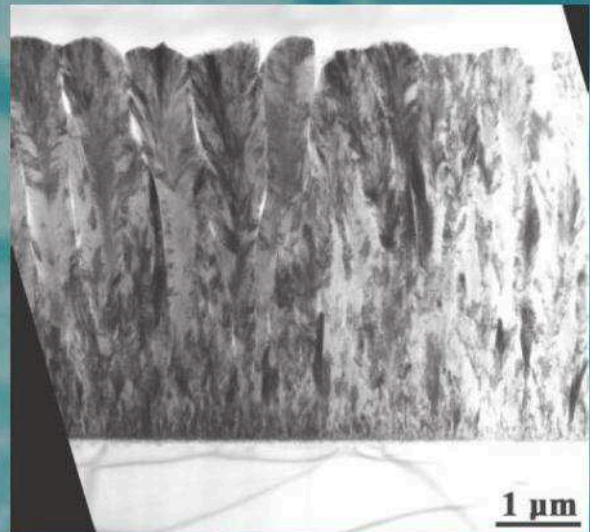
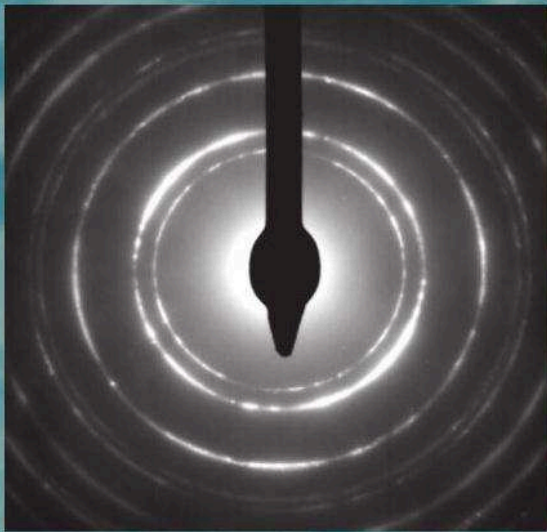


Nanocomposite Coatings and Nanocomposite Materials



Edited by
A. Öchsner, W. Ahmed, N. Ali

Nanocomposite Coatings and Nanocomposite Materials

Preface

1 Nanocomposite Coatings and Nanocomposite Materials

Edited by

Andreas Öchsner, Waqar Ahmed and Nasar Ali

Nanocomposite materials are formed by mixing two or more dissimilar materials at the nanoscale in order to control and develop new and improved structures and properties. The properties of nanocomposites depend not only on the individual components used but also on the morphology and the interfacial characteristics. Nanocomposite coatings and materials is one of the most exciting and fastest growing areas of research with new materials and novel properties being continuously developed which are previously unknown in the constituent materials. Therefore nanocomposite materials and coatings have enormous potential for new applications including aerospace, automotive, electronics, biomedical implants, non-linear optics, mechanically re-enforced lightweight materials, sensors, nanowires, batteries, bioceramics, energy conversion and many other systems with smart functionalities.

This exciting new book comprises of 9 chapters, each written by international experts in an easy understand style and format suitable for students (undergraduate and post graduate), technologists and experts seeking to expand their knowledge in the area of nanocomposite materials and coatings. Even though each topic area covered assumes an elementary knowledge of materials, there is however a comprehensive introduction to each chapter covering the most important literature, details of the experimental methods and techniques used followed by a description of the latest research work. There are four comprehensive chapters covering the design, synthesis and applications of nanocomposite coatings. In the past developments in nanocomposites were hindered by the lack of characterisation techniques available to probe materials at the nanoscale, therefore a complete chapter is dedicated to the latest characterisation techniques available to investigate nanocomposite coatings and nanocomposite materials. Organic/inorganic nanocomposite materials have vast potential for many new applications and by engineering the polymers-host interactions nanocomposites with a broad range of properties can be produced. The synthesis and the applications of hybrid organic-inorganic nanostructured materials are describe in a comprehensive chapter. Novel routes are being developed to synthesise three dimensional nanocomposites hence there are three chapters devoted to nanowires, re-enforced nanocomposites and hierarchical nanocomposites.

It is hoped that the information contained in this book will serve both as an educational aid and a guide to all engaged in the nanocomposites from multidisciplinary subject areas including materials science, physics, chemistry, biology and medical engineering.

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CHAPTER 1

Nanostructured, Nanocomposite Tribological Coatings

^{1a}John J. Moore, ^{1b}In-Wook Park, ^{1c}Jianliang Lin, ^{2d}Jennifer M. Anton,
^{1e}Brajendra Mishra, and ^{3*}Kwang Ho Kim

¹John J. Moore¹, In-Wook Park², Jianliang Lin³, and Brajendra Mishra⁴
Advanced Coatings and Surface Engineering Laboratory (ACSEL),
Colorado School of Mines, Golden, CO 80401, USA

²NIST, 325 Broadway St., MS 853, Boulder, CO 80305, USA

³School of Materials Science and Engineering, Pusan National University,
Keumjung-Ku, Busan 609-735, South Korea

E-mail: ^ajjmoore@mines.edu, ^bipark@mines.edu, ^cjlin@mines.edu,
^djanton@boulder.nist.gov, ^ebmishra@mines.edu,
^{*}kwhokim@pusan.ac.kr

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1. INTRODUCTION

Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique physical–chemical properties [1,2]. A number of sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings [3,4]. There are many types of design models for nanostructured coatings, such as three-dimensional nanocomposite coatings [2,5], nano-scale multilayer coatings [6,7], functionally graded coatings [1,4], etc. The optimized design of nanostructured coatings needs to consider many factors, e.g. ion energy and ion flux of depositing species, interface volume, crystallite size, single layer thickness, surface and interfacial energy, texture, epitaxial stress and strain, etc., all of which depend significantly on materials selection, deposition methods and process parameters [2,8].

Nanostructured, Nanocomposite Tribological Coatings

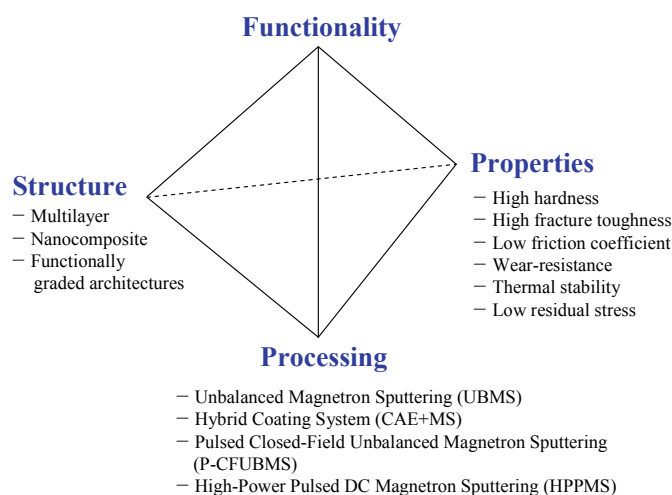


Fig. 1.1. Tetrahedron representing the relationship among processing, structure, properties, and functionality for nanostructured, multifunctional tribological coatings.

In particular, pulsed reactive magnetron deposition techniques have been investigated, more recently, since it is possible to conduct reactive sputtering without arcing during deposition. Pulsed reactive sputtering can also change and control the plasma constituents, increase the ion energy and ion flux, and improve microstructural growth of the thin film through ion bombardment [8]. The applications of pulsing in reactive magnetron sputtering opens up considerable opportunities for the control of ion energy and ion flux to optimize the deposition process and tailor the as-deposited coating structure and properties.

The focus of this chapter is to introduce the relationships between processing, structure, properties, and functionality of nanostructured coatings using various magnetron sputtering deposition processes, such as unbalanced magnetron sputtering (UBMS), hybrid coating system of cathodic arc evaporation (CAE) and magnetron sputtering (MS), pulsed closed-

field unbalanced magnetron sputtering (P-CFUBMS), and high-power pulsed magnetron sputtering (HPPMS), as shown in Fig. 1.1.

2. CLASSIFICATION OF NANOSTRUCTURED, NANOCOMPOSITE TRIBOLOGICAL COATINGS

2.1 NANO-SCALE MULTILAYER COATINGS

Research on using nano-scale multilayers (i.e., “*Superlattices*”) to increase the hardness and toughness of coatings has provided significant advancements in understanding the advantages of employing this type of coating architecture. Early research by Palatnik with multilayers of metals showed that significant improvements in strength were achieved when layer thickness was decreased below 500 nm [6,9]. In early modeling, Koehler [7] predicted that high shear strength coatings could be produced by alternating layers of high and low elastic modulus. Key elements of the concept are that very thin layers (≤ 10 nm) inhibit dislocation formation, while differences in elastic modulus between layers inhibit dislocation mobility. Lehoczy demonstrated [47] these concepts on metallic Al/Cu and Al/Ag multilayers and showed that a Hall-Petch type equation could be used to relate hardness to $1/(\text{periodicity})^{1/2}$ where periodicity is a minimum periodic length between layers in the multilayer coating. Springer and Catlett [10], and Movchan et al. [11] reported on mechanical enhancements in metal/ceramic (e.g., Ti/TiN, Hf/HfN, W/WN, etc.) [12] and ceramic/ceramic (e.g., TiN/VN [13], TiN/NbN [14,15], TiN/V_xNb_{1-x}N [16,17], etc.) laminate structures that followed a Hall-Petch relationship. These pioneering works were followed by intensive research in multilayers [18,19], which has produced coatings significantly harder than the individual components making up the layers. To achieve increased hardness, the layers must have sharp interfaces and periodicity in the 5-10 nm range. The multilayer architectures, as shown in Fig. 2.1, exhibiting high hardness are frequently called superlattices [20]. The different design architectures have been classified and some reports have formalized the multilayer design [4,21]. Multilayer architectures clearly increase coating hardness and have commercial applications, especially in the tool industry. However, they can be difficult to apply with uniform thickness on three-dimensional components and rough surfaces. If the layers are not of the correct periodicity, the superlattice effect is lost. Another relatively new technology, nanocomposites, offers the same advantages as multilayers (plus other benefits) and their properties are not critically dependent on thickness or substrate geometry.

2.2 NANOCOMPOSITE COATINGS

Nanostructured composite (i.e., “*Nanocomposite*”) coatings are usually formed from ternary or higher order systems and comprise at least two immiscible phases: two nanocrystalline phases or, more commonly, an amorphous phase surrounding nanocrystallites of a secondary phase. The most interesting and extensively investigated nanocomposite coatings are

ternary, quaternary or even more complex systems, with nanocrystalline (nc-) grains of hard transition metal-nitrides (e.g. TiN, CrN, AlN, BN, ZrN, etc.), carbides (e.g. TiC, VC, WC, ZrC, etc.), borides (e.g. TiB₂, CrB₂, VB₂, WB, ZrB₂, etc.), oxides (e.g. Al₂O₃, TiO₂, SiO₂, MgO, TiO₂, Y₂O₃, ZrO₂, etc.), or silicides (e.g. TiSi₂, CrSi₂, ZrSi₂, etc.) surrounded by amorphous (*a*-) matrices (e.g. Si₃N₄, BN, C, etc.). The physical, mechanical, and thermal properties of these hard materials are summarized in Table 1 [22]. The synthesis of such nanocomposite (nc-/a-) coatings critically depends on the ability to co-deposit both the nanocrystalline and amorphous phases, such as Ti–Si–N (nc-TiN/nc- and *a*-TiSi₂/*a*-Si₃N₄) [2], Ti–Al–Si–N (nc-TiAlN/*a*-Si₃N₄) [5], W–Si–N (nc-W₂N/*a*-Si₃N₄) [23], Cr–Si–N (nc-CrN/*a*-Si₃N₄) [24], Ti–B–C–N (nc-TiB₂ and TiC/*a*-BN) [25], TiC/DLC (nc-TiC/*a*-C) [26], WC/DLC (nc-WC/*a*-C) [27], etc. as schematically presented in Fig. 2.2(a). A variety of hard compounds can be used as the nanocrystalline phases, including nitrides, carbides, borides, oxides, and silicides. Veprék [28] suggested that the nano-crystalline grains must be 3~10 nm in size and separated by 1~2 monolayers of an amorphous phase as shown in Fig. 2.2(a). For example, Ti–B–N nanocomposite, which consists of nanocrystalline TiN (~5 nm in size) in an amorphous BN matrix, has been synthesized and observed by Lu [32], as shown in Fig. 2.2(b).

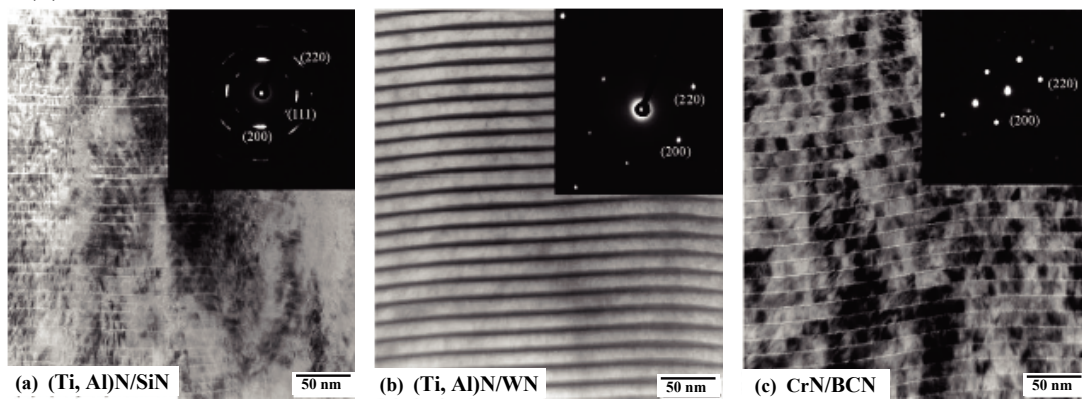


Fig. 2.1. Cross-sectional TEM images and selected area diffraction patterns (SADP) of nano-scale multilayer coatings: (a) (Ti, Al)N/SiN, (b) (Ti, Al)N/WN, and (c) CrN/BCN. [20]

2.3 FUNCTIONALLY GRADED COATINGS

In order to counteract brittle failure and improve fracture toughness, two concepts have been explored. The first involves the use of graded interfaces between the coating and substrate and between layers in the coating. For example, a WC–TiC–TiN (outside layer) graded coating for cutting tools was reported by Fella et al. [29], which showed considerably less wear than single layer hard coatings used in the cutting of steels. This type of coating is functionally and chemically graded to achieve better adhesion, oxidation resistance, and mechanical properties. One example of how functionally graded architectures improve coating performance is the adhesion of DLC to steels. DLC, and especially hydrogen-free DLC, has a very high hardness and generally has a large residual compressive stress. The coatings are relatively inert, and adhesion failures of coated steel surfaces were a roadblock

to success. This problem was solved through designing and implementing a graded interface between the coating and the substrate. Examples of effective gradient compositions are Ti–TiN–TiCN–TiC–DLC for hydrogenated DLC [30] and Ti–TiC–DLC for hydrogen-free DLC [31]. In the development of the latter composition, the importance of a graded elastic modulus through the substrate coating/interface was highlighted as shown in Fig. 2.3. The gradual build-up in material stiffness from the substrate with $E=220$ GPa to the DLC layer with $E=650$ GPa avoids sharp interfaces that can provide places for crack initiation, good chemical continuity, and load support for the hard DLC top-coat. This functionally graded approach can be combined with multilayer and nanocomposite architectures to further enhance tribological properties.

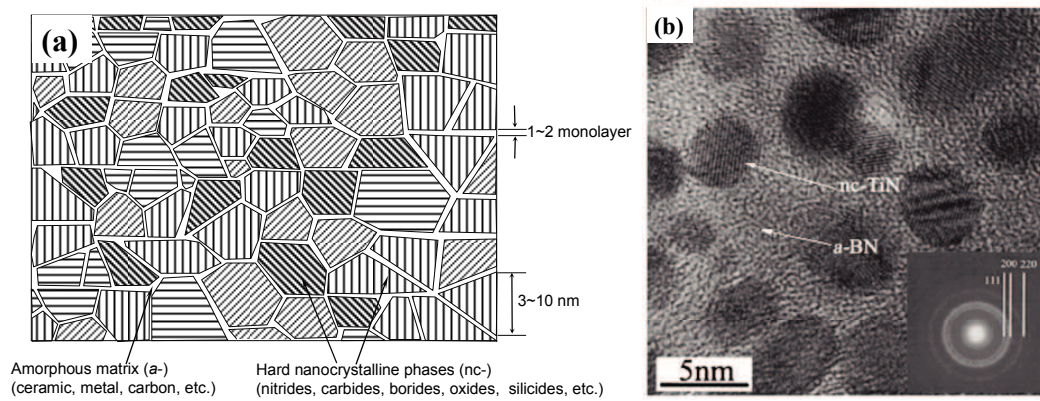


Fig. 2.2. (a) Schematic diagram of a nanostructured nanocomposite coating proposed by Veprék [28], and (b) HRTEM image and selected area diffraction pattern (SADP) of nanocomposite Ti–B–N (nc-TiN/a-BN) [32].

Material	Hardness	Elastic Modulus	Thickness
DLC at 10^{-5} Pa	70 GPa	650 GPa	400 nm
DLC at 10^{-1} Pa	43 GPa	450 GPa	100 nm
Ti _{0.10} C _{0.90}	25 GPa	290 GPa	25 nm
Ti _{0.25} C _{0.75}	27 GPa	350 GPa	25 nm
Ti _{0.30} C _{0.70}	29 GPa	370 GPa	100 nm
Ti _{0.50} C _{0.50}	20 GPa	290 GPa	100 nm
Ti _{0.70} C _{0.30}	14 GPa	230 GPa	100 nm
Ti _{0.90} C _{0.10}	6 GPa	150 GPa	50 nm
Ti	4 GPa	140 GPa	50 nm
440 Steel	11 GPa	220 GPa	Substrate

Ti: 0 at.%
 C: 100 at.%
 Functionally graded
 Ti: 100 at.%
 C: 0 at.%

Fig. 2.3. Schematic diagram of a functionally graded Ti–TiC_x–DLC coating, where chemistry and elastic moduli are transitioned from metallic substrate to hard DLC top layer. [32]

Table 2.1. The physical, mechanical, and thermal properties of hard materials

Phase	Crystal structure	Lattice parameters (nm)	Density (g/cm ³)	Melting point (°C)	Linear thermal expansion, α (10 ⁻⁶ K ⁻¹)	Thermal conductivity, λ (W· m ⁻¹ K ⁻¹)	Electrical resistivity (10 ⁻⁶ Ω cm)	Enthalpy at 298K (kJ· mol ⁻¹)	Young's modulus (10 ⁵ N· mm ⁻²)	Micro hardness (10 N· mm ⁻²)	Oxidation resistance ($\times 100$ °C)
Nitrides											
AlN	hex	0.311/0.498	3.05	2200	6	10	10 ¹¹	288.9	3.15	1200	13
BN	hex	0.251/0.669	2.25	3000	3.8	284.7	3 $\times 10^{14}$	252.5	0.9	4400 HV	10
CrN	fcc	0.415	6.1	1050	2.3	11.72	640	118–124	4	1800–2100	7–7.5
	cub-B1	0.4149	5.39–7.75	1450	2.3	11.72	640	123.1	3.236	1100	
Cr ₃ N	Hex	0.4760/0.4438	5.9	1500	9.4			30.8	3.138	2250 HV	86.3–110.3
HfN	Fcc	0.452	13.8	3310	6.9	11.3	26	369.4	3.33–4.8	1700–2000	
Si ₃ N ₄	hex	0.78/0.56	3.44	1900	2.4	20–24	10 ¹⁸	750.5	2.1	1410 HV	12–14
TaN	hep	0.52/0.29	13.6–13.8	3000	3.6	8.58	128	225.7	5.756	3240	5–8
Ta ₃ N	hex	0.30/0.493	15.8	3000		10.05	263	270.9		3000	
TiN	cub-B1	0.423	5.21	3220	9.35	30	21.7	336.2	2.512	2400 HV	5
VN	fcc	0.41	6.13	2050	8.1	11.3	85–100	147.8	4.6	1520	5–8
ZrN	fcc	0.46	6.93	3000	6	16.75	13.6	365.5	5.1	2000	12
Carbides											
B ₄ C	rhom	0.5631/1.2144	2.52	2450	6	27.63	10 ⁶	72	4.5	3700	11–14
Cr ₃ C ₂	ortho	1.146/0.552/0.2821	6.68	1900	10.3	18.8	75	88.8	4	1500–2000	12
NbC	fcc	0.45	7.78	3490	6.65	14.24	35–74	139.8	3.4	2400	11
SiC	α -hex	β :0.4360	3.2	2200	5.68	15.49	10 ⁵	71.6	4.8	3500	14–17
	β :fcc	α :0.3–7.3/1–1.5	3.17	2700	5.3	63–155	10 ⁵	73.3	3.9–4.1	1400 HV	13–14
TaC	cub-B1	0.4454	14.65	3877	6.04	22.19	25	159.5	2.91	1490	11–14
TiC	cub-B1	0.429–0.433	4.93	3150	7.4	17–23.5	68	179.6	3.22	3200 HV	11–14
VC	cub-B1	0.4173	5.36	2770	6.55	4.2	156	105.1	4.34	2760 HV	8–11
WC	hex	0.29/0.28	15.7	2600	5.2–7.3	121.42	17	35.2	7.2	2080	8
ZrC	cub-B1	0.4989–0.476	6.51	3400	6.93	20.5	42	181.7	4	2600 HV	12
Borides											
AlB ₂	hex	0.3006/0.3252	3.17	1975				67			14–18
CrB	ortho	0.2969/0.7858/0.2932	6.05	1550				75.4	2.15	2250	
CrB ₂	hex	0.279/0.307	5.6	2200	11.1		56	94.6		2800	11–17
HfB ₂	hex	0.3141/0.3470	11.01	3200	5.3	430	10	336.6		1380 HV	11–14
MoB ₂	hex	0.3/0.31	7.8	2100			45	96.3		2600	11–14
NbB ₂	hex	0.31/0.33	6.8	3000	7.1–9.6	16.75	32	150.7	2.6	1910	
SiB ₆	ortho	1.4470/1.8350/0.9946	2.43	1950	8.3		10 ⁷		3.3	2200	11–14
TaB ₂	hex	0.31/0.33		3150	5.1	21.35	68	209.3	2.62	3840	11–14
TiB ₂	hex	0.3/0.32	4.5	2900	6.39	25.96	9	150.7	3.7	2500	11–17
Ti ₃ B	tet	0.61/0.46		2200						2080	13
VB ₂	hex	0.3/0.31	4.8	2400	5.3		16	203.9	5.1	3750	
WB	tet	0.31/1.7	15.5	2860						2350	8–14
W ₂ B	tet	0.56/0.47	16.5	2770	4.7		21.43			3600	
ZrB	fcc	0.47	6.5	3000				163.3			
ZrB ₂	hex	0.32/0.35	6.1	3000	6.83	23.03	9.2	326.6	3.5	2200	11

Table 2.1. Continued

Phase	Crystal structure	Lattice parameters (nm)	Density (g/cm ³)	Melting point (°C)	Linear thermal expansion, α (10 ⁻⁶ K ⁻¹)	Thermal conductivity, λ (W· m ⁻¹ K ⁻¹)	Electrical resistivity (10 ⁻⁶ Ω cm)	Enthalpy at 298K (kJ· mol ⁻¹)	Young's modulus (10 ⁵ N· mm ⁻²)	Micro hardness (10 N· mm ⁻²)	Oxidation resistance ($\times 100$ °C)
Oxides											
Al ₂ O ₃ - α	hex	0.5127	3.99	2043	8	30.1	10 ²⁰	1580.1	4	2100 HV	17
BeO	rhomb	0.513	3.9	2030	7.2-8.6	4.2-16.7	10 ²⁰	1678.5	3.6	2100 HV	20
CrO ₂	hex	0.2699/0.4401	3	2450	9	264	10 ⁻³	569	3	1230-1490 HV	17
CrO ₃	tet	0.441/0.291	4.8					582.8			
Cr ₂ O ₃	ortho	0.573/0.852/0.474	2.81	170-198	6.7		10 ⁻³	579.9		1000 HV	
Cr ₂ O ₃	rhomb	0.536	5.21	2440	5.6			1130.4		2300 HV	
HfO ₂	hex	0.495876/1.35942	5.21	2400	10	3		1130.4		900	
HfO ₂	mono	0.512	9.7	2900	10	36	5 $\times 10^{15}$	1053.4		745 HV	17
MgO	cub	0.4208	3.6	2850	11.2	1.38	10 ⁻²	568.6	3.2	1130-1260	
SiO ₂	quartz	0.4093/0.5393	2.33	1703-1729	0.4	1.2-1.4	10 ⁻²	911	0.5-1.0	1200	
SiO ₂	trigonal	0.421/0.539	2.2	1713	0.5-0.75	10	10 ⁻⁶	911.5	1.114	950 HV	17
ThO ₂	fcc	0.5859	10.05	3250	10	11		1173.1	1.38	1300	
TiO	cub-B1	0.417	4.88	1750	7.6	8	1.2 $\times 10^{10}$	520	2.05-2.80	767-1000 HK	
TiO ₂	tet	0.4593/0.2959	4.19	1900	4.21-4.25			945.4	0.8-2.0	1000 HV	
Ti ₂ O ₃	cub-B1	0.45933/0.29592	4.25	1867	9		10 ⁻⁹ -10 ⁻²⁴	1433.1		980 HV	
Ti ₃ O ₅	rhomb	0.5454	4.6	2130				2461			
ZrO ₂	mono	0.9828/0.3776/0.9898	5.6	1780			10 ⁻⁶	1035	1.63	1200	17
ZrO ₂	cub	0.511		2750	7.5-10.5	0.7-2.4					
Silicides											
CrSi	cub	0.4629	5.38	1550				53.2		1000	
CrSi ₂	hex	0.442/0.655	4.91	1630				100.5		1100	14-18
Cr ₃ Si	cub	0.455	6.52	1710				105.5		900-980	
MoSi ₂	tet	0.32/0.786	6.3	2050	8.4	221.9	21	108.9	3.84	1290	17
NbSi ₂	hex	0.48/0.66	5.5	1950	8.4		6.3	50.2		700	8-11
TaSi ₂	hex	0.4773/0.6552	9.2	2200	8.9/8.8		38	150.7		1410	11
TiSi ₂	ortho	0.8236/0.4773/0.8523	4.39	1520	11.5		18	134.4	2.556	892	11
VSi ₂	hex	0.46/0.64	4.5	1650	11		9.5	95		960	
WSi ₂	tet	0.321/0.788	9.5	2165	6.5	45	12.5	92.1	5.3	1090	16
ZrSi ₂	ortho	0.372/1.416/0.367	4.87	1700	9.7		161	159.4	2.348	1030 HV	8-11

Legend:

HV: Vickers hardness, HK: Knoop hardness

hcp: hexagonal closed-packed, fcc: face-centered cubic

ortho: orthorhombic, hex: hexagonal, cub: cubic, cub-B1: cubic NaCl-type, rhomb: rhombohedral/trigonal, tet: tetragonal, mono: monoclinic, tri: triclinic

3. BACKGROUND OF NANOSTRUCTURED SUPER-HARD COATINGS

Hardness is defined as the resistance to plastic deformation. Plastic deformation of crystalline materials occurs predominantly by dislocation movement under applied load. Therefore, a higher resistance to dislocation movement in a material will generally enhance its hardness. One approach to obtain high resistance to dislocation movement and plastic deformation is to preclude the formation of stable dislocations. “*Super-hard*” coatings, with a hardness value in excess of 40 GPa, have attracted significantly increasing interest during the past 10–15years [33]. A concept for super-hard nanocomposite coatings was suggested by Veprék [34]. The strength and hardness of engineering materials are orders of magnitude smaller than the theoretically predicted values. They are determined mainly by the microstructure which has to be designed in such a way as to efficiently hinder the multiplication and movement of dislocations and the growth of microcracks. This can be achieved in various ways known from physical metallurgy, such as solution, work, and grain boundary hardening [35,36]. In this way, the strength and hardness of a material can be increased by a factor of 3–7 times, i.e., super-hard material should form when such enhancement can be achieved starting from a hard material ($HV > 20$ GPa). Solution and work hardening do not operate in small nanocrystals of about < 10 nm because solute atoms segregate to the grain boundary and there are no dislocations. Therefore, we consider the possibilities of extending the grain boundary hardening in poly- and microcrystalline materials, described by the Hall–Petch relationship [37,38], Eq. (3.1), down to the range of a few nanometers.

$$\sigma_c = \sigma_0 + \frac{k_{gb}}{\sqrt{d}} \quad (3.1)$$

here σ_c is the critical fracture stress, d is the crystallite size, and σ_0 and k_{gb} are constants. Many different mechanisms and theories describe Hall–Petch strengthening [37,38]. Dislocation pileup models and work hardening yield the $d^{1/2}$ dependence but different formula for σ_0 and k_{gb} , whereas the grain–grain boundary composite models also give a more complicated dependence of σ_c on d . The strength of brittle materials, such as glasses and ceramics, is determined by their ability to withstand the growth of microcracks. Brittle materials do not undergo any plastic deformation up to their fracture. Their strength or hardness is proportional to the elastic modulus. The critical stress which causes the growth of a microcrack of size a_0 is given by the general Griffith criterion:

$$\sigma_c = k_{crack} \sqrt{\frac{2E\gamma_s}{\pi a_0}} \propto \frac{1}{\sqrt{d}} \quad (3.2)$$

here E is the Young's modulus, γ_s is the surface cohesive energy, and k_{crack} is a constant which depends on the nature and shape of the microcrack and on the kind of stress applied [35]. Thus, the $d^{1/2}$ dependence of the strength and hardness in a material can also originate from the fact that the size, a_0 , of the possible flaws, such as voids and microcracks that are formed during the processing of the material, also decreases with decreasing grain size. For these reasons, the Hall–Petch relationship, Eq. (3.1), should be considered as a semi-empirical formula which is valid down to a crystallite size of 20–50 nm (some models predict an even higher limit [39,40]). With the crystallite size decreasing below this limit, the fraction of the material in the grain boundaries strongly increases which leads to a decrease of its strength and hardness due to an increase of ‘*grain boundary sliding*’ [40,41]. A simple phenomenological model (i.e., rule of mixtures) describes the softening in terms of an increasing volume fraction of the grain boundary material, f_{gb} , with the crystallite size decreasing below 10–6 nm [42]:

$$H(f_{gb}) = (1 - f_{gb})H_c + f_{gb}H_{gb}, \quad (3.3)$$

here $f_{gb} \propto (1/d)$. Due to the flaws present, the hardness of the grain boundary material, H_{gb} , is smaller than that of the crystallites H_c . Thus the average hardness of the material decreases with d decreasing below 10 nm. The first report of a ‘*Reverse*’ (or ‘*negative*’) *Hall–Petch relationship* was by Chokshi et al.[43] Later on it was the subject of many studies, with controversial conclusions regarding the critical grain size where ‘*Normal*’ *Hall–Petch relationship* changes to the reverse one [39,44]. Various mechanisms of grain boundary creep and sliding were discussed and are described by deformation mechanism maps in terms of the temperature and stress [45,46]. Theories of grain boundary sliding were critically reviewed in Ref. [39]. Recent computer simulation studies [41] confirm that the negative Hall–Petch dependence in nanocrystalline metals is due to the grain boundary sliding that occurs due to a large number of small sliding events of atomic planes at the grain boundaries without thermal activation. Although many details are still not understood, there is little doubt that grain boundary sliding is the reason for softening in this crystallite size range. Therefore, a further increase of the strength and hardness with decreasing crystallite size can be achieved only if grain boundary sliding can be blocked by appropriate design of the material. This is the basis of the concept for the design of super-hard nanocomposites, suggested by Veprek [34].

As mentioned in Sec. 2.1, another possible way to strengthen a material is based on the formation of nano-scale multilayers consisting of two different materials with large differences in elastic moduli, sharp interface, and small bilayer thickness (lattice period) of about 10 nm [7]. Because this design of nanostructured super-hard materials was suggested and experimentally confirmed before super-hard nanocomposites were developed, we will deal with superlattice coatings in Sec. 3.1.

3.1 NANO-SCALE MULTILAYER COATINGS

In a theoretical paper published in 1970 Koehler suggested [7] a concept for the design of strong solids which are nowadays called superlattices. Originally he suggested depositing epitaxial multilayers of two different metals, A and B , having as different elastic constants as possible $E_A < E_B$ but a similar thermal expansion and strong bonds. The thickness of the layers should be so small that no dislocation source could operate within the layers. If under applied stress a dislocation, which would form in the softer layer A , would move towards the A/B interface, elastic strain induced in the second layer B with the higher elastic modulus would cause a repulsing force that would hinder the dislocation from crossing that interface. Thus, the strength of such multilayers would be much larger than that expected from the rule of mixture. Koehler's prediction was further developed and experimentally confirmed by Lehoczky who deposited Al/Cu and Al/Ag superlattices and measured their mechanical properties [47]. According to the rule of mixtures, the applied stress which causes elastic strain is distributed between the layers proportional to their volume fractions and elastic moduli. Lehoczky has shown that the tensile stress–strain characteristics measured on multilayers consisting of two different metals displayed a much higher Young's modulus and tensile strength than that predicted by the rule of mixtures, and both of which increased with decreasing thickness of the double layer (lattice period). For layer thicknesses of <70 nm, the yield stress of Al/Cu multilayers was 4.2 times larger and the tensile fracture stress was 2.4–3.4 times higher than the values given by the rule of mixture [47]. This work was followed by work of a number of researchers who confirmed the experimental results on various metal/metal, metal/ceramic, and ceramic/ceramic multilayer systems (see Sec. 2.1). In all these cases, an increase in hardness by a factor of 2–4 was achieved when the lattice period decreased to about 5–10 nm. For a large lattice period, where the dislocation multiplication source can still operate, the increase of the hardness and the tensile strength (most researchers measured the hardness because it is simpler than the measurement of tensile strength conducted by Lehoczky) [47] with decreasing layer thickness is due to the increase in the critical stress, which is dependent on multiply dislocations such as a Frank-Read dislocation source,

$$\sigma_c = \frac{Gb}{l_{pp}} \propto \frac{1}{l_{pp}} \quad (3.4)$$

where G is the shear modulus, b the Burgers vector, and l_{pp} the distance between the dislocation pinning sites [35]. Usually one finds strengthening dependence similar to the Hall–Petch relationship but with a somewhat different dependence on the layer period (λ^{-n}), instead of the crystallite size d in Eq. (3.1), with $n=1/2$ for layers with different slip systems and $n=1$ for layers with a similar slip system [48]. A more recent theoretical discussion of the Hall–Petch relationship for superlattices was published by Anderson and Li [49]. According to their calculations, strong deviations from continuum Hall–Petch behavior occur when the thickness of the layers is so small that the pileup contains only one to two dislocations.

In a remark added in the proof, Koehler mentioned that the ideas described in his paper would also be valid if one of the layers is amorphous. Recently, several papers appeared in which one of the layers consists of an amorphous CN_x and a transition metal nitride such as TiN [50] or ZrN [51]. However, with decreasing layer thickness the layered structure vanished and a nanocrystalline composite (i.e., “*Nanocomposite*”) structure appeared [50,51]. Such films can also exhibit a high hardness of 40 GPa or more.

3.2 SINGLE-LAYER NANOCOMPOSITE COATINGS

Using similar ideas for restricting dislocation formation and mobility as used in multilayer approaches to “*hardening*”, nanocomposite coatings can also be super-hard [25,28]. These composites have 3-10 nm crystalline grains embedded in an amorphous matrix and the grains are separated by 1-2 monolayers. This design or “*Architecture*” leads to ultra-hard (hardness above 100 GPa) coatings as reported by Veprék and co-authors most recently [2]. The nanocrystalline phase may be selected from nitrides, carbides, borides, and oxides, as shown in Table 1, while the amorphous phase may also include metals and diamond-like carbon (DLC) as shown in Fig. 2.1(a). The initial model proposed by Veprék to explain hardness in nanocomposites is that dislocation operation is suppressed in small grains (3-5 nm) and that the narrow space between them (1-2 monolayers separation) induces incoherence strains [34,52]. The incoherence strain is likely increased, when grain orientations are close enough to provide interaction between matched but slightly misoriented atomic planes. In the absence of dislocation activity, Griffith’s equation, as shown in Eq. (3.2), for crack opening was proposed as a simple description of the nanocomposite strength. This equation suggests that strength can be increased by increasing elastic modulus and surface energy of the combined phases, and by decreasing the crystalline grain sizes. It is noted that elastic modulus is inversely dependent on grain sizes that are in the nm size range due to lattice incoherence strains and the high volume of grain boundaries [2]. In practice, grain boundary defects always exist, and a 3 nm grain size was found to be close to the minimum limit. Below this limit, a reverse Hall–Petch effect has been observed and the strengthening effect disappears because grain boundaries and grains become indistinguishable and the stability of the nanocrystalline phase is greatly reduced [34,43,53].

Nanocomposites with metal matrixes are in a special category for this discussion. They have been demonstrated to increase hardness, but also have good potential for increasing toughness. Mechanisms for toughening within these systems are discussed in the next section, while mechanisms for hardening are discussed here. The composite strength of ceramic/metal nanocomposites may be described by the following form of the Griffith–Orowan model [54] when the dimensions of the metal matrix permit operation of dislocations:

$$\sigma_c = \sqrt{\frac{2E(\gamma_s + \gamma_p)}{\pi a} \frac{r_{tip}}{3d_a}} \quad (3.5)$$

where γ_p is the work done during plastic deformation, r_{tip} is the curvature of the crack tip, and d_a is the interatomic distance. It is noted that crack tip blunting and the work of plastic deformation considerably improve material strength, while the lower elastic moduli of metals cause a reduction in strength as compared to ceramics. However, in nanocomposites, dislocation operation may be prohibited because the separation of grains is very small. For example, the critical distance, l_{pp} , for a Frank-Read dislocation source is very small. Matrix dimensions in hard nanocomposite coatings are from 1 to 3 nm, which is well below the critical size for dislocation source operation, even in very soft metal matrixes. Therefore, the mechanical behavior of such nanocomposites can be expected to be similar to that of ceramic matrix composites.

Composite designs that increase elastic modulus and hardness, do not necessarily impart high toughness. First, dislocation mechanisms of deformation are prohibited and crack opening is the predominant mechanism for strain relaxation when stresses exceed the strength limit. Second, Griffith's equation does not take into account the energy balance of a moving crack, which consists of the energy required to break bonds and overcome friction losses, potential energy released by crack opening, and kinetic energy gained through crack motion [55]. From crack energy considerations, a high amount of stored stress dictates a high rate of potential energy release in the moving crack. In such conditions, a crack can achieve the self-propagating (energetically self-supporting) stage sooner, transferring into a macrocrack and causing brittle fracture. However, nanocomposites contain a high volume of grain boundaries between crystalline and amorphous phases. This type of structure limits initial crack sizes and helps to deflect, split, and blunt growing cracks.

4. NEW DIRECTIONS FOR NANOSTRUCTURED SUPER-TOUGH COATINGS

While super-hard coatings are very important, quite notably for protection of cutting tools, most tribological applications for coatings either require, or would receive significant benefit

from increased toughness and lower friction. In particular, “*High Fracture Toughness*” is necessary for applications where high contact loads and, hence, significant substrate deformations, are encountered [27]. A material is generally considered tough if it possesses both high strength and high ductility. High hardness (H) is directly related to high elastic modulus (E) and high yield strength, but it is very challenging to add a measure of ductility to hard coatings. For example, the super-hard coating designs, as stated earlier, prevent dislocation activity, essentially eliminating one common mechanism for ductility. Therefore, designs that increase ductility must also be considered to provide tough tribological coatings. Pharr [56] has suggested that an indication of fracture toughness (i.e. H/E ratio) can be obtained by examining the surface radial cracks created during indentation, described by the equation:

$$K_c = \alpha_1 \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (4.1)$$

where P is the peak indentation load, c the radial crack length and α_1 an empirical constant related to the indenter geometry. K_c describes the ‘critical stress intensity’ for crack propagation, but it is not an intrinsic parameter that can be used to measure fracture toughness directly. However, it is proportional to fracture toughness. Thus, fracture toughness of coatings would appear to be improved by both a high hardness and a “*Low Elastic Modulus*.” In this work, the H/E values were calculated and discussed relatively for each coating [57].

4.1 FUNCTIONALLY GRADED MULTILAYER COATINGS

An effective route for improving toughness in multilayers is the introduction of ductile, low elastic modulus alternate layers into the coating structure to relieve stress and allow crack energy dissipation by plastic deformation in the crack tip. This approach will result in a decreased coating hardness, but the gain in the fracture toughness improvement may be more important in many tribological applications, excluding coatings for the cutting tool industry. For example, $[\text{Ti}/\text{TiN}]_n$ multilayer coatings on cast iron piston rings relaxed interface stress and improved combustion engine performance [58]. Fig. 4.1(a) shows a schematic of a multilayer $[\text{Ti}/\text{DLC}]_n$ coating on a graded load support foundation, where the ductile Ti layers in the multilayer stack were graded at every DLC interface to avoid brittle fracture[4]. A cross-sectional photograph of this coating with 20 $[\text{Ti}/\text{DLC}]$ pairs is shown in Fig. 4.1(b). The ductile Ti layers reduced the composite coating hardness to 20 GPa as compared to a single layer DLC coating, which has a hardness of about 60 GPa. However, due to dramatic improvement in toughness the multilayer coating design permitted operation during sliding

friction at contact pressures as high as 2 GPa without fracture failure compared to 0.6-0.8 GPa for single layer DLC.

