, S. Tadigadapa, *J. Non-Cryst. Solids* **352**, 657 (2006)
180. J. Grabmaier, G. Kinshofer, R. Plättner, K.H. Eisenrith, U. Deserno, *Siemens Forschungs- und Entwicklungsberichte* **4**(5), 310 (1975)
181. J.G. Grabmaier, H.A. Aulich, *Chem. Ing. Tech.* **51**(6), 612 (1979) (in German)
182. H. Grimm, Patent Specification DE 101 20 384 A1, 2001 (in German)
183. N. Groothoff, N. Jovanovic, G. Marshall, J. Canning, M. Whitford, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. L26, 2007
184. R. Grunow, Doctor Thesis. Friedrich-Schiller-Universität Jena, 1981 (in German)

185. H. Guckel, T. Earles, Klein, in *Deep X-Ray Lithography and Electroplating for Electromagnetic Actuators*. Electrochemical Society Proceedings, vol. 95-18 (1996), p. 407
186. S.T. Gulati, in *Finishing of Advanced Ceramics and Glasses*, ed. by R. Sabia, V.A. Greenhut, C.G. Pantano, Ceramic Transactions, vol. 102 (1999) p. 311
187. T. Haas, A. Hesse, D. Doll, Phys. Rev. B **73**, 045130 (2006)
188. M. Hähnert, Silikattechnik **22**, 241 (1971) (in German)
189. A. Hanneborg, M. Nese, P. Ohlckers, J. Micromech. Microeng. **1**, 139 (1991)
190. A. Harnisch, Doctor Thesis, TU Ilmenau (ISBN 3-8265-4451-x) (1998) (in German)
191. A. Harnisch, D. Hülsenberg, Glastechn. Ber. Glass Sci. Technol. **73**(3), 67 (2000)
192. A. Harnisch, K. Schmidt, D. Hülsenberg, B. Straube, C. Jakob, R. Nutsch, in *Proceedings of 4th International Conference on Joining Ceramics, Glass and Metals*, Königswinter, 1993, p. 367
193. A. Harnisch, K. Feindt, D. Hülsenberg, in *Proceedings of 5th International Conference, Joining'97*, Jena, 1997
194. A. Harnisch, K. Feindt, A. Ehrhardt, D. Baumgart, D. Hülsenberg, E. Kallenbach, in *Proceedings on 6th International Conference on New Actuators*, Bremen, 1998, p. 66
195. A. Harnisch, D. Hülsenberg, B. Straube, A. Ehrhardt, H. Baumgart, in *Proceedings of Sensor 99*, Nürnberg, 1999, vol. 2, p. 263
196. A. Harnisch, U. Brokmann, S. Hecht-Mijic, S. Mrotzek, D. Hülsenberg UV-mikrostrukturierbare Gläser – Werkstoffe, Technologien, Eigenschaftsmodifizierungen und Anwendungen. 5. Chemnitzer Fachtagung Mikromechanik und Mikroelektronik, 2001, p. 188 (in German)
197. A. Harnisch, S. Hecht-Mijic, S. Mrotzek, U. Kucera, D. Hülsenberg, in *Proceedings of FuKoGlas – From the materials research to the application. Materials Week*, München, 2002
198. A. Harnisch, D. Hülsenberg, S. Hecht-Mijic, S. Mrotzek, U. Brokmann, Glass Technol. **43C**, 259 (2002)
199. M. Hashish, J. Eng. Mater. Technol. ASME **111**, 221 (1989)
200. Y. He, D.E. Day, Glass Technol. **33**(6), 214 (1992)
201. S. Hecht-Mijic, Doctor Thesis TU Ilmenau, Germany, 2003
202. S. Hecht-Mijic, V. Christ, B. Straube, A. Harnisch, S. Mrotzek, D. Hülsenberg, U. Kucera, O. Mollenhauer, in *Proceedings of 3rd International Conference Micro Materials, MicroMat 2000*, Berlin, 2000
203. S. Hecht-Mijic, A. Harnisch, D. Hülsenberg, O. Mollenhauer, in *Proceedings of ProcMicrostructured Light Guiding Glass: Materials, Technology and Properties. Materials Week*, Munich, 2001
204. Hecht-Mijic, S. Mrotzek, A. Harnisch, D. Hülsenberg, U. Kucera, S. Herrmann, H. Kaden, Mikrostrukturierbare Gläser mit chemisch-sensitiven Eigenschaften 75. Glastechnische Tagung, Wernigerode, 2001, p. 167 (in German)
205. S. Hecht-Mijic, A. Harnisch, D. Hülsenberg, O. Mollenhauer, in *Proceedings of Summer School of Photosensitivity in Optical Waveguides and Glasses*, Saint-Petersburg, 2002, p. 91
206. S. Hecht-Mijic, D. Hülsenberg, A. Harnisch, H. Kaden, S. Herrmann, C.E. Michelsen, S. Stieber, Fotostrukturierbares ionensensitives Lithiumalumosilikatglas, DE 102 43 442.5, 17 Sept. 2002 (in German), (2002)

207. J. Heiber, Diploma Thesis, TU Ilmenau, Germany, 2002
208. J. Heiber, F. Clemens, T. Graule, D. Hülsenberg, *Glass Sci. Technol.* **77**(5), 211 (2004)
209. J. Heikenwälder, *Wissen. Zeit. Hoch. Mittw.* **14K**, 73 (2000) (in German)
210. J. Heikenwälder, J.R. Matthees, B. Richerzhagen, T. Seim, *Rationelles Tren. Solarz. Werkstat.* **89**(9), 410 (1999) (in German)
211. J. Heikenwälder, J.R. Matthees, B. Richerzhagen, *Laserpraxis* **6**, 36 (2000) (in German)
212. H. Helvajian, in *A Direct-write Technologies for Rapid Prototyping Applications*, ed. by A. Pique, B. Chrisey (Academic, San Diego, 2003)
213. E. Hempel, A. Huwe, K. Otto, F. Janowski, K. Schröter, E. Donth, *Thermochim. Acta* **337**, 163 (1999)
214. T. Henkel, T. Berming, M. Kielpinski, A. Grodrian, J. Metze, J.M. Köhler, *Chem. Eng. J.* **101**, 439 (2004)
215. H. Henmi, S. Shoji, Y. Shoji, K. Yoshimi, M. Esashi, *Sens. Actuators A* **43**, 243 (1994)
216. A. Henning, in *Proceedings of 10th American Waterjet Conference*, vol. 2 (St. Louis, Waterjet Technology Association, 1999), p. 795
217. A. Henning, E. Westkämper, in *Proceedings of 6th Pacific Rim Conference on Water Jetting Technology*, 2000, p. 273
218. A. Henning, E. Westkämper, *Werkstattstechnik* **92**(3), 69 (2002)
219. H. Henschel, O. Köhn, H.U. Schmidt, *IEEE Trans. Nucl. Sci.* **45**(3), 1552 (1998)
220. A. Hesse, Diploma Thesis, TU Ilmenau, Germany, 2004
221. A. Hesse, Y. Ludwig, S. Mrotzek, D. Hülsenberg, in *Proceedings Thüringer Werkstofftag*, Weimar, 2005, p. 72
222. A. Hesse, S. Mrotzek, S. Belau, D. Hülsenberg, *Grundlagenuntersuchungen zum Verziehen von Bündeln aus Glashalbzeugen*, 79. Glastechnische Tagung der DGG, Würzburg, 2005 (in German)
223. V. Hessel, H. Löwe, A. Müller, G. Kolb, *Chemical Micro Process Engineering* (Wiley-VCH, GmbH, Weinheim, 2005)
224. W. Hinz, *Silikate – Einführung in Theorie und Praxis* (Verlag für Bauwesen, Berlin, 1963) (in German)
225. W. Hinz, in *Silikate*, vol. 1 (Verlag für Bauwesen, Berlin, 1970) (in German)
226. W. Hinz, in *Silikate*, vol. 2 (Verlag für Bauwesen, Berlin, 1971) (in German)
227. W. Hinz, G. Solow, G. Kranz, *Silikattechnik* **16**, 210 (1965) (in German)
228. K. Hirao, T. Mitsuyu, J. Si, J. Qiu, *Active Glass for Photonic Devices* (Springer, Berlin Heidelberg New York, 2001)
229. K. Hiromatsu, J.D. Hwang, M. Kim, C.P. Grigoropoulos, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. L3, 2007
230. T. Hirose, M. Fokine, K. Saito, A.J. Ikushima, *J. Non-Cryst. Solids* **352**, 664 (2006)
231. M. Hock, W. Döll, G. Kleer, P. Manns, E. Schäffer, G. Spieß, in *Proceedings of Nanocomposite Coating Materials for Low Cost Production of Refractive and Diffractive Optical Components of Inorganic Glasses*, Materials Week, Munich, 2002
232. H.J. Hoffmann, *Glass Sci. Technol.* **76**, 285 (2003)
233. H.W. Hoffmeister, A. Wenda, in *Proceedings of the 1st International Conference and General Meeting of the European Society for Precision Engineering*, Bremen, 1999, p. 396