In general, the combination of multilayer and functionally graded approaches in the design of wear protective coatings produces exceptionally tough wear protective coatings for engineering applications. One potential drawback slowing the wide spread use of new coatings was the need for reliable process controls to ensure that the correct compositions, structures, and properties are implemented during growth. However, modern process instrumentation and control technologies are able to meet the challenge and permit successful commercialization [59]. Thus, functionally graded and multilayer designs are commonly utilized in the production of modern tribological coatings.

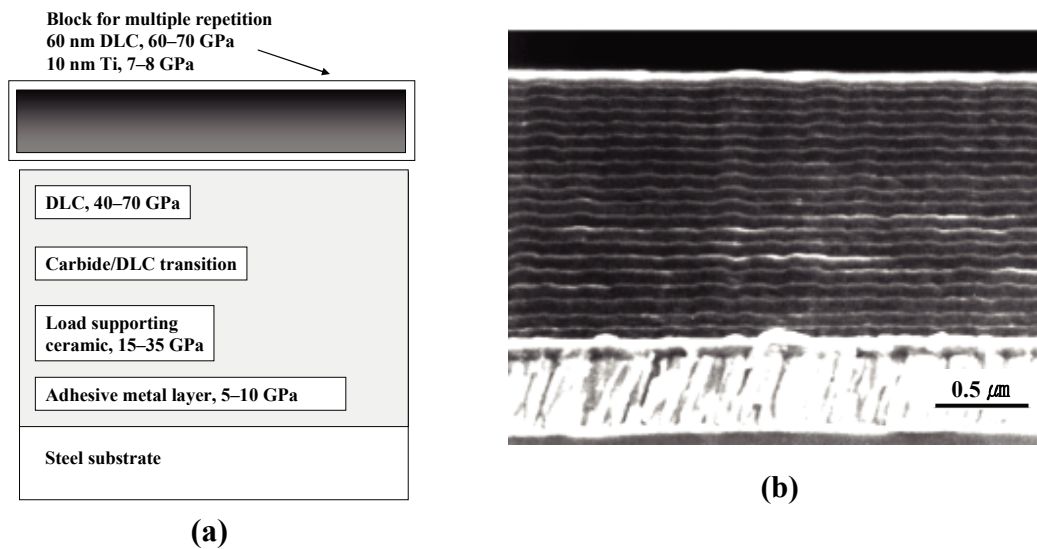


Fig. 4.1. A multilayer coating with multiple Ti/DLC pairs on top of a functionally gradient layer for an optimum combination of cohesive and adhesive toughness: (a) design schematic, and (b) cross sectional photograph of the coating produced with 20 Ti/DLC pairs [4].

4.2 FUNCTIONALLY GRADED NANOCOMPOSITE COATINGS

An alternative to employing multilayers to toughen coatings is embedding grains of a hard, high yield strength phase into a softer matrix allowing for high ductility. This approach has been widely explored in macro-composites made of ceramics and metals which are known as cermets [60]. It was recently scaled down to the nanometer level in thin films made of hard nitrides and softer metal matrixes [28]. Combination of the nanocrystalline/amorphous designs with a functionally graded interface, as shown in Fig. 4.2(a), provides high cohesive toughness and high interface (adhesive) toughness in a single coating. Several examples of tough wear-resistant composite coatings have been reported. Two of them combined nanocrystalline carbides with an amorphous DLC matrix designated as TiC/DLC and WC/DLC composites. In another example, nanocrystalline MoS₂ was encapsulated in an Al₂O₃ amorphous matrix as shown in Fig. 4.2(b). In all cases, the large fraction of grain

boundary phase provided ductility by activating grain boundary slip and crack termination by nanocrack splitting. This provided a unique combination of high hardness and toughness in these coatings. Novel nanocomposite designs suggested by Voevodin and Zabinski [61] for tough tribological coatings are very promising and provide a very attractive alternative to multilayer architectures. One of these novel designs incorporates the “*Chameleon*” approach in which components are added to the coating that provide a low friction coefficient under extreme environmental conditions such as low and high humidity and low and high temperatures [61]. Nanocomposite coatings are more easily implemented, since they do not require precise control in the layer thickness and frequent cycling of the deposition parameters, as is required for fabrication of multilayer coatings. They are however relatively recent developments, and suitable scale-up of deposition techniques is currently under intense study.

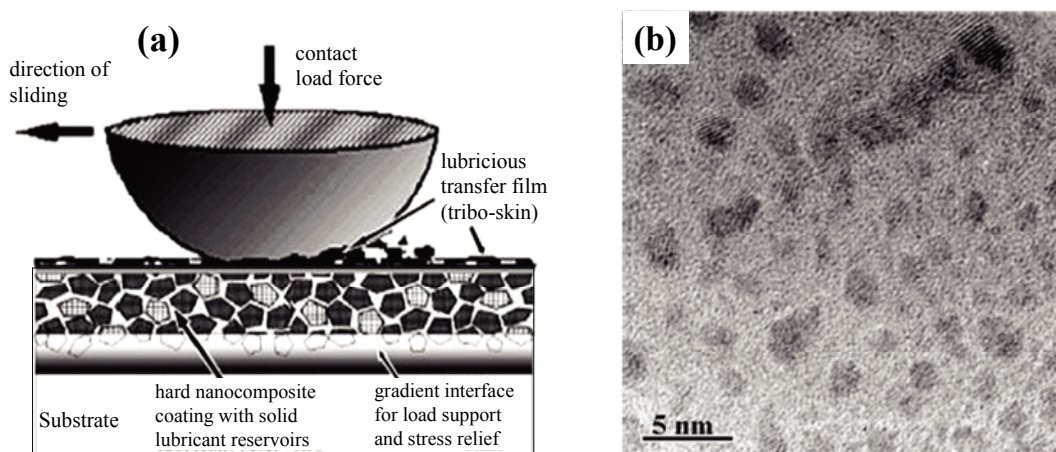


Fig. 4.2. (a) Schematic representation of a tough nanocomposite coating design, combining a nanocrystalline/amorphous structure with a functionally gradient interface, and (b) TEM image of an $\text{Al}_2\text{O}_3/\text{MoS}_2$ nanocomposite coating consisted of an amorphous Al_2O_3 ceramic matrix encapsulating 5–10 nm inclusions of nanocrystalline MoS_2 grains [61].

5. OTHER POSSIBLE PROPERTIES OF NANOSTRUCTURED COATINGS

To prevent tribological failures, there are additional requirements related to the normal (load) and tangential (friction) forces. In general terms, a tough “*Wear-resistant*” coating must support high loads in sliding or rolling contact without failure by wear, cohesive fracture, and loss of adhesion (delamination). A “*Low Friction Coefficient*” reduces friction losses and may increase load capability. Tribological coatings where a low friction coefficient is also required may be obtained by producing nanocomposite coatings with a mix of hard and lubricating phases, in which a hard primary phase (e.g. nitrides, carbides, or borides, etc.) provides wear-resistance and load-bearing capability and a lubricating secondary phase (e.g. $\alpha\text{-C}$, $\alpha\text{-Si}_3\text{N}_4$, $\alpha\text{-BN}$, etc.) reduces the friction between two contacting components. Finally, “*Thermal Stability*” is required to optimize coating performance and lifetime. The amorphous phases in grain boundaries can act as diffusion barriers (e.g. $\alpha\text{-$

Si₃N₄, *a*-SiO₂, etc.) for improved thermal stability. For instance, nc-TiN/*a*-Si₃N₄ coatings with amorphous Si₃N₄ matrix did not show grain growth at temperatures up to 1050 °C as well as super-hardness of about 45 GPa [62]. Moreover, silicon nitride acts as an efficient barrier against oxygen diffusion at the grain boundaries and also by forming an oxidation resistant SiO₂ surface layer, and thus resulting in excellent thermal stability.

In summary, in addition to high hardness, other aspects such as, high toughness, low friction coefficient, and high thermal stability are decisive characteristics of nanostructured coatings for their potential as protective tribological coatings.

6. NEW PROCESSES FOR INDUSTRIAL APPLICATIONS OF MULTIFUNCTIONAL TRIBOLOGICAL COATINGS

6.1 HYBRID COATING SYSTEM OF CATHODIC ARC ION EVAPORATION (CAE) AND MAGNETRON SPUTTERING (MS)

For more than a decade, cathodic arc evaporation (CAE) has been widely used to deposit various kinds of refractory and wear-resistant coatings such as Ti–Al–N [63] and its variants [64] for cutting tools, and CrN [65] coatings for automotive applications. The cathodic arc evaporation process is characterized by a combination of a high deposition rate and a high degree of ionization ($\geq 90\%$) of evaporated species and high ion energies (20–250 eV), which makes this process a versatile deposition technology for many industries. Due to the nature of the high-current vacuum arc discharge, however, only target materials with good electro-conductivity can be used as evaporation sources. Also materials with a too high or low melting point or poor mechanical strength cannot be used. On the other hand, the sputtering process has fewer restrictions concerning the target material. Various kinds of materials, which are hard to use in the arc process, are usable in the sputtering process. One of the drawbacks of the sputtering process for the deposition of hard coatings is its low degree of ionization, which is in the range of a few percents. However, recently, this has been amended by the introduction of unbalanced magnetron sputtering (UBM) [66] and, more recently, by high-power pulsed magnetron sputtering (HPPMS) [67], which enhances plasma irradiation during the deposition or ionization of sputtered species. Recently, more complex coatings in composition and structure such as nanocomposite coatings and multilayer coatings have been under development to increase the service life of the coated tools and machine parts. Considering this situation, combining the arc and the sputtering process can be a way to enhance the possibility of depositing a coating system with a more complex structure and composition for improved performance. In this chapter, the microstructure and mechanical properties of the nanocomposite coating system will be discussed: Ti–Al–N and Ti–Al–Si–N coatings deposited by a hybrid coating system of CAE and sputtering will be introduced and discussed in Sec. 7.1; and Ti–B–C–N and Ti–Si–B–C–N coatings deposited by UBMS will be discussed in Sec. 7.2.

6.2 PULSED CLOSED FIELD MAGNETRON SPUTTERING (P-CFUBMS)

DC magnetron sputtering is a state-of-art deposition technique to produce coatings for diverse industrial applications, such as hard coatings, semiconductor, optical and decorative films etc. In DC magnetron sputtering, a glow discharge is created in low-pressure inert gas by applying a negative voltage on metal targets under a vacuum condition. The use of a magnetic field in the magnetrons behind the metal target allows sputtering to be performed at low pressures and voltages and at high deposition rates [68,69].

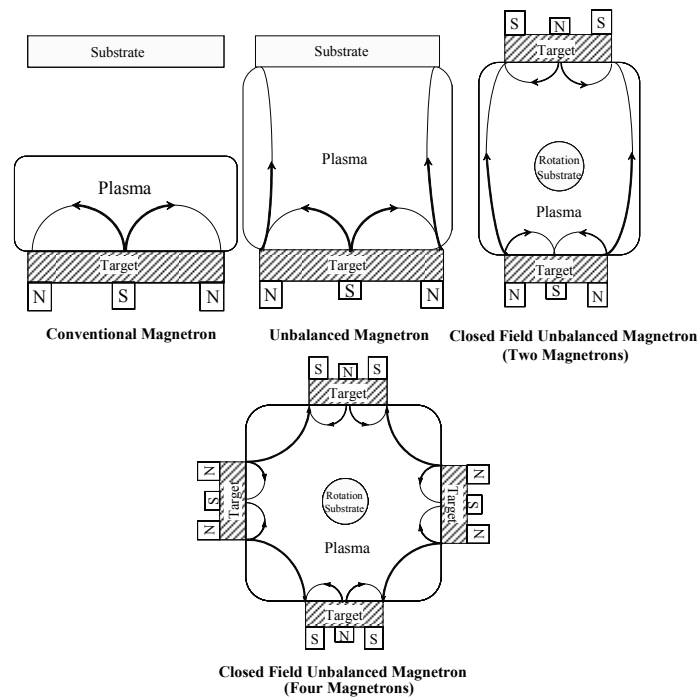


Fig. 6.1. A comparison of the magnetic configuration and plasma confinement in conventional, unbalanced and dual-magnetron closed-field systems [70].

In recent years, there have been many improvements on DC magnetron sputtering. The development of unbalanced magnetron sputtering (the inner magnet and the outer magnet magnetic strength is unbalanced) has significantly increased the plasma generation area away from the target surface, see Fig. 6.1 [70]. With the development of closed field unbalanced magnetron sputtering, a closed magnetic field is created by applying opposite magnetic poles in adjacent magnetrons, thereby resulting in much higher ion current densities and dense, hard well adhered coatings by enhanced chemical reaction at the substrate [70]. A comparison of the magnetic configuration and plasma confinement in conventional, unbalanced and dual-magnetron closed-field systems is presented in Fig. 6.1. Closed field systems can be configured using any even number of magnetrons. The use of multiple magnetrons in conjunction with a two-axis or three-axis substrate rotation system allows for the uniform deposition of large and complex shaped components in the closed field plasma. Applying a negative bias voltage to the substrate can increase the energy of the ions bombarding the substrate. The energetic ions increase the bombardment of the substrate surface therefore producing coatings that exhibit high hardness and good wear resistance and

good adhesion to the substrate. One of the most important improvements in magnetron sputtering has been to reactively deposit ceramic and compound coatings of various components. Under normal magnetron sputtering, the sputtered targets generate a range of species that include energetic ions (1–10%), and neutral atoms (Ti, Cr, Ar, etc.). These species can chemically react with gas atoms that impinge on the substrate surface to form a compound film. Reactive sputtering can be used to deposit most nitride, carbide and oxide thin films with desired composition as a controlled monolithic or compositionally graded structure.

The deposition of hard ceramic coatings such as TiN [71], CrN [72], TiC [73], Ti–Al–N [74], Cr–Al–N [75], Al₂O₃ [76] etc., is achieved using reactive sputtering from the metal targets (Ti, Cr, Al, etc.) in a reactive gas atmosphere, e.g. N₂/Ar, CH₄/Ar or O₂/Ar gas mixture. However, for deposition of insulating films, the insulating film builds up on the surface of the chamber and/or anode. When the insulating layer on the anode becomes thick, the sputtering discharge becomes unstable. This phenomenon is called “*disappearing anode*.” The target can also charge up quickly due to a non-conductive layer formed on the target at which point the target is said to “*poisoned*” which makes sputtering more difficult, decreases the sputtering rate and increases the power in the target. The charges will generate arcing problems in which the micro-particles will be ejected from the target and incorporated into the deposited coatings. This condition leads to non-uniform deposition, and the inhomogeneity and defects in the coatings, as well as reduced deposition rate [77].

In order to overcome this problem, the use of radio frequency (RF) to sputter material was developed in the 1960’s. However, RF sputtering is not used extensively for commercial magnetron sputtering due to its low deposition rate, high cost, and the generation of a high temperature from the self-bias voltage associated with the RF power. In recent years, an alternative technique using a pulsed DC plasma has been developed and is called pulsed DC magnetron sputtering. Pulsed DC magnetron sputtering utilizes a pulsed potential to neutralize the positive charge on the target surface and eliminate the arcing by appropriately controlling the pulsing parameters of the target potential. Fig. 6.2 exhibits some typical target voltage potential waveforms used in pulsed DC magnetron sputtering. The continuous target voltage in DC mode is either turned off periodically in the unipolar mode [Fig. 6.2(b)], or more commonly, switched to a positive voltage [Fig. 6.2(b) and (c)] in pulsed DC magnetron sputtering. During the normal pulse-on (target-on) period (τ_{on}), the negative sputtering voltage is applied to the target as in conventional DC sputtering. However, the target negative potential is periodically interrupted by a positive pulse voltage with a period of τ_{rev} . The reversed positive voltage is variable depending on the power supply allowance, which is reversed to a smaller positive voltage than the nominal negative pulse voltage in the asymmetric bipolar mode [Fig. 6.2(c)] or reversed to the same magnitude of positive voltage as the nominal negative pulse voltage in the symmetric bipolar mode [Fig. 6.2(d)]. The duty cycle is defined as the negative pulse time divided by the period of the pulsing cycle (τ_{cycle}). For a given positive pulse width, the full range of frequencies may not be available due to

the power supply limitation, e.g. for an Advanced Energy Pinnacle Plus power supply, the smallest duty cycle is 50% [78]. In practice, the waveforms are virtually never as intended due to nonlinearities of either the plasma or the power supply circuitry. Therefore, the shapes of the resulting power waveforms are complex [79].

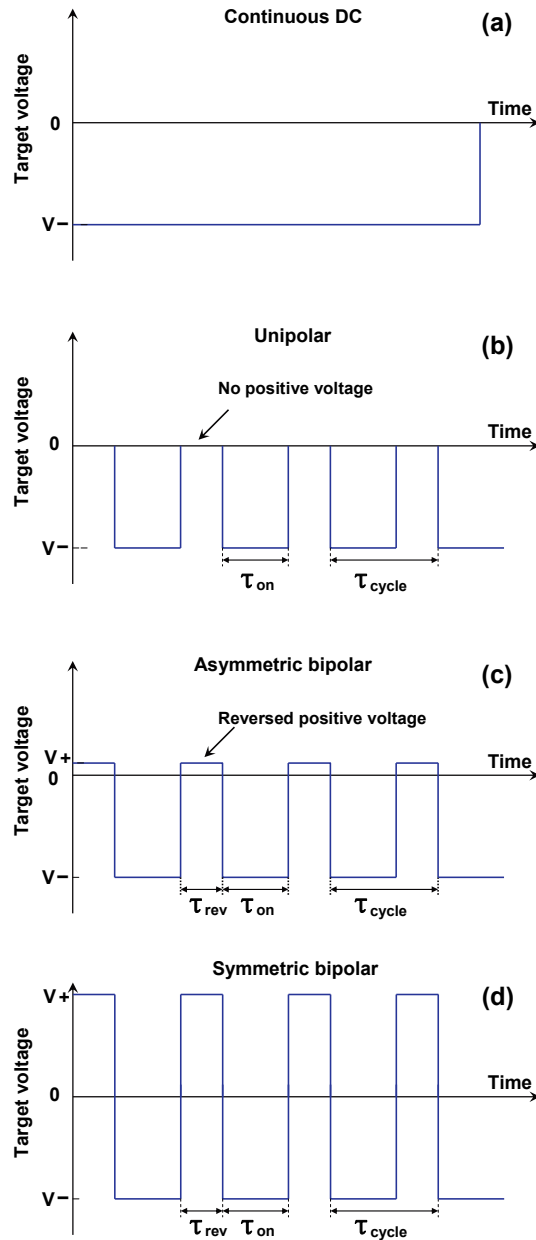


Fig. 6.2. The target voltage waveform when operated in (a) continuous DC, (b) unipolar pulsed mode, and (c) asymmetric bipolar pulsed mode, and (d) symmetric bipolar pulsed mode, (τ_{rev} : the reversed positive pulse period, τ_{on} : the normal negative target potential period, τ_{cycle} : the whole pulse period).

In the closed field configuration, two or more magnetrons are commonly used for reactive sputtering. All magnetrons can be run in pulsing condition, thereby resulting in different combinations of pulsing modes. Normally, the magnetron potential can be pulsed in either asynchronous bipolar mode [Fig. 6.3(a)], in which the two target voltage waveforms are out of phase, or in synchronous bipolar mode [Fig. 6.3(b)], in which the two target voltage waveforms are in phase. The degree of out of phase in asynchronous mode is totally dependent on the frequencies and reverse time on each target.

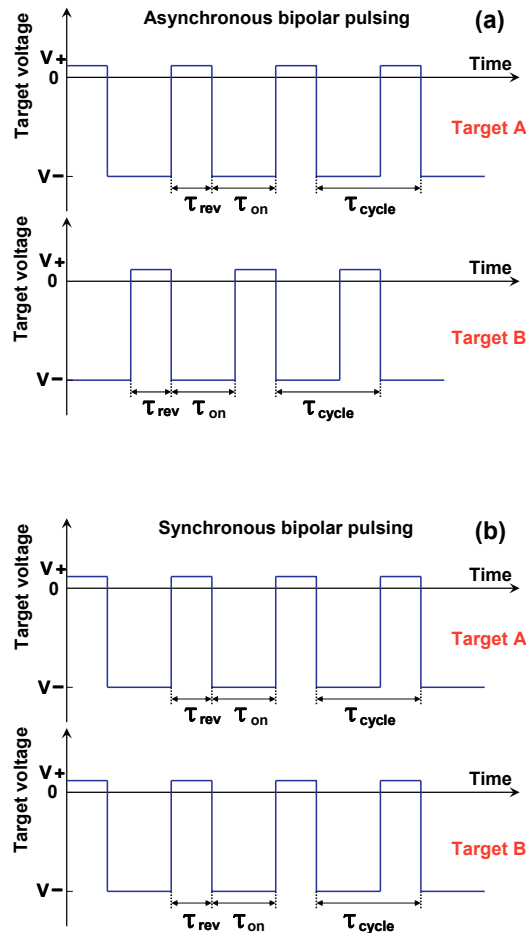


Fig. 6.3. Different target voltage waveforms in a dual magnetron pulsed mode: (a) asynchronous bipolar pulsing, and (b) synchronous bipolar pulsing.

During the reversed positive pulse, the charge built up on the insulating material during the negative pulse period is discharged to eliminate breakdown and arcing. Therefore, a stable deposition process and smooth coating structure can be obtained. Moreover, with precise control of the reactive gas, high deposition rate can be achieved in depositing insulating films. Kelly et al. [80] compared the microstructure of Al_2O_3 films deposited by P-CFUBMS and normal DC magnetron sputtering. A fully dense and smooth surface Al_2O_3 film was produced by P-CFUBMS. On the other hand, the film deposited by DC magnetron

sputtering exhibited a porous structure with micro-particles covering the film surface (Fig. 6.4).

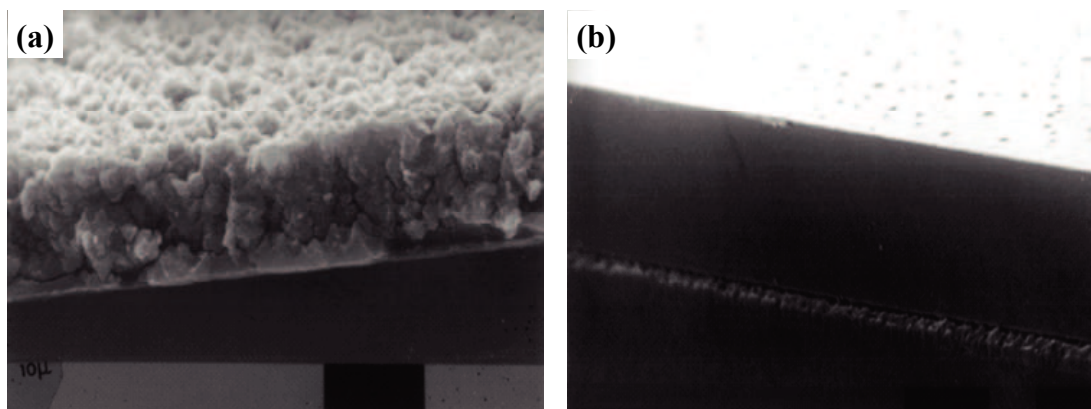


Fig. 6.4. SEM photomicrographs of fracture sections of aluminum oxide coatings deposited by (a) DC reactive sputtering, and (b) pulsed reactive sputtering [80].

6.3 HIGH-POWER PULSED DC MAGNETRON SPUTTERING (HPPMS)

Recently, high-power pulsed magnetron sputtering (HPPMS), operating in an unipolar mode, has attracted wide attention. In this new method, a high-density plasma is created in front of the sputtering source by using pulsed high target power density, ionizing a large fraction of the sputtered atoms [81,82]. In normal DC magnetron sputtering, the degree of ionization is low (typically less than 10%) which is due to the low power density (e.g. 3 Wcm^{-2}) limited by the target overheating from the ion bombardment [83]. However, in high-power pulsed magnetron sputtering, the average thermal load on the target is low by operating the target at high power density (e.g. 3000 Wcm^{-2}) in a pulsed condition; therefore a considerably large fraction of ionized species of the target material can be created by the high probability for ionizing collisions between the sputtered atoms and energetic electrons. It was reported that the fraction of ionized species in high-power pulsed DC magnetron sputtering can be considerably increased up to and beyond 70% [84]. The high degree of ionized ions with high energy makes it possible to control the film growth behavior and thereby produce high quality films. The potential of this emerging new high-power pulsed magnetron sputtering technique includes depositing fully dense films with equiaxed structure, controlling the orientation of the film, and depositing thick (maybe up to $20\mu\text{m}$ or more) films with low residual stress. However, this new technique is in its developing stage, and the deposition rate and cost of the power supply are the most important challenges that need to be considered.

7. CASE STUDIES: PREPARATION – MICROSTRUCTURE – PROPERTIES OF NANOSTRUCTURED COATINGS

7.1 HYBRID COATING SYSTEM OF Ti-Al-Si-N COATINGS

Quaternary Ti-Al-Si-N coatings have been prepared by a hybrid coating system, where CAE was combined with a magnetron sputtering technique. Various analyses (e.g., HRTEM, XPS, XRD) revealed that the synthesized Ti-Al-Si-N coatings exhibited nanostructured composite microstructures consisting of solid-solution (Ti, Al, Si)N crystallites and amorphous SiN_x. The Si addition caused the grain refinement of (Ti, Al, Si)N crystallites and its uniform distribution coupled with a “*percolation*” phenomenon of amorphous silicon nitride similar to that of the Si effect in TiN films [2]. Fig. 7.1 shows dark-field TEM images of Ti-Al-Si-N coatings containing different amounts of Si. The (Ti, Al)N crystallites [in Fig. 7.1(a)] appear to be large grains with a columnar structure. The (Ti, Al)N crystallites became finer with a uniform distribution as the Si content was increased. In Fig. 7.1(b), the crystallites were embedded in an amorphous matrix. These crystallites were revealed to be solid-solution (Ti,Al,Si)N phases of typical fcc crystal structure from the electron diffraction patterns. The (Ti, Al, Si)N crystallites showed partly aligned microstructure penetrated (“*percolated*”) by an amorphous phase, but were not distributed homogeneously in the amorphous matrix. The microstructure, however, changed to that of a nanocomposite, having much finer (Ti, Al, Si)N crystallites (approximately 10 nm) and uniformly embedded in an amorphous matrix as the Si content in films increased to 9 at.% [Fig. 7.1(c)]. Such microstructure as shown in Fig. 7.1(c) was in agreement with the concept of a nanocomposite architecture suggested by Veprék et al. [34]. Therefore, the Ti-Al-Si-N coatings with Si content of 9 at.% exhibited a maximum hardness among the experimental conditions. On the other hand, at a higher Si content of 19 at.% [Fig. 7.1(d)], (Ti, Al, Si)N crystallites decreased (~ 3 nm) and the film consisted mainly of the amorphous phase.

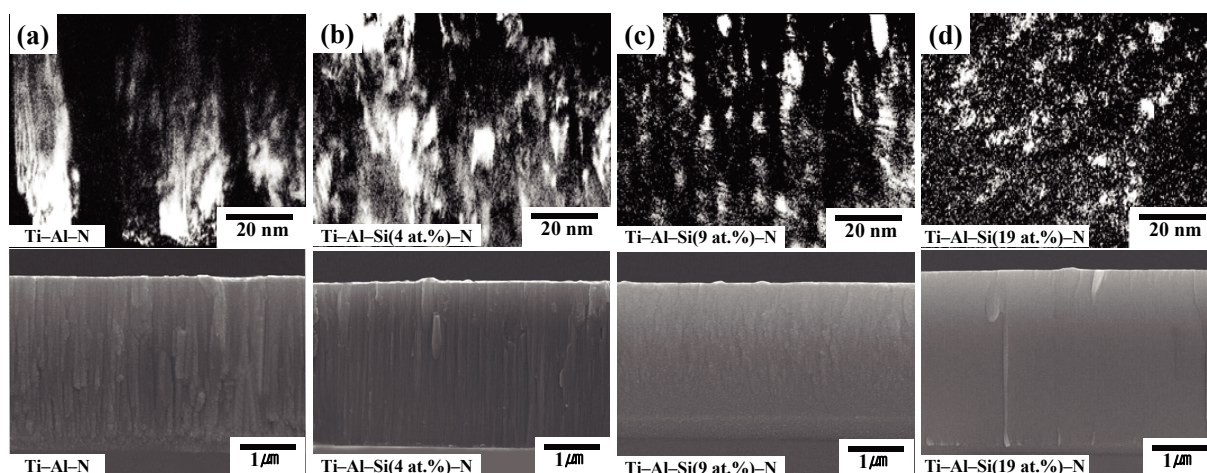


Fig. 7.1. Dark-field TEM and SEM images of Ti-Al-Si-N coatings containing (a) 0, (b) 4, (c) 9, and (d) 19 at.% Si, respectively.[5]

Fig. 7.2(a) shows the nanohardness and Young's modulus of Ti-Al-Si-N coatings with various Si contents and average grain sizes. As the Si content increased, the nanohardness and Young's modulus of the Ti-Al-Si-N coatings steeply increased, and reached maximum values of approximately 55 GPa and 650 GPa at Si content of 9 at.%, respectively, and then dropped again with further increase in Si content. The reason for the large increases in hardness and Young's modulus of Ti-Al-N with Si addition is due to the grain boundary hardening both by strong cohesive energy of interphase boundaries and by Hall-Petch strengthening derived from crystal size refinement, as mentioned in Section 4, which were simultaneously caused by the percolation of amorphous SiN_x ($H = \sim 22$ GPa, $E = \sim 250$ GPa) [85] into the Ti-Al-N film. Another possible reason would be due to solid-solution hardening of crystallites by Si dissolution into Ti-Al-N. The maximum hardness value at the silicon content of about 9 at.% results from the nano-sized crystallites and their uniform distribution embedded in the amorphous SiN_x matrix as shown in Fig. 7.1(c). On the other hand, the hardness reduction with further increase of Si content after maximum hardness as shown in Fig. 7.2(a) has been explained with the thickening of amorphous SiN_x phase with increase of Si content [86]. When the amorphous SiN_x is increased, the ideal interaction between nanocrystallites and the amorphous phase is lost, and the hardness of the nanocomposite becomes dependent on the property of the amorphous phase. On the other hand, Young's modulus, which must be related to density and atomic structure of the film, also largely increased from 470 GPa to 670 GPa with Si addition. This latter result was attributed to the densification of Ti-Al-Si-N films by filling the open structure of the Ti-Al-N grain boundaries with amorphous silicon nitride. Young's modulus reduction with further increase of Si content above 9 at.% was explained by the increase of volume fraction of amorphous SiN_x phase, which has a lower atomic density than crystalline (Ti, Al, Si)N phase. Fig. 7.2(b) shows the friction coefficients of the Ti-Al-N, Ti-Al-Si(9 at.%)–N, and Ti-Al-Si(31 at.%)–N films against a steel ball counterpart. The average friction coefficient of the film decreased from 0.9 to 0.6 with increasing Si content. This result is caused by tribo-chemical reactions, which often take place in many ceramics [87], e.g., SiN_x reacts with H_2O to produce SiO_2 or $\text{Si}(\text{OH})_2$ tribo-layer [88]. The products of SiO_2 and $\text{Si}(\text{OH})_2$ are known to play a role of a self-lubricating layer.

Figure 7.3 shows the surface morphologies of the wear track and composition analyses for the wear debris after a sliding test. The surface morphology of the wear track for Ti-Al-N film was rough, and the width of the wear track relatively narrow as shown in Fig. 7.3(a), whereas, the surface morphology for the Ti-Al-Si(9at.%)–N film was relatively smooth and the width of wear track was wide [Fig. 7.3(b)]. This result is due to the adhesive wear behavior between the hard film (~ 55 GPa) and relatively soft steel ($\sim 700 H_{v0.2}$). Thus, the steel ball is worn and smeared onto the Ti-Al-Si(9at.%)–N film having higher hardness (~ 55 GPa). On the other hand, the surface morphology of wear track for the Ti-Al-Si(31at.%)–N film was very smooth, and the width of wear track narrowed again as shown in [Fig. 7.3(c)]. This reflects that the formation of a self-lubricating tribo-layer such as SiO_2 or $\text{Si}(\text{OH})_2$ was

activated on increasing the Si content. From EDS analyses of the wear debris [Fig. 7.3(a) and 7.3(b)], the peak intensity of Fe for Ti–Al–Si(9at.%)–N film was higher than those for Ti–Al–N film, and the peak intensities of Ti and Al were reversed for the two films. Similar EDS results were found between Ti–Al–Si(9at.%)–N and Ti–Al–Si(31at.%)–N films. This indicates that the harder film was more wear-resistant against the steel counterpart.

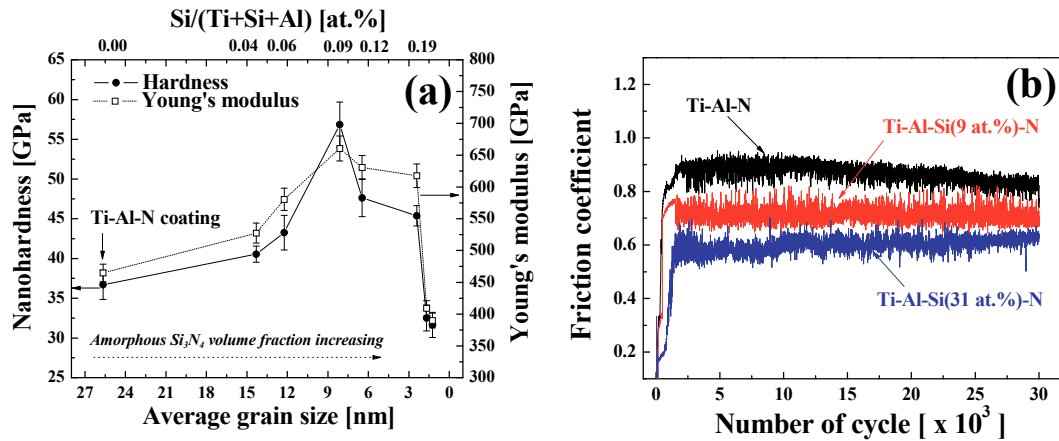


Fig. 7.2. (a) Nanohardness and Young's modulus and (b) friction coefficients of nanocomposite Ti–Al–Si–N [nc-(Ti, Al)N/a-Si₃N₄] coatings as a function of Si content.

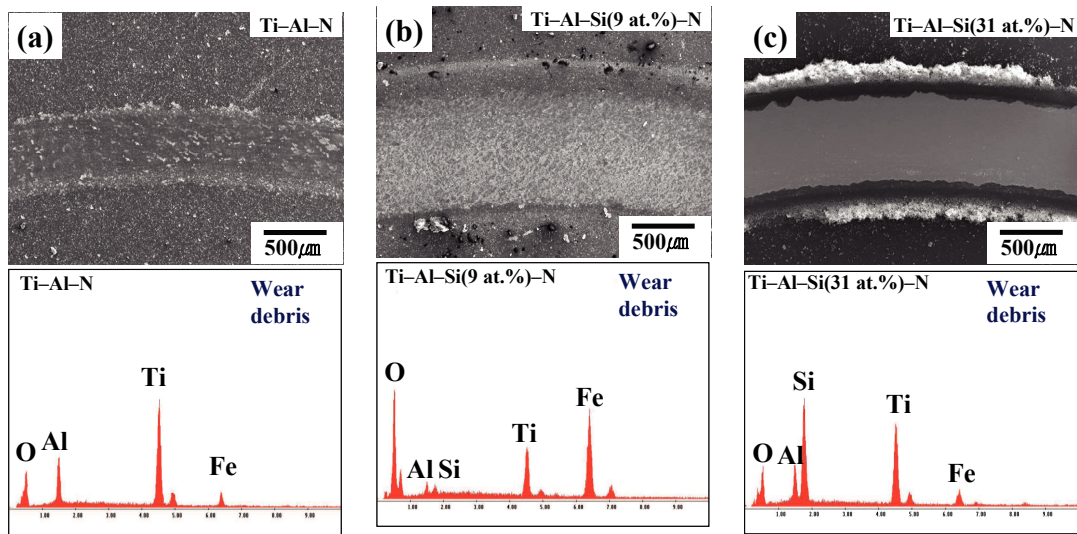


Fig. 7.3. SEM morphologies of wear track and composition analyses for the wear debris after sliding test : (a) Ti–Al–N; (b) Ti–Al–Si(9 at.%)–N; and (c) Ti–Al–Si(31 at.%)–N film.

7.2 UNBALANCED MAGNETRON SPUTTERING OF TI–SI–B–C–N COATINGS

Figure 7.4 shows the X-ray diffraction patterns of Ti–B–C–N and Ti–Si–B–C–N films on AISI 304 stainless steel substrates with various Si target powers at fixed TiB₂–TiC composite target power of 700W. At the Si target power of 0W, the diffraction pattern of Ti–B–C–N film exhibited crystalline hexagonal TiB₂ phase with preferred orientations of (001) or (002) crystallographic planes. Any XRD peaks corresponding to crystalline TiC or TiN phase were

not observed from the Ti–B–C–N diffraction pattern. As the Si target power was increased, the diffraction peak intensities of TiB_2 (001) and (002) gradually decreased and completely disappeared at the Si target power of 300W. At the Si target power of 50W and 100W, the TiB_2 peaks corresponding to the same (001) and (002) planes as well as a small TiC peaks for (111) and (311) crystallographic planes, were present. And, at the Si target power of 150W, very small diffraction TiB_2 peaks for (001) and (002) as well as TiC peaks for (111) and (311) were observed. Furthermore, at the highest Si target power of 300W, the XRD pattern presented no diffraction peaks for the film, indicating that the film is comprised mainly of an amorphous phase. The gradual changes in the XRD patterns of Ti–Si–B–C–N films with Si additions into Ti–B–C–N are similar to the case of the N addition into Ti–B–C, as previously reported by the authors for the Ti–B–C–N nanocomposite system [25].

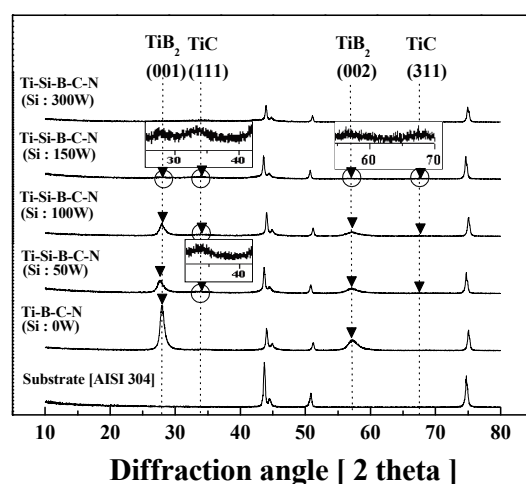


Fig. 7.4. XRD patterns of Ti–B–C–N and Ti–Si–B–C–N films on AISI 304 stainless steel substrates with various Si target powers at fixed TiB_2 –TiC composite target power of 700W.

In the report, it was revealed that the crystallites in Ti–B–C–N films were composed of solid-solution $(\text{Ti}, \text{C}, \text{N})\text{B}_2$ and $\text{Ti}(\text{C}, \text{N})$ crystallites (~ 10 nm in size). Addition of nitrogen into the Ti–B–C film led to grain refinement of the $(\text{Ti}, \text{C}, \text{N})\text{B}_2$ and $\text{Ti}(\text{C}, \text{N})$ crystallites and their distribution is coupled with a percolation phenomenon of amorphous BN and carbon phase. In order to determine the chemical composition and to investigate the bonding status of Ti–Si–B–C–N coating, x-ray photoelectron spectroscopy (XPS) was performed on Ti–B–C–N and Ti–Si–B–C–N coatings deposited by unbalanced magnetron sputtering from a TiB_2 –TiC composite target and a Si target at different Si target powers. Fig. 7.5(a) provides the content of each element in the Ti–Si–B–C–N coating with two different Si target powers and a fixed TiB_2 –TiC target power of 700W. As the Si target power was increased, the Si content was increased in the Ti–Si–B–C–N film from 0 to 14.2 at.%. The boron content steeply decreased. Figures 7.5(b) to (d) present the XPS spectra binding energies of Si [Fig. 7.5(b)], C [Fig. 7.5(c)], and O [Fig. 7.5(d)] for the Ti–B–C–N and Ti–Si(14.2 at.%)–B–C–N coatings. For the Si 2p region [Fig. 7.5(b)], TiSi_2 is clearly present with a smaller amount of

SiC and SiB₄. Examination of the C 1s region [Fig. 7.5(c)] confirms the presence of Ti_xB_yC_z components in amorphous free carbon and CN_x. With addition of Si into the Ti–B–C–N coating, the free carbon peak intensity significantly decreased. The large decrease in the free carbon peak intensity of Ti–B–C–N with the 14.2 at.% Si addition is most likely the result of formation of SiC as shown in Fig. 7.5(b).