234. H.W. Hoffmeister, A. Wenda, Mikrofertigung – Fräsen, Bohren und Schleifen im Mikrobereich Proceedings, 9. Internationales Braunschweiger Feinbearbeitungskolloquium, TU Braunschweig, 1999, p. 18.1 (in German)
235. H.W. Hoffmeister, J. Gäbler, A. Wenda, in *Proceedings of the 9th International Precision Engineering Seminar*, Braunschweig, May 1997
236. S. Honkanen, B.R. West, S. Yliniemi, P. Madasamy, M. Morrell, J. Auxier, A. Schülzgen, N. Peyghambarian, J. Carriere, J. Frantz, R. Kostuk, J. Castro, D. Garaghty, Eur. J. Glass Sci. Technol. B **47**(2), 110 (2006)
237. T. Honma, Y. Benino, R. Sato, T. Fujiwara, T. Komatsu, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. L2, 2007
238. H. Hornberger, R. Weißmann, N. Lutz, Glastechn. Ber. Glass Sci. Technol. **69**(2), 44 (1996)
239. Hoya, Photo sensitive Glass PEG 3. Technical Documentation. Hoya Corporation, Electro-Optics Department, Tokyo, Japan, 1994
240. P. Hrma, D.E. Smith, J. Matyáš, J.D. Yeager, J.V. Jones, E.N. Boulous, Eur. J. Glass Sci. Technol. B **47**(1), 64 (2006)
241. W. Hu, K. Shah, Q. Fu, in *Laser Materials Processing Conference*, Orlando, LIA 94, Congress Proceedings, 2002, p. 2077
242. Z.Q. Huang, M.H. Hong, K.S. Tiaw, Q.Y. Lin, in *Proceedings of 8th International Symposium on Laser Precision Microfabrication*, 2007
243. M. Hug, D. Rieser, P. Manns, Untersuchungen zur Herstellung optischer Komponenten durch schnelles heißprägen anorganischer Gläser. 79. Glastechnische Tagung der DGG, Würzburg, 2005 (in German)
244. D. Hülsenberg, Microelectron. J. **28**, 419 (1997)
245. D. Hülsenberg, in *Aspekte der Forschung vol. 19, Individuum und Kosmos*, edn by H. Fischer (Verlag Humboldt-Gesellschaft, Mainz, Germany, 2004), p. 257 (in German)
246. D. Hülsenberg, R. Bruntsch, K. Schmidt, F. Reinhold, Silikattechnik **41**, 364 (1990) (in German)
247. D. Hülsenberg, A. Harnisch, H.J. Horst, K. Schmidt, B. Straube, in *Proceedings of the Micro Systems Technologies*, Berlin, 1994, p. 259
248. D. Hülsenberg, A. Harnisch, H.J. Horst, M. May, K. Schmidt, B. Straube, in *Proceedings of Microstructuring of Glass Wafers for Kinetic Sensors*, Sensor 95, Nürnberg, 1995, p. 415
249. D. Hülsenberg, A. Harnisch, C. Jakob, M. May, B. Straube, Microsyst. Technol. **2**(3), 109 (1996)
250. D. Hülsenberg, R. Brandes, C. Doppleb, O. Knauf, R. Lipfert, Einkristallines Bariumhexaferritpulver: Herstellung, Eigenschaften, Anwendung in der Mikrotechnik, Keramische Werkstoffe, 52nd Erg. Lfg, 1999, 40p (in German)
251. D. Hülsenberg, E. Kallenbach, Funktionsintegrierte Konstruktionsgläser – Entwicklung, Herstellung, Verarbeitung und Anwendung. Final Research Report, TU Ilmenau, Germany, 2002 (in German)
252. D. Hülsenberg, S. Hecht-Mijic, A. Harnisch (2003) Herstellung mikrostrukturierter Glasbauteile durch Prägen (in German). Final Research Report, TU Ilmenau, Germany
253. D. Hülsenberg, B. Halbedel, G. Conrad, A. Thess, Y. Kolesnikov, U. Lüdtke, Glass Sci. Technol. **77**(4), 186 (2004)
254. D. Hülsenberg, U. Brokmann, A. Hesse, Y. Ludwig, S. Mrotzek, Galvanotechnik **98**(10), 2530 (2007) (in German)

255. I. Ichiro, in *Proceedings of the 3rd International Micro Materials Conference, ddp goldenbogen, Dresden*, ed. by B. Michel, T. Winkler, M. Werner, H. Fecht, 2000
256. C. Iliescu, J. Miao, *Electron. Lett.* **39**(8), 658 (2003)
257. I. Inaski, in *Proceedings of the 3rd International Micro Materials Conference, ddp goldenbogen, Dresden*, ed. by B. Michel, T. Winkler, M. Werner, H. Fecht, 2000
258. J.C. Ion, *Laser Processing of Engineering Materials* (Elsevier, Butterworth-Heinemann, 2005)
259. T. Izawa, S. Kobayashi, S. Sudo, F. Hanawa, in *Proceedings on International Conference on Integrated Optics and Optical Fiber Communication*, Tokyo, 1977, p. 375
260. J. Jablonowski, *J. Am. Machinist* **21**(9), (1989)
261. M. Jacquorie, Doctor Thesis, Shaker Verlag, Aachen, 2001 (ISBN 3-8265-9356-1)
262. M. Jacquorie, M. Vos, Verfahren zur Herstellung von Microtiterplatten, German Patent, DE 102 12 266 C1, 2002 (in German)
263. F. Janowski, W. Heyer, Poröse Gläser-Herstellung, Eigenschaften und Anwendung, Deutscher Verlag für Grundstoffindustrie, Leipzig 1982 (in German)
264. F. Janowski, D. Enke, in *Porous Glasses*, ed. by F. Schüth, K.S.W. Sing, J. Weitkamp. Handbook of Porous Solids, vol. 3 (Wiley-VCH, Weinheim, 2002)
265. K. Jansen, U.S. Patent 5,173,097, 1990
266. H. Jian-jun, Z. Hua, R. Jian, Z. Xiu-jian, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. L9, 2007
267. R.W. Johnstone, M. Parameswaran, *An Introduction to Surface Micromachining* (Kluwer Academic, Boston, 2004)
268. S. Juodkazis, K. Yamasaki, A. Marcinkevicius, V. Mizeikis, S. Matsuo, H. Misawa, T. Lippert in *Microstructuring of Silica and Polymethylmethacrylate Glasses by Femtosecond Irradiation for MEMS Application*. Materials Research Society Symposium, Proceedings, vol. 687 (Materials Research Society, 2002), p. 173
269. M. Kaempfe, T. Rainer, K.J. Berg, G. Seifert, H. Graener, *Appl. Phys. Lett.* **74**(9), 1200 (1998)
270. T. Kanamori, Y. Terunuma, Y. Nishida, K. Hoshino, K. Nakagawa, Y. Ohishi, S. Sudo, *J. Non-Cryst. Solids* **213/214**, 121 (1997)
271. F.P. Kapron, D.B. Keck, R.D. Maurer, *Appl. Phys. Lett.* **17**(10), 423 (1970)
272. P. Keiper, H. Exner, U. Löschner, T. Kuntze, Drilling of Glass by Excimer Laser Mask Projection Technique, ICALEO 1999
273. Y. Kikutani, H. Hisamoto, M. Tokeshi, T. Kitamori, In Ramsey, J.M. and van den Berg, A. (eds.) *Micro Total Analysis Systems*. Kluwer Academic Publishers, 161, (2001)
274. J. Kirchhof, K. Gerth, J. Kobelke, K. Schuster, in *Proceedings 2002 Glass Odyssey, 6th ESG Conference*, Montpellier, 2002, p. 196
275. T. Kirner, J. Albert, M. Günther, G. Mayer, K. Reinhäkel, J.M. Köhler, *Chem. Eng. J.* **101**, 65 (2004)
276. Kitano, K. Koizumi, H. Matsumura, U.S. Patent 3,941,474, 1971
277. G. Kleer, R. Kassner, E.M. Meyer, M.G. Schinker, W. Döll, *Surf. Coat. Technol.* **54/55**, 167 (1992)