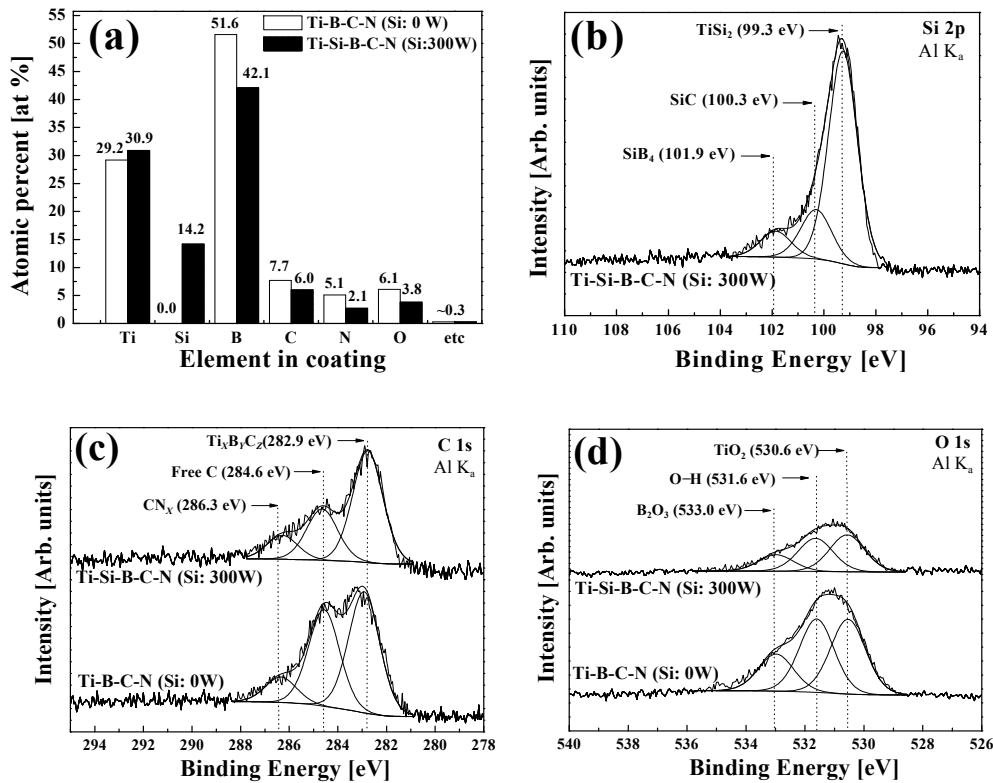


Fig. 7.5. XPS data for: (a) Content of Ti, Si, B, C, N, and O, and XPS spectra of (b) Si 2p, (c) C 1s, and (d) O 1s for Ti–B–C–N with Si target power of 0W and Ti–Si–B–C–N coating with Si target power of 300W (14.2 at.% Si in film).

Based on the results from the XRD and XPS analyses, it was concluded that the Ti–Si–B–C–N coatings are nanocomposites consisting of nanosized (Ti,C,N)B₂ and Ti(C,N) crystallites embedded in an amorphous TiSi₂ and SiC matrix including some carbon, SiB₄, BN, CN_x, TiO₂, and B₂O₃ components.

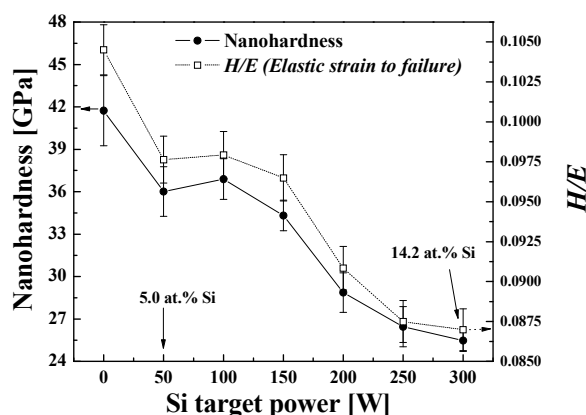


Fig. 7.6. Nanohardness and H/E values of Ti-Si-B-C-N coating as a function of Si target power.

Figure 7.6 presents the nanohardness and H/E values of the Ti-Si-B-C-N coatings as a function of Si target power. The hardness of the Ti-Si-B-C-N coating decreased from ~42 GPa at 0W Si target power to ~36 GPa at 50W Si target power (5.0 at.% Si in coating). The hardness was constant at about 35 GPa from 50W to 150W Si target power and decreased again with the further increase in Si target power to about 25 GPa at Si target power of 300W (14.2 at.% Si in coating). The decrease in hardness of Ti-B-C-N with 50W Si target power is most likely due to a reduction in hard TiB_2 based crystallites. The supporting evidence is shown in Fig. 7.5(a), where boron content decreases with increasing silicon content. However, the Ti-Si-B-C-N coating with Si target power of from 50W to 150W exhibited a high hardness of about 35 GPa. The reason for maintaining the high hardness (~35 GPa) in Ti-Si-B-C-N coatings with a small amount of Si is most likely due to percolation of amorphous TiSi_2 and SiC in the grain boundaries. Veprek et al.[28] have found that ultra-hardness ($80 \text{ GPa} \leq H_v \leq 105 \text{ GPa}$) is achieved when the nano-sized and/or amorphous TiSi_2 precipitate in the grain boundaries in their Ti-Si-N (nc-TiN/a- Si_3N_4 /a- and nc- TiSi_2) nanocomposites. On the other hand, the hardness reduction with further increase in Si target power above 200W can be explained by either an increase in the soft amorphous TiSi_2 , SiC, and SiB_4 phases and/or reduction of hard TiB_2 based crystallites. When the amount of amorphous phase is increased the ideal interaction between nanocrystallites and the amorphous phase can be lost, and the hardness of the nanocomposite becomes dependent on the property of the amorphous phase [89]. In addition, H/E values, the so-called ‘elastic strain to failure criterion’, were calculated from the obtained hardness (H) and Young’s modulus (E). Recently, Leyland and Matthews [57] have suggested that a high H/E value is often a reliable indicator of good wear-resistance. In Fig. 7.6, the H/E values exhibited a similar tendency with hardness. As the Si target power increased, the H/E value of Ti-Si-B-C-N coatings decreased from ~0.105 to 0.087. From the results of hardness and H/E , it can be suggested that the Ti-Si-B-C-N coating with Si target power up to 150W could provide a better wear-resistance with higher fracture toughness than that of Ti-Si-B-C-N coating with Si target power above 200W.

Fig. 7.7(a) shows the friction coefficients of the Ti–Si–B–C–N coating against a WC–Co ball as a function of Si target power. The average friction coefficient of Ti–Si–B–C–N coating rapidly decreased by increasing the Si target power and showed a minimum value of approximately 0.15 at Si target power of 50W, and then rebounded with the further increase in the Si target power above 100W. This large decrease in friction coefficient of Ti–Si–B–C–N coating with the 50W Si target power is most likely due to the formation of smooth solid-lubricant tribo-layers formed by tribo-chemical reactions during the sliding test. For example, silicon compounds such as TiSi_2 , SiC , or SiB_4 in the coating react with ambient H_2O and oxygen to produce SiO_2 or $\text{Si}(\text{OH})_2$ tribo-layers. These by-products of SiO_2 and $\text{Si}(\text{OH})_2$ have been known [87] to play a role as a self-lubricating layer. This Si effect on tribological behavior in nanocomposites, has also been found [90] by other authors. In addition, the carbon and hydroxide phases in the coating, as shown in Fig. 7.5(c) and (d), with a small Si content may also contribute to the minimum friction coefficient value.

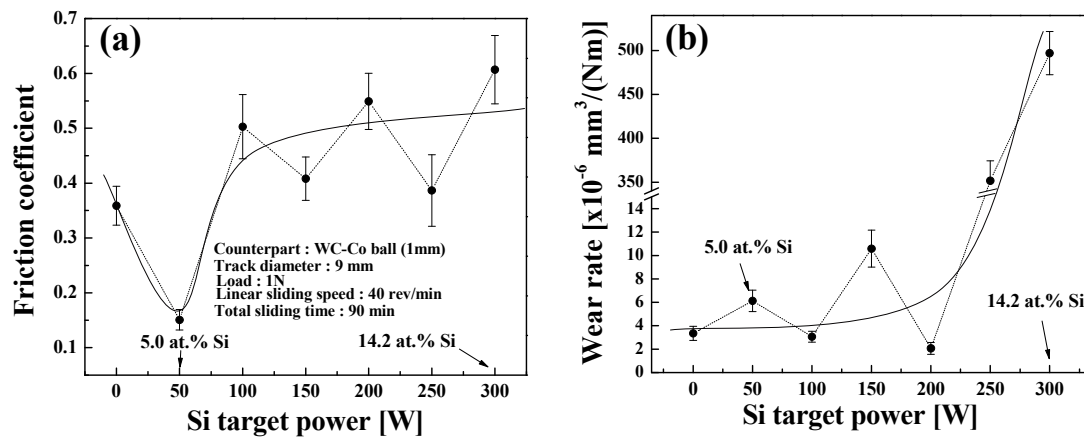


Fig. 7.7. (a) Friction coefficients and (b) wear rates of Ti–Si–B–C–N coating against WC–Co ball as a function of Si target power.

However, the friction coefficient slightly increased with further increase in Si content in the coating. The increase in friction coefficient with increase target power is most likely due to a reduction in free carbon and hydroxide phase, which are self-lubricating phases, in the Ti–Si–B–C–N coating as shown in Fig. 7.5(c) and (d). Fig. 7.7(b) represents the wear rates of Ti–Si–B–C–N coating on AISI 304 substrates as a function of Si target power. The wear rate of the Ti–Si–B–C–N coating slightly increased from $\sim 3 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ at 0W to $\sim 10 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ at Si target power around 200W. These very low wear rates would be due to the adhesive wear behavior between the hard coating ($\sim 35 \text{ GPa}$) and relatively soft WC–Co ($\sim 22 \text{ GPa}$) ball. On the other hand, at the Si target power above 250W, the wear rate of the Ti–Si–B–C–N coating steeply increased to about $500 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ at Si target power of 300W. This large increase in wear rate would be due to the abrasive wear behavior between the relatively soft coating ($\sim 25 \text{ GPa}$) and the WC–Co ball. Combining the results of the H/E [Fig. 7.6] values and wear rates [Fig. 7.6(b)], the Ti–Si–B–C–N coating with a higher H/E of

above ~ 0.090 had a better wear-resistance against WC–Co ball in agreement with Leyland and Matthews [57].

7.3 PULSED CLOSED FIELD MAGNETRON SPUTTERING OF Cr–Al–N COATINGS

7.3.1 CHARACTERIZATION OF ION ENERGY AND ION FLUX CHANGE IN THE P-CFUBMS

As described in the previous section, pulsed DC magnetron sputtering has been used to eliminate arcing problems during the reactive sputter deposition of insulating films, stabilize the discharge and reduce the formation of defects in the film. Besides its primary goal of eliminating arcing, it has been found that applying pulsing in DC magnetron sputtering has significant influence on the ion energy and ion flux change within the plasma. In addition, coating structure and properties will benefit from additional ion bombardment by the increased ion energy and ion flux. In recent years, time and space-resolved Langmuir probe and electrostatic quadrupole plasma mass spectrometer measurements have been intensively used to investigate the plasma condition in pulsed DC magnetron sputter deposition [91,92]. Bartzsch et al. [93] found that the ion current density was increased at the substrate during pulsed bipolar magnetron sputtering. The ion current increased nearly linearly with sputtering power for both bipolar and unipolar pulsing modes. In addition, the ion current density increased with a decrease in the duty cycle at a constant frequency and sputtering power. Muratore et al. [91] compared the ion energy distributions (IED) of pulsed DC magnetron sputtering and conventional DC magnetron sputtering during deposition of titanium oxide films using a Hiden Analytical Ltd., electrostatic quadrupole plasma analyzer (EQP). An increased ion energy up to 140 eV was observed in pulsed DC magnetron sputtering compared with a 17 eV in the DC discharge. Increase of crystallographic texture and an 11% increase in hardness were observed in the TiO films processed with the pulsed magnetron sputtering. Backer et al. [94] calculated the ion energy impinging on the pulsed DC magnetron sputtering of Ti and TiO₂ films from the measurements of plasma parameters using a planar Langmuir probe and found that the ion energy values during the positive pulse period increased more than 10-fold the time-average value.

The use of high ion energy and ion flux from the pulsed plasma for the reactive sputtering deposition is still a new field. Only a very limited number of coating materials, such as Cr–Al–N [95], TiC [96], TiO₂ [91,97], BN [98], Al₂O₃ [99] have been studied in some detail. More investigation in this field is needed in understanding the nature of the pulsed plasma and its influence on the film structure and properties. One approach to understanding the nature of these states employs both laboratory measurements and theoretical studies aimed at using an EQP to characterize the positive ion energies and the flux change within the plasma. Using this latter approach, it was possible to control ion bombardment energy and

ion flux to deposit nanostructured films. This research program will be described here in an effort to explain the use of P-CFUBMS to produce nanostructured Cr–Al–N films.

Lin et al. [100] first investigated the ion energy and ion flux change in the pulsed closed field dual magnetron sputtering of Cr–Al–N films. To demonstrate how the dual magnetron pulse influences the energy spectra of the ions, the evolution of the IED in response to pulsing only one target and pulsing both targets (Cr and Al) asynchronously and synchronously was considered, see Fig. 7.8(a). A significant increase in maximum pulsed ion energy up to 150 eV and 170 eV were observed when both targets were pulsed asynchronously and synchronously at 350 kHz and 1.4 μ s reverse time respectively. On the other hand, when only one target was pulsed, the ion energy remained at 20 eV which is similar to that of the threshold of conventional DC sputtering. The low ion energy region also increased up to 30–40 eV when both targets were pulsed compared with the 10 eV value when only one target was operated in pulse mode [Fig. 7.8(a)].

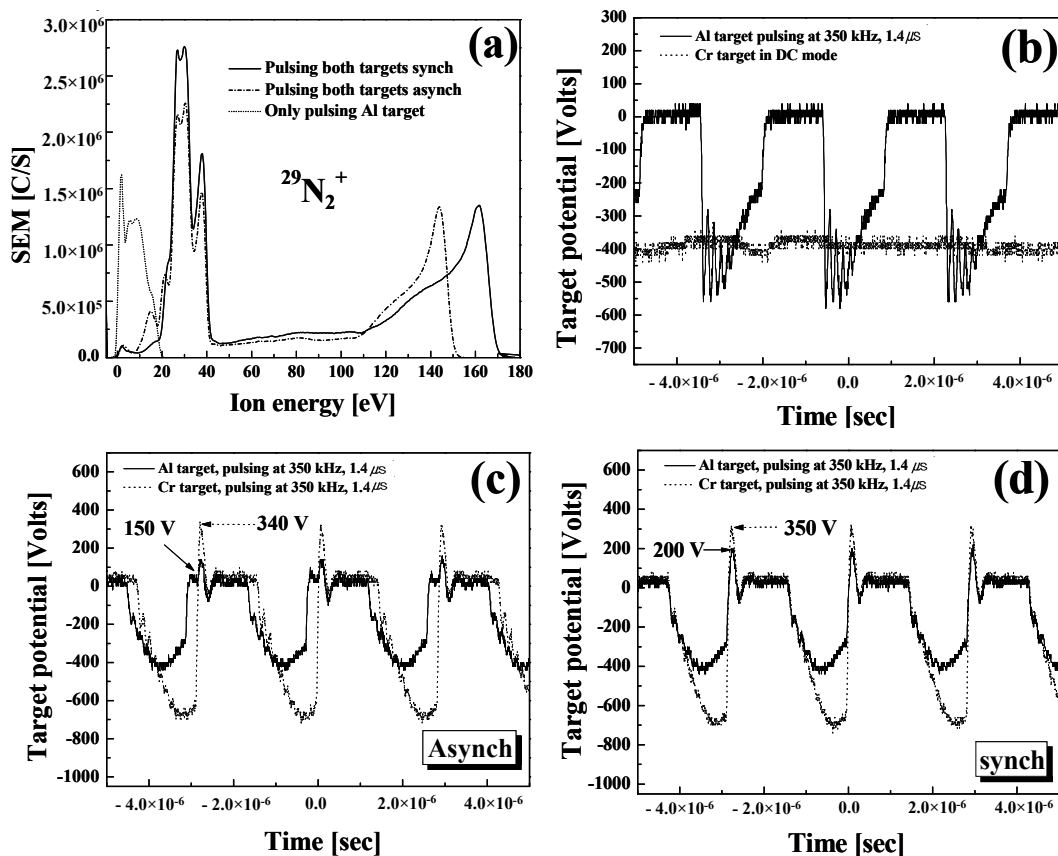


Fig. 7.8. (a) The ion energy distributions of $^{29}\text{N}_2^+$ during pulsed discharge for pulsing only Al target and pulsing both targets synchronously and asynchronously at 350 kHz, 1.4 μ s. (b) The voltage waveforms of targets for pulsing the Al target at 350 kHz, 1.4 μ s and keeping the Cr target in a DC discharge. (c) The voltage waveforms of targets for pulsing both targets asynchronously at 350 kHz, 1.4 μ s. (d) The voltage waveforms of targets for pulsing both targets synchronized at 350 kHz, 1.4 μ s [100].

It was also found that a target positive voltage overshoot is developed at the beginning of the positive pulse period and the positive voltage overshoot can result in an increase in the ion energy, which can greatly improve the film structure and properties due to the increased ion bombardment of the substrate [91,100]. The voltage waveforms on the Cr and Al targets measured when only pulsing one target and pulsing both the Cr and Al targets asynchronously and synchronously at 350 kHz and 1.4 μ s are presented in Fig. 7.8(b), c and d respectively. In Fig. 7.8(b), when only the Al target is pulsed, the Cr target potential has a constant DC negative value reaching -400 V, and the Al target negative potential pulse is periodically interrupted by the positive pulse voltage, which is about 10% of the nominal negative pulse voltage, 40 V in this case. On the other hand, when both the Cr and Al targets are running in the pulse mode [Fig. 7.8(c) and (d)], steep and large amplitude positive voltage overshoots appear at the start of the positive pulse period in both targets and collapse to the nominal positive pulse voltage value after 200-300 ns. Misina et al. [101] demonstrated that the total ion energy at the substrate is mostly determined by the plasma potential. The fast voltage overshoot was observed at the beginning of the positive pulse period and contributed to an increase in the plasma potential and the ion energy. Some physical models have been proposed to explain the effect of the positive voltage overshoot on the increased plasma energy [92]. Moiseev and Cameron [102] proposed that at the beginning of the positive pulse time, a high positive potential is developed on the targets, and therefore a large electron current is extracted from the plasma bulk. Due to the slow ion movement, compared with that of electrons, the equilibrium cannot be reached in a short time period, therefore a negative charge density gradient and a positive charge density gradient will be created in the plasma bulk resulting in an electron field potential being established under this charge gradient. Ions will be accelerated by the electron field potential and will gain energy from it.

It was found that pulsing provides a wide range of ion energies and ion fluxes in the plasma. In general, three different ion energy regions in a pulsed plasma have been well documented. Figure 7.9(a) shows a typical time averaged $^{29}\text{N}_2^+$ ion energy distributions in a discharged plasma for Cr–Al–N film deposition when the Cr and Al targets were pulsed synchronously at 100 kHz and 5.0 μ s. The Al target voltage waveform is shown in Figure 7.9(b). It can be seen that pulsed ion energies generally consist three regions which are corrected to distinct phases of the discharge voltage.

The low ion energy region ‘A’ in Figure 7.9(a) usually is in the range of 0–10 eV, which corresponds to the negative pulse period (sputtering period) in the target voltage waveform [Figure 7.9(b)]. The plasma potential is several volts above the grounded chamber wall surface potential during this period. The ‘B’ middle ion energy region (20 ~ 50 eV) is the energy gained from the target potential in the reverse positive pulse period [see Fig. 7.9(b)], which has an average positive value of fixed percentage of the nominal sputtering voltage. The ‘C’ ion energy tail region is the kinetic energy gained from the fast and high positive voltage overshoot at the beginning of the positive pulse period. When the fast and steep

positive voltage overshoot is developed on the target, a large electron current is extracted from the bulk plasma towards the target. Due to the slow ion movement, compared with that of electrons, the equilibrium cannot be reached in a short time period, therefore a negative charge density gradient and a positive charge density gradient will be created in the bulk plasma resulting in an electric field potential being established under this charge gradient. Ions will be accelerated by the electric field potential and will gain energy from it.

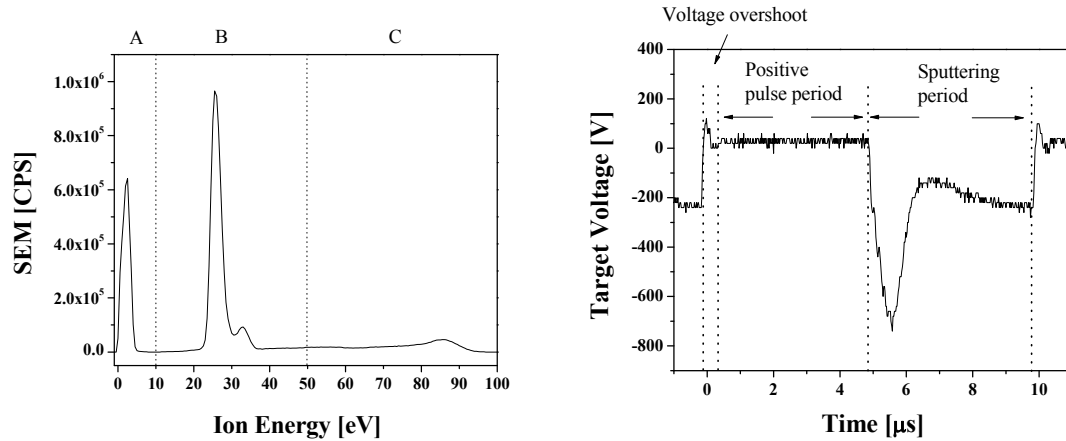


Fig. 7.9. (a) A typical time averaged $^{29}\text{N}_2^+$ ion energy distributions in a discharged plasma for CrAlN film deposition when the Cr and Al targets were pulsed synchronously at 100 kHz and 5.0 μ s, (b) The Al target voltage waveform.

In pulsed closed field dual magnetron sputtering, the pulsed discharge can not only change the ion energy but can also vary the ion flux in the plasma. The frequency and duty cycle of the applied pulses play an important role in determining the ion energy and ion flux because the frequency sets the timescale of the pulsing cycle, while the duty cycle establishes the time within the cycle the pulse is set to positive and negative voltage [103]. As a result, different combinations of pulsing frequencies and duty cycles can change the ion flux and the ion energy values in the plasma, which have a great influence on the deposition process and the film structure and properties. Fig. 7.10(a) and (b) exhibit the maximum ion energy evolution ($^{29}\text{N}_2^+$) as a function of duty cycle at different pulsing frequencies in the synchronized and asynchronous pulsing modes, respectively. The corresponding integrated ion flux values in the two pulsing modes are plotted in Fig. 7.10(c) and (d) [100].

The ion energy will have higher values when both targets are pulsing at higher frequencies in most cases. In the asynchronous mode, the maximum ion energy decreases with increasing the duty cycle at most frequencies and drops suddenly to the low energy region at certain duty cycles due to the total separation of the two target positive pulse periods [100], see Fig. 7.10(b). The ion flux decreases with an increase in the duty cycle at all frequencies in both the synchronized and asynchronous pulsing modes [Fig. 7.10(c) and (d)]. As the duty cycle decreases (the positive pulse time increases), the cathode is switched proportionally to a positive voltage for a longer period of time, which in turn provides more time for positive

ions to stream away from the target. This increased escape time results in a higher number of ions gaining the additional kinetic energy available from the positive potential switch, thereby increasing the flux of higher energy ions at the substrate. The negative voltage overshoot developed on the targets at the beginning of the negative pulse period also contributes to the ion flux change within the plasma. Bradley et al. [92] investigated the time evolution of the electron density, the electron temperature, and the plasma potential using a Langmuir probe in pulsed DC magnetron sputtering. It was found that both the effective electron temperatures and densities were elevated during pulse periods compared to the DC equivalent discharge. During the positive pulse time of the cycle, electrons are drawn to the positive potential on the target. When the target voltage switches back to negative, these electrons are now reflected and accelerated back into the plasma, causing a spike in the electron temperature. Under these latter conditions electrons will gain higher kinetic energy from the higher negative voltage overshoot and may also contribute to ionization.

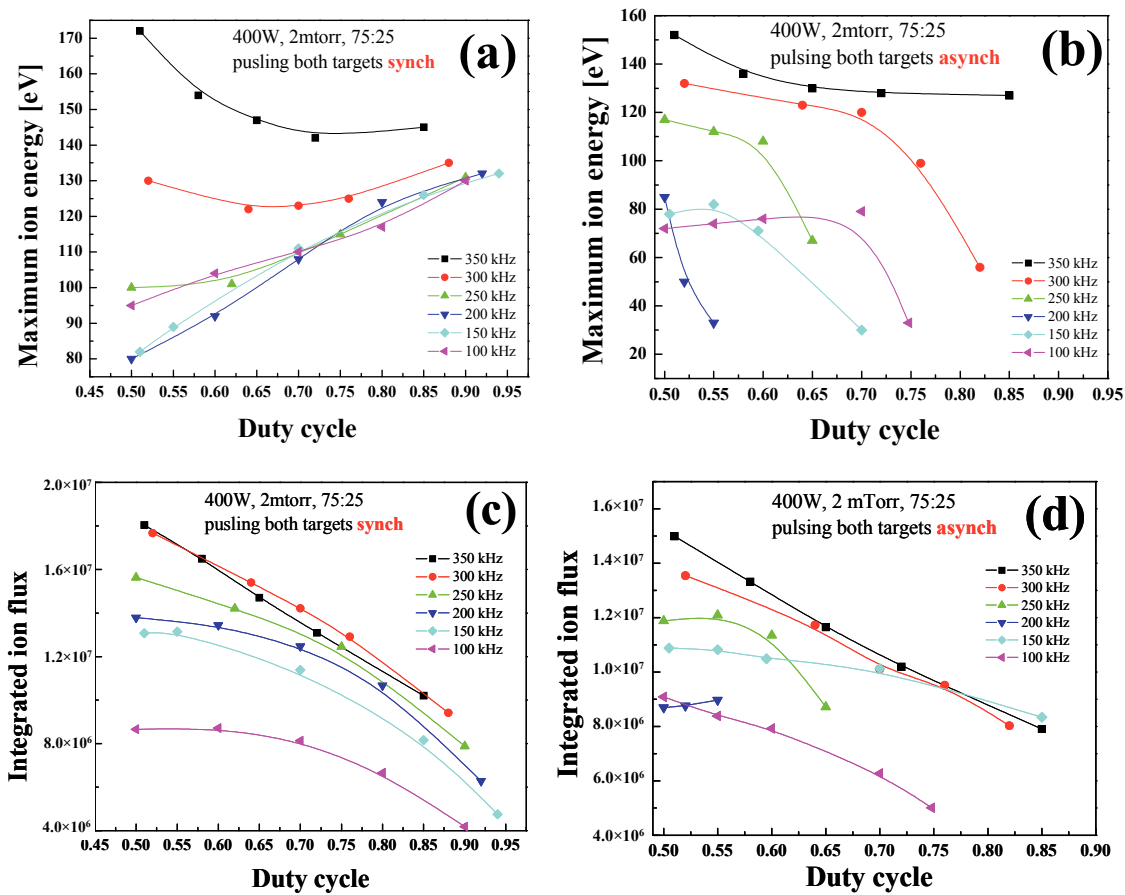


Fig. 7.10. The maximum ion energy ($^{29}\text{N}_2^+$) as a function of the duty cycle at different pulsing frequencies in (a) synchronized mode, and (b) asynchronous mode; The integrated ion flux as a function of the duty cycle at different pulsing frequencies in (c) synchronized mode, and (d) asynchronous mode [100].

The change of the plasma composition in pulsed reactive magnetron sputtering plays an important role in determining the as-deposited coating composition. During the deposition of Cr–Al–N thin films using P–CFUBMS, the change in the Cr–Al–N coating composition was found to be influenced by the Cr^+ , Al^+ , and N^+ ion fluxes in the plasma, resulting in improvements in film density, hardness, and stoichiometry [95]. In addition, some other studies [104] have also demonstrated the importance of applying a pulsed DC substrate bias to control the film properties, such as adhesion, texture, morphology, and density of the film.

7.3.2 MICROSTRUCTURE AND PROPERTIES OF Cr–Al–N COATINGS

The increased ion energy and ion flux in P–CFUBMS as discussed in the previous section will strongly affect the structure and properties of the films. The high ion energy and ion flux will apply additional ion bombardment, increase the mobility of the atoms on the substrate, and reduce the shadowing effect of the columnar structure, thereby changing the film growth microstructure. Fig. 7.11 shows the cross-section SEM images of Cr–Al–N films deposited at two ion energy levels by changing the pulsing parameters in P–CFUBMS. For a total ion energy at 72 eV (maximum pulsed ion energy of 22 eV + substrate bias of -50 V), which is obtained by pulsing the Cr and Al targets asynchronously at 100 kHz and 1.0 μs , a typical columnar structure with grain size of 60 nm is observed [Fig. 7.11(a)]. On the other hand, the film deposited at total ion energy of 122 eV (maximum pulsed ion energy of 72 eV + substrate bias of -50 V), which is obtained by pulsing both targets asynchronously at 100 kHz and 5.0 μs , exhibits a denser structure with nanocrystallized and equiaxed grains of less than 20 nm [Fig. 7.11(b)] [105].

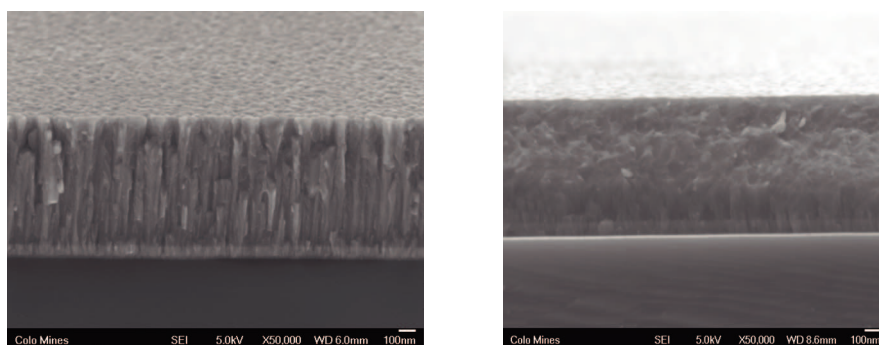


Fig. 7.11. Scanning electron micrographs of cross section of Cr–Al–N films deposited asynchronously at: (a) 100 kHz and 1.0 μs , and (b) 100 kHz and 5.0 μs [105].

In the case when high ion energy and ion flux bombardment are used in the film growth, the grain size and the surface roughness of the films will be reduced. For example, a comparison of the grain size and surface roughness of Cr–Al–N films deposited by P–CFUBMS through an increase in ion flux by 7 fold near the substrate region is presented in Fig. 7.12. Fig. 7.12(a) and (b) are the 2D and 3D AFM images of Cr–Al–N film surfaces deposited at relatively low ion flux. The morphology of film indicates separated mounds of grains of relatively large lateral and vertical sizes which indicate a large average grain size

and porous structure with a surface roughness of about 23.45 nm. On the other hand, the mounds become smaller ($<100\text{nm}$), more continuous when the ion flux is increased by 7 fold in the plasma, thereby showing more nuclei and a denser microstructure [Fig. 7.12(c) and (d) [106]

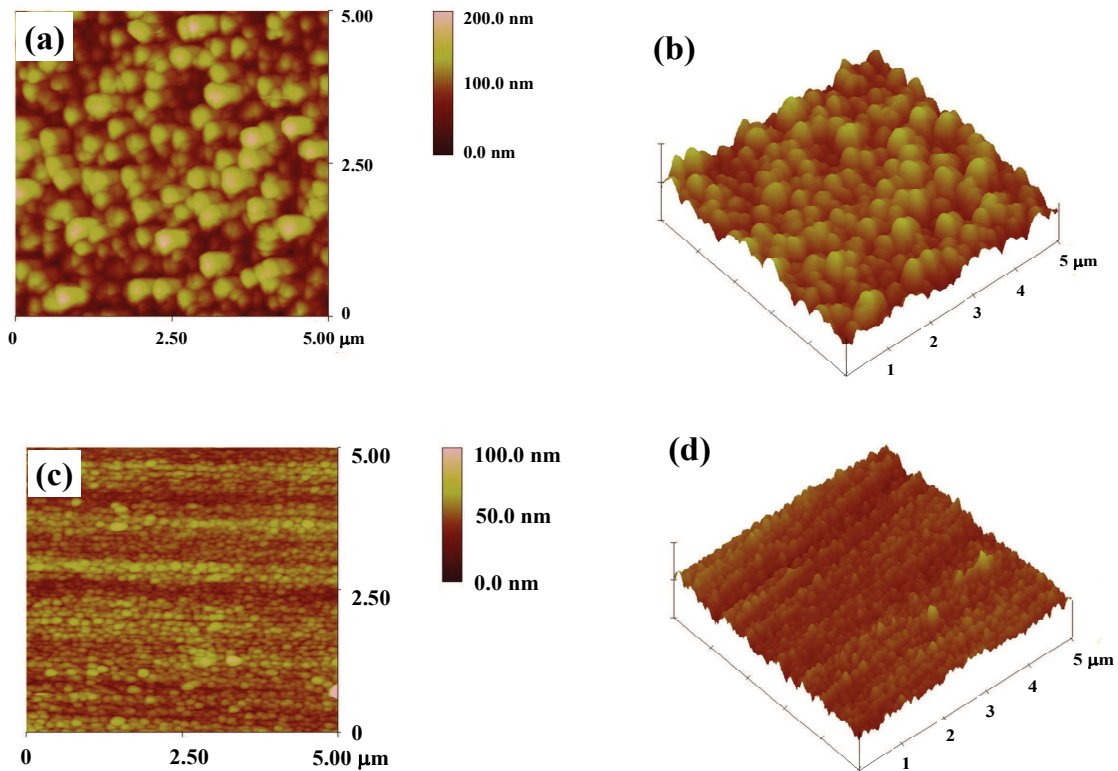


Fig. 7.12. Two and three dimensional AFM images of Cr-Al-N films deposited at: (a) and (b) relatively low ion flux, (c) and (d) high ion flux [7 fold higher than in (a)] [106].

The high ion energy bombardment created by pulsing in reactive sputtering deposition can result in different film surface growth processes. The most dominant energy impact to the film is the direct implantation of the energetic ions into the near-surface region. The ions carrying high energy can be directly implanted into the voids of the growing film. This process can increase the film density as well as the compressive stress of the film. The energy imparted to the film also results in increase in the film growth temperature, and can thus aid in surface diffusion and relaxation, which can result in a higher defect annealing rate than the defect generation rate in the film, thereby lowering the film internal stress. The temperature at which this occurs depends on several factors such as; film material, impinging ion energy. However, as the temperature is increased the thermal stress will also increase [107]. Another high ion energy effect on the film growth is the knock-on implantation, which takes place when the incoming particles collide with the surface atoms of the film. The ions with high energy can knock the surface atoms out of their original lattice positions and move them deep into the voids (interstitial) of the lattice structure of the film, thereby increasing film density. The already bonded atoms in the near surface region of the film may be removed again due to the high energy bombardment, resulting in re-sputtering, which

may change the film growth orientation and decrease the deposition rate. A schematic representation of the surface processes during the ion bombardment in Cr–Al–N films deposition is presented in Fig. 7.13 [108].

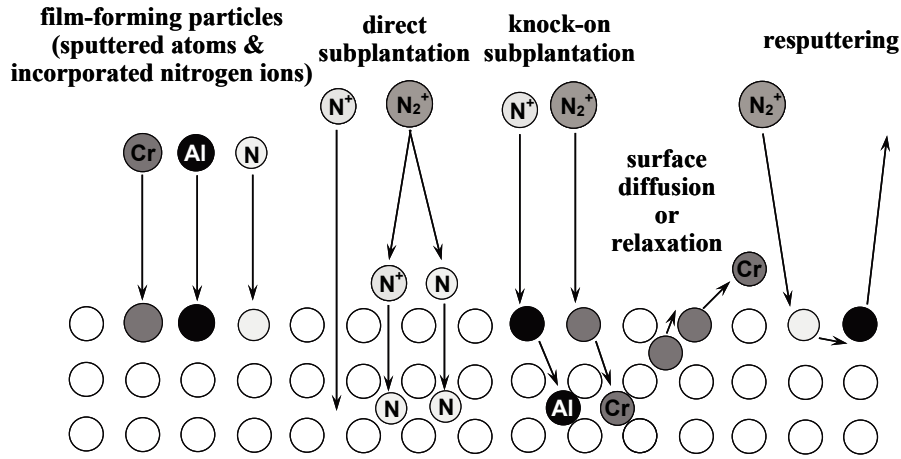


Fig. 7.13. Schematic drawing of surface processes during film growth [108].

7.3.3 PROPERTIES OF Cr–Al–N COATINGS

The improved microstructure of films at controlled ion energy and ion flux levels by pulsing the targets results in significant improvement of the mechanical and tribological properties. Fig. 7.14 shows the increase in hardness obtained by increasing ion energy from 72 eV to 200 eV (including -50 V substrate bias) in Cr–Al–N films deposited using P–CFUBMS system. The different maximum ion energy was achieved by varying the pulsing parameters asynchronously on the Cr and Al targets [105]. The film hardness increased from 34 GPa to 48 GPa when the maximum ion energy in the discharged plasma increased from 72 eV to 200 eV accordingly. The Young's modulus of film exhibits a similar trend.

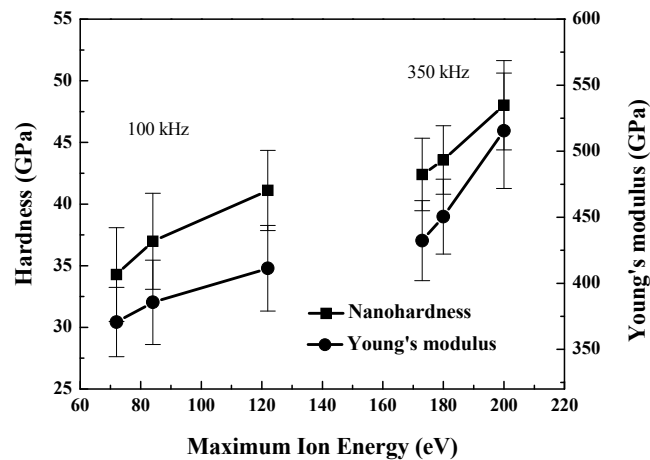


Fig. 7.14. The hardness and Young's Modulus values of Cr–Al–N films deposited in asynchronized mode as a function of maximum ion energy (including -50 V substrate bias) in the plasma.

The increased hardness of the films on using the high ion energy and ion flux bombardment is directly related to the denser microstructure and decreased (nanocrystalline) grain size. According to the Hall-Petch relationship [37,38], the hardness of the material increases with decreasing crystallite size. The contribution of development of internal residual stress also needs to be considered. The bombarding particles will be implanted in the growing film resulting in increased defect incorporation, provided their energy is high enough. The density of defects such as dislocations, point defects, trapped gases, etc., will strongly affect the stress state of the film. The variation in the in-plane residual stress as a function of the maximum ion energy in the discharged plasma is shown in Fig. 7.15 for P-CFUBMS Cr–Al–N films. The internal stress increases with increased maximum ion energy in the plasma and develops rapidly when the ion energy is between 122 eV to 200 eV. The film deposited with 200 eV ion energy exhibits a high residual stress of ~13 GPa. Since stresses result from a change in the average distance between atoms in the lattice away from their equilibrium positions, the elastic response of the material will change. It is understandable that highly compressive stressed materials will show large hardness values. Also, a high defect concentration in a compressively stressed material will restrict the plastic flow, and thus, be a contributing factor in enhancing the hardness [107].

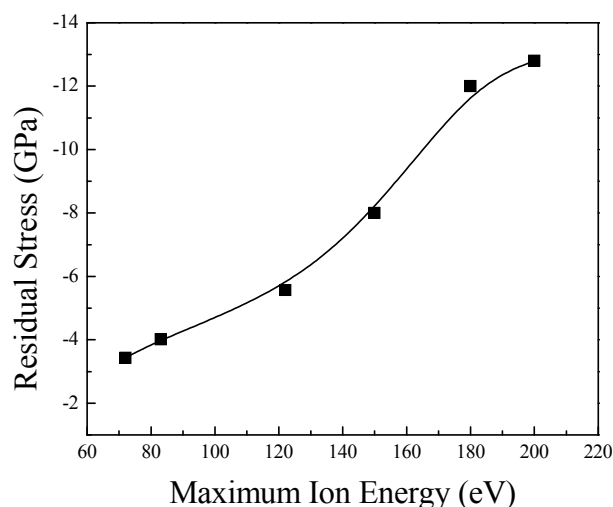


Fig. 7.15. The internal residual stress in Cr–Al–N films as a function of maximum ion energy (including -50 V substrate bias) incorporated in deposition by P–CFUBMS.

The wear-resistance of hard films is determined by many parameters such as contact geometry, surface roughness, applied load, adhesion, etc. Usually for hard coatings, with a combination of good surface finish and adhesion strength, the wear mechanism is mainly governed by the surface interaction between the tip and the coating itself. On the other hand, if there is low adhesion strength between the film and the substrate, the adhesion of the film will totally control the wear properties. The steady-state coefficient of friction (COF) value and calculated wear rate of Cr–Al–N films deposited in asynchronized mode with different

maximum ion energy are plotted in Fig. 7.16. The COF and wear rate of Cr–Al–N films increased with an increase in the maximum ion energy.

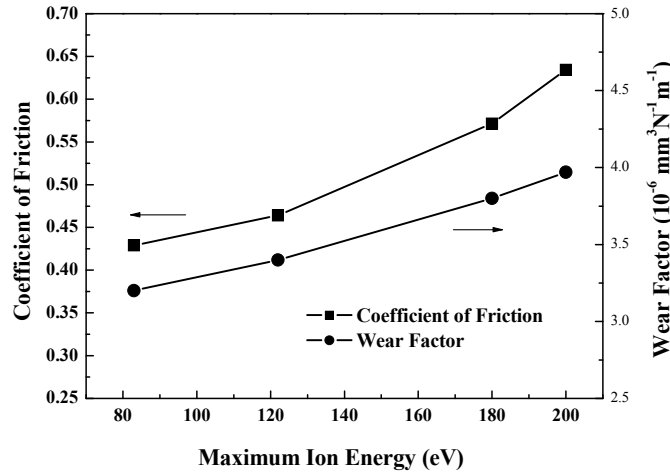


Fig. 7.16. Friction coefficient and wear rate of Cr–Al–N films deposited in asynchronous mode with different maximum ion energy (including -50 V substrate bias).

In the case of high ion energy and ion flux assisted deposition, the increased ion energy and ion flux can facilitate the ion bombardment on the substrate, increase the mobility of the atoms on the substrate surface, resulting in a denser film with decreased grain size, and films with super hardness (Fig. 7.14). The super hard Cr–Al–N films deposited at high ion energy and ion flux (hardness above 40 GPa) can change the wear behavior between the film and the WC ball. Since the hardness of the WC ball (16–20 GPa) is much lower than the super hard Cr–Al–N films (48 GPa in this case), the main abrasive wear body can switch from the coating to the WC ball, and this was confirmed from SEM observations of the WC ball after the wear test. Therefore, the increased contact surface between the WC ball and the films due to the ball wear can result in an increase in the COF of the films, nevertheless the film can still have a low wear rate due to the super hardness of the film. However, if the film receives excessive ion energy and flux bombardment, the internal residual stress and concentrations of point and line defects in the films will increase. Excessive high residual stress and point defect concentration can reduce the film toughness and increase the brittleness of the film, thereby reducing the film wear resistance. Therefore, care should be taken to control both the ion energy and ion flux during film deposition in P–CFUBMS to achieve both high hardness and wear resistance in the film. The high in-plane stress built up with excessive ion bombardment can be converted to a stress gradient by depositing compositionally graded structure between the substrate and film, and varying the pulsing conditions throughout the deposition processes.

7.4 PULSED CLOSED FIELD MAGNETRON SPUTTERING OF TiC–C COATINGS

Three primary coatings of interest were deposited as follows: *Film A* was deposited with DC power to both targets, *Film B* was deposited with DC power to the graphite target and pulsed power (at a reverse time of 1 μ s and a frequency of 100 kHz, hereafter denoted as 1 μ s/100 kHz) to the titanium target, *Film C* was deposited with synchronous pulsed power (1 μ s/100 kHz) to both targets. XPS analysis of *Film B* indicated an overall coating composition of 51.8 at.% C, 41.1 at.% Ti, 5.8 at.% O, and 1.3 at.% Ar. Of the total carbon in the coating, 78% was bound as carbide (40.4 at.% overall), while the remaining 22% was present as amorphous and/or graphitic C–C bonds (11.4 at.% overall). These results suggest that nearly all of the Ti was bound as TiC while there remained a small amount of excess carbon. XRD patterns (see Fig. 7.17) did not show evidence of a graphite peak, nor a broad low angle amorphous bump, so it is unclear if the excess carbon was amorphous, graphitic, or a combination of both. Hardness values for *Film A*, *B*, and *C* were 39 ± 3 , 40 ± 2 , and 35 ± 2 GPa, respectively. It appears there was little significant change in the friction coefficient in terms of numerical values ($0.201 \sim 0.220 \pm 0.011$), however a large amount of small particulate debris was present in and around the wear track after the test for *Film C*.

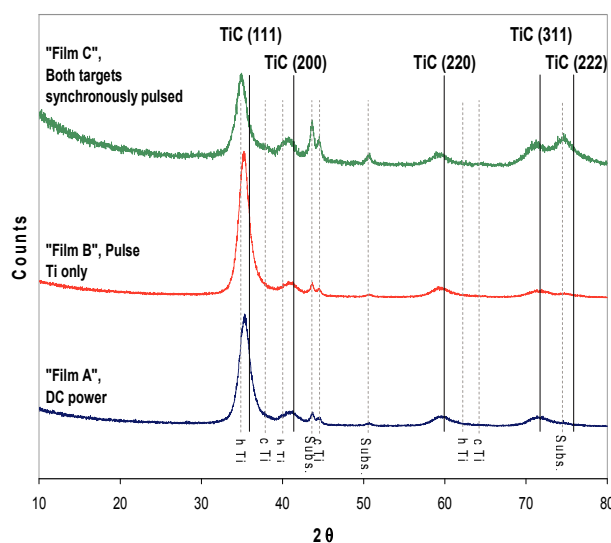


Fig. 7.17. Glancing angle XRD patterns for three different pulse configurations: DC power to both targets (*Film A*), pulsed power at to the titanium target only (*Film B*), and pulsed power to both targets (*Film C*). Dashed lines indicate peaks for titanium from the interlayer (cubic and hexagonal) and the substrate. All TiC peaks are shifted to lower 2θ values indicating compressive stress in the coating.

Glancing angle XRD patterns for the coatings are shown in Fig. 7. 17. All of the TiC peaks are shifted to lower 2θ values indicating compressive stress in the coating. The shift is even more pronounced for *Film C*. *Films A* and *B* have very similar patterns where the TiC (111) peak is clearly dominant. *Film C* exhibits stronger (200), (311), and (222) peaks in relation

to the (111) peak. This observation is consistent with reports in the literature of texture control with increased ion energy and flux [109].

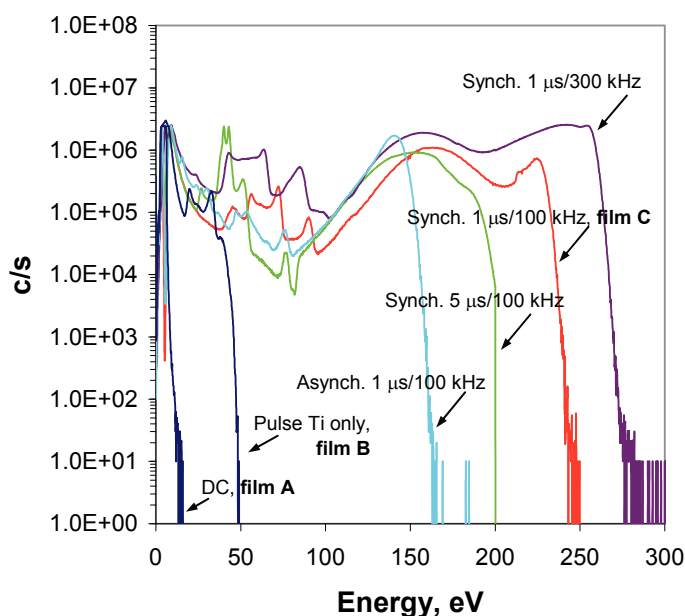


Fig. 7.18. Log scale ion energy distribution (IED) of argon (Ar^+) for DC power, pulsing the Ti target only, and pulsing both targets synchronously and asynchronously. Synchronous pulsing of both targets results in ion energies as high as 280 eV.

Figure 18 shows the IEDs for conditions corresponding to *coatings A, B, and C*, as well as additional asynchronous and synchronous conditions. Given that the ion flux at the substrate (or probe in this case) is determined by the number of ions per unit time per unit area, the intensity (counts/second) at a particular energy is directly proportional to the ion flux since the area is constant. With DC power to both targets, there is a single peak centered at 4.7 eV with a maximum detected energy at 10 eV. Pulsing the titanium target (with DC power to the graphite target), extended the ion energy range out to 48 eV with an appreciable flux of ions between 10 and 45 eV. Pulsing both targets expands the ion energy range up to 280 eV for synchronous pulsing at $1\mu\text{s}/300\text{ kHz}$ with a very high flux of ions.

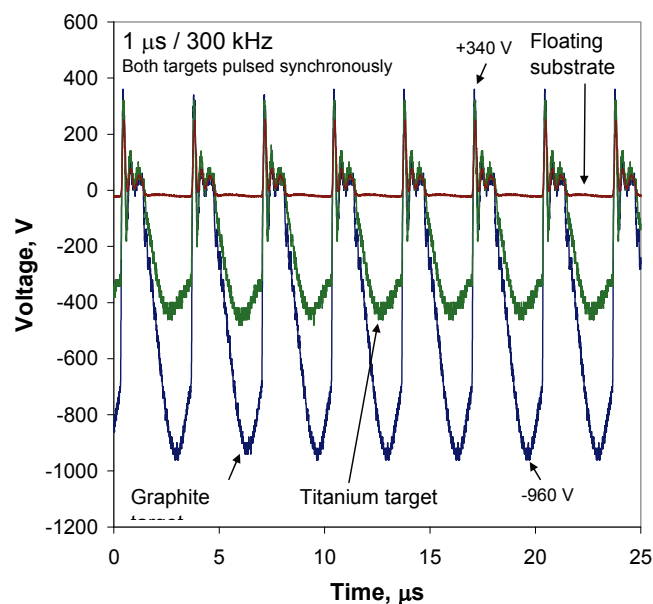


Figure 7.18. Voltage waveforms for synchronous pulsing of both targets at 300 kHz and 1 μ s. The positive overshoots for graphite and titanium are +340 and +320 V, respectively. The negative overshoots for graphite and titanium are -960 and -480 V, respectively.

The target voltage waveforms suggest that the large voltage overshoot in switching between the positive and negative regimes may contribute to the increased ion energy for the pulsed discharges. When only the Ti target is pulsed at 1 μ s/100 kHz (corresponding to *Film B*), the potential difference between the positive and negative overshoot is 640 V. Figure 18 shows the waveform when both targets are pulsed synchronously at 1 μ s/300 kHz. In this case the potential difference between overshoots is 1300 V. For the asynchronous condition, the difference between overshoots was 1200 V. During the “off” time of the cycle, electrons are drawn to the positive potential on the cathode while the positive ions stream away. When the voltage switches to negative, the electrons are now reflected and accelerated back into the plasma, causing a spike in electron temperature which has been observed by Bradley et al. [92]. It is possible that some of the reflected electrons acquire the full sheath potential associated with the negative overshoot, between -520 and -890 V. The ionization cross section for argon increases with electron energy up to a maximum at about 100 eV and remains significant out to about 1000 eV. Therefore these “hot” electrons may also contribute to ionization. As the frequency is increased, the cathodes spends more time in the positive regime, allowing more positive ions to stream away, which increases the flux of ions at the substrate. Pulsing both targets generates a much larger potential difference upon voltage switching than pulsing only one target, and there is a corresponding increase in maximum ion energy. The potential differences for asynchronous and synchronous pulsing are similar, yet the maximum synchronous pulsing ion energy is more than twice as high. It is possible that the potential differences on each cathode are additive, such that for synchronous pulsing the ion energy is boosted by the cathode voltages switching

simultaneously. It should be noted that the graphite target runs at a substantially higher voltage than a metallic target for an equivalent power.

Figure 20(a) is a TEM image of *Film B*, where the top of the image is a thinner region of the coating due to shadowing during deposition. At the edge of the carbon support, the coating grew in the plane of the support, providing a cross-sectional view which highlights the columnar structure. Figure 20(b) shows a similar image for *Film C*. The cross-section at the edge of the carbon support lacks a columnar structure and consists of very small (3~10 nm) equiaxed crystallites.

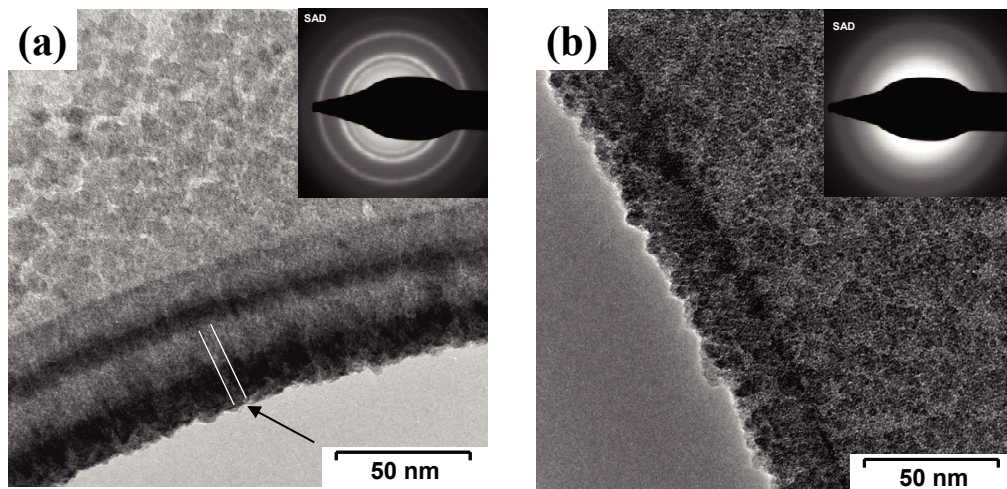


Fig. 7.20. TEM images taken at the edge of a holey carbon support of (a) a coating deposited by pulsing the titanium target only, showing a columnar structure; and (b) a coating deposited by pulsing both targets synchronously, showing 3~10 nm sized equiaxed crystallites.

The high ion energy (up to 280 eV) produced by pulsing both targets synchronously had a distinct and significant influence on the microstructure of the TiC coatings. It is likely that the substantial amount of energy has induced a considerable defect density in the growing coating resulting in a high rate of re-nucleation. This occurrence has been observed in the growth of TiN coatings with ion energies in excess of 160 eV [82]. While possessing a hardness value in line with the other coatings in this study (35 ± 2 GPa), *Film C* did not perform well in other tribological tests, such as the wear test and scratch test. In both cases a significant amount of particulate debris was generated. It is probable that the coating was under considerable levels of stress (indicated by the shift in the XRD peaks) created by the high ion energy bombardment (280 eV) and failed at the grain boundaries, causing particles of coating to separate from the bulk. This coating was not optimized for composition and it is possible that additional carbon may alleviate these issues.

8. CONCLUDING REMARKS

A number of multi-component, nanostructured coatings have been prepared and summarized for a range of tribological applications. The relationship among processing, structure, properties, and performance of nanostructured coating systems: Ti–Al–N, Ti–Al–Si–N, Ti–B–C–N, Ti–Si–B–C–N, Cr–Al–N, and TiC–C produced by various deposition processes, such as unbalanced magnetron sputtering (UBMS), hybrid coating system of cathodic arc evaporation (CAE) and magnetron sputtering (MS), pulsed closed-field unbalanced magnetron sputtering (P–CFUBMS), and high-power pulsed DC magnetron sputtering (HPPMS) was discussed with concepts of design for their industrial application in detail. In each case, the coating system needs to exhibit a range of tribological properties to meet the required application, such as high wear resistance, low friction coefficient, self-lubrication, high oxidation and/or corrosion resistance. In particular, the effect of the film chemistry, pulsing the magnetron and utilizing a closed field configuration was discussed as suitable control parameters in tailoring the structure and properties of the coatings to meet specific tribological applications.

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CHAPTER 2

Nanocharacterisation of Nanocomposite Materials

Yizhong Huang

Department of Materials, University of Oxford
Parks Road, Oxford, OX1 3PH
UK
yellowh@hotmail.com

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1. INTRODUCTION

Nanocomposite materials/coatings are normally formed by incorporating nanosized particles into a matrix of inorganic/organic standard materials. The idea for the design of nanocomposites is based on the thermodynamically driven segregation in binary, ternary or quaternary systems. The segregation leads to spontaneous self-organization of a stable nanoscale structure. Thus, a nanocomposite material/coating consists of at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. It is of particular interest that nanocomposites can have excellent combination of properties including mechanical strength, toughness, electrical or thermal conductivity, high hardness, low friction and high oxidation/corrosion resistance that cannot be achieved from solely materials with a single phase. To date, a wide variety of nanocomposite materials/coatings with the desired properties have been produced. Ceramic nanocomposite hard coatings, for example, mainly used for cutting tools have undergone significant development over the past few years. Initial success in the development of the hard coatings was based on simple binary compounds such as TiC, TiN, CrN and Al₂O₃ which enable the lifetime of tools to be significantly increased in a number of applications [1-6]. However, these coatings show the high friction coefficients against steels or counterparts, and thus fluid lubricants and/or coolants are needed during cutting processes. Moreover, the poor adaptability of all these coatings to the diverse properties such as hardness, friction, oxidation resistance as well as mechanical properties means that the improvements are still necessary. This has been achieved by designing appropriate multi-components (e.g. ternary compounds like TiAlN) and multi-phases (e.g. multilayer coatings like TiN/NbN) hard coating materials.

In ternary compounds the incorporation of a third element provides the possibility of enhancing special coating properties significantly. As an example, TiAlN has considerably higher temperature oxidation resistance than TiN. The twist drills coated by TiAlN can last approximately 8 times longer when cutting cast iron, and 2 or 3 times longer when cutting high-alloy steel, compared to the TiN-coated drills [7]. Ti(C,N) has also been found to be harder [8], higher erosion resistance [9] and have a lower coefficient of friction than TiN [10, 11]. The properties of multilayer coatings benefit from the dramatically increased interface volume caused by periodic layers of different materials on a nanometer sized scale [12-14]. For example, TiC/TiN, TiN/TiAlN or TiN/NbN multilayer coatings show higher hardnesses and cracking resistances than single layer coating of the same material. Although these rearranged coatings show much better improvement in some mechanical properties, some other properties are still not optimized and may even deteriorate. For example the friction coefficients, are still quite high for all above coatings during metal treatment after optimization for multilayer coatings.

Dry lubricant coatings such as amorphous carbon or diamond-like carbon (DLC) and MoS₂ have been used in specialised applications [12, 15-19]. The industrial commercialization of

such coatings is hindered by severe problems in the process technologies needed to synthesize these materials with the desired combination of properties. For example, superhard diamond-like carbon coatings show extremely low friction coefficients against steels and metals, but their applicability suffers from very poor adhesion on metal substrates due to high internal stress on the coatings [20-23]. MoS₂ thin films also show ultra-low friction coefficients, especially in dry atmospheres, but they are very soft and have very high wear rates [24-28].

Recently, the need for new coatings with improved properties has led to research investigations based on the nanocrystalline dispersion coatings with metals, carbon and solid lubricants deposited apart from the hard material components [29-31]. This advanced nanocomposite coating design should give optimized combination of properties such as hardness, residual film stress, elastic behaviour and friction behaviour.

Other types of nanocomposites like polymer nanocomposites that represent a new class of materials are attractive alternatives to conventional filled polymers and these have also been developed considerably in recent years [32-36]. In this emerging class of materials, nanosized inorganic fillers (at least one dimension) are dispersed in polymer matrix offering tremendous improvements in the performance properties of polymers.

The excellent properties that nanocomposites exhibit are believed to be due to the specific microstructures and nanostructures contained in the materials. However, due to the scale of the nanostructures/microstructures in order to obtain a better understanding it is important to choose and develop material characterization techniques suitable for determining the structure and composition at the micro/nano scale. The aim of this chapter is to give an overview of a wide range of techniques that enable characterization to be carried out at micro/nano scale with microstructural analysis of nanocomposite coatings being investigated.

2. MORPHOLOGICAL CHARACTERIZATION OF NANOCOMPOSITE MATERIALS

2.1 SCANNING ELECTRON MICROSCOPY (SEM)

The first and true scanning electron microscope (SEM) was developed in 1942 by Zworykin *et al.* [37]. The instrument consisted of an inverted column (an electron gun at the bottom), three electrostatic lenses and electromagnetic scan coils placed between the second and third lenses. In 1948, C. W. Oatley at Cambridge University began constructing an SEM based on Zworykin's Graduate student D. McMullan [38] who described his work in a doctoral dissertation where they had claimed a resolution of 500 Angstroms. Further work, reported by K. C. A. Smith [39], made large changes to the electron optics. The electrostatic lenses were replaced with electromagnetic coils; a double deflection scanning system was added as

were stigmator coils. In addition, Smith utilized non-linear signal processing (gamma processing) to improve the imaging capability.

The SEM is a microscope that uses electrons as a source rather than light to form an image. It is a surface analysis technique and capable of viewing the morphology of the materials surface with a high resolution and a large focal depth of field.

Traditionally, a beam of electrons in SEM is generated thermionically from a tungsten or lanthanum hexaboride (LaB_6) filament, which is now being replaced by an field emission (FE) electron source. This source offers a higher brightness and greater resolution but requires a better vacuum and is more costly. Electrons are usually accelerated to an energy with a value ranging from a few hundred eV to 50 keV and are then focused by a series of lenses (including two condenser lenses and a objective lens) into a small probe with a spot size of 1 nm - 5 nm and finally raster scanned over the sample surface.

Many different types of signals are produced when electrons hit the surface of the sample and interact with the sample atoms in which secondary electrons are most common and useful. A secondary image is formed when these secondary electrons are collected by a detector. X-rays, which are also produced by the interaction of electrons with the sample materials, are valuable because they can be detected in an SEM equipped for energy-dispersive X-ray spectroscopy and wavelength dispersive X-ray spectroscopy and form the bases of chemical analysis. These analysis techniques will be describe in more detail later in this chapter.

In addition to the secondary electrons, backscattered electrons are also generated and can be used to detect contrast between areas with different chemical compositions. These can be observed especially when the average atomic number of the various regions is different. Backscattered electrons can also be used to form an electron backscatter diffraction (EBSD) image which is useful for determining the crystallographic structure of the specimen. However, there are fewer backscattered electrons emitted from a sample than secondary electrons. The number of backscattered electrons leaving the sample surface upward may be somewhat lower than those that follow trajectories toward the sides. Additionally, in contrast to the case with secondary electrons, the collection efficiency of backscattered electrons cannot be significantly improved by a positive bias common on Everhart-Thornley detectors. This detector positioned on one side of the sample has low collection efficiency for backscattered electrons due to the small acceptance angles. The use of a dedicated backscattered electron detector above the sample in a "doughnut" type arrangement, with the electron beam passing through the hole of the doughnuts, greatly increases the solid angle of collection and enables the detection of more backscattered electrons.

The spatial resolution of the SEM depends on the size of the electron spot but is limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are very large compared to the distances between atoms, so the resolution of an SEM is not high enough to image down to

the atomic scale, as is possible in the transmission electron microscope (TEM). However, the SEM has a number of advantages in the characterization of materials. These include less sample preparation time, a wide magnification range capable of revealing both bulk and nano-structured materials (including thin film coatings, an example shown in Figure 1 [40]) and availability of the variety of analytical modes for measuring the composition and nature of the specimen. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. In general, SEM images are much easier to be interpreted than TEM images.

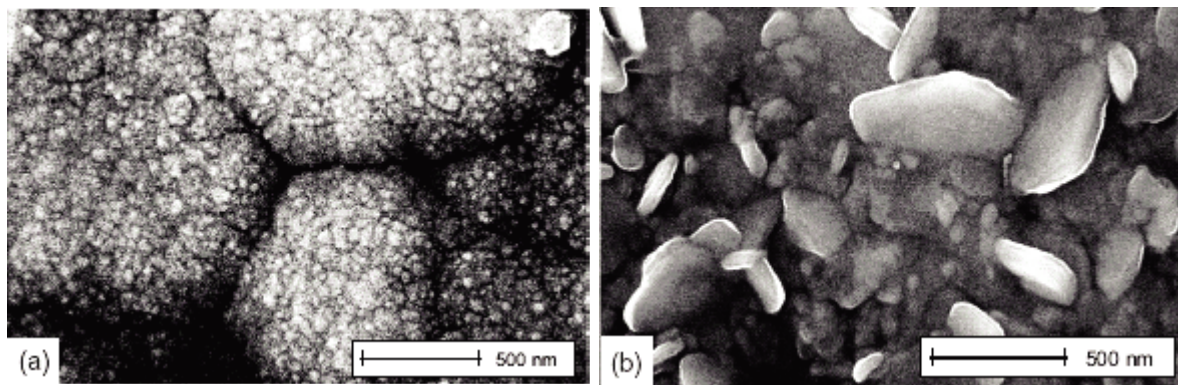


Fig. 1. FEG-SEM micrographs of the surface of the (a) as-received sample of co-sputtered MoS_x-Ti, (b) after exposure to a temperature of 350 °C.

2.2 TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM is one of most powerful techniques in materials science and has been widely used in the characterization of nanocomposites. It has ability to examine the constitutional characteristics of these nanocomposites such as grain shape and size, crystallinity and chemical variations at a resolution down to nanometer scale. Modern TEM using advanced designs are capable of seeing lattice defects, atoms and even their movements.

TEM was invented in the 1930s and used as an optical instrument for imaging samples at high resolutions. Since then, the TEM has developed rapidly and is becoming a versatile tool for characterization in material science and biology. In terms of its construction (a schematic diagram shown in Fig. 2), a general TEM usually consists of six basic components as following.

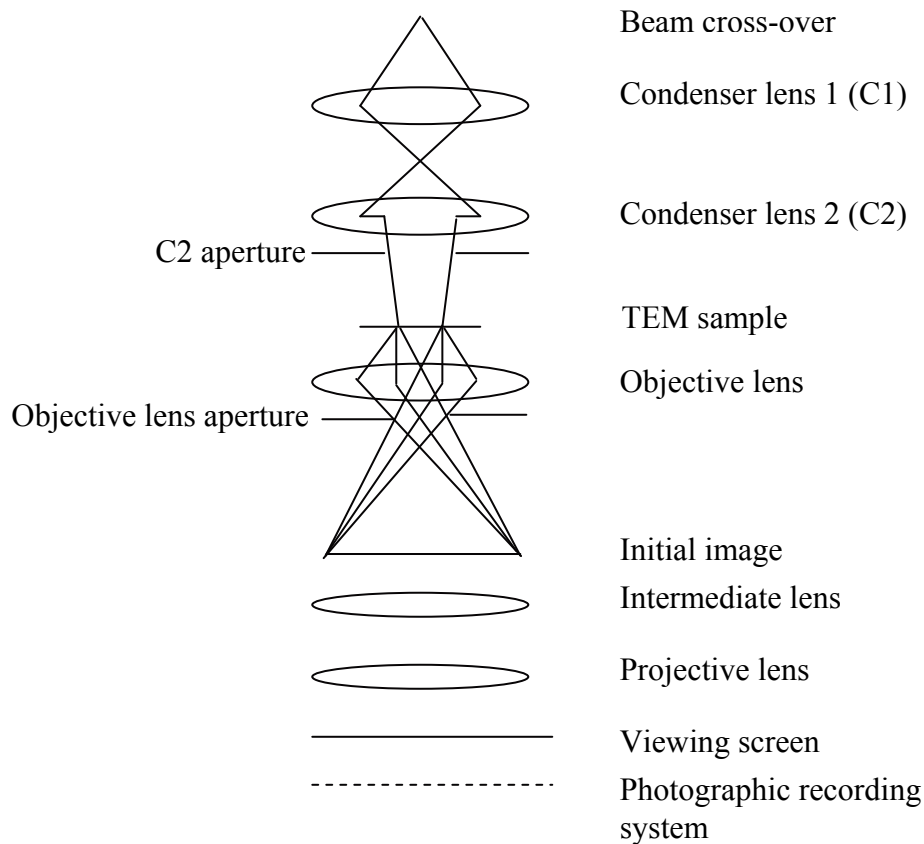


Fig 2. Schematic diagram of transmission electron microscope.

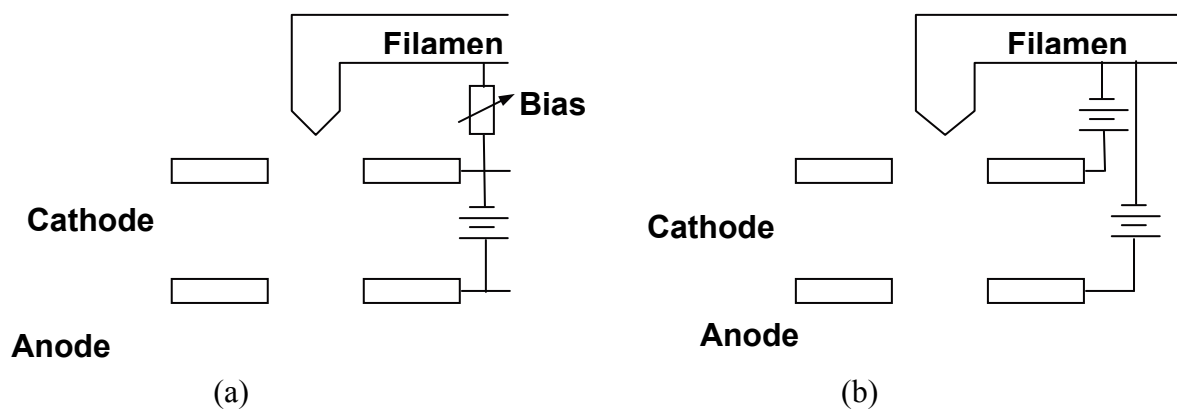


Fig. 3. A schematic diagram showing two different sources generating electrons.

- **Source providing illumination.** An electron source, commonly used in all TEMs, comprises of a filament, which emits electrons either by thermal heating (so-called thermoionic filament as shown in Fig. 3a) or through application of a high electric field to a metal filament tip generating field emission electrons (so-called field-emission filament as shown in Fig. 3b). The field-emission filament is a lot more

expensive and requires much higher vacuum than the thermoionic one but offers a very stable source with a higher resolution and longer life.

- **Electrodes.** These include a cathode which accelerates electrons generated from the filament to a high energy ranged from a few hundreds to over million voltages dependent of voltage generators used. Although a higher voltage can produce a higher resolution, in fact, most of TEM instruments are operated at an energy between 100 kV and 400 kV to reduce sample damage and reasonable instrumental cost balanced by achieving an electron wavelength as short as possible.
- **Optical system.** This consists of a series of electromagnetic lenses, such as condenser lens, objective lens, projective lens as well as intermediate lens. These lenses help to focus electrons to produce a small probe beam and form images of samples. Objective lens is the heart of the microscope. The spherical and chromatic aberrations inherent in objective lens is the major limitation to the resolution of the TEM instrument.
- **Sample chamber.** This is the place where the sample is positioned and right above the objective lens. It is important that the chamber is spacious enough to allow the samples to be viewed with a wide range of tilting necessary for crystal orientation examination and chemical analysis.
- **Camera(s).** Images of the samples can be acquired using a video/scanned camera located beneath a phosphor screen where images are seen. The photographs are taken by lifting up the screen and exposing the negatives in the camera. However, this recording method has been gradually replaced by using a CCD camera, which collects digital images without developing the negatives saving a considerable amount of time.
- **Vacuum system.** The TEMs run at a very high vacuum, which is maintained by vacuum system. In most cases, such a system comprises a combination of two types of pumps, i.e. mechanical and diffusion pumps.

Analysis capacity of TEM has been significantly enhanced by integration of the advanced techniques to the instrument. These techniques include spectrometers (such as energy-dispersive X-rays analysis (EDX) and electron energy-loss spectroscopy (EELS)) described in section 3.

2.2.1 RESOLUTION

The high-resolution of TEM benefits from the filament of source, which emits electrons through either thermal heating or field extraction forming an electron beam. Due to the lens aberrations, electrons that pass over the objective lens are unlikely focused at one point but forming a disc with its radius d , which is given by

$$d = C_s \beta^3 \quad (2.1)$$

where C_s is the spherical aberration constant and is typically 1 or 2 mm for an objective lens and β is half the angle of the cone of light from specimen plane accepted by the objective, which is ultimately determined by the size of objective aperture.

It is an advantage that electrons have an extremely short wavelength dependant of their energy. For example, the wavelength of electrons, accelerated to a high energy through a potential of 100 kV, is 0.0037 nm. The instrument resolution (without consideration of the effects from the type of sample itself) is proportional to the electron wavelength (λ), i.e.

$$d = 0.61 \lambda / \beta. \quad (2.2)$$

From the equation (2.1), it is clear that a very small aperture that minimizes the spherical aberration is recommended in order to obtain a high resolution. However, the diffraction at the aperture occurs when the aperture becomes too small, which inversely degenerates the resolution. However, according to equation (2.2), the resolution increases with increasing aperture size. Combining equations (2.1) and (2.2), an optimized aperture size, which takes both the spherical aberration and diffraction limit into account, can be written as

$$\beta = (0.61 \lambda / C_s)^{1/4}. \quad (2.3)$$

Therefore, a maximum resolution can be obtained

$$d = 0.88 C_s^{3/4} \lambda^{1/4}. \quad (2.4)$$

Since the beam is focused by a series of condenser lenses resulting in a very small probe, the spatial resolution is defined by measuring the size of this probe. This is a very important parameter in determining the capability of the machine for compositional analysis (i.e. elemental mapping) of a small region of the sample.

2.2.2 IMAGING AND DIFFRACTION

When the sample is sufficiently thin, some electrons can transmit through the thin foil without scattering, so called transmitted beam (as illustrated in Fig. 4a)). However, the interaction of electrons with crystalline samples could scatter them at different manners dependent on the specific lattice planes (denoted as (hkl) in crystallography). In particular, when the electrons are incident at a Bragg angle with respect to the transmitted beam, these

electrons are reflected by these planes, and then focused by the objective lens resulting in various spotted beams, so called diffraction beam (as shown in Fig. 3b)).

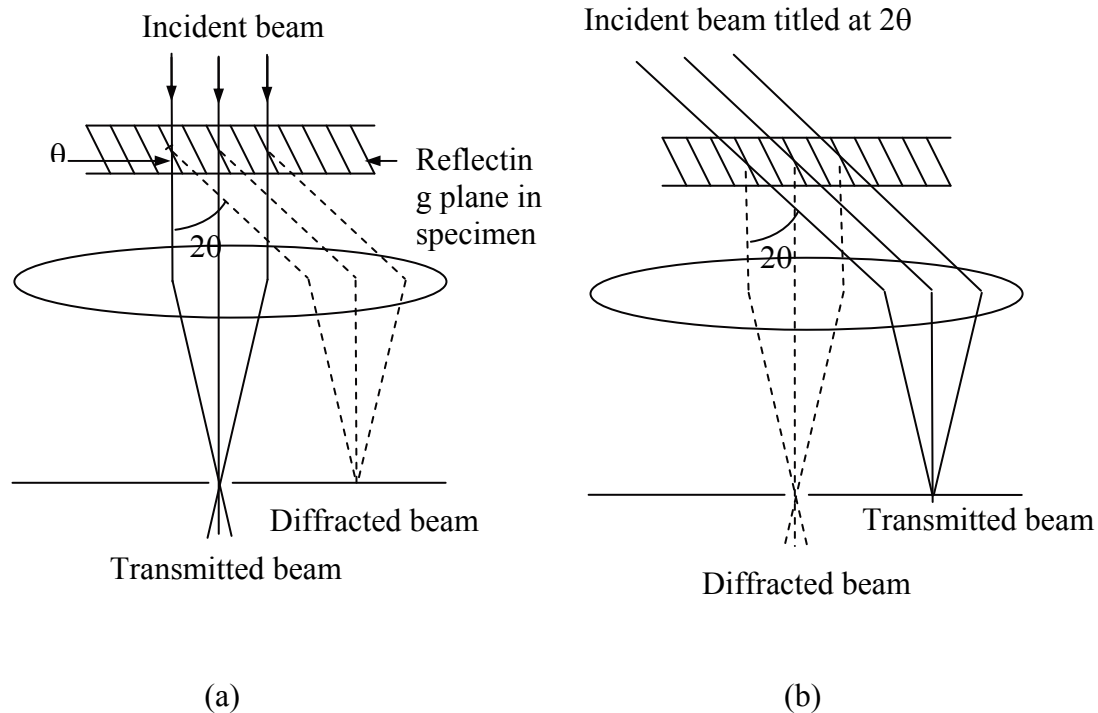


Fig. 4. A schematic diagram showing the mechanism of bright-field (BF) and dark field (DF) image formation.

A bright field image is formed when the transmitted beam is selected for imaging. In contrast, if a diffracted spot is used, one can obtain a dark field image. The selection of individual beam is made by an aperture strip, which locates in the back of the focal plane of the specimen where diffraction pattern is formed. This aperture strip contains a few holes (normally four) of different sizes at order of magnitude of a micron. Using such aperture, it is possible that only the transmitted beam or diffracted beam can be allowed to pass through it leading to a bright field or dark field image. Both image modes are most commonly used in the examination of crystalline materials with the dark field mode more favorable than the bright field mode in terms of crystal orientation, defect and phase analysis at a microscale. Firstly, the dark field image offers better contrast than the bright field image allowing features to be more visible. Secondly, the individual diffracted spot reflects a specific diffracted lattice plane in the crystal, which involves the information of that plane in the image. This dark field imaging technique is particularly useful in the analysis of defects and crystalline grain orientation. As a matter of fact, defects as a result of lattice plane distortion or disorder are shown in the dark field image with a specific form of morphology dependent on their types. For example, a dislocation (edge or screw type) has a geometry of straight/wavy line and a dislocation loop shows a ring-like pattern.

However, to characterize of nanocomposites, the bright field imaging and even dark field imaging are not very useful. As mentioned above, both techniques are suitable for the examination of crystalline grains with fairly large sizes (scaled above micron order of magnitude). This is due to the limit of the physical diameter of the selected area aperture in TEM, the scale of which is not as small as micron. As a result, when the grain size is reduced down to nano scale, individual grains cannot be selected by inserting a single aperture so that a single grain is unlikely to be illuminated within a field of view. The involvement of polynanograins (randomly oriented) in the event of diffraction will result in a diffraction pattern which consists of a series of concentric rings other than spotty points. Each ring corresponds to a particular set of lattice planes. Fig. 4(a) shows an example generated from Fig. 4(b), a bright field image of TiAlCN nanocomposite hard coating (grown by a reactive magnetron deposition method [31, 41]). By indexing the diffraction pattern, a major phase in the nanocomposite can be identified using the equation

$$L\lambda = Rd \quad (2.5)$$

where $L\lambda$ is TEM camera length used in recording the image; R refers to radius of each ring in the diffract pattern and d represents the lattice constant of the phase. In addition, the dominated direction of grain growth is easily revealed from the bright field image. Although this information is very useful and valuable, the further details such as minor phases contained in the nanocomposite, fine defects, measurement of accurate size of nanograins and their orientation relationship are cannot be obtained at this level. A dark field image can be produced by selecting a small segment of a ring from the diffraction pattern, but it doesn't help too much to access more information except slightly enhancing the image contrast. However, many other well developed techniques capable of examining nanostructured materials have been integrated into the TEM. These techniques include convergent beam diffraction, high resolution TEM and HAADF.

2.2.3 MICRODIFFRACTION PATTERN

Microdiffraction pattern in TEM is one of techniques capable of working on a small area in the sample down to a nano scale, which is performed using a fine convergent probe without inserting a physical selected-area aperture. It is a feature of this method that the diffraction patterns formed on the back focal plane of the objective lens are shaped as a disc rather than a sharp spot. The diameter of the disc is proportional to the convergent angle of the probe. In this technique, the spatial resolution of the beam (i.e. probe size) is a critical issue. Generally, the diameter of probe is determined by the condenser lenses in the TEM, which are functioned to focus the beam. There are usually at least two condenser lenses integrated in the TEM column and located right below the electron gun. The first condenser lens (C1)

allows forming a beam cross-over at its back focal plane and thus controls the minimum spot size for the rest of the condenser system. This crossover then acts as a point light source that illuminates the second condenser lens at a divergent angle leading to a very broad beam. This broad beam subsequently is brought to be a convergent probe by focusing the second condenser lens (C2). A ray diagram of such two condenser lens system is shown in Fig. 1. Since the diameter of this convergent probe determines the illuminated area of sample, efforts have been made to reduce the probe size, which include: (1) reduce the spot size by increasing the lens current of C1; (2) increase the convergent angle of beam probe through increasing the lens current of C2; (3) insert a small condenser lens aperture; (4) prepare the sufficiently thin samples.