278. G. Kleer, E. Kaiser, W. Döll, Surf. Coat. Technol. **79**, 95 (1996)
279. G. Kleer, E. Schäffer, M. Bodmann, J. Kraft, Y. Qiang, H. Haberland, Material. Werkstofftech. **29**, 545 (1998) (in German)
280. G. Kleer, W. Döll, M. Hock, P. Manns, E. Schäffer in *Glass Science and Technology*, ed. by W. Pannhorst, J. Deubener, vol. 76, C2 (Verlag der Deutschen Glastechnischen Gesellschaft, Offenburg, 2003) p. 7
281. F. Klocke, M. Hilleke, Feinwerktech. Mikrotech. Messtech. **104**(1–2), 81–84 (1996) (in German)
282. F. Klocke, M. Hilleke. Ind. Diam. Rund. **30**(2), 90 (1996) (in German)
283. F. Klocke, S. Hambrücker, in *Progress in Precision Engineering and Nanotechnology* ed. by H. Kunzmann (N.W. Wirtschaftsverlag, Braunschweig, 1997)
284. F. Klocke, O. Ruebenach, OSA Tech. Dig. Ser. **12**, 130 (1998)
285. F. Klocke, O. Ruebenach, Ind. Diam. Rund. **34**(2), 133 (2000) (in German)
286. F. Klocke, O. Ruebenach, Ind. Diam. Rev. **60**(3), 227 (2000)
287. F. Klocke, O. Ruebenach, in *International Seminar on Precision Engineering and Microtechnology 2000. Proceedings*, ed. by M. Weck (Voerde, Rhiem, 2000), p. 179
288. F. Klocke, W. Weck, S. Fischer, H. Özmeral, R.B. Schroeter, S. Zamel Ind. Diam. Rund. **3**, 172 (1996)
289. F. Klocke, W. König, M. Hilleke, in *Werkstoffe für die Fertigungstechnik*, ed. by A. De Padi (DGM- Informationsgesellschaft Verlag, Frankfurt, 1997) (in German)
290. F. Klocke, O. Auer, M. Hamers, Werkstattstechnik **90**(1/2), 46 (2000) (in German)
291. F. Klocke, D. Paehler, in *Japan Society of Precision Engineering, Tokyo, Initiatives of Precision Engineering at the Beginning of Millennium, Yokohama, Proceedings*, 2001, p. 411
292. J.C. Knight, T.A. Birks, P.S.t.J. Russell, D.M. Atkin, Opt. Lett. **21**(19), 1547 (1996)
293. J. Kobelke, J. Kirchhof, M. Scheffler, A. Schwuchow, J. Non-Cryst. Solids **256/257**, 226 (1999)
294. W. Koenig, in *Wettbewerbsfaktor Produktionstechnik* (VDI, Duesseldorf, 1989), p. 212 (in German)
295. W. Koenig, V. Sinhoff, Ind. Diam. Rund. **1**, 30 (1994) (in German)
296. W. Koenig, M. Hilleke, in *Technology of Ultrasonic Machining of Advanced Ceramics*. Ceramic Forum International CFI, DKG 72, No. 4, 1995, p. 175
297. G. Köhler, DDR-Patent 129, 413, 1977
298. M. Köhler, *Etching in Microsystem Technology* (Wiley-VCH, Weinheim, 1999)
299. G. Köhler, R. Emmrich, H.P. Köllner, Diffusionsschweißen extrem genauer Glas-Glas-Verbindungen (in German). Jenaer Ingenieurtag, Fügen von Glas, Keramik und Metall, Wissenschaftliche Beiträge der Friedrich Schiller Universität, 1984, p. 23
300. A. Koike, M. Tomozawa, J. Non-Cryst. Solids **353**, 2318 (2007)
301. K. Koizumi, Y. Ikeda, I. Kitano, M. Furukawa, T. Sumimoto, Appl. Opt. **13**(2), 255 (1974)
302. R. Komanduri, D.A. Lucca, Y. Tany, Ann. CIRP, Manuf. Technol. **46**(2), 545 (1997)
303. N. Kondo, H. Ono, Patent Specification U.S. 005314522, 1994
304. Y. Kondo, T. Suzuki, H. Inouye, K. Miura, T. Mitsuyu, K. Hirao, Jpn. J. Appl. Phys. **37**, L94 (1998)