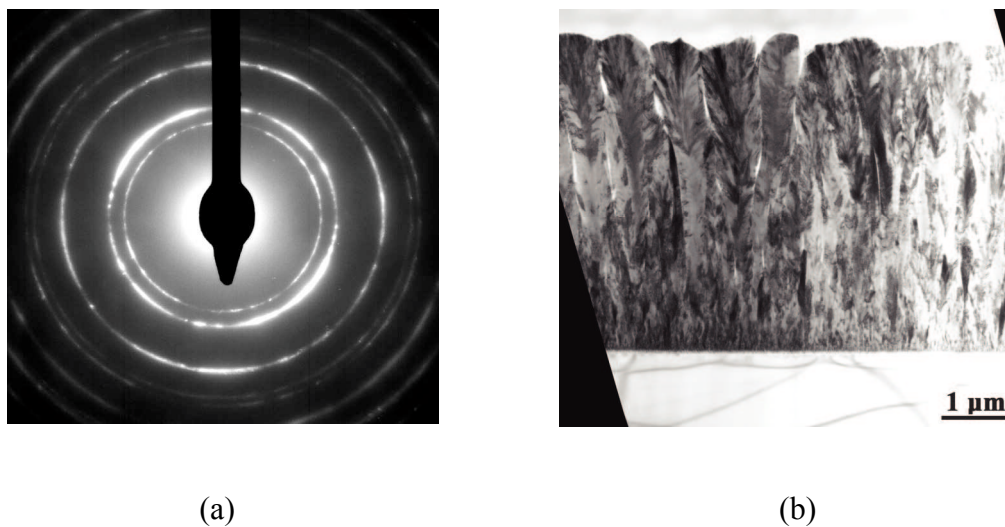


Fig. 5. A diffraction pattern (a) generated from the TiAlCN nanocomposite coating, a bright-field image of which is showed in (b).

The microdiffraction pattern technique is a straight forward, fast, effective method to analyze the small structures (such as precipitates, nanoparticles) in terms of chemical composition, nanograin orientation and phase identification. Here is an example [42, 43] showing how to use microdiffraction pattern technique to perform the relationship between the nanograins within the matrix. The crystallography of the oxide layers was characterized by electron microdiffraction using a convergent probe with a diameter of 15–50 nm, depending on the width of the individual layers. First, the foil was tilted until the beam was parallel to a low index zone axis of one of the grains adjacent to the crack. Second, the orientations of the oxide layers adjacent to the matrix grain were examined by deliberately moving the specimen under the static, focused probe both across and along the layers. Likewise, the same procedure was applied to the other grain. Fig. 5(a) and (b) shows diffraction patterns (DPs) from the grain (A) and outer layer (region B) in Fig. 6 of a type 316 steel. Careful comparison of the patterns shows that the outer layer adjacent to the grain has a parallel orientation relationship to the $\langle 110 \rangle$ and $\langle 200 \rangle$ austenite directions. These phases are spinels. However, there are additional reflections and considerable diffuse scattering in Fig.

5(b) that suggests that the layer is nano-crystalline and composed of a number of nano-grains (~ 5 nm), with some grains only partially coherent or incoherent with the matrix grain. Moreover, examination of microdiffraction patterns from the inner layer showed that the individual crystals (identified, by analysis of diffraction patterns in combination with high-resolution image of polycrystals, as a spinel: NiFe_2O_4) were oriented exactly with either one or the other matrix grain. This was verified by observing almost identical DPs from tens of individual grains in the inner layer. A specific example is presented in Fig. 5(c), from the crystal labelled C in Fig. 6, acquired at the same foil orientation as for Fig. 5(a) and (b). Equivalent results at $\langle 211 \rangle$ steel foil orientation from the same region in Fig. 6 are presented in Fig. 5(d)–(f). High-resolution observations of the sandwiched layer verify that the outer-layer consists of an array of nano-particles (the so-called nano-crystalline layer (NL)) with lattice fringes by space of 0.485 nm, some of which are oriented with respect to each other and are the same as the adjacent grain (as indicated by parallelism of lattice fringes).

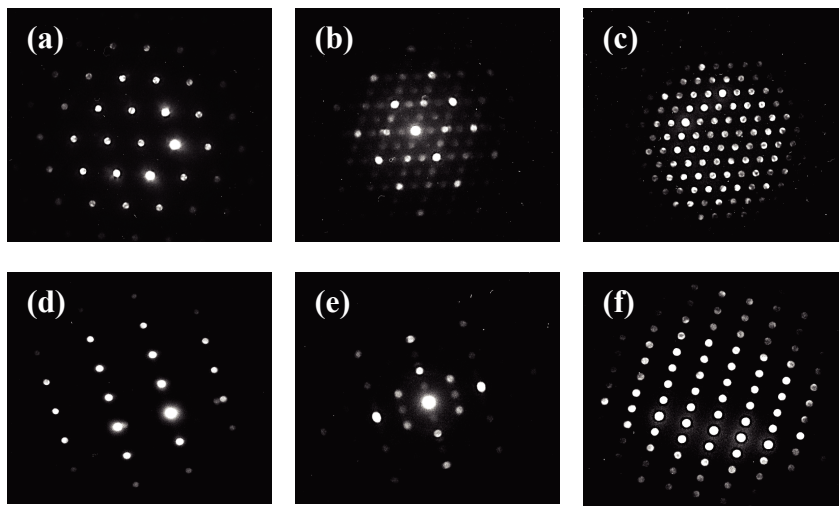


Fig. 6. (a) shows $\langle 110 \rangle$ mDP from steel grain A (in Figure 6) and (b) from adjacent NL layer and (c) a PL grain at same tilt. (d) - (f) show equivalent results at $\langle 211 \rangle$ steel orientation. Parallel reflections from the three regions demonstrate coherency.

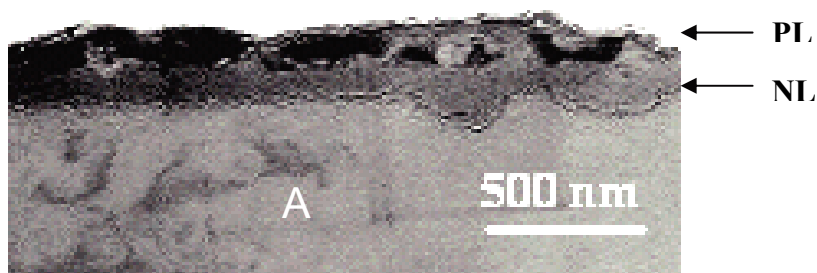


Fig. 7. Spinal oxide layers grown on the stainless steel matrix grain A.

Likewise, this microdiffraction pattern detection can be applied to microstructural characterization of nanocomposites, in particular, chemical phases and orientation relationship of micro/nano grains within nanocomposites. Furthermore, by pointing a single micro/nano grain using a convergent probe, a microdiffraction pattern with sharp discs can be produced. As a result, this technique makes it possible to obtain a dark field image of a single micro/nano grain using an objective aperture to allow an individual microdiffraction disc to pass through it forming an illumination beam.

2.2.4 HIGH RESOLUTION TEM

Increasing number of techniques are becoming available to produce images at an atomic level so that the lattice arrangements within crystalline materials can be visualized. One popular technique is high resolution TEM (HRTEM). A very high magnification is necessary in order to obtain a high-resolution atomic image. However, atomic images are not obtained by simply zooming in an image to a sufficient magnification through an imaging system (comprising of both intermediate and projection lenses) in TEM. The atomic images are formed by interference of the transmitted beam with one or more diffracted beams. As a result, a phase contrast, which contributes to the atomic lattice image, is achieved due to a small variation of phase angles between the two beam waves. Figure 7 shows a cross-sectional high resolution image of a nanocomposite Ti-Al-C-N where lattice fringes are clearly visible with different configurations. Each configuration can be interpreted as a crystalline nanoparticle. By simply measuring the distance between the neighbouring lattice fringes, the phase can be identified with the help of known compositional constituents of the nanocomposite. Furthermore, other information can be retrieved from this image such that some crystalline particles are separated by some amorphous regions (without lattice fringe appearance), which are actually carbon phases confirmed by Raman microspectroscopy (more details are given below in the section of Raman microspectroscopy).

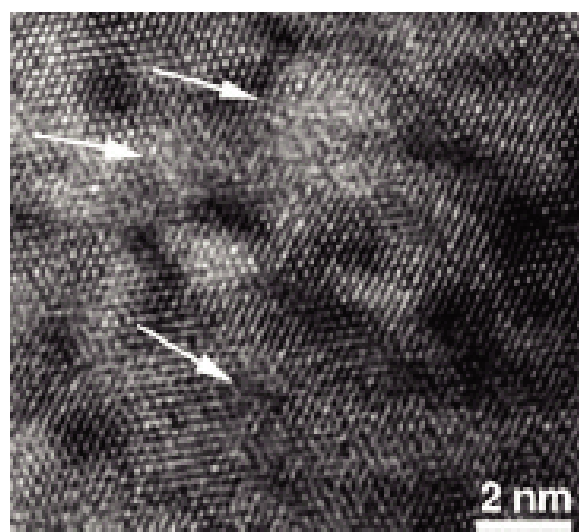


Fig. 7. HRTEM image of TiAlCN coating with carbon content of approximately 16 % at.

To acquire a good quality HRTEM image, several factors must be taken into account. Firstly, TEM column alignment needs to be carried out as accurately as possible, which includes electron gun and condenser lenses' alignment, astigmatism correction of condenser lenses and objective lens. Since a high resolution TEM image is limited by the resolution, which is imposed mainly by the spherical aberration that the objective lens is remained, efforts need to be made to minimize them. A well-aligned objective lens is in the first instance extremely important. This is usually done through checking the high-voltage centre of the objective lens (i.e. apply a small voltage oscillation onto the objective lens coils whilst watch the beam if it is concentrically moving in and out). Conventionally, the correction of the spherical aberration was usually performed using the Fresnel fringes along the edge of a small hole viewed with the objective lens overfocused. In modern TEM instrument, the astigmatism can be adjusted with the assistance of a CCD camera, which acquisition of a live FFT (fourier transformation) pattern. This pattern is a direct real-time image from the objective lens and thus reflects the spherical aberration status of the objective lens. Ideally, the pattern should appear to be a series of concentric round circles when the objective lens has a small spherical aberration, which is not significant. However, in most cases, the FFT pattern is distorted and not even a circle shape. This demonstrates a large spherical aberration that the objective lens is suffering and action should be taken to minimize it. The process of this action involves to gently adjust the objective lens stigmators until the FFT pattern becomes round as perfectly as possible. Most recently, spherical aberration correctors (Cs correctors) have been developed which consists of a series of quadpole and octodupole lenses. They are incorporated into electron column to help reduce and even eliminate the spherical aberration of the condenser and objective lenses. Therefore, no artefacts or delocalization effects are observed in phase contrast imaging of non periodic regions of the specimen. Secondly, in a

HRTEM, an atomic image of a crystal structure is only possible if certain conditions are satisfied. Thus choosing the optimum defocus is crucial. In Gaussian focus one sets the defocus to zero, the sample is in focus. As a consequence, contrast in the image plane gets its image components from the minimal area of the sample, the contrast is localized (no blurring and information overlap from other parts of the sample) leading to a minimum phase contrast. Only at a Scherzer focus (i.e. $f = -1.2\sqrt{Cs\lambda}$) where weak phase object approximation is met, atom columns are imaged dark and spaces between atoms bright. Moreover, the HRTEM simulations (such as using exit wave function method) have been very helpful and enable to significantly improve the HRTEM image, with which a lot of researchers have been working.

2.2.5 TEM SAMPLE HANDLING

To examine materials by TEM requires a sample that should normally be less than 3 mm in a diameter with the area of interest sufficiently thin to allow electrons to penetrate it. It is important to prepare a good TEM sample, which is a prerequisite for any analysis using various TEM techniques (including imaging, EDX and others). Not only is it difficult to thin the bulk sample down to a desired thickness (mostly less than 100 nm), but also preparation (such as mechanical/electrochemical polishing and ion sputtering) can bring a lot of artifacts into the sample, which may give rise to unexpected false information of the materials. As for nanocomposites, a greater challenge involves preserving the nanostructures within a thin foil so that they can be visible in TEM. A number of new techniques for preparing TEM samples have been developed to supplement techniques currently employed. These methods allow materials such as ceramics, semiconductors, nanocomposites and even biomaterials, which cannot be prepared using traditional TEM sample preparation methods (i.e. mechanical polishing and electropolishing) to be thinned into TEM samples. It is worth mentioning that some techniques such as a focused ion beam system can prepare a TEM sample with a specific site within half an hour's time. Two major methods currently used for TEM sample preparation are discussed and their suitability to the types of materials as well as their advantages and disadvantages are considered below.

2.2.5.1 BROAD ION BEAM MILLING

Broad ion beam milling, usually utilizes a source of Ar^+ ions, which are accelerated by a high voltage (up to 5 KeV). These irradiate the sample surface at an adjustable angle (between 1 to 10 degrees) and bombard the surface to sputter away atoms from the material. Such removal of materials enables a reduction in the thickness of the sample resulting in a thin foil suitable for TEM observation. Commonly, the equipment widely used for this purpose is known as precise ion polishing system (i.e. PIPS) which is a GATAN product. It is a very powerful instrument that allows preparation of a large variety of materials including metals and alloys, ceramic, semiconductor as well as nanocomposite materials/coatings. The technique has a lot of advantages - cheap, easy to be operated and with little maintenance requirement and low

service-cost. Of greater importance is the excellent reliability of the technique and its use can achieve a very high yield of success in the TEM sample preparation.

A common problem of TEM specimen preparation by ion milling and all surface analysis techniques utilizing ion beam depth profiling is the roughening of the specimen surface due to ion bombardment. It is well known that sample rotation and decrease of the angle of incidence can help to reduce this problem. However, it cannot be fully eliminated this way. Therefore a new, low energy ion gun has been developed which can be used at ion energies as low as 100 eV still producing high enough intensity for effective milling [44]. The new gun was designed from materials suitable for ultra high vacuum (UHV) conditions in order to apply it also in Auger electron spectrometers.

The new, low energy ion gun may be incorporated as the second gun in the IV3 equipment of Technoorg Co. or it will also be available in a separate instrument under the commercial name “Gentle mill”. In either case it is suitable for final stage ion polishing of TEM specimens produced in a conventional ion miller by removing the damaged surface layer thus making them capable for high resolution electron microscopy.

Features of the low energy ion gun are as follows:

- Extremely low ion energy operation range: 100 eV- 2 keV
- High thinning rate due to hot cathode discharge
- Substantially reduced surface damage for HREM examination
- Vacuum-load lock system
- Computer-control

2.2.5.2 FOCUSED ION BEAM MILLING

Focused ion beam (FIB) systems have been commercially manufactured for approximately twenty years primarily for large semiconductor manufacturers. FIB systems operate in a similar fashion to a scanning electron microscope (SEM) except, rather than a beam of electrons and as the name implies, FIB systems use a finely focused beam of ions (such as gallium) that can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling at nano-meter scale.

The use of ions in a focused beam accelerated in a FIB apparatus to energies up to 30 keV is now well established as a means both of depositing films at selected locations and of selectively milling to reveal structural features in integrated circuits [45]. The FIB has more recently been used for generating electron transparent TEM specimens from selected regions of a bulk sample [46]. Potential artefacts from the TEM preparation method are the implantation of the milling ions, the generation of crystal defects within the specimen by the high-energy ions, local specimen heating, stress generation, phase-dependent variable etching

rates and the deposition of ion-sputtered material over free surfaces. Such artefacts can also arise when using more conventional broad beam ion milling TEM foil preparation. Although these artefacts can be minimized by selection of appropriate ion energy and specimen geometry, particularly in the final stages of preparation, they are always present to some extent.

There are two established methods for preparing TEM foils using FIB: (a) the 'trench' technique [47, 48, 49] and (b) the 'lift out' technique [46, 50]. Foils are prepared with a cross-sectional orientation in both cases. With the trench technique the location of the transparent area can be selected within the limits imposed by the ability to mechanically cut and polish a thin cross-section from a bulk sample containing the volume of interest. In the lift out technique, a small transparent area can be extracted at any location on the surface of the bulk sample.

Trench technique involves milling of an H-shaped membrane on both sides of the sample using a series of reduced beam currents until the membrane is thinned down to around a hundred nanometer becoming electron transparent in TEM. Before FIB ion beam milling, a slice of the material with the area of interest (approximately 2 mm long and less than 60 μm wide) is prepared by either dicing or polishing. The thinner the slice is made the shorter time is required for FIB milling. The slice is then glued to a slotted TEM grid with its top part being cut off to provide a clear path between the sample top surface and the ion beam. It is recommended that the conductive epoxy such as silver glue be used to avoid charging in the FIB imaging.

Lift-out technique involves cutting out a cross-section sample from its substrate and transferring it into a support grid with a thin support membrane using a micro-manipulator. Similar to the trench technique, lift-out technique are processed by ion beam milling using a series reduced beam currents until the sample becomes thin enough for TEM observation. However, instead of being ready to place into TEM for the sample prepared by trench technique, the thin membrane prepared by lift-out technique has to be cut so that it is free and allows to be lifted out by the use of a micro-manipulator with the help of a glass/metal needle.

The two techniques outlined above have their relative advantages and disadvantages. In the lift-out technique the pre-FIB preparation time is minimal, whilst in the trench technique the time taken for grinding and polishing the sample into a slice for mounting onto a TEM grid is considerable. The post-FIB preparation times for the two techniques are also different. Trench cross-section samples can be placed immediately into a TEM but the plucking of a cross-section sample from its substrate and placing into a support membrane can be very difficult and time consuming. More problems are encountered with the lift-out technique during TEM sample preparation for example, the specimen can get broken during plucking or drop off when transferring into the TEM grid. Sometimes, when a cross-section sample slides

up the needle, it is very challenging to place the sample onto the TEM grid. Since a cross-section sample prepared using the trench technique is surrounded by the substrate materials at its three dimensions, the rotation angle is limited when viewing in a TEM. This causes a problem during EDX analysis, in which X-rays can be blocked by sidewalls of the trench and additional X-ray may be generated from them. However, it is advantageous that the cross-section TEM sample prepared by life-out technique is left intact without the substrate material surrounding the thin membrane. It is very important to understand the differences between these two TEM sample preparation techniques so that users can make an informed choice between the two according to the specific requirements.

Compared with many other methods, FIB provides a faster and more reliable method for preparing TEM samples. It has no preferential choices to the type of materials and is suitable for most cases and a wide range of materials, such as metal and alloys, ceramic, semiconductors and biomaterials. However, it allows better control if the materials are relatively conducting. To prepare TEM samples for nanocomposite materials, especially nanocomposite coatings, FIB is widely used.

The main drawback that FIB prepares TEM samples is that it brings artifacts to the materials. This is due to ion damage and implantation into the sidewalls of the cross-section samples during the ion beam milling process. The depth of the damage and implantation depends on the ion species, the incident energy, the angle of incidence and the type of material. Considerable efforts have been made to reduce these artifacts, depositing a protective layer on the area of interest before sectioning, the use of gas-assisted enhanced milling and dual-beam FIB system, for instance.

2.3. ATOMIC FORCE MICROSCOPY (AFM)

The AFM can be classed as a scanning probe microscope with a very high-resolution at an atomic level. Invented by Binnig, Quate and Gerber in 1986, it uses a cantilever (typically made of silicon/silicon nitride) probe with a sharp tip that has a radius of nanometer order of magnitude. Scanning this probe over the sample surface allows imaging, measurement and manipulation at the nanoscale.

Depending on the specific application, the AFM can be operated at a number of different modes. Commonly, imaging modes can be split into two major types of mode: static mode (such as contact mode) and dynamic mode (such as tapping mode).

When the tip is sufficiently close to a sample surface, several types of forces between the tip and the sample are generated. These forces can be mechanical contact force, van der Waals force, capillary force, chemical bonding, electrostatic force, magnetic force, Casimir force, solvation force etc. leading to different types of AFMs. Direct characteristics of the materials can be easily measured using these AFMs through force imaging. For example, a magnetic force microscope (MFM) can be used to map the spatial distribution of magnetism by

measuring the magnetic interaction force between a tip and a sample. Since magnetic devices have become smaller and smaller, an evaluation technique with nanoscale spatial resolution has become necessary. To meet this demand, the MFM has been developed.

Recently, AFM has been a most widely used tool in performing the surface analysis of nanocomposite materials/coatings [51-58]. Fig. 8 shows three surface morphological images of TiAlCN nanocomposite coatings with different carbon contents conducted using a Nanoscope IIIa AFM, with the standard contact mode Si tips by scanning an area of $5\mu\text{m} \times 5\mu\text{m}$ at a scan rate of 0.5 Hz. Results show that the structure for pure TiAlN without C content was columnar, with grains on the surface sized between 300-700 nm. The addition of low levels of carbon (in the 5 - 8 at.% range) show that the columnar structure is retained. At higher carbon contents in the 8-30 at. % range, a fine nanostructure is observed with grain size in the range of 30 - 50 nm.

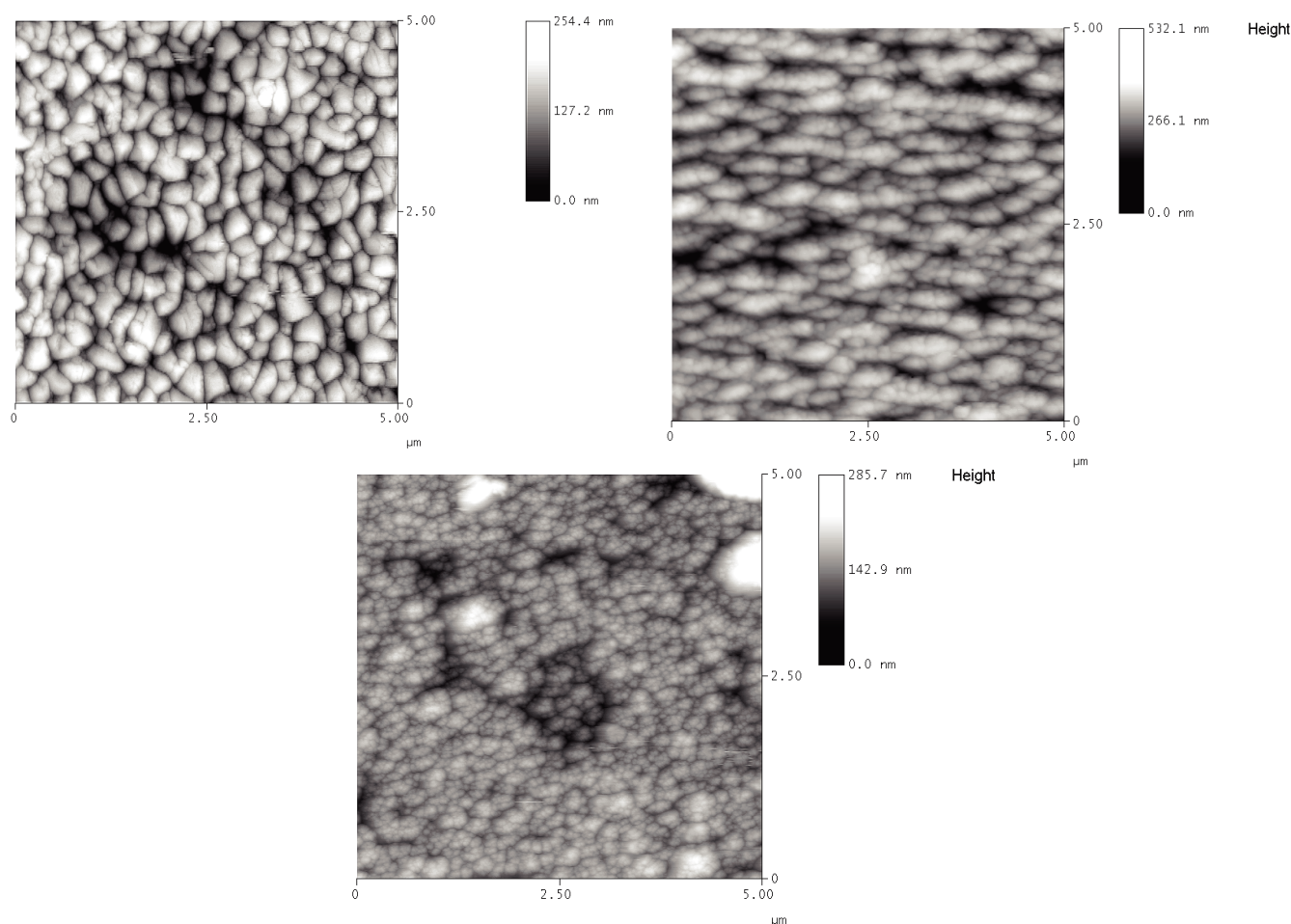


Fig. 8. AFM images for TiAlCN nanocomposite coatings with different carbon contents: (a) 0 at.%, (b) 13.5 at.% and (c) 28.0 at.%.

The variations in the uppermost surface morphology and roughness of coatings were analyzed by AFM. Figure 8 (a), shows a surface image of pure coating of TiAlN, with very uniform grains of average size of around 250 nm. The surface also revealed a fairly smooth

topography with a RMS roughness estimated about 39.0 nm. The height contrast image suggests the presence of vacancies on the top surface with grains in triangle-like shape indicating that the structure of grains are more likely columnar, parallel with the normal to the original surface of the substrate, which is consistent with the previous XRD investigation above. With comparison to the pure coating, two surface images for both TiAlN-13.5 at.%C (b) and TiAlN-28 at.%C (c) coatings with different carbon contents were obtained using the same scanning conditions, which were shown in Figures 5 and 6, respectively. Different from the pure TiAlN coating, the appearances of both coatings were displayed as consisting of many clusters formed by the segregation of a lot of small grains although some individual grains can be seen clearly. The grains are not very uniform and with a large range of magnitude in size. The values of their grain sizes and roughnesses in contrast to the pure TiAlN coating were measured and presented in Table 1.

Table 1. The comparison of three representative coatings in terms of average grain size and roughness.

Coating	TiAlN	TiAlN-13.5 at.%C	TiAlN-28 at.%C
Grain size (nm)	250	120	30
Roughness (nm)	39.0	37.6	26.9

The decrease in both grain size and roughness was found when carbon was introduced into the TiAlN coating, which then kept decreasing with increasing carbon content. Note that the RMS roughness here is defined by the shape of overlapping grains, of which thin films were composed, other than by the local roughness of the individual grains. To get the value as accurate as possible, the grain size was measured by averaging several tens of individual grains ranged between the smallest and largest.

The AFM has several advantages over the scanning electron microscope (SEM). Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM is able to provide a true three-dimensional surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms. In principle, AFM can provide higher resolution than SEM and gives atomic resolution in ultra-high vacuum (UHV). UHV AFM is comparable in resolution to Scanning Tunneling Microscopy and Transmission Electron Microscopy.

A disadvantage of AFM compared with the scanning electron microscope (SEM) is the image size. The SEM can image an area on the order of millimetres by millimetres with a depth of field on the order of millimetres. The AFM can only image a maximum height on the order of micrometres and a maximum scanning area of around 150 by 150 micrometres. Another disadvantage is that at high resolution, the quality of an image is limited by the radius of curvature of the probe tip, and an incorrect choice of tip for the required resolution can lead to image artifacts. Traditionally the AFM could not scan images as fast as an SEM, requiring several minutes for a typical scan, while an SEM is capable of scanning at near real-time (although at relatively low quality) after the chamber is evacuated. The relatively slow rate of scanning during AFM imaging often leads to a thermal drift in the image, making the AFM microscope less suited for measuring accurate distances between artifacts on the image. However, advances in speed are being made in what is being termed videoAFM, where reasonable quality images are being obtained at video rate - faster than the average SEM.

2.4 SCANNING TUNNELING MICROSCOPY (STM)

Similar to the AFM, the scanning tunneling microscope (STM) is also a scanning probe microscope in which an electrical probe (also called stylus) is used to scan over a surface. The stylus is so sharp that its tip has only one atom on top of the tip. An image is formed by collecting a weak electric current flowing between the stylus tip and the conductive surface. The STM was invented in 1981 by Gerd Binnig and Heinrich Rohrer of IBM's Zurich Lab in Zurich, Switzerland who were awarded a Nobel Prize in Physics in 1986. It provides a very high resolution enabling an image at an atomic scale to be obtained. Thus, direct atomic arrangements on the surface of a conductive sample can be visualized and imaged without additional interpretation processes unlike other techniques such as HRTEM. This allows the STM a very good technique for in-situ observation of evolution of atomic structures. Thus, it is an highly effective method for characterizing nanocomposite materials/coatings [59-62]. Fig. 9 shows such an example of the surface topography of the as-deposited titanium and the anodized titanium using cyclic voltammetry as a function of different E_{max} [63].

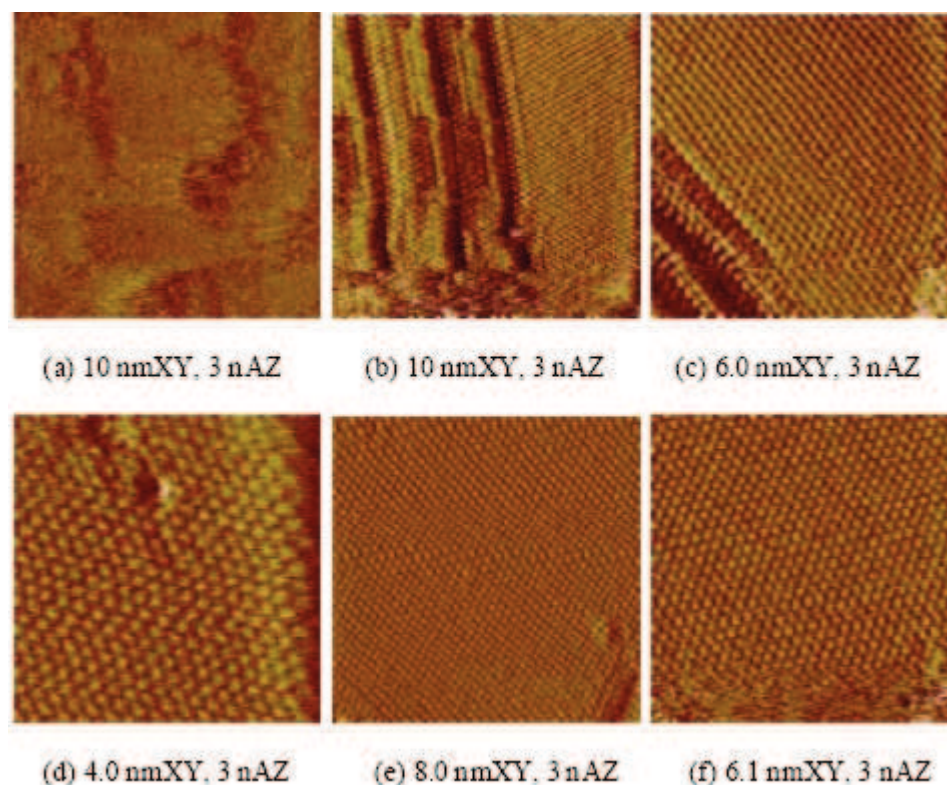


Fig. 9. STM image of (a) the as-deposited titanium and the anodic oxide layer formed at (b) $E_{max} = -50$ mV, (c) $E_{max} = 200$ mV, (d) $E_{max} = 500$ mV, (e) $E_{max} = 1000$ mV and (f) $E_{max} = 1500$ mV in 0.1M H_2SO_4 solution. Current mode, $I_{setpoint} = 2.0\sim 2.5$ nA, $V_{bias} = 100\sim 300$ mV.

Besides acquiring high resolution imaging, the STM has the ability to manipulate individual atoms, trigger chemical reactions, or reversibly produce ions by removing or adding individual electrons from atoms or molecules.

3. CHEMICAL ANALYSIS OF NANOCOMPOSITE MATERIALS

3.1 X-RAYS DIFFRACTION (XRD)

It is well known that x-rays have the wavelengths at the same order of magnitude as the distances between atoms or ions in a molecule or crystal and as a result, the molecule or crystal should act as a 3-D diffraction grating. X-rays were used to carry out diffraction experiments on the crystals for the first time in 1912 by Prof. Max von Laue, a professor of physics at the University of Munich in Germany and his group, who were awarded Nobel Prizes in Physics. It has been demonstrated that occurrence of X-rays diffraction depends on the X-ray wavelength, the crystal structure and orientation between X-rays incidence and the crystal lattice plane. For a given wavelength (λ), diffraction can only take place at a certain angle (θ) for a given d-spacing. The relationship between them can be written as

$$\lambda = 2d \sin\theta$$

which is the famous equation, i.e. Bragg law, where the angle θ is called Bragg angle.

X-rays diffraction (XRD) provides an easy, fast and convenient means that enables to determine the elements present in a sample because of the unique wavelengths produced by each unique element. A lower energy process that involves the interaction of electrons with the nucleus of an atom in the target metal produces a continuum of lower intensity X-radiation over a broad energy range known as Bremsstrahlung. Likewise, by varying the angle of X-rays incidence, a continuous diffraction pattern spectrum can be generated that reflects characteristic of the sample.

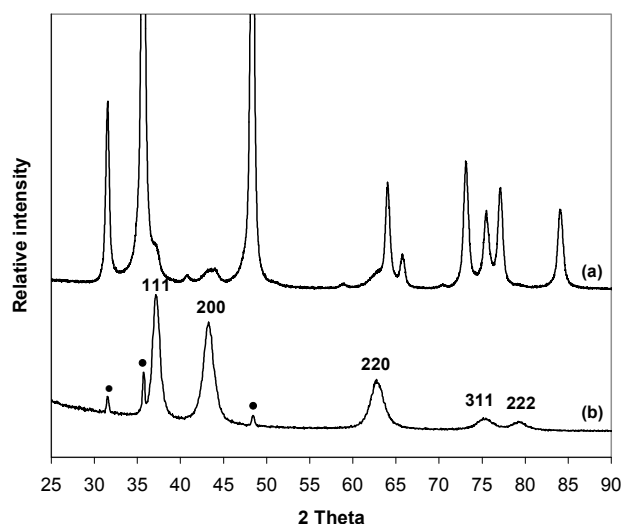


Fig. 10. The Bragg-Brentano XRD pattern from substrate (a) showing strong diffraction reflections of substrate, which are considerably suppressed (marked by •) in XRD pattern (b) from the coated substrate containing 5.51 at.%C for sample NCP18, which was measured using a low glancing angle x-rays.

Figure 10 shows the XRD spectra of the nanocomposite TiAlCN coating with a carbon content of 5.51 at.% grown on the surface of Si substrate scanned in the Bragg-Brentano in the region between 25° and 90° [41]. Three peaks generated from the coatings were identified as (111), (200) and (222) separately. X-ray diffraction was performed on a Philips PW-3710 diffractometer equipped with Cu K α radiation with wavelength $\lambda = 1.5406$ nm subject to a tube current of 30 mA at the generator voltage 40 kV. However, the visibility of peaks from the coatings is much lower than those from the substrate. Furthermore, all corresponding peaks from TiN, TiAlN, TiAlCN or TiAlC are likely to overlap. Hence, the detailed phase information is impossible to retrieve. In order to eliminate the strong reflections from the substrate, XRD measurements were taken at a low glancing angle, which was found more applicable and reliable to the thin films in particular [64]. As a comparison between both spectra in Figure 10, obtained from scanning the coating TiAlN-5.5 at.%C using the Bragg-

Brentano and a low glancing angle, respectively, peaks from coatings were revealed much more evidently whilst substrate peaks are considerably suppressed.

One of examples is presented in Figure 11 showing low angle XRD (111) peak patterns, ranging from 36° to 40° , of five coatings with different carbon contents. Based on the measurement of the interplanar spacing $d_{111} = 2.402 \text{ \AA}$ at the position I in Figure 11, the phase lattice parameter was determined as $4.161 \text{ \AA}$, that corresponds to TiAlN component with the standard lattice parameter $a = 4.170 \pm 0.005 \text{ \AA}$ [65]. The small decrease, thought to be due to effect of internal stress, indicates this coating (TiAlN without C) is likely in a state of tensile stress, which will be confirmed further by internal stress analysis below. The (111) peak shift took place when carbon content was added into TiAlN and moved continuously from the position I, II to III with the increase of carbon up to 30%. This may be due to a structural transition as carbon is incorporated into TiAlN and partially or completely replaces nitrogen at its lattice position resulting in the formation as TiAlCN (II) and TiAlC (III). Since the atomic volume of carbon is larger than that of nitrogen, the TiAlN cell was increasingly increased with higher carbon content until nitrogen is fully substituted by carbon. The increasing boardness of the peak demonstrates the reduction of grain sizes of the coatings in the magnitude from microcrystalline to nanocrystalline. Carbon appears to act as a diffusion inhibitor that restrained the growth of coating grains and thereby resulting in coatings being more randomly oriented. This is supported from Figure 3 and Figure 4, where pure TiAlN coating showed a preferred growth direction $\langle 111 \rangle$, which is dramatically suppressed but the $\langle 200 \rangle$ texture increases strongly when the carbon content increases from 0 to $\sim 8\%$.

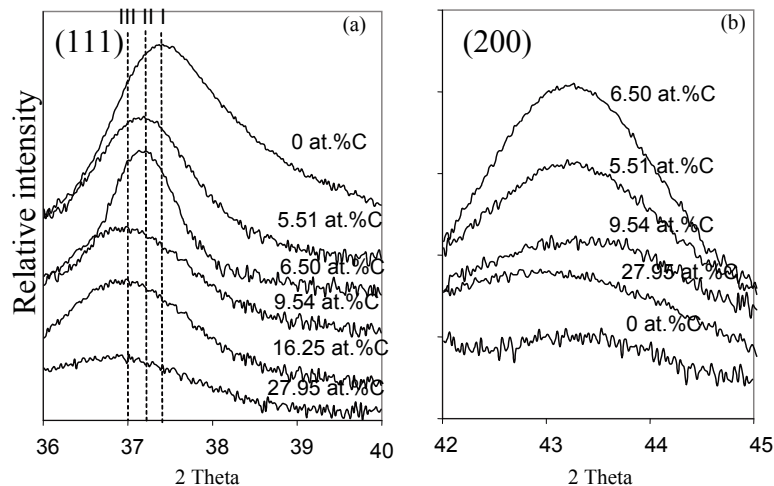


Fig. 11. The shift of (111) and (200) peaks with the increase of carbon content.

In addition to the useful of XRD for chemical analysis it has also been applied to analysis of the growth texture of nanocomposite coatings and their internal strain/ stress measurements, the study of phase equilibrium, measurement of particle size, as well as growth texture of coatings.

The texture of the coatings has also been examined using the pole-figure. Figure 12 shows the (111) peak and (200) peak for the TiAlCN coatings with different carbon contents. The pole-figures indicate that the (200) orientation is present in all coatings but with a maximum intensity for low carbon content below 9.5 at.%. The (111) peak intensity drops while (200) peak intensity increases with the increase of carbon content. This change could be due to a shift in the preferred (111) orientation of the coatings to a more mixed orientation.

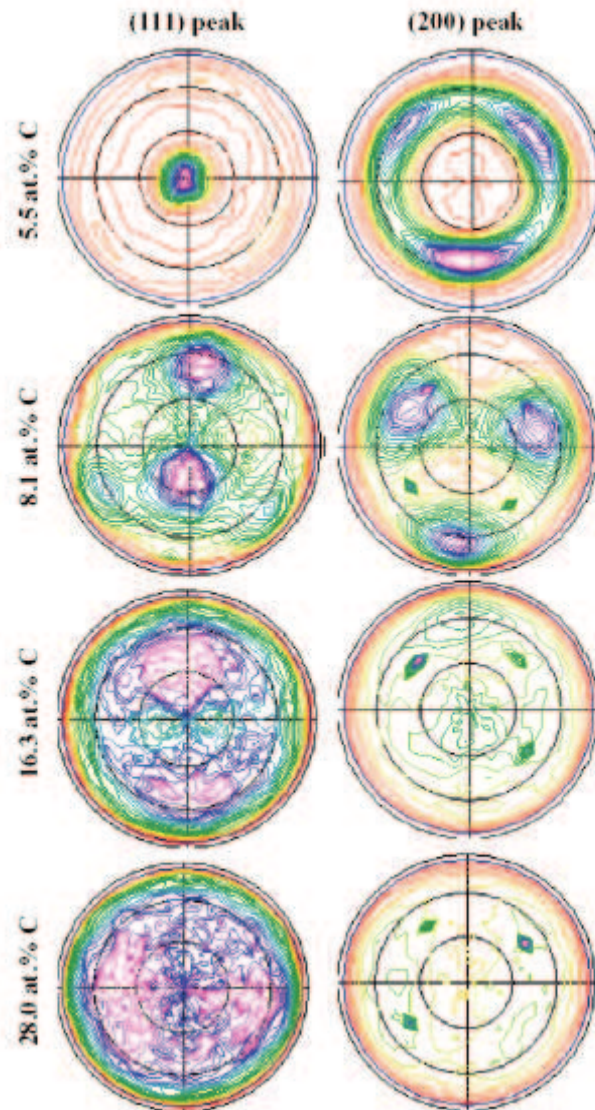


Fig. 12. X-Ray Diffraction pole figures of the (111) and (200) peaks for the TiAlCN nanocomposite coatings with 5.5, 8.1, 16.3, and 28.0 at.% carbon.

Internal stresses present in pure TiAlN, TiAlN-5.51 at.%C and TiAlN-28 at.%C have been determined using glancing angle parallel beam geometry. The method is based on the equation given by

$$a_{\psi} = \sigma a_0 \{[(1+\nu)/E]\sin^2\psi - 2\nu/E\} + a_0.$$

The stress can be worked out from the slope obtained by the least-squares fit of the plot of a_{ψ} against $\sin^2\psi$. The details of this method have been described in elsewhere [66]. Table 2 summaries the internal stress measurements for three coatings with various carbon contents where unstressed lattice parameter a_0 , elastic modulus E and Poisson's ratio ν of TiN were assumed to be 4.240 Å, 400 GPa and 0.3, respectively.

Table 2. The variation of internal stresses measured for three coatings with difference carbon contents.

Coating	TiAlN-0C	TiAlN-0.05C	TiAlN-0.28C
Internal stress (GPa)	0.7	-0.5	-2.14

These results show that the transition of the internal stress statement of TiAlN coating from tensile to compress occurred after addition of carbon element into the coating.

3.2 X-RAYS PHOTOELECTRON SPECTROSCOPY (XPS)

XPS is a surface analysis technique that can be used to analyze the chemical and electronic state of the elements on a surface of the sample. Kai Siegbahn in Sweden was awarded a Nobel Prize in 1981 for his significant contribution to the development of a very powerful chemical analysis instrument known as X-ray Photoelectron Spectroscopy. It is a quantitative spectroscopic technique that measures the number of electrons detected (electron emission intensity plotted as Y-axis) versus the binding energy of the electrons detected (X-axis) to form a spectrum. This spectrum is produced by irradiating a material with a beam of X-rays generated from a metal source such as copper whilst measuring the kinetic energy (KE) and number of electrons escaping from the surface (1 -10 nm in depth) of the material. The spectrum consists of various peaks with each peak being characteristic of a specific element. Measuring these peak areas at nominal binding energies enables to quantitative determination of the concentration of the elements within samples. Meanwhile, small shifts in these binding energies (chemical shifts) provide powerful information about chemical states and short-range chemistry from which the bonding state of the element with

another or others can be determined. Furthermore, ion etching is available in most XPS instruments, which allows elemental composition as a function of depth (i.e, depth profiling) to be elucidated.

XPS is capable of examining a various types of materials including both conductors and insulators and suitable for undertaking nano-structured materials, in particular nanocomposite coatings [67-72].

Following shows an example by using XPS to investigate the elemental composition of TiAlCN nanocomposites, in particular, carbon [31, 41]. XPS revealed carbon contamination on the surfaces of the four selected as-received samples with various carbon contents. The presence of three C1s peaks (Figure 13) at the binding energies of 285.5 eV, 287.1 eV and 289.2 eV, were attributed to the atomic binding statements of C-C, C-O and carbon bonding in organic compounds correspondingly. This is quite common and inevitable during XPS analysis. However, the similarity in the shape of these spectra proves that the vacuum environment in the sample chamber to be fairly stable for all the samples when x-rays examination was in progress. This is important because it provides assurance that the chemical analysis of all coatings was performed in the identical working conditions. In addition, the XPS data of all spectra in the present work has also been normalized for an accurate comparison both prior to and after ion beam sputtering.

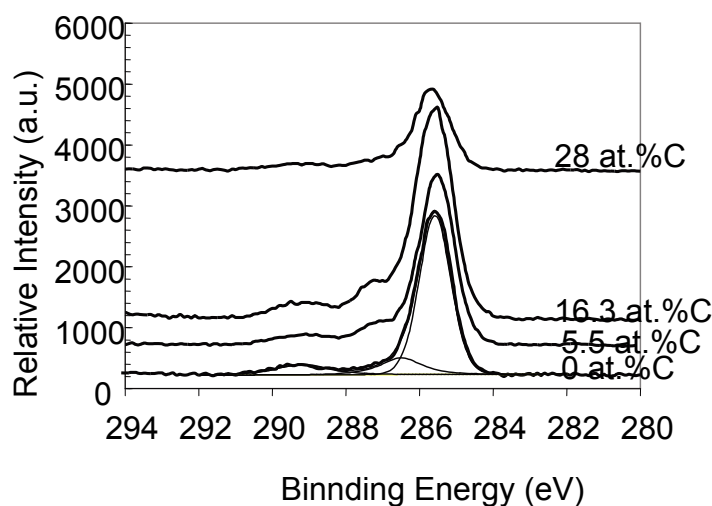


Fig. 13. XPS spectra revealing carbon contamination on the surfaces of as-received (Ti,Al)(C,N) nanocomposite samples with various carbon contents where C1s three peaks are visible.

To minimize the above carbon contamination, the removal of outermost surfaces of coatings was generally conducted using Ar^+ ion beam etching prior to x-ray analysis. However, the difficulties in the chemical composition and phase determination have been still encountered with samples especially at low carbon contents due to adventitious carbon contributing to the

C1s spectra even after ion beam etching. An example was shown in Figure 14 with the C1s spectra acquired from the polished surfaces of both non-carbon TiAlN and 5.5 at.% carbon TiAlN coatings after they have been Ar⁺ ion beam etched for 5 minutes. A peak at binding energy of 282.1 eV was presented in both spectra. The corresponding component is believed to be a metallic carbide suggested

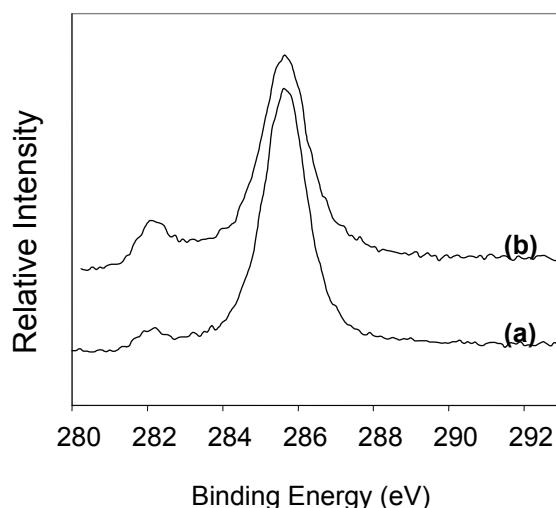


Fig. 14. XPS spectra showing C1s peaks acquired from the polished surfaces of both non-carbon TiAlN coating(a) and 5.5 at.% carbon (Ti,Al)(C,N) nanocomposite coating (b) after being Ar⁺ ion etched for 5 minutes.

from the binding energy of Ti-C (281.9 eV) and should be attributed to the adventitious carbon at least partially for 5.5 at.% C TiAlN coating where some introduced carbon atoms may have incorporated into the lattice structure and bonded with Ti and/or Al. However, the effect of adventitious carbon on XPS C1s spectrum tends to be not significant when a sufficiently high carbon species were added into the coating, as shown in Figure 15. Two C1s spectra for 16.3 at.% carbon TiAlN and 28 at.% carbon TiAlN coatings were generated from the surfaces after being Ar⁺ ion beam etched for 5 minutes. There are two components being revealed through curve-fitting at binding energies of 283.2 eV and 286.2 eV with the former component being believed to be (Ti,Al)-CN. But, the latter component can not be quite certain which is likely to be C-N or C-C. A smaller increase of carbon binding energy of (Ti,Al)-CN component than C-TiN component (282.9 eV) is reasonably due to partial Ti atoms being replaced by Al atoms in the lattice space and C bonds to both Ti and Al where Al atoms are more electropositive than Ti atoms. The exhibition of this component can be also confirmed from N1s spectra (Figure 16). It is strongly evident that TiAlC-N component dominates within the high carbon coatings whilst TiAl-N does in the relatively low carbon coatings. In particular, an extra C1s peak at a low binding energy (282.6 eV) is visible in the spectrum (Figure 10) of 28 at.%C TiAlN coating. The component has a very small FWHM (0.6 eV) and is thereby considered to be associated with an isolated TiAl-C phase. The fraction of this phase tends to increase when the distance towards the interface of substrate and the coating decreases. This heterogeneity was demonstrated by the depth profiling

analysis of 28 at.%C TiAlN coating shown in Figure 17, where the fraction of TiAlCN phase was found to decrease down to the substrate in the thickness.

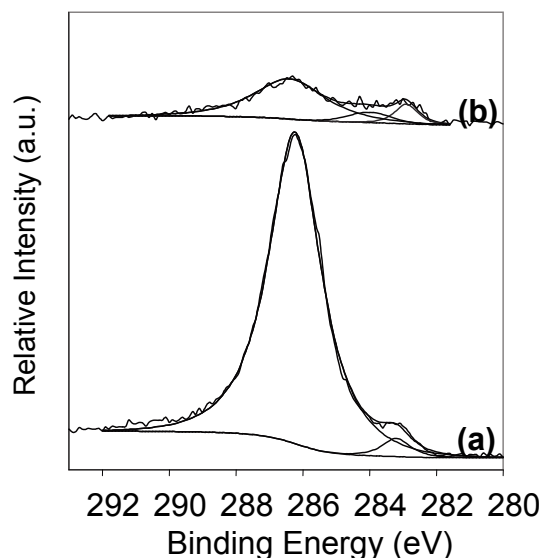


Fig. 15. XPS spectra showing C1s peaks acquired from the polished surfaces of both (TiAl)(C,N) nanocomposite coatings with carbon contents of (a) 16.3 at.% and 28 at.% (b) after being Ar^+ ion etched for 5 minutes.

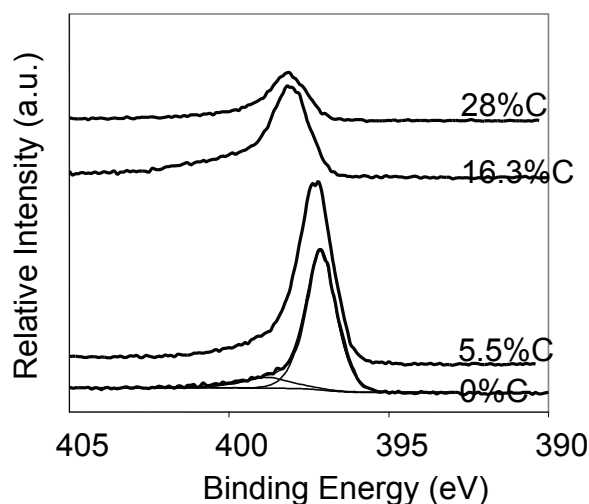


Fig. 16. XPS spectra showing N1s peaks acquired from the polished surfaces of both (TiAl)(C,N) nanocomposite coatings with carbon contents after being Ar^+ ion etched for 5 minutes.

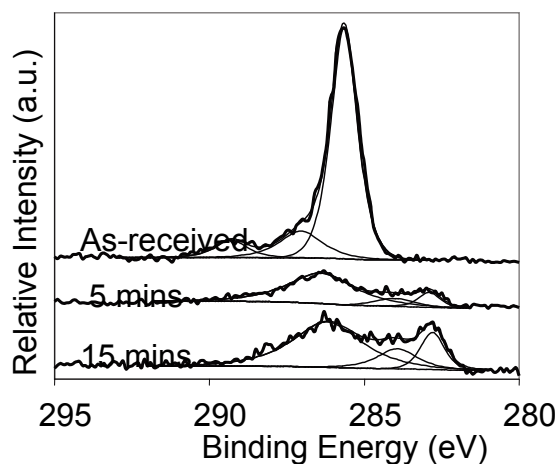


Fig. 17. Depth profiling of 28 at.%C (Ti,Al)(C,N) coating.

3.3 ELECTRON MICROPROBE ANALYSIS (EMPA)

Electron microprobe analysis (EMPA) is a non-destructive method for determining the chemical composition of very small amounts of solid materials. It was developed by R. Castaing in Paris as his 1950 Ph.D. dissertation. Commercial electron microprobes became available in the 1960s, and have become standard analytical tools.

EMPA uses a high-energy focused beam of electrons to generate X-rays characteristic of the elements within a sample from volumes as small as 3 micrometers (10^{-6}m) across and deep. The resulting X-rays are diffracted by analyzing crystals (TAP, PET, LIF) and counted using gas-flow and sealed proportional detectors. Chemical composition is determined by comparing the intensity of X-rays from standards (known composition) with those from unknown materials and correcting for the effects of absorption and fluorescence in the sample.

The electron microprobe is designed specifically for detecting and measuring characteristic X-rays. It uses an electron beam current from 10 to 200 nanoamps, roughly 1000 times greater than that in a scanning-electron microscope (SEM). These higher beam currents produce more X-rays from the sample and improve both the detection limits and accuracy of the resulting analysis. Locations to be analysed are selected using a transmitted-light optical microscope, which allows accurate positioning to about 1 micrometer, a feature not available on an SEM. The resulting data yield quantitative chemical information of a textural nature. Variations in the chemical composition within a material, such as a mineral grain or metal, can be readily determined.

The electron microprobe can quantitatively analyze light elements such as C, N and O with a detection limit and sensitivity of about 500-1000 ppm and the heavier elements Na up to uranium ($Z = 92$) at routine levels as low as 100 ppm. Therefore, it is an accurate and convenient chemical measurement technique, ideal for nanocomposite coatings that are constituted by multiple elements with some having low atomic numbers [72-74].

We have grown TiAl(N,C) samples by reactive sputtering of TiAl in a mixture of N_2 and CH_4 gas. The chemical composition analysis determined by EPMA of the coatings show that the level of carbon in the films varied from 0 at. % (i.e. pure TiAlN) to 28 at. % carbon (given in table 3) [31].

Table 3. Chemical composition and constitution of (Ti,Al)(N,C) coatings deposited by reactive dc magnetron sputtering from a TiAl alloy target under variation of the methane gas flow.

Sample No.	Coating type and microstructure	Elemental composition (at.%)				
		Ti	Al	N	C	O
1	nc fcc TiAlN	26.7	26.5	45.0	0.7	1.0
2	nc fcc TiAlNC	21.7	26.5	45.3	5.5	0.9
3	nc fcc TiAlNC+a-C	20.6	24.1	46.4	8.1	0.8
4	nc fcc TiAlNC+a-C	21.2	23.0	45.5	9.5	0.7
5	nc fcc TiAlNC+a-C	20.4	22.6	42.7	13.5	0.7
6	nc fcc TiAlNC+a-C	19.5	21.8	41.4	16.3	1.1
7	nc fcc TiAlNC+a-C	17.0	19.0	34.9	28.0	0.9

3.4 ENERGY DISPERSIVE X-RAY ANALYSIS (EDX)

Energy dispersive X-ray spectroscopy (EDX) is a very powerful yet simple technique for chemical characterization of the surface of materials and can provide rapid qualitative microanalysis. It is often incorporated within electron microscopes such as SEM and TEM and consists of the beam source, the X-ray detector, the pulse processor and the analyzer.

Electrons are arranged around the nucleus of an atom in a number of electron shells labeled as K L M N starting from the innermost shell (K) away from the nucleus. A vacancy can be induced when a primary electron from electron source with a high energy strikes an electron in an inner shell. The atom relaxes by filling up this vacancy with another electron moving from outer shell which produces excess energy, which is released in the form of X-rays that reflects characteristic of the atom (element). In EDX the X-rays are analysed and presented as a spectrum rather like XPS comprising of a series of peaks with each peak corresponding to a specific element. Modern EDXs is able to perform both point scans (i.e. probe scanning by a pixel) and line scans (i.e. probe scanning over the surface as a line). A point scan allows the

chemical composition of a tiny target such as a nanoparticle to be characterized however a line scan can do elemental mapping of an entire area. The spatial resolution is dependent of the probe size of primary beam, the thickness of the specimen and the effect of back scattered electrons from the specimen around the point analyzed.

Figure 18 shows a bright field image of the FePtCr nanocomposite film which annealed at 700 °C for 1 h [75]. EDS elemental analyses of the pointed areas of I, II, and III illustrated in the TEM image of Fig. 3(a) are shown in Fig. 3(b), 3(c) and 3(d), respectively. The EDS analyses indicate that the composition of inner grain (position I) consists of Fe and Pt, the composition of grain surface area II consists of Fe, Pt as well as Cr, and the composition of grain boundary III consists of only purely Cr.

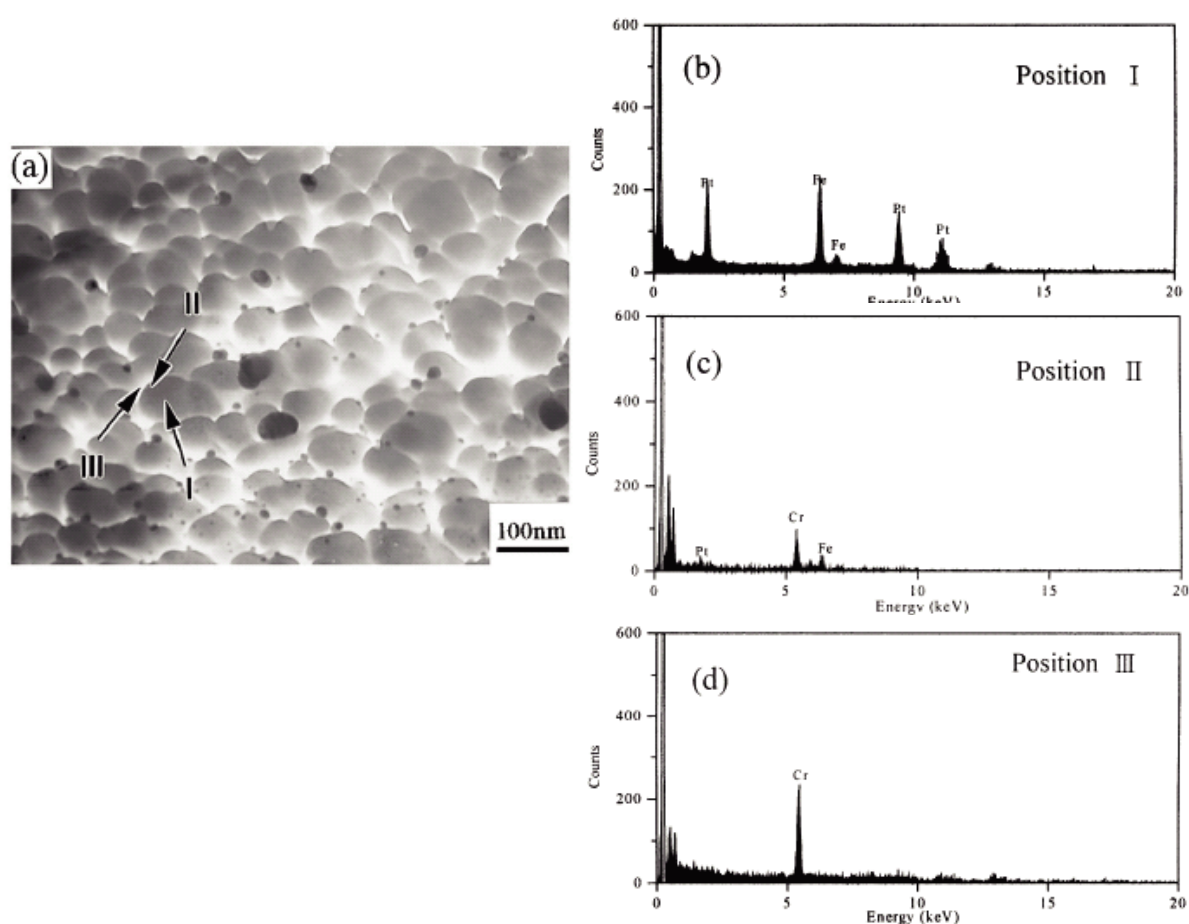


Fig. 18. (a) TEM bright field image of the (FePt) Cr film annealed at 700 °C for 1 h. (b) shows the composition of the (FePt) Cr grain shown in position I, (c) the composition of the grain surface area shown in position II, and (d) the composition of grain boundary shown in position III.

3.5 ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)/ ENERGY FILTER IMAGE (EFTEM)

EDX is fairly convenient and powerful technique for chemical analysis however it suffers from a major drawback its insensitivity in detecting the light elements such as C, N and O. In contrast, EELS has been proved to be a very powerful technique for chemical analysis of materials at the nano-meter scale and is capable of analyzing elements with low atomic number [76-83].

The experimental arrangement of EELS involves illuminating the specimen with a focused probe of electrons. When an electron beam is incident onto a thin TEM specimen at a high energy, some electrons may lose energy due to their inelastic interaction with the specimen atoms. Elastically scattered electrons have no energy loss and therefore, it is possible to collect an energy-loss spectrum from a small area (down to nanometer scale) of the specimen. Scattered electron intensity as a function of energy loss of those electrons that transmit the thin specimen is obtained in the spectrum. A typical EELS spectrum is configured as following [84]:

- I. A zero-loss peak, which represents those electrons that are scattered elastically during the interaction.
- II. Plasmon peak, as resulted by inelastic scattering from out-shell or valence electrons. The energy loss is normally between 5 eV - 50 eV.
- III. High energy loss peaks, which in fact appear as edges, i.e. a sharp rise followed by a slow fall. These edges correspond to excitations of inner shell electrons which are determined by the relevant binding energies of electrons in the specimen. Thus, by measuring the position and area under each edge (after taking account of the background intensity), an estimate of which elements are present in the vicinity of the probe and in what proportions can be made.

The TEM can be operated in the imaging mode and diffraction mode for acquiring EELS spectra [9]. In TEM imaging mode, a magnified image appears on the viewing screen and the spectrometer object plane contains a diffraction pattern. The angular distribution of electrons entering the spectrometer is independent of the entrance aperture size. In this mode, the spectrometer is diffraction coupled. The value of convergence semi-angle is determined by the size of the objective aperture. However, with the microscope in diffraction mode, the object plane of the spectrometer (the back-focal plane of the projector lens) contains an image of the specimen and the electron diffraction pattern is on viewing screen. Convergence semi-angle is determined by the effective diameter of the spectrometer entrance aperture projected back into the plane of the diffraction pattern and the system is thus image coupled.

Energy filtered TEM, used to obtain images showing the chemical distribution at a small area in the specimen, is performed by an additional set of electron optics incorporated into the microscope with configuration of either post-column or in-column. To form these images, it

is important to select only those electrons that have been inelastically scattered and have lost a specific amount of energy using an energy slit as an illumination.

EFTEMs can be operated in a variety of ways. First of all, the contrast of normal TEM images (i.e. bright-field and dark-field) can be significantly enhanced with only allowing zero-loss electron to pass through the slit for image formation. This is particularly useful when the image contrast is considerably degraded by the inelastic electron or specimens with low atomic number, such as biological samples, are examined in TEM. On the other hand, inelastic scattering can degenerate convergent beam diffraction patterns. Therefore filtering them gives more accurate measurements of the lattice parameters and symmetry analysis of microstructures present in a material. A second widely-used image mode in EFTEM is set by allowing only electrons from a specific EELS core-loss edge to contribute to an image. A pictorial map with compositional variations within a specimen can be imaged at a high-resolution, which is equivalent to but more quantitative than EDX mapping.

The spatial resolution in EFTEM, especially imaging from an EELS edge, is very important, which is imposed by chromatic aberration effects of the objective and projector lenses. The nature of the inelastic scattering itself and combined effects of spherical aberration and diffraction at the objective aperture are also very important. For particular energy-loss ranges, resolutions to the order of 1 nm are feasible but rely on high resistance to beam damage and to specimen drift at the extremely high exposure times required.

3.6 RAMAN SPECTROSCOPY

Raman spectroscopy is a spectroscopic technique commonly used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. Phonons or other excitations in the system are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy is a similar and but complementary information.

Typically, a sample is illuminated with a laser beam and then light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line (due to elastic Rayleigh scattering) are filtered out and those in a certain spectral window away from the laser line are dispersed onto a detector.

Spontaneous Raman scattering is typically very weak and it is difficult to separate the weak inelastically scattered light from the intense Rayleigh scattered laser light. Raman spectrometers typically use holographic diffraction gratings and multiple dispersion stages to achieve a high degree of laser rejection. A photon-counting photomultiplier tube (PMT) or, more commonly, a CCD camera is used to detect the scattered light. In the past, PMT were

the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, recently the use of CCD detectors have made dispersive Raman spectral acquisition much more rapid.

Raman spectroscopy offers several advantages for microscopic analysis and since it is a scattering technique, specimens do not need to be fixed or sectioned. Spectra can be collected from a very small volume ($< 1\mu\text{m}$ in diameter); these spectra allow the identification of species present in that volume. Water does not interfere very strongly and therefore Raman spectroscopy is highly suitable for the microscopic examination of minerals, materials such as polymers and ceramics, biological cells and large molecules such as proteins. A Raman microscope begins with a standard optical microscope, and adds an excitation laser, a monochromator, and a sensitive detector (such as a charge-coupled device (CCD) or photomultiplier tube (PMT)). FT-Raman has also been used with microscopes.

The use of Raman spectroscopy has been well established for multicomponent structural determination and quantitative analysis through wavelength shift between the incident light and scattered light. In this work, a system 2000 Renishaw Raman microscope was used, equipped with a slit ($15\mu\text{m}$ wide) and a CCD array detector (4×576 pixels) in order to avoid the problems with alignment of pin holes. The instrument was set up in confocal mode with an $\times 100$ short working-length objective ($\text{NA} = 0.95$) during experiment.

Raman microspectroscopy was undertaken on the TiAlCN nanocomposite films (listed in 3.3). There is no evidence of carbon existing as a separate phase until the carbon content is up to 8 at.%. A bump (as called D-G band) is clearly visible in Figure 6. The intensity of these bands increases as the carbon content increases to 28 at.%. Combined with the XRD results, this is unambiguous evidence that above 8 at.% carbon, there is the coexistence of a cubic TiAlC(N) like structure and a separate carbon phase. More information is available in literature [41].

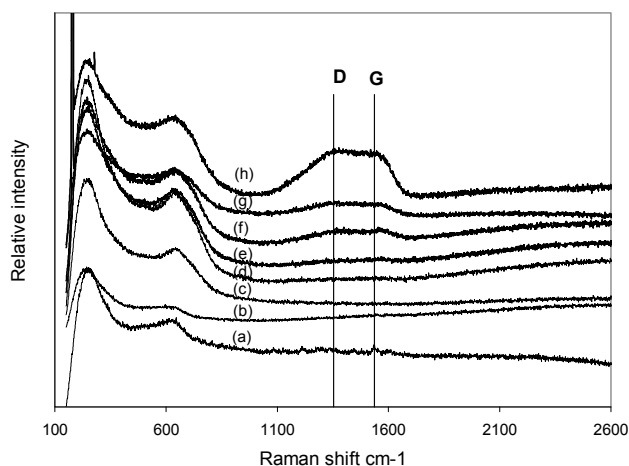


Fig. 19. Raman spectra showing the onset of the D-G band characteristic for amorphous carbon with increasing carbon content in the (Ti,Al)(N,C) coatings.

4. SUMMARY

Nanocomposite materials are formed by multiple atoms of various elements that react and are incorporated into the material in a controlled environment. They are made of multi-phases with a range of sizes generally at a nano-scale. These size characteristics and composition make nanocomposites one of the most complicated materials which is very difficult to be examined and analyse using conventional techniques. However, peculiar and sometimes outstanding properties that nanocomposites can offer have been a driving force leading to the development of a number of advanced characterization techniques. A limited number of these techniques have been described in this chapter. There are two types of techniques, one emphasises microscopy to characterize the micro/nano-structures of nanocomposites and the other on the spectroscopy to analyze the chemical compositions of nanocomposites. There are many other techniques that are being developed that enable nanocomposites to be characterized. These include atom probe, nanoSIMS and cathodoluminescence spectroscopy.

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CHAPTER 3

Hierarchical Nanocomposites

Mehrdad N. Ghasemi Nejhad

Hawaii Nanotechnology Laboratory
Department of Mechanical Engineering
University of Hawaii at Manoa
Honolulu, Hawaii 96822, USA

nejhad@hawaii.edu

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1. INTRODUCTION

Nanotechnology can be broadly defined as, “The creation, processing, characterization, and utilization of materials, devices, and systems with dimensions of the order of 0.1–100 nm, exhibiting novel and significantly enhanced physical, chemical, and biological properties, functions, phenomena, and processes due to their nanoscale size” [1]. Nanocomposites are of significant importance in the rapidly developing field of nanotechnology. Recently, researchers have investigated nano-composites containing polymer-nanoparticles to improve their physical, mechanical, and chemical properties. Nano-particles embedded in polymer matrix have attracted increasing interest because of the unique properties displayed by nanoparticles and their inclusion in polymers. Due to the nanometer size of these particles, their physicochemical characteristics differ significantly from those of micron size and bulk materials. When two or more phases are mixed together to make a composite, one can often obtain a combination of properties, in the resulting composite, that are not available in either one constituent.

The field of nanocomposites involves the study of multiphase materials where at least one of the constituent phases has one dimension less than 100 nm. This is the range where the phenomena associated with the atomic and molecular interaction strongly influence the macroscopic properties of materials. Since the building blocks of nanocomposites are at nanoscale, they have an enormous surface area and there are numerous interfaces between the two intermix phases. The special properties of the nanocomposite arise from the interaction of its phases at the interface and/or interphase regions. By contrast, in a conventional composite based on micrometer sized filler such as carbon fibers, the interfaces between the filler and matrix constituents have a much smaller surface-to-volume fraction of the bulk materials, and hence influence the properties of the host structure to a much smaller extent. The optimum amount of nanoparticles in the nanocomposites depends on the filler size, shape, homogeneity of particles distribution, and the interfacial bonding properties between the fillers and matrix. The promise of nanocomposites lies in their multifunctionality, i.e., the possibility of realizing unique combination of properties unachievable with traditional materials. The challenges in reaching this promise are tremendous. They include control over the distribution in size and dispersion of the nanosize constituents, and tailoring and understanding the role of interfaces between structurally or chemically dissimilar phases on bulk properties. Motivated by the recent enthusiasm in nanotechnology, development of nanocomposites is one of the rapidly evolving areas of composites research.

Scientists and engineers working with fiber-reinforced composites have practiced this “bottom-up” approach in processing and manufacturing, at micron level, for decades. When designing a composite, the material properties are tailored for the desired performance across various length scales. From the selection and processing of matrix and fiber materials and architecture, to the lay-up of laminae in laminated composites, and finally to the net-

shape forming of the macroscopic composite parts, the integrated approach used in composites processing is a remarkable example in the successful use of the “bottom-up” approach (even prior to the development of nanocomposites, albeit at the micron level).

In this chapter, the current state of knowledge in processing, performance, and characterization, of nanocomposites is addressed. This will be logically followed by the composite schemes involved in processing and performance of hierarchical nanocomposites using the bottom-up approach. Dispersion, functionalization, exfoliation, and optimization are of utmost importance in processing of composites using the bottom-up approach. Next, the newly developed and popular bottom-up manufacturing of multi-functional hierarchical nanocomposites is explained. Techniques used to develop nanocomposites will be discussed with major emphasis on the multifunctionality of such composites.

2. NANOCOMPOSITES

The composites of the future will offer many advances over composites of today. Using nanocrystalline materials mixed in with traditional materials to create nanocomposites will allow new materials with novel properties to be realized, including completely stain proof cloth, armor only a few millimeters thick, televisions of any size less than a millimeter thick, completely scratch-proof optics, new lighter/high-efficiency/low-cost/durable fuel cells, new high-efficiency/low-cost/durable solar cells, super-performing/light-weight/low-cost composites, and many others. Composites will create new products which have not yet been considered. Nanocomposites offer the chance to combine organic polymers with inorganic ceramics or to add nanoparticles and nanotubes to polymers and ceramics for improved properties.

Recent developments in production and characterization of various nanoparticles have created numerous new opportunities to develop nanocomposites for different applications. The progress made in the production and purification of nanotubes in the last few years has made it practical to use nanotubes as reinforcements in polymer composites [2-4]. The potential to develop carbon nanotube (CNT) reinforced nanocomposites looks promising for a wide range of applications including high mechanical damping, strength, fracture toughness, and electrically and thermally conductive polymer nanocomposites [5-9]. However, the CNTs applications as structural reinforcements depend on their ability to transfer load from the matrix to the nanotubes [5].

Significant improvements in the in-plane mechanical properties of CNTs reinforced composites compared to their unreinforced counterparts have been reported [10-11]. For example, Qian et al. [12] dispersed multi-walled carbon nanotubes (MWCNTs) homogeneously throughout polystyrene matrices by a simple solution-evaporation method. Tensile tests on composite films show that 1 wt% nanotube additions result in 36%–42% and 25% increases in elastic modulus and break stress, respectively. Yeh et al. [13] found

improvements in tensile strength (25%) of MWCNTs/phenolic composites compared to pure phenolic. Similarly, Schadler et al. [14] studied the mechanical behavior of MWCNT/epoxy nanocomposites in both tension and compression. It was found that the compression modulus is higher than the tensile modulus, indicating that the load transfer to the nanotubes in the composite is much higher in compression.

Gojny et al. [15] evaluated the influence of different types of nanofillers on the mechanical properties of epoxy-based nanocomposites and the relevance of the nanotube surface functionalization. The nanocomposites produced exhibited enhanced strength and stiffness. Maa et al. [16] compounded carbon nanofibers (CNFs) (5 wt%) with Poly-ethylene-terephthalate (PET) resin. Compounding methods included ball-milling, high shear mixing in the melt, as well as extrusion. The resulting composites had good dispersion of CNFs in PET matrix with considerably higher compressive strength compared to the conventional Carbon fiber.”

2.1. NANOPARTICLE-NANORESIN NANOCOMPOSITES

Nanoparticle nanocomposites are being used increasingly for enhancement of structural, thermal, electrical, and optical properties. Researchers [17-20] developed polypropylene (PP)-based nanocomposites by the incorporation of a novel nano-sized precipitated calcium carbonate (NPCC) filler and polyethylene-octene elastomer (POE). Talc and calcium carbonate (CaCO_3) are the most common mineral fillers used for PP due to their availabilities in readily useable form and low cost. Zuiderduin et al. [21] reported that adding 60 wt% of stearic acid treated CaCO_3 particles of 0.7 μm diameter into a PP matrix increased the impact strength and the modulus significantly. Thio et al. [22] also obtained considerable improvement in impact performance using 0.7 μm diameter stearic acid coated CaCO_3 particles at 30 vol. % loading. Chan et al. [23] successfully prepared PP/ CaCO_3 nanocomposites and reported an impact enhancement of about twice that of the neat PP. Zhang et al. [24] carried out further studies to improve the dispersion of CaCO_3 nanoparticles in the PP matrix by adding a nonionic modifier. Studies on phase structure of ternary PP/Elastomer/ CaCO_3 composites were carried out by Premphet and Horanont [25]. The NPCC used in this study had a measured average primary particle size of 50 nm. CaCO_3 filler is known to have a spherical shape with an aspect ratio of close to one. Without any POE, the inclusion of up to 15 wt% of NPCC improved the flexural modulus of PP by about 30% and increased the impact strength by 1.5 times. At both 10 and 15 wt% NPCC levels studied, the impact strength of the neat PP increases dramatically with increasing POE content. When comparing the compositions with the same POE content, the nanocomposite with higher NPCC loading of 15 wt% showed better impact enhancement as compared to the nanocomposite loaded with 10 wt% NPCC (this behaviour is shown schematically in Figure 1). Thus, although the main contributor to the impact enhancement in PP appears to be from the POE phase, the addition of NPCC provided further synergistic toughening effect on the PP.

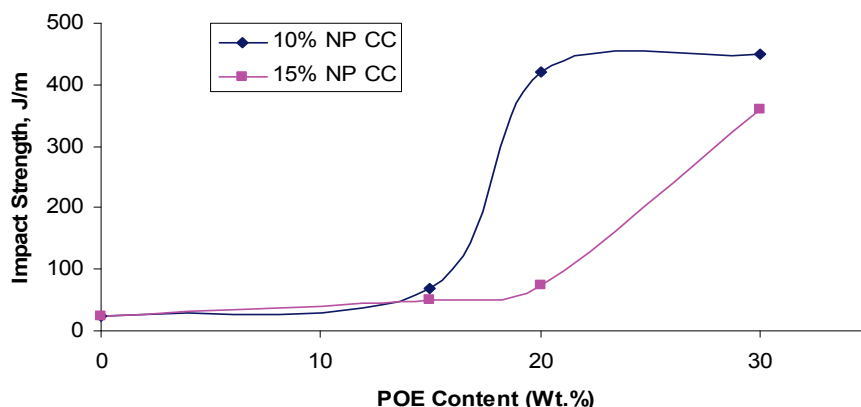


Fig. 1. Effects of POE & NPCC on Impact Strength of Nanocomposite.

Additions of NPCC and POE have resulted in improvements in mechanical properties of interest of the ternary PP/POE/CaCO₃ nanocomposites. The impact strength has been greatly improved albeit at the expense of the tensile strength and flexural modulus. Although the main contributor to the impact enhancement in PP was from POE, the addition of NPCC provided further synergistic toughening effect on the PP. The observed decrease in stiffness with increasing NPCC content in the presence of POE could possibly be due to the encapsulation of NPCC particles by the POE phase. The size of the dispersed POE domains within the continuous PP matrix influenced the impact strength of the nanocomposites, and the average size of about 0.6 μm was found to be the most optimum for the impact enhancement.

Veedu et al. [26] employed SiC nanoparticles with the size range of 45 to 55 nm to develop nanoresin/nanocomposites using a high temperature epoxy. They obtained remarkable improvements in properties such as tensile strength (by about 100%), strain-to-failure (by about 150%), and fracture toughness (by about 200%-300%). Tensile properties of both neat epoxy and nanocomposite specimens were measured according to ASTM D638. To measure fracture toughness quantified by the critical-strain-intensity factor (K_{IC}) and the critical strain energy release rate (G_{IC}), single edge notch bend (SENB) tests were performed according to ASTM standard D 5045, for both neat epoxy and nanocomposite specimens.

2.2. NANOCCLAY-NANORESIN NANOCOMPOSITES

Over the last decade, the mechanical and thermal properties of nanoclay/epoxy nanocomposites have been investigated extensively. This has been best demonstrated by the works of Lam and Lau [27] and Hamidi et al. [28]. In the first paper, the authors [27] demonstrate the optimum reinforcement of nanoclay in epoxy nanocomposites for enhanced micro hardness. Enhanced mechanical and thermal performances of conventional polymer-based composites reinforced with a relatively small amount of layered silicates typically in

the range of 3 – 5 wt% has been reported [29, 30]. Researchers from Toyota [31-36] pioneered the utilization of nanoclay in thermoplastics.

Improved properties are obtained only when nanoclay is intercalated and/or exfoliated into the polymeric matrix [30-32]. Alexandre and Dubois [37], for instance, showed that mechanical and barrier properties, transparency, and toughness are directly proportional to the degree of exfoliation. Nanoclay dispersion into epoxies also induces significant enhancements in mechanical properties. For example, Advani and Shonaike [38] observed more than 100 and 120% increase in tensile modulus and strength, respectively, after the addition of 5 wt% nanoclay into an epoxy adhesive. Furthermore, Shah et al. [39] reported a reduction in moisture absorption diffusivity after the introduction of Closite[®]10A nanoclay into a molded Derkane epoxy part. A nanoclay load as low as 0.5 wt% reduced moisture diffusivity by more than 50%, while a 5 wt% clay load resulted in an 86.4% reduction in moisture diffusivity. Increases in Tg and tensile modulus with increasing nanoclay contents were also reported [39]. Kinloch and Taylor [40] studied Tg improvements in an epoxy due to the introduction of 10 wt% of nanoclay. The authors reported a small improvement from 78 to 79°C for exfoliated Nanomer[®]I30E, and a higher Tg of 85°C for intercalated Closite[®]25A.

Akkapeddi [41] studied both short and continuous glass-fiber-reinforced clay-polyamide 6 nanocomposites manufactured by a melt compounding technique. The author reported improved flexural modulus, strength, and heat distortion temperature under load as well as improved moisture resistance at 2 and 5 wt% nanoclay contents. Haque et al. [42] reported significant improvements in mechanical and thermal properties of S2-glass/epoxy composites with low nanoclay contents manufactured by vacuum assisted resin infusion molding (VARIM). The authors observed that dispersing 1 wt% clay resulted in a 26°C increase in Tg as well as 44, 24, and 23% improvement in interlaminar shear strength, flexural strength, and fracture toughness, respectively. Hussain and Dean [43] utilized the VARIM process to fabricate a series of S2-glass/vinylester nanocomposites containing 0.5, 1, 2, 5 and 10 wt% clay. They reported significant improvements in Tg, interlaminar shear strength, flexural strength, flexural modulus, and fracture toughness [43]. Becker et al. [44] investigated intercalated clay-epoxy nanocomposites reinforced with 49% unidirectional carbon fibers. The addition of layered silicate to the prepregs resulted in tougher composites with more than 50% increase in fracture energy reported for composites containing 2.5, 5, and 7.5 wt% nanoclay.