305. H. Korn, W. Hinz, Silikattechnik **23**(3), 80 (1972) (in German)
306. J. Körner, Students Research, TU Ilmenau, Germany, 2003 (in German)
307. J. Körner, R. Mayerhofer, M. Hartmann, H.W. Bergmann, Appl. Phys. A **63**, 123 (1996)
308. D. Krabe, W. Scheel, in *IEEE Electronic Components and Technology Conference*, San Diego, California, 1999, p. 1164
309. M. Kraus, F. Raether, M. Talkenberg, N. Siedow, German Patent DE 10 2004 026257.8, 2004 (in German)
310. M. Kraus, E.W. Kreutz, A. Horn, G. Ligbado, M. Talkenberg, D. Hoffmann, N. Siedow, Farbige Innenmarkierung von Glas durch Laserstrahlung. 79. Glastechnische Tagung der DGG, Würzburg, 2005 (in German)
311. U. Krieger, C. Gießler, B. Halbedel, A. Thess, D. Hülsenberg, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. I9, 2007
312. C. Kröger, L. Sörström, Glastechn. Ber. **38**, 313 (1965) (in German)
313. J. Krüger, Ph.D. Thesis, Technische Universität Cottbus, 1999 (in German)
314. J. Krüger, W. Kautek, Appl. Surf. Sci. **96–98**, 430 (1996)
315. Küppers, J. Koenings, H. Wilson, J. Electrochem. Soc: Solid-State Sci. Technol. **123**(7), 1079 (1976)
316. K. Kuribayashi, M. Sakai, H. Monji, M. Aoki, H. Okinaka, H. Torii, Patent Application EP 0 191 618 B1, 1986
317. J.H. Kyung, N.M. Lawandy, Electron. Lett. **32**(5), 451 (1996)
318. J.H. Kyung, N.M. Lawandy, Opt. Lett. **21**(3), 174 (1996)
319. B. Lan, M.H. Hong, K.D. Ye, Z.B. Wang, S.X. Cheng, T.C. Chong, Jpn. J. Appl. Phys. **43**(10), 7102 (2004)
320. K. Lange, S. Grigull, M. Harz, U. Kreissig, B. Schmidt, in *Proceedings of 3rd International Symposium on Semiconductor Wafer Bonding*, Reno (Nevada), 1995
321. A. Langsdorf, B. Löffelbein, J. Adler, G. Stephani, in *Proceedings of the Materials Week 2002*, Munich, 2002
322. B.R. Lawn, *Fracture of Brittle Solids*, 2nd edn. (Solid State Science Series, Cambridge, 1993)
323. B.R. Lawn, R. Wilshaw, J. Mater. Sci. **10**, 1049 (1975)
324. K.B. Lee, L. Lin, Sens Actuators A **111**, 44 (2004)
325. F. Legewie, L. Bosse, A. Gillner, R. Poprawe, in *Werkstoffwoche 98*, vol. 1, ed. by H. Kempter (Wiley-VCH, 1998) p. 371 (in German)
326. S. Lehnice, B. Löffelbein, O. Zimmer, M. Füting, T. Burkhardt, D. Grimme, S. Piltz, in *Proceedings of the Materials Week*, Munich, 2002
327. S. Lehnice, B. Löffelbein, O. Zimmer, M. Füting, T. Burkhardt, D. Grimme, C. Gärtner, S. Piltz, ZWF, **97**(5), 238 (2002) (in German)
328. Lengtenberg, S. Bouwstra, M. Elwenspoek, J. Micromech. Microeng. **1**, 157 (1991)
329. A. Lenk, L. Morgenthal, Glastechn. Ber. Glass Sci. Technol. **73**(9), 285 (2000)
330. L. Li, T.D. Bennett, in *Proceedings of 34th National Heat Transfer Conference*, Pittsburgh, 2000, p. 263
331. H.J. Ligthart, P.J. Slikkerveer, F.H. In't Veld, P.H.W. Swinkels, M.H. Zonneveld, Phillips J. Res. **50**(3/4), 475 (1996)
332. H.J. Lin, F.Y. Hsu, W.K. Chang, Eur. J. Glass Sci. Technol. B **48**(3), 123, (2007)
333. S. Lindroth, Glas-Email-Keramo-Technik **3**, 146 (1952) (in German)

334. K.L. Loewenstein, *The Manufacturing Technology of Continuous Glass Fibers. Glass Science and Technology 6* (Elsevier, Amsterdam, 1993)
335. M. Lončar, D. Nedeljković, T. Doll, J. Vučković, A. Scherer, T.P. Pearsall, *Appl. Phys. Lett.* **77**(13), 177 (2000)
336. H. Löwe, H. Mensinger, W. Ehrfeld, *Jahrbuch Oberflächentechnik 1994*, vol. 50 (Metall Verlag, Heidelberg, 1994), p. 77 (in German)
337. Y. Ludwig, Under-Graduated Scientific Thesis, TU Ilmenau, 2003 (in German)
338. Y. Ludwig, Diploma Thesis, TU Ilmenau, 2004 (in German)
339. D. Maas, B. Büstgens, J. Fahrenberg, W. Keller, D. Seidel, in *Proceedings of Application of Adhesive Bonding for Integration of Microfluidic Components, ACTUATOR'94*, Bremen, 1994, p. 75
340. D. Maas, B. Büstgens, J. Fahrenberg, W. Menz, W.K. Schomburg, D. Seidel, in *Seminar on Handling and Assembly of Microparts, Proceedings and Lectures, Vienna*, ed. by H. Detter 1994
341. D. Maas, J. Fahrenberg, W. Keller, D. Mihalj, D. Seidel, in *Microsystem Technologies 1994, 4th International Conference on Micro, Electro, Opto, Mechanical Systems and Components, Berlin*, ed. by H. Reichl (VDE-Verlag, 1994)
342. M. Madou, *Fundamentals of Microfabrication*, 2nd edn. (CRC, Boca Raton, 2002)
343. P. Manns, W. Döll, G. Kleer, *Glastechn. Ber. Glass Sci. Technol.* **68**(12), 389 (1995)
344. P. Manns, G. Kleer, W. Döll, Heißprägung von Mikrostrukturen in anorganische Gläser für die Anwendung in der optischen Sensorik, 74. Glastechnische Tagung, Ulm, 2000, p. 102 (in German)
345. A. Marcinkevicius, S. Juodkazis, V. Mizeikis, M. Watanabe, S. Matsuo, J. Nishii, H. Misawa, in *Laser Applications in Microelectronic and Optoelectronic Manufacturing VI*, ed. by M. Gower C, H. Helvajian, K. Sugioka, J. Dubowski, *Proceedings of SPIE*, vol. 4274 (2001) p. 469
346. A.C. Marques, H. Jain, R.M. Almeida, *Eur. J. Glass Sci. Technol. B* **48**(2), 65 (2007)
347. D.M. Marsh, *Proc. R. Soc. Lon. A* **282**, 33 (1964)
348. Y.Y. Maruo, T. Tanaka, T. Ohyama, T. Hayashi, *Sens Actuators B* **57**, 135 (1999)
349. Mashiro, M. Keiichi, M. Hiroyuki, H. Tadaaki, M. Yoshido, K. Hiroshi, European Patent Application, 0 671 372 A2, 1995
350. R.D. Maurer, *Proc. Inst. Electric. Eng.* **123**(6), 581 (1976)
351. M. May, D. Hülsenberg, in *Proceedings Ilmenauer Symposium für Mikrosystemtechnik*. Ilmenau, Germany, 1995 (in German)
352. H. Mehlhorn, Theoretische Grundlagen des Diffusionsschweißens und Schlussfolgerungen für die Anwendung, Jenaer Ingenieurtag, Fügen von Glas, Keramik und Metall, Wissenschaftliche Beiträge der Friedrich Schiller Universität, 1984, p. 6 (in German)
353. M. Mehmel, *Sprechsaal* **90** **4**, 90 (1957); **5**, 111 (1957) (in German)
354. W. Menz, P. Bley, *Mikrosystemtechnik für Ingenieure* (VCH Verlagsgesellschaft mbH, Weinheim, 1993) (in German)
355. J. Merker, H.J. Ullrich, M. Schlaubitz, *Schweiß. Schneid.* **46**(7), 328 (1994) (in German)
356. T.A. Michalske, S.W. Freiman, *J. Am. Ceram. Soc.* **66**(4), 284 (1983)

357. L.L. Mishnaevsky Jr., *Int. J. Mach. Tools Manufact.* **34**(4), 499 (1994)
358. M. Moenster, P. Glas, R. Iliew, R. Wedell, G. Steinmeyer, *IEEE Photon. Technol. Lett.* **18**(23), 2502 (2006)
359. Möncke, D. Ehrt, *Glass Sci. Technol.* **77**(5), 239 (2004)
360. W.M. Moreau, *Semiconductor Lithography* (Plenum, New York, 1991)
361. G.W. Morey, *J. Soc. Glass Technol.* **35**, 270 (1951)
362. G.W. Morey, N.L. Bowen, *J. Soc. Glass Technol.* **9**, 226 (1925)
363. Moriwaki, E. Shamoto, in *Proceedings of the 8th International Precision Engineering Seminar*, 1995, p. 298
364. T. Moriwaki, E. Shamoto, K. Inoue, *Ann. CIRP* **41**(1), 141 (1992)
365. S. Mrotzek, Doctor Thesis, TU Ilmenau, 2005
366. S. Mrotzek, G. Hungenbach, H. Strahl, A. Harnisch, D. Hülsenberg, in *Proceedings of the 5. Chemnitzer Fachtagung Mikromechanik & Mikroelektronik* (2001) p. 196 (in German)
367. S. Mrotzek, A. Harnisch, G. Hungenbach, H. Strahl, D. Hülsenberg, *Glass Sci. Technol.* **76**(1), 22 (2003)
368. S. Mrotzek, Y. Ludwig, K. Pfeifer, D. Hülsenberg Modifizierung von fotostrukturiertem Glas durch Ionenaustausch. 79. Glastechnische Tagung der DGG, Würzburg, 2005 (in German)
369. R. Müller, in *Proceedings of the 5th Otto-Schott-Colloquium* Jena, 1994, p. 93 (Glastechn. Ber. Glass Sci. Technol. 67 C)
370. J.J. Müller, H.E. Gorny, J. Schmalz, U. Heinemann, *J. Appl. Crystallogr.* **28**, 853 (1995)
371. H. Müller-Simon, J. Bauer, P. Baumann, *Glass Sci. Technol.* **74**(10), 283 (2001)
372. H. Münch, H. Crazzolara, Spannungsarme Aufbautechnik piezoresistiver Siliziumsensoren durch Einsatz von Glasloten (in German). VDI Berichte, vol. 939, p. 513 (1992)
373. F. Munoz, O. Pritula, J. Sedláček, C. Rüssel, *Eur. J. Glass Sci. Technol. A* **47**(4), 97 (2006)
374. L. Murugesh, R.O. Scattergood, *J. Mater. Sci.* **26**, 5456 (1991)
375. D.J. Nagel, in *Direct-write Technologies for Rapid-Prototyping Applications* ed. by A. Pique, D.B. Chrisey, (Academic, San Diego, San Francisco, 2002)
376. Y. Nakata, T. Okada, M. Maeda, *Jpn. J. Appl. Phys.* **42**, L379 (2003)
377. M. Nalin, E.J. Carvalho, L. Cescato, G. Poirier, S.J.L. Ribeiro, Y. Messaddeq, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* **47**(2), 186 (2006)
378. Y. Namba, M. Abe, *Ann. CIRP* **42**(1), 417 (1993)
379. K. Nassau, J.W. Shiever, *Ceram. Bull.* **54**(11), 1004 (1975)
380. U. Natura, D. Ehrt, *Formation of radiation defects in silicate and borosilicate glasses caused by UV lamp and excimer laser radiation*. Glastechn. Ber. Glass. Sci. Technol. **72**(9), 295 (1999)
381. R. Neugebauer, A. Schubert, J. Böhm, T. Burkhardt, in *Proceedings on EUSPEN 2nd International Conference*, Turin, vol. 1, 2001, p. 184
382. M. Nienhaus, F. Michel, A. Wolf, T.R. Dietrich, in *Micro Engineering 97, Stuttgart, Proceedings* (1997), p. 1 (in German)
383. Nölle, *Technik der Glasherstellung*, 3rd edn. (Deutscher Verlag für Grundstoffindustrie, Stuttgart, 1997) (in German)
384. S. Nolte, Doctor Thesis, Universität Hannover, Germany, 1999 (in German)
385. M.E. Nordberg, *J. Am. Ceram. Soc.* **27**, 299 (1944)
386. R. Nowak, S. Metev, G. Sepold, K. Großkopf, *Glastechn. Ber.* **66**(9), 227 (1993)

387. Obermeier, S. Hein, K. Holzner, German Patent Application, DE 4446704 C1, 1994
388. E. Obermeier, K. Holzner, T. Diepold, German Patent Application, DE 4409068 A1, 1994
389. M. Opyd, G.H. Frischat, M.L. Aigner, D. Köpsel, Glass Technol.: Eur. J. Glass Sci. Technol. A **48**(3), 130 (2007)
390. M. Opyd, G.H. Frischat, M.L. Aigner, D. Köpsel, Glass Technol.: Eur. J. Glass Sci. Technol. A **48**(1), 31 (2007)
391. J. Orava, T. Wagner, M. Krbal, T. Kohoutek, M. Vlcek, M. Frumar, J. Non-Cryst. Solids **353**, 1441 (2007)
392. H. Orgura, Y. Yoshida, Jpn. J. Appl. Phys. **42**, 2881 (2003)
393. A.D. Osmanis, A.K. Snijedze, V.M. Äglitis, in *19th Symposium on magneto-hydro-dynamics in Riga-Salaspils. Proceedings* (1987), p. 179 (in Russian)
394. H. Ostendarp, Patent Application EP 0 867 418 A1; Patent Application EP 0 867 417 A1, 1998
395. Pähler, R. Brückner, Glastechn. Ber. **58**(2), 33 (1985); **58**(3), 45 (1985) (in German)
396. W.J. Pan, D. Furniss, H. Rowe, C.A. Miller, A. Loni, P. Sewell, T.M. Benson, A.B. Seddon, J. Non-Cryst. Solids **353**, 1302 (2006)
397. H. Paschke, Fügen mit Glasphasen, die Anwendung von Glasloten, DVS-Berichte 66, Deutscher Verlag für Schweißtechnik, 1980 p. 45 (in German)
398. L. Pauling, *The nature of the Chemical Bond* (Cornell University Press, New York, 1945)
399. N.M. Pavluskina, *Vitrokeramik – Grundlagen der Technologie* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1986) (German translation from the Russian)
400. N.D. Payne, W.A. Gambling, Electron. Lett. **10**(15), 289 (1974)
401. U.C. Peak, R.B. Runk, J. Appl. Phys. **49**(8), 4417 (1978)
402. D.H. Pearson, R.J. Tonucci, Adv. Mater. **8**(12), 1031 (1996)
403. K.W. Peter, J. Non-Cryst. Solids. **5**, 103 (1970)
404. Pfeufer, Glastechn. Ber. Glass Sci. Technol. **70**(4), 113 (1997)
405. F. Pigeonneau, Glass Technol.: Eur. J. Glass Sci. Technol. B **48**(2), 66 (2007)
406. R. Pini, R. Salimbeni, G. Toci, M. Vannini, Opt. Quant. Electron. **27**, 1243 (1995)
407. A. Pique, D.B. Chrisey, C.P. Christensen, in *Direct-Write Technologies for Rapid Prototyping Applications*, ed. by A. Pique, B. Chrisey (Academic, San Diego 2002)
408. G. Pollack-Diener, Techn. Messen tm **56**(11), 422 (1989) (in German)
409. H.M. Pollicove, in *Replication and Molding of Optical Components*, SPIE, vol. 896 (1988), p. 158
410. D.I. Pomerantz, G. Wallis, J.J. Dorsey, U.S. Patent 3,417,456, 1968
411. F.W. Preston, Trans. Opt. Soc. **23**(3), 141 (1922)
412. B. Proctor, Phys. Chem. Glasses **3**, 7 (1962)
413. K.E. Puttick, M.R. Rudman, K.J. Smith, A. Franks, K. Lindsey, Proc. R. Soc. Lond. A **426**, 19 (1989)
414. D.L. Pye, A. Montenero, J. Innocent, *Properties of Glass-Forming Melts* (CRC, Taylor and Francis, USA 2005)
415. H.J. Quenzer, W. Henke, W. Hoppe, W. Pilz, P. Wagner, in *Proceedings of Micro System Technologies*, Berlin, 1994, p. 163