Manufacturing industries have also started to investigate the development of this type of nanocomposites to fabricate materials with high strength and thermal stability [45-47]. However, it is found that a fully exfoliated inter-planar structure of nanoclay platelets inside polymer matrices is needed to achieve the desired properties of the composites [48-50]. Six types of samples were made in this study; namely, pure epoxy (0 wt% nanoclay), and nanoclay/epoxy nanocomposites with 2 wt%, 4 wt%, 6 wt%, 10 wt%, and 15 wt% of

nanoclays. It was found that the hardness increases from pure epoxy to the nanoclay/epoxy nanocomposite with 4 wt% nanoclay content and decreases with further increase in the nanoclay content. The average diameter of the nanoclay clusters measured at different locations was about 125 nm, whereas at 15 wt% of nanoclay loading the cluster size was about 400 nm. At higher weight percentage of nanoclay in polymer nanocomposites, the tendency to form agglomerates is increased [51], and hence larger clusters of nanoclay would be easily formed.

The average cluster size of different wt% of nanoclay/epoxy nanocomposites is given schematically in Fig. 2a [27]. The cluster size increased with increasing wt% of the nanoclay content. Fig. 2b shows the schematics of the stiffness variation of the nanoclay/epoxy nanocomposite samples with respect to the nanoclay content by weight percentage from the flexural strength test. The optimum stiffness occurs at the 4 wt% of nanoclay content, after which the stiffness of the nanoclay/epoxy nanocomposites drop with the increase of nanoclay content. The authors attribute the maximum stiffness at 4 wt% to the optimum contact surface area of the nanoclay at this weight loading [27]. The second paper [28] studied the effects of nanoclay content on morphology and spatial distribution of voids in resin transfer molded nanoclay/E-glass/epoxy composite disks. Nanocomposites with nanoclay loads of 0, 2, 5, and 10 wt% were studied [28]. Voids in the samples of nanocomposites were evaluated via microscopic image analysis. The addition of nanoclay was found to result in a significant increase in the apparent viscosity of the clay-epoxy mixture, thus increasing the molding pressure. It was found that void content increased considerably with increasing nanoclay content; however, the nanocomposite with 2 wt% nanoclay yielded the lowest void content of 0.7%. The presence of nanoclay in the impregnated resin induced at least 60% reduction in voids located inside fiber tows, which were trapped by the fluid front motion during impregnation. Irregularly shaped voids were also observed to decrease with increasing nanoclay content. A nonuniform void content and morphology was observed radially, which seems to be affected by the flow kinematics as well as possible breakdown and filtration of clay clusters [28].

Almost six-fold increase in the injection pressure was estimated for the resin containing 10 wt% nanoclay [28]. Overall void content was observed to increase from 2.1% in the composite disk molded without nanoclay to 5.1 and 8.3% in the nanocomposites containing 5 and 10 wt% nanoclay, respectively. The addition of 2 wt% nanoclay yielded the lowest void content at 0.7%. The increased void content in nanocomposites molded with 5 and 10 wt% nanoclay was due to the pre-existence of air pockets embedded in nanoclay clusters, which could not be removed by mechanical mixing, sonication, or degassing. These air pockets usually appeared as 40- to 60- μm , circular voids surrounded by the epoxy resin, thus forming bulk of so-called matrix voids. Voids were observed to be smaller on average after the addition of nanoclay at all concentrations investigated. The presence of nanoclay in the resin induced at least 60% reduction in voids located within the fiber preform. Irregularly shaped voids were also observed to decrease with increasing nanoclay content. Along the

radial direction of the molded disks, an increase in preform voids, which were formed by mechanical entrapment, was observed at higher nanoclay levels [28].

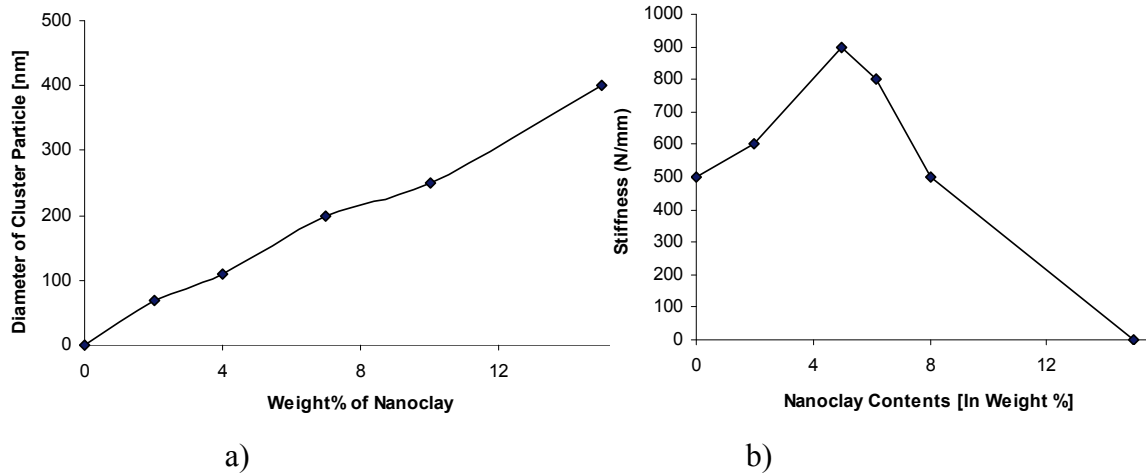


Fig. 2. Schematics of the variation of the a) cluster size and b) stiffness at different wt% of nanoclays [27].

2.3. NANOTUBE-NANORESIN NANOCOMPOSITES

Much of the previous work was performed in the area of nitrile substituted polymers including polyacrylonitrile (PAN) [52, 53], poly(vinylidenecyanide vinylacetate) (PVDCN/VAc) [54, 55], polyphenylethernitrile (PPEN) [56] and poly(1-bicyclobutanecarbonitrile) [57]. Development of multifunctional materials using SWCNT in polymers is best demonstrated by the work of Ounaies et al. [58-60].

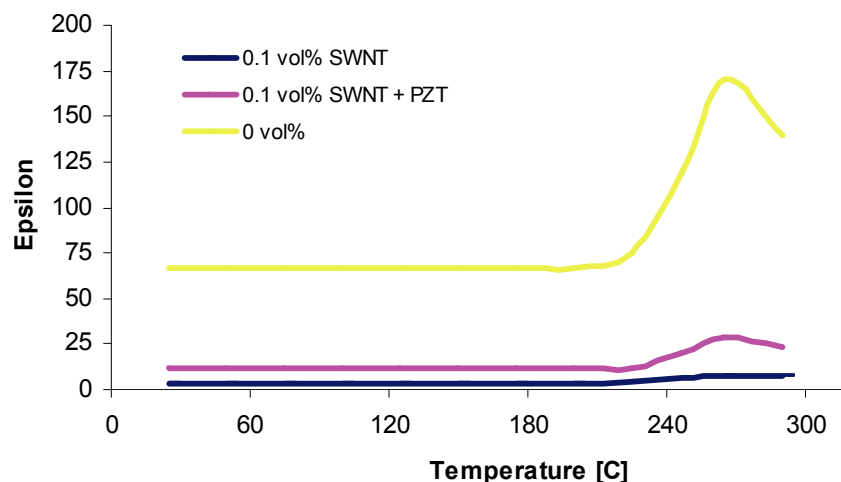


Fig. 3. Schematics of the dielectric constant as a function of temperature.

In these papers [58-60], the authors studied the effects of incorporating lead zirconate titanate (PZT) powder and SWCNT to the polyimide matrix. The authors have developed

amorphous polyimides containing polar functional groups and investigated their potential use as high temperature piezoelectric sensors. In these studies, a small volume fraction of SWCNT was added to the polyimide for obtaining improvements in the thermal, dielectric, mechanical, and piezoelectric properties of the resulting SWCNT-polyimide nanocomposites. Later, the three-phase SWCNT-PZT-polyimide nanocomposites were manufactured and assessed for resulting mechanical, dielectric, and piezoelectric properties. Both SWCNT and PZT showed good dispersion in polyimide matrix without any bundling or percolation. Improvement in the mechanical and thermal properties of the SWCNT-polyimide nanocomposites resulted from the incorporation of SWCNT. Dielectric measurements as a function of SWCNT content revealed a low percolation threshold of 0.06 vol%. The overall dielectric constant increase with increasing inclusion content. The presence of the SWCNT allows for a better poling of the polyimide and yields higher P_r [58-60] values at the same poling conditions. In addition, a small amount of SWCNT facilitates the simultaneous poling of the polyimide and PZT inclusions, resulting in a value of P_r one order of magnitude higher than that of the pristine polyimide (this is shown schematically in Figure 3). This increase in P_r was achieved at a relatively low loading of PZT particles (20 vol%). The mechanical properties of the two-phase and three-phase composites were measured by DMA to assess the effects of SWCNT and PZT inclusions on the modulus of the polyimide. At 2.0 vol% SWCNT loading, both modulus and strength increased with the same elongation at break. At 5.0 vol% SWCNT, the modulus increased by 44%. PZT loading did not affect the mechanical properties.

2.4. NANOTUBE/NANOPARTICLE-NANOADHESIVE NANOCOMPOSITES

The optimal amount of nanofillers inclusion, carbon nanotubes, and alumina nanopowder for enhanced tensile debonding and shear properties in hierarchical nanocomposites is best demonstrated by the work of Meguid and Sun [61] for composite adherends made of carbon fiber/epoxy laminate and aluminum alloy 6061-T6. In view of their importance and utility in aerospace, automotive, and communication fields, carbon fiber reinforced polymers (CFRP) are currently being extensively studied. This is because this class of materials possesses admirable properties, low weight, high fracture toughness, and relatively high strength. The influence of the incorporation of nanoscale particles into epoxy adhesives for the purpose of joining two dissimilar composite materials has not been investigated thoroughly. This may be due to the large variance in function, intricacy of geometry, incompatible materials, and operating conditions. Structural bonded joints can fail at different locations and by a variety of failure modes. Failure can occur or initiate in the adhesive or in the adherend, depending on the geometrical configuration, the materials of the adherends, the adhesive as well as the manufacturing process. It is difficult to describe and define all the possible failure modes of adhesive bonded joints. The authors [61] classify the failure modes of adhesive bonded joints into the following four general categories: (i) adherend failure due to tension, (ii) interfacial failure due to shear, (iii) debonding cohesive failure, and (iv) out-of-plane failure

due to delamination in composite adherends. However, the presence of the interface in adhesively bonded joints governs the strength of that joint. Therefore, a strong interface, which possesses high toughness, is highly desirable.

Carbon fiber reinforced laminates were fabricated by autoclave at specified pressure and temperature. Carbon nanotubes and alumina nanopowders were dispersed into an epoxy adhesive. The dispersion was carried out by stirring the mixture for 30 min at 50°C followed by the addition and blending of the remaining components of the adhesive. This technique ensured homogeneous dispersion of the nanofillers into the adhesive. The authors obtained uniform dispersion of carbon nanotubes and alumina nanopowder within the epoxy adhesive. The weight concentration in these two cases was 2.5%. Additional nanomixtures with nanofillers at nominal weight percentages of 1.5%, 5%, 7.5%, 10%, 12.5%, and 15% were also prepared. The substrates were then bonded together and carefully cured at a controlled room temperature for seven days. The authors utilized test set ups used for the tensile debonding and shear testing of the new interface. Tensile debonding was employed for determining the tensile stress–strain characteristics, modulus of elasticity, and ultimate tensile strength of the nano-reinforced interface. Shear testing was employed for determining the shear modulus and shear strength of the nano-reinforced interface.

Three different cases, i.e., epoxy adhesive with alumina nanopowder (EANP), epoxy adhesive with carbon nanotube (EANT), and epoxy adhesive (EA) were considered. The authors demonstrated that the bonding strength increases as a result of the presence of uniformly dispersed carbon nanotubes and alumina nanoparticles. In the tensile tests, the critical load for EANT and EANP was 1.2 and 1.4 times of that for EA, respectively. In addition, the stiffness for the EANT and EANP were about 50% and 100% better than that for the EA samples, respectively. The sample size was three in these experiments. Remarkable improvement was found in Young's modulus as well as the ultimate tensile strength for the cases involving different weight fractions of homogeneously dispersed nanofillers used in the study. The increase continues with the increase in the weight percentage of the nanofillers. However, for percentages above 10%, the properties degrade to below the EA level, possibly due to agglomerations.

The same three different cases, i.e., EANP, EANT, and EA were also considered for the shear lap tests, and again, the weight fraction ratio of the filler concentration was 2.5% for EANP and EANT. Once again, the authors demonstrated the strengthening of the shear resistance as a result of dispersed carbon nanotubes and alumina nanoparticles. The critical shear load for EANT and EANP was 1.1 and 1.3 times of that for EA, respectively. Again, remarkable improvement was found in the shear modulus as well as the shear strength for the cases involving different concentrations of dispersed alumina nanopowders and carbon nanotubes. Analogues to the tensile tests, the results also revealed the sensitivity of the shear properties to the concentration of the nanofillers. An increase in the weight fraction of the nanofillers beyond 7–8% resulted in a reduction in the shear properties of the adhesive.

The authors [61] attributed the dependence of the tensile and shear properties of nano-reinforced interface adhesive to the presence of nanoparticles, which play a major role in determining the strength of the interface at a given weight (volume) percent. The experimental results show that there is a limit to the amount of dispersed nanofillers beyond which a drop in the properties is observed. It is also believed that agglomeration of the nanoparticles could act as failure initiation sites, which could result in lowering the strength and stiffness of the adhesive. The results reveal that at a given weight (volume) percent, the presence of nanoparticles plays a major role in determining the strength of the interface, and for the most favorable response, this amount should be optimized, often experimentally.

3. HIERARCHICAL NANOCOMPOSITES

Through nanotechnology, it is envisioned that nanostructured materials will be developed using a bottom-up approach. “More materials and products will be made from the bottom-up, that is, by building them from atoms and molecules, and nanoscale powders, fibers, and other small structural components made from them.” [62]. A “hierarchical composite” is a composite the constituents of which are increased in size hierarchically, i.e., a nanostructure material such as a nanoparticle, nanoclay, nanofiber, and/or nanotube is manufactured first. Next, this nanostructure is mixed with a resin to give a “nanoresin/nanocomposite”. Finally, a micron-size fiber is mixed with this “nanoresin/nanocomposite”, as one would do in tradition fiber-reinforced polymer composites to yield “hierarchical nanocomposites.” Here, an attempt is made to provide a brief overview of recent advances in hierarchical nanocomposites research, and critical issues in hierarchical nanocomposites research are discussed. Subramaniyan et al. [63] used vacuum assisted wet lay-up (VAWL) process for the inclusion of dispersed nanoclay in resin as reinforcement in conventional fiber-reinforced composites. The addition of 5% nanoclay produced a substantial increase in longitudinal compressive strength (33.9%) of glass fiber reinforced composites. Yutaka et al. [64] studied the effects of reinforcing carbon nanofiber, CNF, (5 and 10 wt% with aspect ratio of 10 and 50) in epoxy used for the manufacture of fiber reinforced composites. The addition of CNFs in epoxy reinforced fiber composites increased compression and flexure properties considerably [64, 65]. Miyagawa et al. [66] reported mechanical and thermophysical properties of biobased epoxy nanocomposites reinforced with organo-montmorillonite clay and PAN-based carbon fibers. Dynamic mechanical analysis (DMA) was conducted and yielded an increase of 0.9 GPa for the storage modulus of biobased epoxy at 30°C with the addition of 5.0 wt% exfoliated clay nanoplatelets. It was observed that the interlaminar shear strength (ILSS) of the carbon fiber reinforced polymer (CFRP) improved by adding 5.0 wt% intercalated clay nanoplatelets [66].

3.1. NANOPARTICLE-NANORESIN HIERARCHICAL NANOCOMPOSITES

Ceramic Matrix Composites (CMCs) are being developed for applications that require light-weight structural materials, oxidation resistance, and high temperature resistance capabilities

including high strength and modulus [67-69]. These applications include advanced aircraft, space vehicles that re-enter the earth's atmosphere, engine parts, and high temperature furnaces. An important type of ceramic matrix composite that is currently being investigated is the Continuous Fiber-reinforced Ceramic Composite (CFCC). However, one of the important areas of concern is that even the best processed ceramic materials used in applications pose many unsolved problems; among them, relatively low fracture toughness and strength, degradation of mechanical properties at high temperatures, and poor resistance to creep, fatigue, and thermal shock. Attempts to solve these problems may involve incorporating secondary phases such as particulates, platelets, whiskers, and fibers in the micron and nanometer size range at the matrix grain boundaries. However, the results obtained have been generally disappointing when micron-size fillers are used to achieve these goals [70]. By scaling the particle size to the nanometer scale, it has been shown that novel material properties can be obtained.

The optimal amount of nanoparticle inclusion for enhanced mechanical performance in hierarchical nanocomposites is best demonstrated by the work of Gudapati et al. [71, 72] in continuous fiber ceramic composites (CFCCs). These authors initially reported considerable (up to 25%) improvements in flexural strength of CFCCs with nanoparticle inclusions. It has been reported that the mechanical properties of the composites could be improved by adding an optimal amount of nanoparticles into polymer-based composites. In Reference [71], the authors investigate the effects of various nanoparticles (such as silicon carbide, SiC; carbon, C; titanium oxide, TiO₂; yttrium oxide, Y₂O₃; and zinc oxide, ZnO) at 5% inclusion by weight within CFCCs with plain weave SiC woven fabric. In this work, Ni/CE referred to a CFCC that was not reinforced with nanoparticles and was considered as a base/control material, where Ni stood for NicalonTM silicon carbide fiber and CE stood for KiON CERASET[®] preceramic polymer [71]. The effects of various nanoparticle reinforcements on the processing and flexural mechanical performance of CFCCs using Polymer Infiltration Processing (PIP) were investigated. Glycerol Monooleate was used as surfactant agent to provide good dispersion of nanoparticles in the KiON CERASET[®]. Ni/CE-*n* referred to a manufactured base/control composite reinforced with *n* (referring to the type of) nanoparticles in the polymer, and with preceramic polymer pyrolysis/reinfiltration route, where the initial matrix had nanoparticles but reinfiltration matrix did not. Ni/CE-*n*-R-*n* referred to a Ni/CE composite that used matrix reinforced with *n* nanoparticle for both fabrication and corresponding reinfiltration. Detailed description of the manufacturing of various nanocomposites and materials used can be found in the work reported by the authors [71]. It was shown, in this study, that a) yttrium oxide, Y₂O₃, performed the best and increased the flexural strength by 25% as compared to the base/control CFCC without any nanoparticle. In addition, it was shown that the reinfiltration using preceramic polymer with nanoparticle inclusion performed better than the reinfiltration using preceramic polymer without nanoparticle inclusions.

In a follow up work, the authors [72] experimentally investigated the effects of different weight percentages of yttrium oxide, Y_2O_3 , nanoparticle inclusions on the processing and in-plane flexural properties of the CFCCs. The CFCCs were manufactured using SiC fibers, and KiON CERASET[®] preceramic polymer with increasing weight percentage of nanoparticles to find the optimum amount of these nano-inclusions. Five different types of CFCCs were manufactured with varying weight percentage of nanoparticles 0, 5, 10, 15, and 20. The nanoparticle used was yttrium oxide with an average size of 29 nm. The effects of varying weight percentage of nanoparticle reinforcements on processing and flexural mechanical performance of CFCCs using Polymer Infiltration Processing (PIP) was investigated. Glycerol Monooleate was used as surfactant agent to provide good dispersion of nanoparticles in the KiON CERASET[®]. Ni/CE- n referred to a base composite reinforced with yttrium oxide nanoparticles, with n referring to the percentage of nanoparticles in the polymer, manufactured with preceramic polymer pyrolysis/reinfiltration route, where the initial matrix had nanoparticles but these were not present in the reinfiltration matrix. Ni/CE- n -R- n referred to a Ni/CE composite that used matrix reinforced with n percentage of yttrium oxide nanoparticles for both fabrication and corresponding reinfiltration. Detailed description of the manufacturing of various nanocomposites and materials used can be found in the work reported by the authors [72].

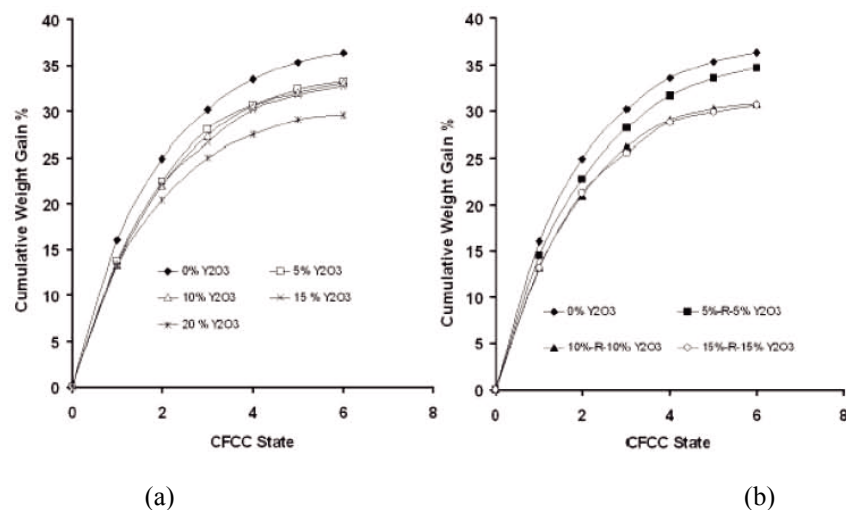


Fig. 4. Comparison of cumulative weight gain (%) for different types of CFCCs after each pyrolysis cycle; a) Ni/CE- n vs. Ni/CE, b) Ni/CE- n -R- n vs. Ni/CE [72].

Figure 4 is a plot of the cumulative weight gain percentages of the two types of CFCCs against pyrolysis/reinfiltration cycles. This figure shows that the cumulative percentage weight gain for both Ni/CE- n and Ni/CE- n -R- n type CFCCs, after each pyrolysis step is lower than that of the base/control Ni/CE CFCCs. Also, from Fig. 4, a consistent decrease in cumulative percentage weight gain is observed with increasing nanoparticle weight percentage, which the authors attributed to a better matrix densification at B-staging for composites reinforced by the nanoparticles. The authors attributed the decrease in

cumulative percentage weight gain for Ni/CE-n-R-n samples with increasing nanoparticle weight percentage to the difficulties in reinfiltrations with increasing weight content of the nanoparticles. It is apparent that the viscosity of the nanoparticle filled polymer increases with increasing weight percentage of nanoparticles.

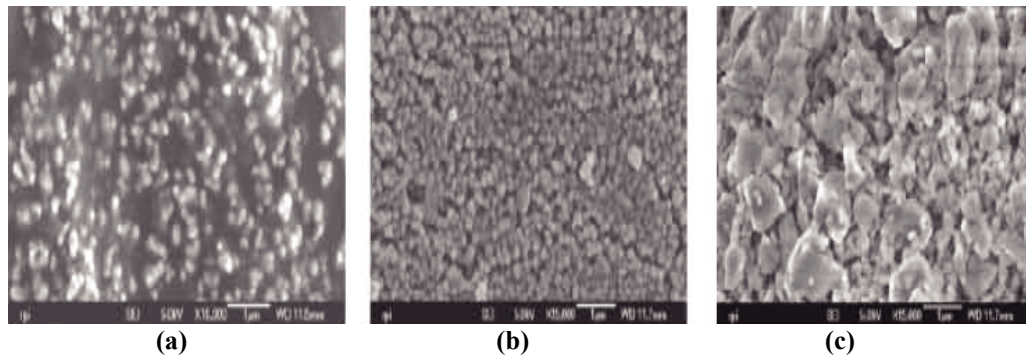


Fig. 5. SEM micrographs of nanoparticles reinforced CERASET preceramic polymer matrix: a) CERASET reinforced with 10% nanoparticles b) CERASET reinforced with 15% nanoparticles, c) CERASET reinforced with 20% nanoparticles [72].

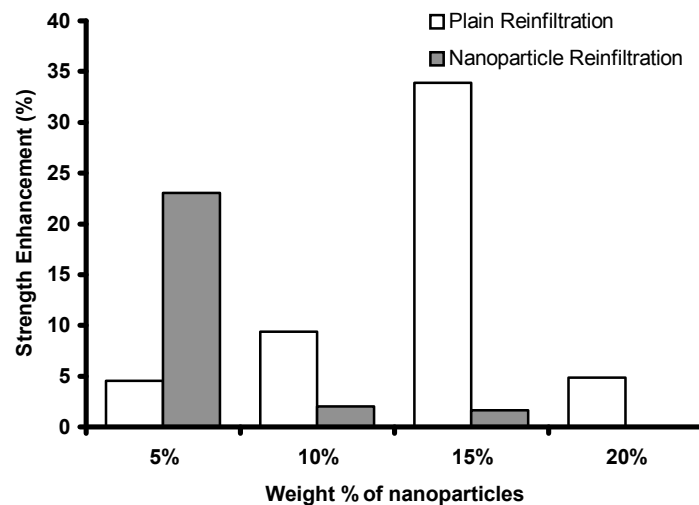


Fig. 6. CFCC strength enhancement for different types of nanocomposites [72].

Dispersion is an important factor in the performance of nanoparticle-reinforced nanocomposites. Improper dispersion leads to agglomeration of particles and the agglomerated inclusions act as defects with high stress concentrations, instead of acting as uniform reinforcements. The authors here [72] used 5-wt% of glycerol monooleate as surfactant agent to disperse the nanoparticles in the preceramic polymer followed by a mechanical stirring system. The SEM studies have revealed uniform dispersion up to a weight percentage of 15% without any agglomeration (see Figs. 5a and 5b). As shown in Figure 5c, particles started to agglomerate at a threshold weight percentage of 20%

suggesting the inability of the surfactant used in dispersing the nanoparticles. From Figure 6, it is observed that the flexural strength of the base/control material is increased by approximately 5 - 34% by adding nano-sized particles to it. It should also be mentioned that the CFCC flexural strength improves significantly with nanoparticle reinforced preceramic polymer reinfiltration route, when the reinfiltration polymer contains 5-wt% of nanoparticles. Further increase in weight fraction of nanoparticles in the reinfiltration polymer resulted in problems during reinfiltration stage leading to the degradation of flexural properties, as compared with Ni/CE-5-R-5. Figure 6 shows that, in general, the nanoparticle addition to CFCC enhances its strength, and the optimum strength enhancement is reached with lower weight percentage of nanoparticle inclusion for the Ni/CE-n-R-n samples (i.e., 5%) as compared with that for the Ni/CE-n samples (i.e., 15%).

3.2. NANOCLAY-NANORESIN HIERARCHICAL NANOCOMPOSITES

The feasibility of integrating polypropylene/montmorillonite nanocomposite matrices into conventional fiber-reinforced composites has been efficiently demonstrated by Boigny et al. [73]. Reinforcing polymer matrices with inorganic fillers in the nanometer size range, exemplified by exfoliated montmorillonite (MMT) clay platelets, in addition to improving the mechanical performance, also broadens their range of functionality to include flame resistance and modified transport properties [74-76]. Hence, it is of significant importance to study the resulting “nanocomposites” as matrices for conventional fiber-reinforced thermoplastic composites. In this feasibility study for integrating nanocomposite matrices into conventional composites, two processing routes for hybrid iPP/MMT nanocomposite fiber-reinforced composites have been considered: long glass fiber-reinforced composites based on co-woven yarns, as a step towards the fabrication of nanocomposite-based co-mingled yarns [77], and glass mat reinforced thermoplastic (GMT) composites [78].

iPP/MMT nanocomposite granulates were prepared from an iPP homopolymer, and a commercial iPP/40-50 wt% organically modified MMT concentrate (Nanocor), which also contained a PP-based compatibilizer, by melt compounding at 200 °C in a twin-screw extruder. Melt spun iPP/MMT fibers were prepared from the nanocomposites. Precursor fabrics were prepared by co-weaving as-spun iPP/MMT yarns with glass fiber (GF) yarns or with poly-ether-ether-ketone (PEEK) yarns. The iPP/MMT precursors for the GMT were films of about 1 mm in thickness, produced by extrusion through a planar die at 180 °C of granulates produced as described above from a low viscosity iPP homopolymer grade specifically tailored for GMT applications.

TEM images of an as-compounded nanocomposite extrudate with an MMT content of 3.4 wt% showed that the MMT was well dispersed within the polymer. However, exfoliation could not be achieved and many of the MMT particles consisted of stacks of individual MMT layers rather than isolated layers. Un-drawn fibers showed far less orientation of both the MMT stacks and the iPP lamellae than the drawn fibers. In the case of the oriented films, the orientation and aspect ratios of the MMT particles were similar to those in the un-

drawn fibers. The reinforcing effect of the MMT on the axial stiffness, as inferred from static tensile tests, was generally greater in the drawn fibers than in the un-drawn fibers, in which the MMT layers showed less orientation.

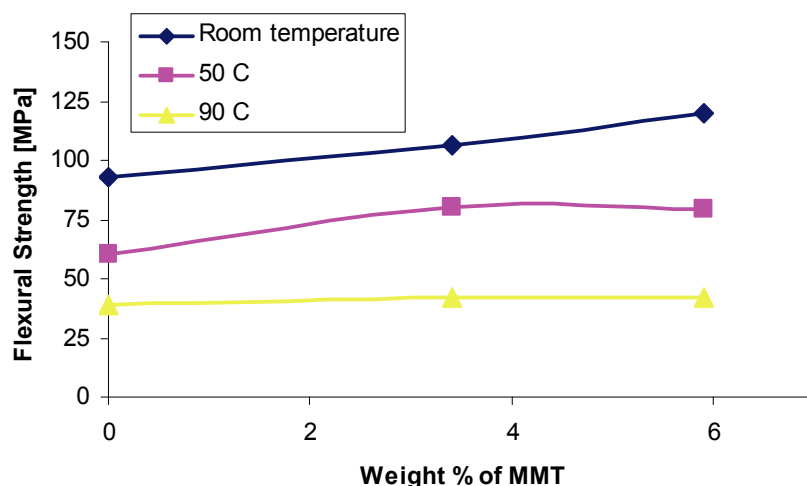


Fig. 7. Flexural strength of glass mat-based composites for different MMT contents and temperatures (glass mass fraction of 30%).

Unidirectional hybrid fiber reinforced nanocomposites were prepared by compression molding a precursor fabric. In initial tests, glass fiber yarns and iPP yarns containing either 0 or 3.6 wt% MMT were wound consecutively onto a pre-form to give an overall glass fiber content in the final composite of about 60 vol%. Simple co-weaving of the iPP/MMT and GF yarns was considered as a means of obtaining a more controlled distribution of the GF fibers in the precursor. iPP/3.6 wt% MMT fibers were melt spun with glass fiber yarns using a table-top loom to produce a simple woven textile containing about 50 vol% GF. The warp consisted of the iPP/MMT yarn and the weft was made up of both iPP/MMT and the reinforcing fibers. Impregnation was significantly improved with respect to that in the co-wound yarn, 10 minutes at 220 °C and 2 MPa, being sufficient to reduce the porosity to 1 vol%. Next, a similar composite processed under identical conditions where the GF tows were replaced by PEEK filament tows. In spite of the relative coarseness of the MMT particles present in the manufactured specimen, MMT was clearly present within the PEEK tows, i.e. in the interstices between the PEEK filaments, which is encouraging for this type of processing. Sections taken perpendicular and parallel to the fiber direction confirmed the MMT to have lost any orientation acquired during fiber spinning.

Three-point bend tests were carried out to investigate the mechanical properties in the presence of the MMT. Results for the flexural strength are shown schematically in Figure 7. The observed improvements in stiffness of the nanocomposite precursors were reflected by corresponding systematic strength improvements in the GMT specimens. However, while these results are encouraging, the experimental scatter was large, reflecting the relatively small specimen sizes and extrinsic factors considered for experimentation. It will therefore

be necessary to verify the observed trends in more detail before determining the extent of a reinforcing effect of the MMT.

3.3. NANOTUBE-NANORESIN HIERARCHICAL NANOCOMPOSITES

In the past decade, carbon nanotube nanocomposites have been extensively used to investigate their mechanical, thermal, electronic, and optical properties. A novel area, where nanotube nanocomposites can have major impact is in the damage detection and health monitoring of fiber reinforced composites. Very recent breakthroughs have demonstrated the myriad of opportunities that can be explored by dispersing nanotube networks in the host matrix. Recent studies by Thostenson and Chou [79] have shown the ability to detect damage in the composite by using electrical conductivity measurements. Zhang et al. [80] used a similar approach to demonstrate damage detection in dynamic loadings by using electrical conductivity measurements. These recent studies show more promise for research in the area of nanotube reinforced hierarchical nanocomposites. Electrical techniques have been used before to detect damage in carbon fiber reinforced composites both under static and dynamic loading [81-84]. However, this technique does not apply to composites reinforced with non-conductive fibers. In Reference [49], glass fibers which are non-conductive are used as fiber reinforcements. Carbon nanotubes dispersed in the epoxy are used to detect the damage mechanisms. It is well established that nanotubes can form a conducting network in polymers at low concentrations similar to the nervous system in human beings. Recent studies have shown that multi-walled carbon nanotubes (MWCNTs) show highest potential for enhancement of electrical conductivity [85] (see Figure 8). The most beneficial aspect of nanotubes being used for hierarchical sensing is the creation of an in-situ network of sensors which is noninvasive to the inplane properties of the composite.

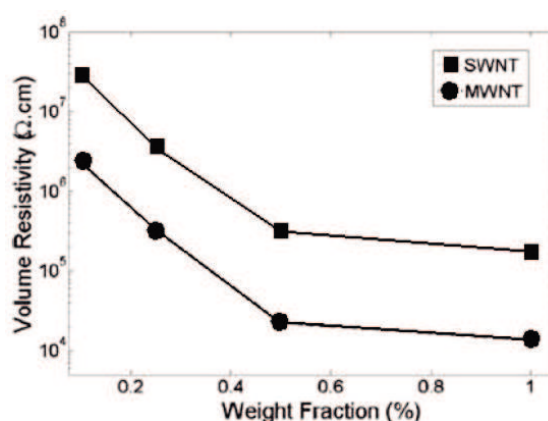


Fig. 8. Resistivity of polymer as a function of weight % reinforcement.

In Reference [49], unidirectional and bidirectional composites were manufactured and tested. Both mechanical and electrical readings were recorded concurrently during tensile and fracture tests. The resistance of the sample tested in tension increased linearly with

initial deformation. A sharp increase in resistance was observed when delamination initiated. Similar trends were observed for both unidirectional and bidirectional composites. Zhang et. al. [80] used similar approach to study the dynamic behavior of nanocomposites in fatigue and self healing. Similar relationship between resistivity and mechanical parameters was observed. In summary, in-situ monitoring of carbon nanotubes offers tremendous potential for damage sensing, self-healing, and in-situ health monitoring techniques in nanocomposites.

4. MULTISCALE HIERARCHICAL NANOCOMPOSITES

In previous sections, nanocomposites with the inclusion of nanomaterials such as nanoparticles, nanoclays, and nanotubes as reinforcing materials are discussed. In this section, multiscale hierarchical nanocomposites employing a bottom-up approach by in-situ manufacturing of nanoscale materials (such as MWCNT) onto microscale materials (such as carbon or SiC fibers) and finally combining these with resins to give macroscale materials and structures (such as hierarchical continuous fiber nanocomposites) are discussed with their multifunctional properties. In this section, a brief overview of recent advances in “bottom-up” multiscale hierarchical nanocomposites research is presented. Critical issues in this research area as well as promising techniques for processing precursors for macroscopic nanocomposites are discussed.

4.1. HYBRID MULTISCALE HIERARCHICAL NANOCOMPOSITES

The controlled surface growth of carbon nanotube is best illustrated by the work of Thostenson et al. [86] using carbon fibers. Recent advances in the synthesis of carbon nanotubes have enabled the growth of carbon nanotubes on carbon fibers using chemical vapor deposition ~CVD [87,88]. With carbon nanotubes, the change in reinforcement scale relative to carbon fibers offers opportunity to combine potential benefits of nanoscale reinforcement with well-established fibrous composites to create hybrid, multiscale, hierarchical micro-/nano-composites. By varying the reinforcement scale, it is possible to tailor the mechanical and physical properties of the composites. In this work [86], carbon nanotubes grown on carbon fibers are used to create hybrid, multiscale, hierarchical carbon nanotube/carbon fiber composites where individual carbon fibers, which are several microns in diameter, are surrounded by nanotubes. Figures 9a and 9b show the surfaces of a single carbon fiber before and after the growth of carbon nanotubes by CVD, as a typical hybrid multiscale hierarchical manufacturing technique for nanocomposites. The thickness of the nanotube region surrounding the fiber ranged between 250 and 500 nm.

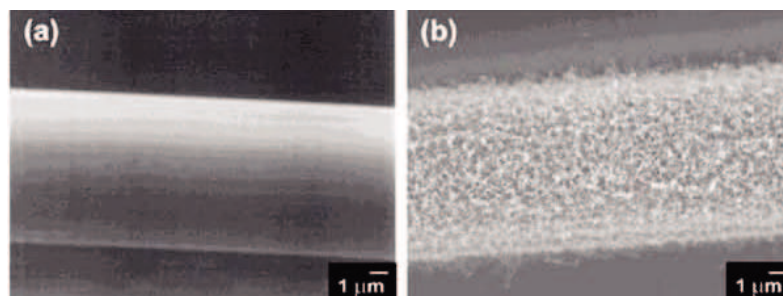


Fig. 9. SEM micrographs of carbon fibers a) before and b) after nanotube growth [86].

In the synthesis of carbon nanotubes on the surfaces of carbon fibers to create hybrid, multiscale, hierarchical nanocomposites, a thin layer of stainless steel was applied to bundles of carbon fiber using magnetron sputtering. Prior to the application of the catalyst, the carbon fiber bundles were heat-treated at 700 °C in a vacuum to remove any polymer sizing applied to the fiber. For nanotube growth, the flowing hydrogen was replaced with acetylene (C_2H_2). The growth time for the nanotubes was 1/2 h.

After the CVD, the fibers were examined with an SEM to verify the nanotube growth. The surfaces of the fibers after each step in the synthesis process for growing carbon nanotubes (heat treatment, catalyst application, exposure to growth conditions) were examined with the SEM, and no pitting of the fiber surfaces was observed.

The authors [86] used single-fiber fragmentation test method to assess the properties of the fiber/matrix interface. The fiber fragmentation experiments for four different fiber specimens (i.e., Catalyst, CVD/No Catalyst, Unsized, and Nanotube) were carried out. The results show that the critical aspect ratio (l/d) is inversely proportional to the interfacial shear strength. The growth of carbon nanotubes on the surface of the fibers resulted in the strongest interface, and both the application of stainless steel catalyst and exposure to CVD conditions without nanotube growth resulted in a significant degradation of the fiber/matrix interface and increased scatter in experimental data as compared with the unsized (baseline) fiber and the carbon nanotube-modified fiber. Compared to the unsized fiber, the nanotube—modified fiber shows a 15% improvement in interfacial strength while the catalyst and CVD (no catalyst) fibers show a 37% and 32% degradation in the interface strength, respectively.

Before preparing fiber-fragmentation specimens with the nanotube-coated fibers, the authors [86] viewed the individual filaments under an optical microscope. It was clear that there were variations in the surface of the fiber. During the catalyst application, the catalyst layer may not always be deposited uniformly on the surface of the individual fiber. As a result, there will be local areas on the fiber where amorphous carbon is deposited instead of nanotubes. Individual nanotube-modified fibers are also quite difficult to extract from the

fiber bundle because of nanotube entanglement. Thus, some carbon nanotubes are stripped from the fiber bundle as they are extracted. This surface variation could clearly be seen when viewing the carbon fiber under an optical microscope [86]. Carbon fiber surfaces are relatively smooth and, therefore, reflect light. In contrast, the presence of carbon nanotubes on the fiber surface results in light scattering. Therefore, in a micrograph, the dark areas would correspond to fibers, where carbon nanotubes are attached to the surface, and the bright areas would correspond to bare fiber.

4.2. MULTIFUNCTIONAL MULTISCALE HIERARCHICAL NANOBRUSH NANOCOMPOSITES

The controlled surface growth of carbon nanotubes on silicon carbide fibers to demonstrate nanobrush nanocomposites for multifunctional applications is best illustrated by the work of Cao et al. [89]. Typical materials for constructing brush bristles include animal hairs, synthetic polymer fibers, and metal wires. The performance of these bristles has been limited by the oxidation and degradation of metal wires, poor strength of natural hairs, and low thermal stability of synthetic fibers. Here, the authors [89] demonstrate an innovative approach to construct multifunctional, conductive brushes with carbon nanotube bristles grafted on fiber handles, and perform several unique tasks such as cleaning of nanoparticles from micro-trenches of micro-/nano-electronics, coating of the inside of micro-capillaries, selective chemical adsorption with environmental cleaning applications, and as movable electromechanical brush contacts and micro-switches.