416. R.S. Quimby, *Photonics and Lasers* (Wiley, New York, 2006)
417. T. Rainer, Ph.D. Thesis, Martin-Luther-Universität Halle-Wittenberg, 2002 (in German)
418. N.F. Raley, J.C. Davidson, J.W. Balch, SPIE Proc., **2639**, p. 40 (1995)
419. M. Rammo, E. Roeder, Glastechn. Ber. Glass Sci. Technol. **67**(3), 61 (1994)
420. K.J. Rao, *Structural Chemistry of Glasses* (Elsevier, Amsterdam, 2002)
421. K. Raulin, O. Cristini, G. Ehrhart, B. Capoen, M. Bouazaoui, S. Turrell, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. K1, 2007
422. H. Rawson, *Properties and Applications of Glass* (Elsevier, Amsterdam, 1980)
423. M. Reuter, Ph.D. Thesis, Universität Kaiserslautern (1993) (in German)
424. M. Rexer, Z. Techn. Phys. **20**, 4 (1939) (in German)
425. Robu, Sinterfilter VitraPor, Technical Dokumentation Robu Glasfilter-Geräte, 1998 (in German)
426. E. Roeder, G. Wagner, in *Joining Ceramic, Glass and Metal*, ed. by H. Krappitz, H.A. Schaeffer. Proceedings of the 4th International Conference, Königswinter (Verlag der Deutschen Glastechnischen Gesellschaft, Frankfurt am Main, 1993), p. 279
427. M. Rongen, R. Beerkens, A.J. Faber, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. E2, 2007
428. S.E. Rosenberg, H. Papamichael, I.N. Miaoulis, Glass Technol. **35**(6), 260 (1994)
429. A. Rosenberg, R.J. Tonucci, H.B. Lin, A.J. Campillo, Opt. Lett. **21**(11), 830 (1996)
430. A. Roßwang, G. Naundorf, Galvanotechnik **83**(3), 824 (1992) (in German)
431. R. Roy, E. Osborn, J. Am. Chem. Soc. **71**(6), 2086 (1949)
432. P.S.J. Russell, Science **299**, 358 (2003)
433. C. Rüssel, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. E1, 2007
434. Y. Rytz-Froidevaux, R.P. Salathe, H.H. Gilgen, Appl. Phys. A **37**, 121 (1985)
435. R. Salim, Doctor Thesis, TU Ilmenau (ISBN 3-932633-15-6), 1998 (in German)
436. R. Salim, H. Wurmus, A. Harnisch, D. Hülsenberg, Microsyst. Technol. **4**(1), 32 (1997)
437. H.A. Schaeffer, *Technologie des Glases* (Institut für Werkstoffwissenschaften III, Universität Erlangen Nürnberg, 1990) (in German)
438. E. Schäffer, G. Kleer, Surf. Coat. Technol. **133–134**, 215 (2000)
439. Schatt, H. Worch, *Werkstoffwissenschaft*, 8th edn. (Deutscher Verlag für Grundstoffindustrie, Stuttgart, 1996) (in German)
440. D.E. Schaudel, W. Dümig, Adhäsion, **3**, 70–79 (1978) (part 1, in German)
441. H.C. Scheer, H. Schulz, T. Hoffmann, C.M. Sotomayor Torres, J. Vac. Sci. Technol. B **16**, 3917 (1998)
442. A.V. Scherbakov, The Technology Equipment Glass Structure Company (TEGS), prospectus of the company in Saratov/Russia (1999)
443. M.G. Schinker, Prec. Eng. **13**(3), 208 (1991)
444. M. Schinker, J. Bormann, D. Stahn, W. Döll, G. Kleer, P. Manns, Patent Applications U.S. 4,921,519, 1988
445. M.G. Schinker, W. Döll, SPIE, **802**, 70 (1987)
446. K. Schmidt, Doctor Thesis, TU Ilmenau (ISBN 3-8265-0294-9), 1994 (in German)

447. U. Schmidt, G. Köhler Verbindungen von optischem Glas mittels Diffusionsschweißen (in German). Jenaer Ingenieurtag, Fügen von Glas, Keramik und Metall, Wissenschaftliche Beiträge der Friedrich Schiller Universität, p. 93 (1984)
448. H. Scholze, *Glastechn. Ber.* **35**, 37 (1962) (in German)
449. H. Scholze, *Glas-Natur, Struktur und Eigenschaften*, 2nd edn. (Springer, Berlin Heidelberg New York, 1977) (in German)
450. H. Scholze, *Glas-Natur, Struktur und Eigenschaften*, 3rd edn. (Springer, Berlin Heidelberg New York London, 1988) (in German)
451. H. Scholze, D. Helmreich, J. Bakardijev, *Glastechn. Ber.* **48**, 237 (1975) (in German)
452. Schott, SIRAN[®] carriers – for the immobilization of microorganisms – open new routes for high grade biotechnological products. Technical Dokumentation, Schott Engineering, Mainz (1992)
453. Schott, Foturan – ein Werkstoff für die Mikrosystemtechnik. Technical Documentation, Schott Glaswerke, Mainz (in German) (1995)
454. A. Schubert, T. Burkhardt, J. Kadner, R. Neugebauer, in *Proceedings of 1st International Conference and General Meeting of the European Society for Precision Engineering and Nanotechnology (EUSPEN)*, vol. 1 (1999), p. 530
455. A. Schubert, J. Edelmann, T. Burkhardt, *Microsyst. Technol.* **12**(8), 790 (2006)
456. H. Schulz, D. Lyebiedev, H.C. Scheer, K. Pfeiffer, G. Bleidiesel, G. Grützner, J. Ahopelto, *J. Vac. Sci. Technol. B* 18(6), 11/12, 3582 (2000)
457. A.B. Seddon, W.J. Pan, D. Furnis, C.A. Miller, H. Rowe, D. Zhang, E.M. Bearty, Y. Zhang, A. Loni, P. Sewell, T.M. Benson, *J. Non-Cryst. Solids* **352**, 2515 (2006)
458. B. Sepeur-Zeitz, M. Mennig, H. Krug, H. Schmidt, Mikrostrukturierung organisch – anorganischer Nanomere durch Prägeverfahren. 72. Glastechnische Tagung, Münster, p. 76 (1998) (in German)
459. P.J. Severin, NATO ASI Ser., Ser. B: Phys., **91**, 101 (1989)
460. E. Shamoto, C. Ma, T. Moriwaki, in *Proceedings of 1st International Conference and General Meeting of the European Society for Precision Engineering and Nanotechnology (EUSPEN)*, vol. 1, 1999, p. 408
461. L. Shartsis, W. Capps, *J. Am. Ceram. Soc.* **35**, 155 (1952)
462. G.L. Sheldon, I. Finnie, *J. Eng. Ind. Trans. ASME* **88B**, 387 (1966)
463. M. Shimizu, H. Iwakuro, *Jpn. J. Appl. Phys.* **35**(Part 2, 12A) L1622, (1996)
464. Y. Shimotsuma, K. Hirao, J. Qiu, K. Miura, *J. Non-Cryst. Solids* **352**, 646 (2006)
465. S. Shoji, M. Esashi, in *Photoetching and Electrochemical Discharge Drilling of Pyrex Glass*, Technical Digest of the 9th Sensor Symposium (1990), p. 27
466. F.B. Siebers, N. Greulich, W. Kiefer, *Glastechn. Ber.* **62**(2), 63 (1989)
467. J.H. Simmons, K.S. Potter, *Optical Materials* (Academic, San Diego, 2000)
468. J. Singer, U.S. Patent 4,127,398, Single-chip combinatorial synthetic reactor, in *Micro Total Analysis Systems 2001* ed. by J.M. Ramsey, van den A. Berg (Kluwer Academic, New York) p. 161 (1995)
469. V.R. Sinhoff, in *Berichte aus der Produktionstechnik*, ed. by W. Eversheim, F. Klocke, W. Koenig, T. Pfeifer, M. Weck (Shaker, Aachen, 1997) (in German)
470. W. Skatulla, L. Horn, *Exp. Techn. Phys.* **8**(1), 1 (1960) (in German)
471. W. Skatulla, W. Vogel, H. Wessel, *Silikattechnik* **9**, 51 (1958) (in German)

472. P.J. Slikkerveer, PhD Thesis, Eindhoven University of Technology, 1999
473. P.J. Slikkerveer, P.C.P. Bouten, F.H. in't Veld, H. Scholten, *Wear* **217**, 237 (1998)
474. P.J. Slikkerveer, P.C.P. Bouten, F.C.M. de Haas, *Sens. Actuators* **85**, 296 (2000)
475. A. Smekal, *Glastechn. Ber.* **22**, 278 (1949) (in German)
476. G.P. Smith, *Glass Technol.* **20**(4), 149 (1979)
477. G.P. Smith, *Mater. Design*, **2**, 121 (1989)
478. R.B. Sosman, *The Properties of Silica* (The Chemical Catalog Company, New York, 1927)
479. C.M. Sotomayor-Torres, *Alternative Lithography*. (Kluwer Academic/Plenum, New York, 2003)
480. U. Sowada, H.J. Kahlert, D. Basting, *Laser + Optoelektron*, **20**(2), 69 (1988)
481. B. Speit, *F&M* **101**, 339 (1993) (in German)
482. G.A.C.M. Spierings, *J. Mater. Sci.* **26**, 3329 (1991)
483. G.A.C.M. Spierings, *J. Mater. Sci.* **28**, 6261 (1993)
484. G.A.C.M. Spierings, J. van Dijk, *J. Mater. Sci.* **22**, 1869 (1987)
485. G. Spur, E. Uhlmann, S.E. Holl, in *9th Cimtec-World Ceramic Congress, Ceramics: Getting into the 2000s – Part D*, by ed. P. Vincenzini (Techna Srl, 1999) p. 181
486. J. Stanek, *Electric Melting of Glass* (Elsevier, Amsterdam, 1977)
487. G. Staupendahl, *Viertes Symposium Zukunft Glas*, Zwiesel, 2002, p. 137 (in German)
488. G. Staupendahl, P. Gerling in *Strahl-Stoff-Wechselwirkung bei der Laserbearbeitung 2*, ed. by G. Sepold, M. Geiger. Proceedings of the DFG-Symposium, 18–19 February 1998, Bremen/Germany, p. 117 (in German) (ISBN 3-9805011-6-7)
489. G. Staupendahl, J. Grabow, K. Herrmann, in *Thüringer Werkstofftag 2002, Proceedings*, ed. by J.D. Schnapp, U. Glatzel, K.D. Jandt, H. Knake (Verlag Dr. Köster, Berlin, 2002), p. 185 (in German)
490. W. Steger, R. Haller, in *Meister des Kupferferrädchens* ed. by Joska-Kristall (Ohetaler Verlag, 2006) (in German)
491. M. Stehle, R. Brückner, *Glastechn. Ber.* **53**(5), 130 (1980) (in German)
492. M. Stehle, R. Brückner, *Glastechn. Ber.* **54**(3), 74 (1981) (in German)
493. R. Stemmer, *Metall* **22**(11), 1103 (1968) (in German)
494. A.F. Stewart, A.H. Guenther, *NIST Spec. Publ.* 775 (1989) p. 176
495. M. Stjernström, J. Roeraade, *J. Micromech. Microeng.* **8**, 33 (1998)
496. S.D. Stookey, *Ind. Eng. Chem.* **41**, 856 (1949)
497. S.D. Stookey, *U.S. Patent* 2, 628, 160, 10 Feb. 1953
498. S.D. Stookey, *Ind. Eng. Chem.* **45**, 115 (1953)
499. S.D. Stookey, *Ind. Eng. Chem.* **46**, 174 (1954)
500. S.D. Stookey, *Chemtech*, **8**, 458 (1971)
501. S.D. Stookey, *Explorations in Glass. An Autobiography* (American Ceramic Society, Westerville Ohio/USA, 2000)
502. S.D. Stookey, F.W. Schuler, in *Proceedings of the IV. International Congress on Glass*, Paris 1956, p. 390
503. B. Straube, Doctor Thesis, TU Ilmenau (ISBN 3-8265-3060-8), 1997 (in German)
504. A.M. Streltsov, N.F. Borrelli, *J. Opt. Soc. Am. B* **19**(10), 2496 (2002)

505. J.S. Stroud, *J. Chem. Phys.* **35**(3), 844 (1961)
506. M. Sugawara, *Plasma Etching, Fundamentals and Applications* (Oxford University Press, New York, 1998)
507. K. Sugioka, M. Masuda, T. Hongo, Y. Cheng, K. Shihoyama, K. Midorikawa, *Appl. Phys. A* **79**, 815 (2004)
508. K.H. Sun, *J. Amer. Ceram. Soc.* **30**, 277 (1947)
509. T. Suratwala, L. Wong, P. Miller, M.D. Feit, J. Menapace, R. Steele, P. Davis, D. Walmer, *J. Non-Cryst. Solids* **352**, 5601 (2006)
510. S. Surinach, E. Illekova, G. Zhang, M. Poulain, M.D. Baro, *J. Mater. Res.* **11**(10), 2633 (1996)
511. K. Suzuki, S. Matsui, Y. Ochiai, *Sub-Half-Micron Lithography for ULSIs* (Cambridge University Press, Cambridge, 2000)
512. G. Tammann, *Der Glaszustand*. L. Voß, Leipzig
513. B.V. Tanikella, R.O. Scattergood, *Scripta Mater.* **34**(2), 207 (1996)
514. E.W. Taylor, *J. Soc. Glass Tech.* **34**, 69 (1950)
515. S. Thiel, S. Lehnicke, O. Zimmer, D. Grimme, U. Doll, S. Piltz, *VDI-Z Spec. Werkzeug-/Formenbau* **11**, 26 (2000) (in German)
516. L. Thielen, A.M. Lankhorst, A.F.J.A. Habraken, D. Hegen, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. F10, 2007
517. T.B. Thoe, D.K. Aspinwall, M.L.H. Wise, *Int. J. Mach. Tools Manuf.* **38**(4), 239 (1998)
518. V. Tikomirov, P. Hertogen, G. Adriaenssens, V. Krasteva, G. Sigel, J. Kirchhoff, J. Kobelke, M. Scheffler, *J. Non-Cryst. Solids* **227–230**, 694 (1998)
519. H. Tokura, I. Kondoh, M. Yoshikawa, *J. Mater. Sci.* **24**, 991 (1989)
520. H.K. Tönshoff, v.W.Schmieden, I. Inasaki, W. König, G. Spur, *Ann. CIRP* **39**(2), 621 (1990)
521. H.K. Tönshoff, D. Hesse, H. Kappel, in *Proceedings of LANE'94*, vol. 2, 1994, p. 627
522. R.J. Tonucci, B.L. Justus, U.S. Patent 5,332, 681 (1992)
523. R.J. Tonucci, B.L. Justus, A.J. Campillo, in *Nanometer Array Glass Technology for Quantum Dot and Quantum Wire Applications*. Technical Digest, International Quantum Electronics Conference, Wienen, 1992, p. 60
524. F.V. Tooley, *The Handbook of Glass Manufacture*, vol. 2 (Books For Industry, 1974)
525. M. Toyoda, Y. Fujiya, M. Nayama, T. Yamada, *Trans. Jpn. Weld. Soc.* **24**(2), 3 (1993)
526. W. Trier, *Glass Furnaces – Design, Construction and Operation* (Society of Glass Technology, Sheffield, 1987)
527. D.M. Trotter, *Sci. Am.* **56** (1991)
528. H. Tsuchiya, T. Inoue, M. Miyazaki, in *Proceedings of the 5th International Conference on Production Engineering*, Tokyo, 1984, p. 413
529. T. Tsukada, H. Nogami, Y. Nakagawa, E. Wani, K. Mashimo, H. Sato, S. Samukawa, *Thin Solid Films* **341**, 84 (1999)
530. E. Uhlmann, N.A. Daus, in *Deutsche Keramische Gesellschaft e.V. –DKG-Ceramic Materials and Components for Engines: 7*, ed. by J.G. Heinrich. International Symposium – Applications in Energy Transportation and Environment Systems (Wiley-VCH, Weinheim, 2001), p. 417
531. E. Uhlmann, S. Piltz, U. Doll, *Werkstattstechnik online* **91**(12), 733 (2001) (in German)

532. P.M. Valov, *Glass Phys. Chem.* **20**(3), (1994)
533. P.A. Van Nijnatten, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. F16, 2007
534. H. Varel, D. Ashkenasi, A. Rosenfeld, M. Wähmer, E.E.B. Campbell, *Appl. Phys. A* **65**, 367 (1997)
535. A.K. Varshneya, *Fundamentals of Inorganic Glasses* (Academic, New York, 1994)
536. F. Vizethum, PhD Thesis, Universität Erlangen-Nürnberg, 1986
537. W. Vogel, *Glaschemie*, 1st edn. (VEB Deutscher Verlag für Grundstoffindustrie Leipzig, 1979) (in German)
538. W. Vogel, *Glaschemie*, 3rd edn. (Springer, Berlin Heidelberg New York, 1992) (in German)
539. W. Vogel, *Glasfehler* (Springer, Berlin, Heidelberg, New York, 1993) (in German)
540. W. Vogel, H.G. Byhan, *Silikattechnik* **15**, 239 (1964) (in German)
541. W. Vogel, K. Gerth, *Silikattechnik* **9**, 353, 495, 539 (1958) (in German)
542. W. Vogel, K. Gerth, *Glastechn. Ber.* **31**, 15 (1958) (in German)
543. W.J. Wadsworth, A. Ortigosa-Blanch, J.C. Knight, T.A. Birks, T.P.M. Man, P.S.t.J. Russell, *J. Opt. Soc. Am. B* **19**(9), 2148 (2002)
544. D.B. Wallace, W.R. Cox, D.J Hayes, in *Direct-write Technologies for Rapid-Prototyping Applications*, ed. by A. Pique, D.B. Chrisey, (Academic, San Diego, 2002)
545. G. Wallis, D.I. Pomerantz, *J. Appl. Phys.* **40**(10), 3946 (1969)
546. B.E. Warren, *Zeitschrift Kristallogr. Mineralog. Petrogr.* **86**, 349 (1933)
547. D. Washington, V. Duchenois, R. Polaert, R.M. Beasley, *Acta Electron.* **14**(2), 201 (1971)
548. F. Wauro, F. Bartels, *Mst News* **19**, 14 (1997)
549. F. Wauro, F. Bartels, in *Proceedings on 1st International Conference on Motion Systems*, Jena, 1997, p. 98 (in German)
550. W. Wawrziniak, *Sci. J. Friedrich-Schiller-Universität Jena*, **25**(5), p. 553 (1976) (in German)
551. J. Weber, in *Elektroschmelzen von Glas*, Hüttentechnische Vereinigung der Deutschen Glasindustrie (1990) (in German)
552. M. Weck, J. Luderich, M. Vos, H.B. Schroeder, in *Progress in Precision Engineering 95*, ed. by M. Bonis, Y. Alayli, P. Revel (Elsevier, Amsterdam, 1995)
553. R. Wedell, *Phys. Bl.* **52**(11), 1134 (1996) (in German)
554. M. Wegmann, J. Heiber, F. Clemens, T. Graule, D. Hülsenberg, K. Schuster, *Glass Sci. Technol.* **78**(2), 69 (2005)
555. A. Wenda, M. Beck, V. Hüntrupp, M. Meisel, M. Rothenburg, O. Rübenach, J. Schmütz, C. Schwietering, J. Gäbler, *F&M* **107**(11), 64 (1999) (in German)
556. H. Wensink, H.V. Jansen, M.C. Elwenspoek, in *Proceedings on 10th Micromechanics Europe Workshop*, Giv sur Yvette, France, 1999, p. 199
557. H. Wensink, J.W. Berenschot, H.V. Jansen, M.C. Elwenspoek, in *Proceedings of 13th IEEE MEMS Conference*, 2000, p. 769
558. E. Westkämper, H.W. Hoffmeister, J. Gäbler, *F&M* **104**(7/8), 525 (1996) (in German)
559. E. Westkämper, A. Henning, G. Radons, R. Friedrich, T. Ditzinger, in *Proceedings on International Seminar on Intelligent Computation in Manufacturing Engineering*, Salerno, 2000, p. 179

560. W.A. Weyl, *Glastechn. Ber.* **23**(6/7), 174 (1950) (in German)
561. W.A. Weyl, E.C. Marboe, *The Constitution of Glasses, vol. 1: Fundamentals of the Structure of Inorganic Liquids and Solids; vol. 2: Constitution and Properties of Some Representative Glasses* (Interscience, New York, London, 1962)
562. S.M. Wiederhorn, *J. Am. Ceram. Soc.* **50**(8), 225 (1967)
563. M. Wiemer, K. Hiller, T. Gessner, T. Kloss, K. Schneider, U. Leipold-Haas, J. Bagdahn, M. Petzold, in *Proceedings on 3rd International Conference Micro Materials*, MicroMat, Berlin, 2000, p. 1280
564. A. Winkelmann, O. Schott, *Ann. Phys.* **51**, 730 (1884) (in German)
565. V. Winter, Forschungszentrum Karlsruhe, Wissenschaftliche Berichte FZKA6173 (1998) (in German)
566. J.L. Wiza, *Nucl. Instrum. Meth.* **162**, 587 (1979)
567. A. Yabe, H. Njino, N. Kondo, H. Ono, T. Takahashi, Y. Takahashi, T. Matsumura, U.S. Patent Specification 005,374,291, 1994
568. K. Yamada, W. Watanabe, T. Toma, K. Itoh, J. Nishii, *Opt. Lett.* **26**, 19 (2001)
569. M. Yamane, Y. Asahara, *Glasses for Photonics* (Cambridge University Press, Cambridge, 2000)
570. T. Yano, N. Uno, S. Shibata, M. Yamane, in *Proceedings of the XXI International Congress on Glass in Strasbourg*, Ref. A49, 2007
571. S. Yoshida, H. Ito, *Bull. Jpn. Soc. Prec. Eng.* **24**(4), 239 (1990)
572. Y. Yoshida, Y. Kobayashi, T. Zhang, H. Yajima, Y. Hashidate, H. Ogura, in *First International Symposium on Laser Precision Microfabrication*, ed. by I. Miyamoto, K. Sugioka, T.W. Sigmon. *Proceedings of SPIE*, vol. 4088, 2000, p. 187
573. S.W. Youn, C.G. Kang, *J. Non-Cryst. Solids* **351**, 3065 (2005)
574. W.J. Zachariasen, *J. Am. Ceram. Soc.* **54**, 3841 (1932)
575. J. Zeng, T.J. Kim, in *Proceedings on 11th International Conference on Jet Cutting Technology*, St. Andrews, Scotland, 1992, p. 483
576. J. Zhang, K. Sugioka, K. Midorikawa, *Appl. Phys. A* **69**, S879 (1999)
577. H. Zhang, P. Shi, D. Li, K. Du, *Appl. Opt.* **42**(9), 1681 (2003)
578. Z.W. Zhong, Z.Z. Han, *Mater. Manuf. Process.* **17**(3), 339 (2002)
579. K. Zimmer, K. Otte, A. Braun, S. Rudschuck, H. Friedrich, H. Schulz, H.C. Scheer, T. Hoffmann, C.M. Sotomayor-Torres, R. Mehnert, F. Bigl, in *Proceedings on 1st International Conference and General Meeting of the European Society for Precision Engineering and Nanotechnology (EUSPEN)*, 1999
580. E. Zimmermann, T. Koliwer, G. Köhler, in *Joining Ceramic, Glass and Metal. Proceedings of the 4th International Conference*, ed. by S. Krappitz (Verlag der Deutschen Glastechnischen Gesellschaft, Frankfurt am Main, 1993), p. 374
581. V. Zöppig, G. Christen, K. Feindt, T. Gramsch, A. Harnisch, H. Pfefferkorn, *Microgripping devices with functional elements of micro structured glass materials*. Seminar on Handling and Assembly of Microparts, Vienna, 1997

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