The nanotube brush consists of a silicon carbide fiber (SiC, diameter 16 μm) as the handle and aligned MWCNTs grafted on the fiber ends as bristles. The nanotubes (average diameter 30 nm) were grown by selective chemical vapor deposition (CVD) with ferrocene and xylene as the precursors. Before CVD, individual SiC fibers were partially masked by a 15-nm Au layer except for the top ends (see Fig. 10a) and placed vertically in the furnace. Figure 10b shows the scanning electron microscope (SEM) image of the top morphology of as-grown nanotubes on fibers. Here, the nanotubes grew in three prongs symmetrically distributed around the centre fiber (like a dust sweeper), and have a uniform length ($\sim 60\mu\text{m}$ after 30 minutes growth) along the fiber axis. Figure 10c shows an individual brush with 60- μm -long nanotube bristles spanning over 75 μm . The trim length can be varied from hundreds down to a few micrometers depending on the growth time. The authors have obtained brushes with bristle spans ranging from several micrometres to millimetres. For example, Fig. 10d shows a brush with 200- μm span and 70- μm trim length formed from nanotubes grown for a rather short time of ~ 35 minutes. The geometry of the bristles can also be made different, such as three prongs like a dust-sweeper (see Fig. 10b), two prongs resembling a hand-held fan, a one-prong toothbrush (see Fig. 10c), and alternating bristle brush (see Fig. 10d).

The authors [89] performed tensile tests to measure the adhesion of MWCNT to the SiC microfibers by mechanically pulling away nanotubes from the handle. Here, the nanotubes

experienced a shear stress at the nanotube–SiC interface, which eventually strips their ends away from the SiC fiber. The stress–strain curve of an as-grown brush (see Fig. 11) shows a maximum stress of 0.28 MPa before the bristles detached from the handle (ten brushes were tested, this stress ranged over 0.2–0.3 MPa). The authors demonstrated that the adhesion strength can be improved by a subsequent annealing of the brush at 950 °C for several hours in argon (the failure stress nearly doubles, see red curve in Fig. 11). Here, the annealing strengthens the interaction between carbon and the underlying silicon (SiC bonding); thereby, substantially enhancing the bristle–handle adhesion. The authors performed extensive contact-brush operations to evaluate the brush lifetimes; for example, the rotating brush, contacting a metal surface in every rotation, after over 0.1 million cycles remains robust without shedding the nanotube bristles. The flexibility of nanotubes can relieve the contact stresses as the brush touches a solid surface on each cycle. In addition, the nanotube brush was glued to the shaft of a micromotor and then immersed into a solution housed in a capillary and stirred for 5 min at 2,000 r.p.m., and no shedding of the nanotube bristles was observed [89].

The developed nanotube brushes are multifunctional and possess a number of useful functions, among which cleaning of nanomaterials and nanoparticles from surfaces and micro-trenches (e.g., 10 μm wide and 100 nm deep), painting and cleaning inside micro-capillaries, chemical and metallic ion adsorption using brush MWCNT bristles chemical functionalizations, electrical contact and switching are described by the authors [89]. These durable nanotube brushes could also serve as versatile, anti-static, heat tolerant tools in many industrial and environmental applications.

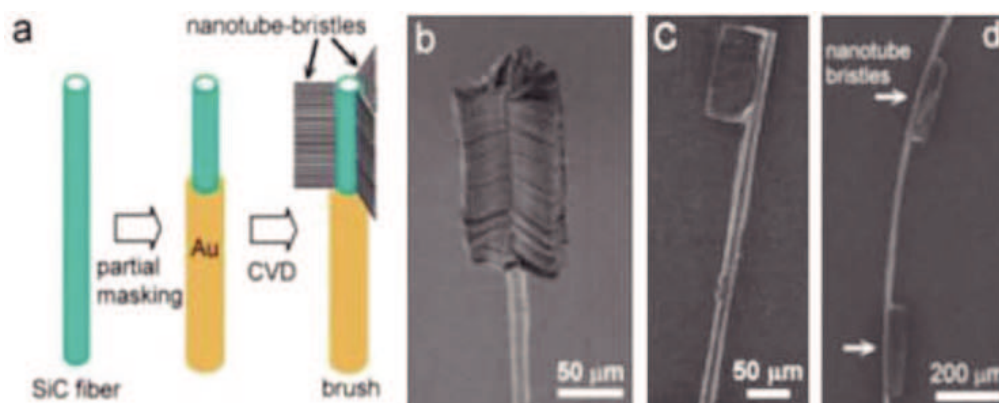


Fig. 10. a) Illustration of partial masking of SiC fibers to grow nanotubes only on the fiber top, b) as-grown nanotubes on top of SiC fibers, c) a single nanobrush (resembling a toothbrush). d) a brush with alternating bristles.

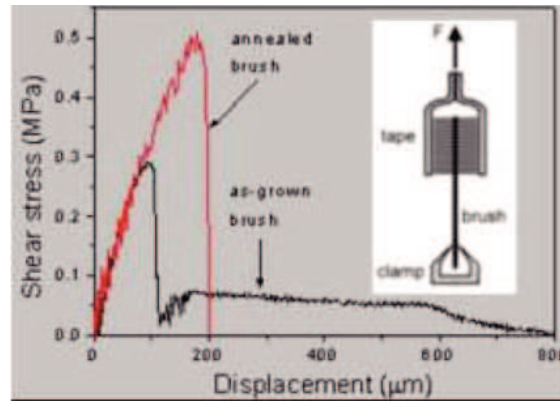


Fig. 11. Tensile testing of brushes (shear-stress versus displacement) for measuring the adhesion strength of nanotube bristles, for both as-grown (black) and annealed (red) brushes.

The nanobrush technology described in this section can be employed and create nanobrushes with various numbers of prongs (see Figure 12) and fiber lengths. These nanobrushes can then be included into a resin to produce hybrid multiscale hierarchical nanocomposites.

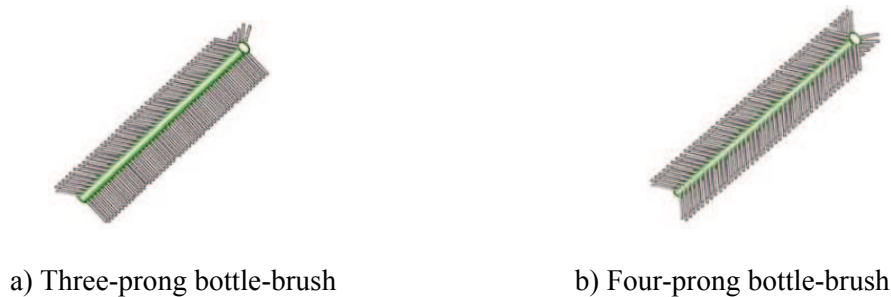


Fig. 12. Schematic models of two types of bottle-brushes as the reinforcements for the hybrid multiscale hierarchical nanocomposites.

4.3. MULTIFUNCTIONAL MULTISCALE HIERARCHICAL NANOFOREST NANOCOMPOSITES

The controlled surface growth of carbon nanotubes on fibers to manufacture 3D nanocomposite is best illustrated by the work of Veedu et al. [90] using silicon carbide fibers. For many decades, advanced fiber-reinforced polymer- and ceramic-matrix composites have been used as viable primary load-bearing structures. Although the in-plane loading and stresses have been handled by various configurations of fiber architectures, such as 1D (i.e., unidirectional tapes) and 2D (i.e., woven fabrics), the intralaminar and interlaminar stresses have remained major issues, resulting in relatively weak interlaminar fracture toughness. Despite huge promise of studies using carbon-nanotube reinforcements in polymer composites, the real use of nanotubes in composites for structural applications has often been rather disappointing, due to issues such as dispersion, alignment, and

interfacial strength. In this study [90], the authors demonstrate an innovative approach using nanotubes in composites, to influence and increase the 3D composite interlaminar properties, using unique bottom-up multiscale hierarchical manufacturing of carbon-nanotube forests grown on fibers present in adjacent plies to give 3D nanocomposites. To optimize the interfacial effect, well-aligned MWCNTs were grown perpendicular to 2D woven fabrics of SiC to produce 3D fabrics. A brief manufacturing route for this type of nanocomposites is shown in Figure 13.

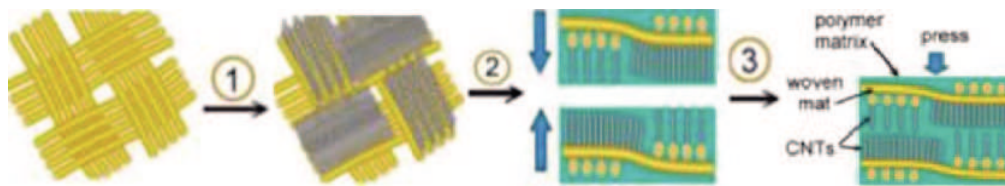


Fig. 13. Schematic diagram of the steps involved in the multiscale hierarchical nanomanufacturing of a multifunctional 3D nanocomposite. (1) Aligned nanotubes grown on the fiber cloth. (2) Stacking of matrix-infiltrated MWCNT-grown fiber cloth. (3) 3D multifunctional nanocomposite plate fabrication by lay-up technique.

Figure 14a shows a scanning electron micrograph of the top of a piece of SiC fiber cloth consisting of 16- μm fibers (see inset) woven into a 2D plain-weave fabric. The SiC fiber cloth after growing MWCNTs on its surface, by the CVD process, is shown in Fig. 14b, and its close-up view is shown in Fig. 14c. MWCNTs are grown uniformly on all of the exposed fibers on the surface of the fiber cloth. The nanotubes grown on the fibers were about 60- μm long. MWCNTs were successfully grown uniformly on SiC fiber cloths of up to 120 mm $\times$ 40 mm. The nanotube-grown fabrics were infiltrated with a high-temperature epoxy, then stacked to yield a ‘sandwich’ structure, and the laminated structure was cured in an autoclave. Generally, the proposed fabric reinforcement can be infiltrated with polymers or preceramic polymers with appropriate viscosities to produce polymer-matrix or ceramic-matrix composites, respectively. An optical photograph of the fabricated 3D multiscale multifunctional hierarchical nanoforest nanocomposite (1 $\times$ 1 inch) is shown in Fig. 14d.

Several experiments such as double-cantilever beam (DCB) and end-notched flexure (ENF) were carried out to demonstrate the transverse mechanical properties improvement, and the effects of the MWCNT nanoforests bridging the plies. To characterize the local behavior of the 3D reinforced composite, the hardness and indentation modulus were measured using a nanoindenter. At an approximate indentation depth of 2.5 nm, the percentage improvements in the indentation modulus and hardness of the 3D nanocomposite compared with those for the base/control 2D composite samples were 30% and 37%, respectively. The authors [90] attributed this to partial misalignment of the MWCNTs during the fabrication of the 3D nanocomposites.

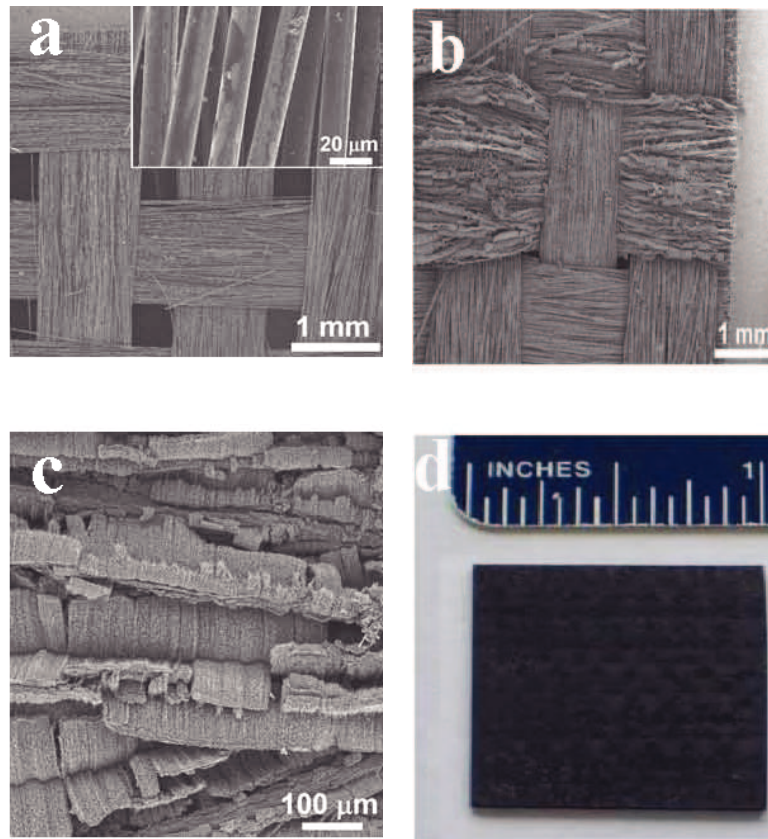


Fig. 14. The growth of MWCNTs on the SiC woven cloth. a) Plain weave SiC fabric cloth. Inset: individual bare fibers of the woven cloth. b) The cloth with MWCNTs grown perpendicularly on its surface. c) Close view of the MWCNTs grown on the SiC woven cloth. d) Photograph of a manufactured 3D multiscale multifunctional hierarchical nanoforest nanocomposite.

Table 1 gives the multifunctional properties of the 3D multiscale hierarchical nanoforest nanocomposite specimens as compared with their 2D woven composite counterpart. From the fracture toughness values, the 3D hierarchical nanocomposite shows a Mode I GIC of 4.26 kJ m^{-2} , that is a 348% improvement compared with the base/control 2D composite with a GIC of 0.95 kJ m^{-2} (see Table 1). The interlaminar shear fracture toughness of the 3D nanocomposite for Mode II GIIC was 140 J m^{-2} which showed an improvement of about 54% as compared with that for the base 2D composite at 91 J m^{-2} (see Table 1). An investigation of the scanning electron micrographs of the fracture surface of the base 2D composite and the 3D composite reveals that the superior fracture performance of the 3D nanocomposite results from a mechanical interlocking between the fibers and the matrix by means of the nanotubes [90]. The interlocking effect between the adjacent plies due to the MWCNT nanoforests makes it difficult to open the plies, leading to the high interlaminar fracture toughness, GIC, of the 3D nanocomposite.

Table 1. Multifunctional properties of the 3D multifunctional multiscale hierarchical nanoforest nanocomposite

Material Property Type		2D Composite	3D Nanocomposite
Fracture toughness test results	GIC (kJ/m ²)	0.95	4.26
	Enhancement in GIC		348%
	GIIC (J/m ²)	91	140
	Enhancement in GIIC		54%
Flexure test results	Flexural Modulus (GPa)	$23.1 \pm 0.3 = 100\%$	$24.3 \pm 0.2 = 105\%$
	Flexural Strength (MPa)	$62.1 \pm 2.1 = 100\%$	$150.1 \pm 1.4 = 140\%$
	Flexural Toughness (N-mm)	$5.8 = 100\%$	$30.4 = 424\%$
Structural dynamic properties	(Hz)	753.8	598.2
		0.0095	0.0731
	(Hz)	753.9	601.4
		7.162	43.963
	Enhancement in Damping		514%
Average CTE over 0° to 150°C (ppm/°C)		$123.9 \pm 0.4 = 100\%$	$47.3 \pm 0.3 = 38\%$
Through thickness thermal conductivity at 125°C (W/m.K)		$0.33 = 100\%$	$0.5 = 151\%$
Through thickness electrical conductivity (S/cm)		0.075×10^{-6}	0.408

The composite specimens were also tested under a three-point flexural loading to measure the in-plane mechanical performance. The measured in-plane strength, modulus, and toughness of the 3D nanocomposite show 140%, 5% and 424% enhancements compared with the base 2D composite (see Table 1), indicating that the enhancement of the through-the-thickness mechanical properties does not compromise the in-plane properties. In addition to the large-scale improvements in mechanical properties, the 3D nanocomposite also shows superior multifunctional performances such as damping, coefficient of thermal expansion (CTE), and thermal and electrical conductivities. The natural frequencies as well as the damping ratios of the 3D nanocomposite with those of its 2D counterpart were measured and compared using a cantilevered-specimen experiment. The data in Table 1 compare the results of structural dynamic properties of the 3D nanocomposite with the base 2D composite, where f_n and ζ are the natural frequency and damping ratio, respectively. It is shown that the nanotube-fastened 3D nanocomposite has improved ζ by 669% compared with the 2D composite counterpart (see Table 1). In addition, the damping characteristics,

$f_{\text{a}\zeta}$, enhancement is more than five times (i.e., 514%) for the 3D nanocomposite compared with the base 2D composite counterpart. These results are very encouraging for the use of 3D nanotube nanoforest nanocomposites in many structural areas where such properties are highly desired.

Through-the-thickness thermal conductivities of the base 2D composite and the 3D nanocomposite were also measured for comparison. The thermal conductivity of the 3D nanocomposites showed consistent improvements compared with the base 2D composite over the range of 0-150 °C. Here, it is noteworthy that the high thermal conductivity of the MWCNTs grown in the thickness direction improves the transverse thermal conductivity of the base 2D composite by about 50% (see Table 1). The electrical conductivity of the 3D nanocomposite was also measured. The average through-the-thickness conductivity of the 3D nanocomposite (i.e., 0.408 S cm^{-1}) was significantly higher than that of its 2D composite counterpart (i.e., $0.075 \times 10^{-6} \text{ S cm}^{-1}$). The measured average in-plane electrical conductivities of the 3D nanocomposite and base 2D composite are 3.44 S cm^{-1} and $0.75 \times 10^{-6} \text{ S cm}^{-1}$, respectively; indicating that the interfacial nanoforest nanotubes provides conducting paths along all directions in the 3D nanocomposite structure. The much-improved through-the-thickness electrical conductivity observed in the 3D nanocomposites would potentially impart to these structures an electrical sensing capability for structural health monitoring during delaminations (i.e., crack initiations and/or propagations).

For the 3D nanocomposites fabricated with nanotube nanoforests, the authors [90] demonstrated remarkable improvements in the interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties, damping, thermoelastic behaviour, and thermal and electrical conductivities making these structures truly multifunctional. The multifunctional multiscale nanoforest hierarchical 3D nanocomposite introduced by the authors [90] is the first real instance where the nanotubes are used in a value-added proposition to effectively improve traditional composite performance by many folds. The vertical arrays of nanoforest nanotubes in the thickness direction of the composite improve the mechanical properties without compromising the in-plane properties, and also alleviate the problem of agglomeration when nanotubes are randomly introduced in the composites. Such 3D nanocomposites could pave the way for the application of CNTs in structural composite materials.

5. NANORESIN-BASED COMPOUND MULTISCALE HIERARCHICAL NANOCOMPOSITES

Nanoresin reinforced by nanoparticles, nanoclays, and/or nanotubes have potential applications as the matrix materials for the multiscale hybrid and/or multifunctional hierarchical nanocomposites to produce super-performing compound nanocomposites. This class of nanocomposites are called compound, here, since both composites constituents, i.e., the resin and the fiber are both reinforced by nanomaterials. In the case of the resin, the

nanoresin, explained earlier in this chapter, uses nanomaterials (i.e, nanoparticles, nanoclays, and nanotubes) to reinforce the resin to give nanoresins (or nanocomposites) with superior properties compared with just the resin without such nanomaterials. For the fiber structure, it has been shown that for the multiscale hierarchical nanocomposites, the fiber structure can be reinforced using CNTs. Therefore, when the nanoresins are used as the matrix materials for the CNT-grown fiber structures to produce composites, the resulting structure will be a “compound multiscale hierarchical nanocomposite,” with both constituents, i.e., the fiber and the matrix, taking advantage of nanomaterials to give super-performing compound nanocomposites.

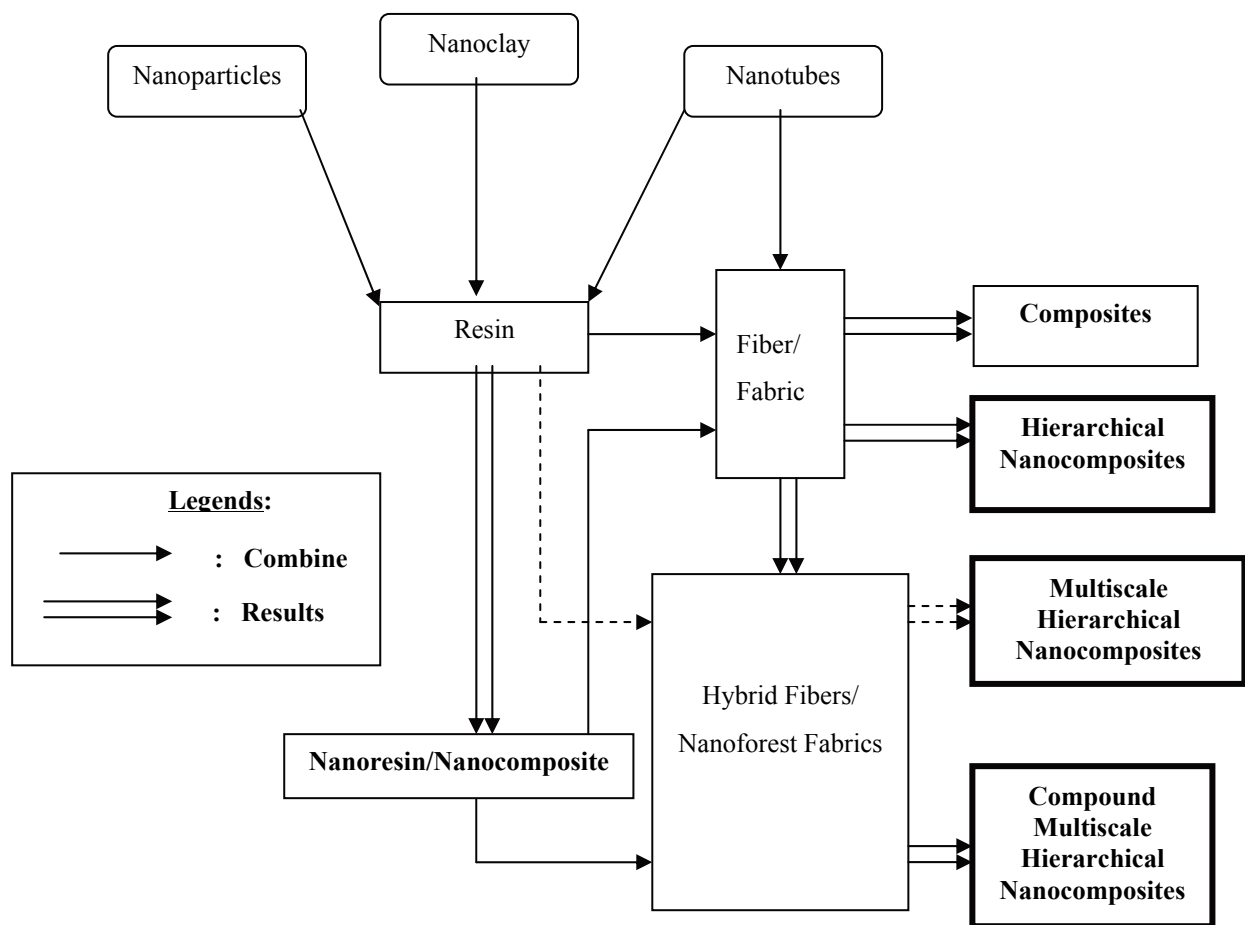


Fig. 15. Development Flow Chart for Hierarchical Nanocomposites.

6. CONCLUSIONS

This chapter *firstly* explains the developments of *nanocomposites (nanoresins)* where a matrix material is reinforced by various nanomaterials such as nanoparticles, nanoclays, and nanotubes. *Secondly*, it explains the developments of *hierarchical nanocomposites*, where the nanoresins, instead of pure resins, are used for the manufacture of composite materials. *Thirdly*, it explains the developments of *multiscale hierarchical nanocomposites*, where the

fiber structure is reinforced by the in-situ growth of carbon nanotubes (CNTs) on their surfaces and the resulting CNT-grown fibers are used with a resin system to produce nanocomposites. Finally, *compound multiscale hierarchical nanocomposites* are explained, where both of the composites constituent materials, i.e., the fiber and the matrix, are reinforced by nanomaterials first and are then combined to produce super-performing nanocomposites. Figure 15 summarizes the development of Hierarchical Nanocomposites explained in this chapter.

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CHAPTER 4

Fumed Silica Reinforced Nanocomposites

Dimitrios N. Bikiaris* and Alexandros A. Vassiliou

Laboratory of Organic Chemical Technology, Department of Chemistry,
Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

* dbic@chem.auth.gr

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1. INTRODUCTION

A wide range of natural minerals have been introduced in thermoplastic polymers since the 1930s for various reasons, but mainly to reduce the cost of the end-products. The term “mineral fillers” has also been used fairly broadly, including any particulate inorganic, natural or synthetic in origin material, as well as short glass fibers [1]. However, it was demonstrated that fillers have a substantial role in modifying the properties of various thermoplastics and has been proven that their addition offers an effective way of improving the mechanical properties of polymeric materials. Due to this enhancement, the cost reduction factor became less important over the years and the research attention was focused on the property improvements that could be achieved due to the filler’s addition. Several factors influencing the processability and mechanical properties of polymer composites are taken into account. These include the amount of added filler, the average particle size, interactions between filler and polymer matrix, as well as interactions between filler particles themselves yielding strong agglomerations [2-6]. After the introduction of the filler some of the polymer’s properties, like stiffness, heat deflection temperatures, dimensional stability, flammability, etc., are improved, while other, and especially toughness, are altered detrimentally.

Traditional fillers like calcium carbonate, talk, mica, silica, alumina, magnesium hydroxide, etc., require high loading amounts to achieve a significant improved performance. However, the weight increase of the final product is undesirable, especially when compared to the light weight of polymers. To overcome the above drawback, during the last few years a new class of mineral-reinforced thermoplastics, termed nanocomposites, has been extensively investigated. In this case the particulate fillers are in the nanometer size range, preferably less than 100 nm, providing miscibility with the polymer matrix and exploiting unique synergisms between the combined materials.

This radical alternative to conventional-filled polymers has generated much enthusiasm in the scientific community since the advantages compared to the pristine polymeric materials seem almost endless. Due to the high aspect ratios of the nanoscopic filler particles, an ultra large interfacial area per volume is formed with the polymer matrix. Thus, such composites exhibit the excellent flexibility, low density and easy processability of polymers in conjunction with the high strength, rigidity and heat resistance of inorganic materials. The observed enhancements are usually on mechanical properties, thermal stability, gas barrier properties, electric properties, even on biodegradation rates [7-9]. Especially the use of biodegradable materials as the organic phase has recently been the subject of great interest. Many excellent reviews reveal the vast obtainable improvements, which broaden the potential applications of such materials, without, concurrently, seriously compromising the biodegradability characteristics of the final material compared with the pristine material [10-12]. The small

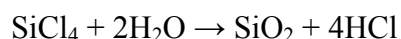
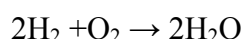
amount of filler does not affect recycling processes. Also, most of these fillers, such as montmorillonite and fumed silica, are considered environmentally benign [11, 13].

Thus, the addition of such nanoparticles in polymeric materials offers many advantages when compared with traditional fillers, forming revolutionary materials. The promise of industrial uses of such materials seems to be undiminished, especially for the preparation of composites. Contributing towards such a direction could also be the increasing renewed interest towards toughness enhancement of thermoplastics with filler addition. There are several scientific works, claiming that rigid nanoparticle fillers can increase polymer toughness in thermoplastic matrices like HDPE and PP [14-17]. Nanofillers can be three-dimensional materials, such as zeolites, or two-dimensional layered materials such as clays, metal oxides etc. However, one of the few disadvantages associated with the nanoparticles addition is their high cost. Nonetheless, this negative effect is counterbalanced by the relatively small amounts (2-5 wt%) of nanoparticles needed, in contrast to traditional fillers which require a much higher loading to achieve a similar performance. Usually, a maximum in mechanical properties appears in such materials at low filler contents. Higher nanoparticles content results in diminished properties, which is attributed to the increasing tendency of the nanoparticles to form agglomerates as their concentration is increased. Significant effort is focused on the ability to obtain control over the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parent materials, but also on their morphology and interfacial characteristics.

2. FUMED SILICA

2.1 PREPARATION AND PROPERTIES

Fumed silica nanoparticles are extensively used in industry as active filler for the reinforcement of elastomers, as a rheological additive in fluids and as a free flow agent in powders. Aerosils and Cab-O-Sils are typical commercially available fumed silicas. Its macroscopic appearance is that of a white, fluffy powder-like solid, odorless and tasteless, consisted by almost spherical primary particles. More scientifically referred to as pyrogenic silicon dioxide, it is produced by a hydrothermal process from silica tetrachloride. The precursor material is purified by multiple distillations and introduced as aerosol in an oxygen-hydrogen flame under a controlled atmosphere at temperatures usually between 1200-1600 °C. The following reactions occur inside the flame:



Highly viscous droplets of amorphous silica are created, forming the spherical primary particles, which collide and fuse together building up stable aggregates by intergrowth [18]. No conventional model of primary particle bonding in these aggregates exists, some assuming the occurrence of hydrogen and electrostatic bonding, while others believe that primary particle bonding occurs through Si-O-Si bridges. The size of the primary particle can be controlled by adjusting the synthesis conditions, such as the temperature map in the flame, the flame length, the flow turbulence and velocity, and the ratio of the reactants [19]. Particle-size distribution becomes narrower with decreasing primary particle size. Rapid cooling of the silica aggregates, which takes place in a few thousandth of a second, is responsible for the complete amorphous nature of fumed silica. A process is then used to remove any hydrochloric acid residue that might be adsorbed on the material to less than 250 ppm, which is adequate for most applications, thus leading to an extremely pure product ($> 99.8\% \text{ SiO}_2$).

The aggregates tend to stick together forming loosely bonded agglomerates through surface interactions. Although primary particles can be identified by TEM, it is not possible to distinguish aggregates from agglomerates. The size of the agglomerates actually present in a liquid or powder mixture depends mainly on the dispersion and mixing intensity during preparation. Typical BET specific surface areas of fumed silica range from 50 to 400 m^2/g . The high surface area is not related to the occurrence of micropores, but can be understood from sizes of primary particles in the range of 10-20 nm. Primary particles form stable three-dimensional chain-like structures, so-called aggregates (DIN 53206). A simple geometrical approximation of the aggregates composed of spherical primary particles leads to a specific surface area $SA = 6/d$.

Fumed silica exhibits a refractive index of 1.45, similar to that of silica glass, and is only slightly influenced by the particle size and the surface chemistry. Thus, transparent mixtures can be easily obtained from pyrogenic silicas and most organic polymers. Ultraviolet radiation reflectivity of the material is greater than 83%. Pure pyrogenic silicas are thermally quite stable. Heating for 7 days at a temperature of 1000 °C doesn't result in any change of morphology or crystallization. The thermal stability is, however, significantly lower if other substances are present. Traces of alkali or alkaline-earth metal ions in particular act as mineralizers. Pyrogenic silicas are largely inert chemically. They only dissolve in strong alkali solutions, forming silicate, and in hydrofluoric acid with the formation of silicon tetrafluoride. The solubility in pure water is similar to that of quartz ($\sim 150 \text{ mg/L}$). Typical physical properties of fumed silica are summarized below:

Density: 2.203 g/cm ³	Thermal conductivity: 1.3 W/(m·K)
Hardness: 7; 5.3–6.5 (Mohs)	Heat capacity: 45.3 J/mol
Tensile strength: 48.3 MPa	Softening point: c. 1665 °C
Compressive strength: >1.1 GPa	Annealing point: c. 1140 °C
Bulk modulus: ~37 GPa	Strain point: 1070 °C
Rigidity modulus: 31 GPa	Electrical resistivity: >10 ¹⁸ Ω×m
Young's modulus: 71.7 GPa	Dielectric constant: 3.75 at 20 °C 1 MHz
Poisson's ratio: 0.16	Dielectric loss factor: less than 0.0004 at 20 °C 1 MHz
Coefficient of thermal expansion: 5.5×10 ⁻⁷ cm/(cm·K) (average from 20 °C to 320 °C)	Index of refraction at 587.6 nm (<i>n_d</i>): 1.4585

Due to the X-ray amorphous nature of the material [60], fumed silica doesn't promote silicosis upon inhalation [56], contrary to silica nanoparticles prepared by sol-gel methods. When taken orally it passes through the gastrointestinal system without any detectable amount being absorbed. The LD₅₀ values were found to be > 2 g/kg for rats and > 10 g/kg for rabbits. Fumed silica is also harmless when in contact with the skin. However it can cause a droughty sensation which is, however, easily removed with washing and proper skincare. Because of the high reaction temperatures, fumed silica is sterile immediately after manufacture. This does not preclude the possibility of subsequent contamination. Comprehensive studies have shown that gram-negative and gram-positive bacteria cannot survive longer than several hours to several days on dry fumed silica. However, this does not completely rule out the possibility that some sporogenic microorganisms could survive under these conditions. It does not affect bacterial metabolism in aqueous suspensions. Research has shown that, in conditions such as those prevalent in the biosludge beds of effluent treatment plants, the biological processes are not adversely affected within the effluent. Tests for fish toxicity showed no visible damage nor did they display any deviant behaviour in comparison to a control group. In the Ames test, which is a biological assay to assess the mutagenic potential of chemical compounds, no such mutagenic potential was revealed. It does not affect groundwater, especially as dissolved silicon dioxide can often be found in drinking water. Nevertheless, chemical modification of the material can potentially have a detrimental effect upon its benign character.

2.2 SURFACE PROPERTIES AND CHARACTERIZATION

Silanol groups are formed on the surface by two main processes [20]. During the condensation polymerization of Si(OH)₄ in the course of silica synthesis the supersaturated solution of the acid transforms to its polymeric form, resulting in spherical colloidal particles

containing $\equiv\text{Si-OH}$ groups on the surface. Upon drying, the hydrogel yields a xerogel, retaining some or all of the surface silanol groups. Furthermore, rehydroxylation of dehydroxylated silica when treated with water or aqueous solutions can form surface OH groups. The surface silicon atoms tend to have a complete tetrahedral configuration and in an aqueous medium their free valence becomes saturated with hydroxyl groups.

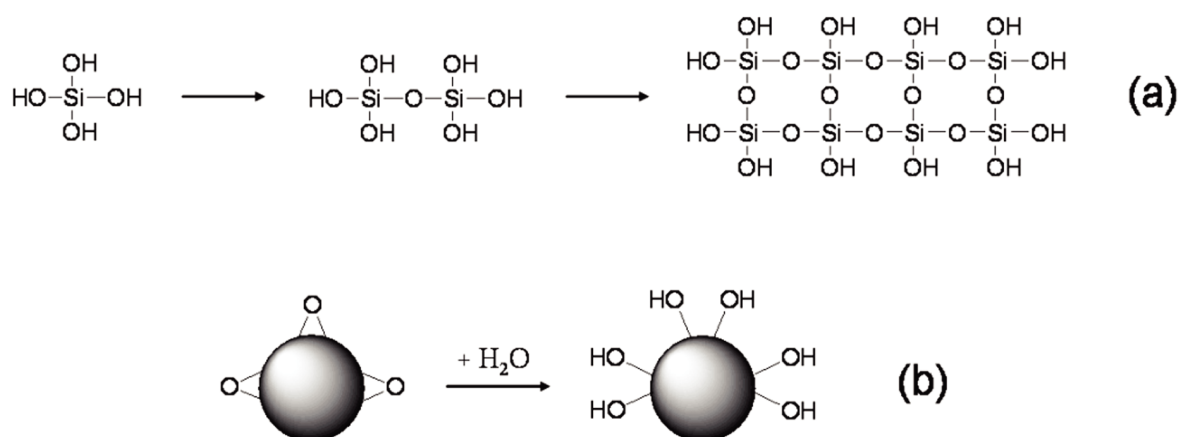


Fig. 1. Formation of silanol groups on the silica surface by (a) condensation and (b) rehydroxylation.

Fumed silica bears three kinds of surface hydroxyl groups; (i) isolated free (single silanols), $\equiv\text{SiOH}$, (ii) geminal free (geminal silanols or silanediols), $=\text{Si(OH)}_2$ and (iii) vicinal, OH groups bound together through hydrogen bond (H-bonded single silanols, H-bonded geminals and their H-bonded combinations) [49, 50]. Single silanols are more reactive than H-bonded vicinal silanols, contrary to what is expected due to the enhanced acidity of the proton not engaged in the H-bond. This is probably because H-bonding engages more than two silanol groups and forms a rather linear or two-dimensional structure in which there is no reactive hydrogen, as all hydrogens are involved in H-bonding. Fully hydroxylated silica contains more bonded than isolated silanols. Rehydroxylation can increase the ration of bonded silanols to isolated ones. The surface also contains exposed siloxane bonds, $\equiv\text{Si-O-Si}\equiv$ bridges with oxygen atoms on the surface, which can be converted to silanols when rehydroxylated. In the course of time adsorbed water reacts with strained siloxane groups and forms bridged silanol groups. This aging can easily be followed by IR spectroscopy [61]. Lastly, there is structurally bound water inside the silica skeleton and very fine ultramicropores (<1 nm), i.e. internal silanol groups. The concentration of all the aforementioned groups depends on the conditions of thermal treatment of the silica sample.

When at a sufficient concentration these OH groups give to the surface a hydrophilic nature. They act as centers of molecular adsorption during their interaction with adsorbates capable of undergoing a donor-acceptor interaction, such as hydrogen bonding. The surface acquires

more and more hydrophobic properties as the concentration of the surface hydroxyl groups is decreased. Siloxane sites are considered hydrophobic. The δ bonds in the Si-O-Si moiety are strengthened by $d_{\pi}-p_{\pi}$ interaction. Both lone pairs on the oxygen are involved in π interaction, which is responsible for the inability of the siloxane moiety for donor-acceptor interactions [20, 22].

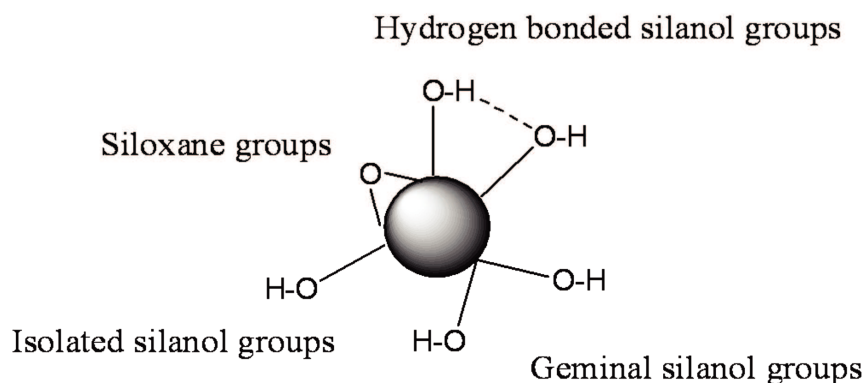


Fig. 2. Types of silanol groups and siloxane bridges on the surface of the amorphous silica.

Table 1. Effect of temperature treatment in vacuo on surface concentration of the different types of OH groups, Si atoms and Si-O-Si bridges (free of OH groups), with the initial state corresponding to the maximum degree of surface hydroxylation(first line) [21].

Temperature of vacuum pretreatment (°C)	Total OH groups (nm ⁻²)	Isolated OH groups (nm ⁻²)	Geminal OH groups (nm ⁻²)	Vicinal OH groups (nm ⁻²)	Si atoms (nm ⁻²)	Si-O-Si bridges (nm ⁻²)
180-200	4.60	1.20	0.60	2.80	0	0
300	3.55	1.65	0.50	1.40	1.05	0.53
400	2.35	2.05	0.30	0	2.25	1.13
500	1.80	1.55	0.25	0	2.80	1.40
600	1.50	1.30	0.20	0	3.10	1.55
700	1.15	0.90	0.25	0	3.45	1.73
800	0.70	0.60	0.10	0	3.90	1.95
900	0.40	0.40	0	0	4.20	2.10
1000	0.25	0.25	0	0	4.35	2.18
1100	0.15	0.15	0	0	4.45	2.23
1200	0	0	0	0	4.60	2.30

The surface characteristics of fumed SiO_2 are very important in the adsorption process of many adsorbates, included single compounds or polymers. The silica's surface has a negative charged surface, due to its hydroxyl groups and ethereal linkages, prone to adsorption of electron deficient species [51, 52]. Sonication of an aqueous suspension of fumed silica or its interaction with polymers can break down a portion of silica aggregates into primary particles. It was reported that sonication of concentrated aqueous suspensions of fumed silica at ≥ 3 wt% can give a dispersion composed mainly of primary particles up to 99.9 % of the total number of particles [52].

The surface concentration of silanols can be determined by a variety of physical and chemical methods. However, all methods require the complete removal of physically adsorbed water, which can be accomplished by heating at temperatures higher than 180°C under vacuum [23]. Amongst the physical methods IR spectrometry, ^{29}Si CP-MAS NMR and ^1H MAS NMR are particular useful when relative measurements are used, and can distinguish between different kinds of silanol. IR can distinguish free and bonded silanols but not free and geminal sites, ^{29}Si CP-MAS NMR can distinguish between single and geminal silanols but not free and bonded sites, while ^1H MAS NMR can differentiate isolated and H-bonded silanols. Free and bonded silanols can also be quantified by IR [24]. Chemical methods used are (i) isotopic exchange with D_2O [25], HTO [26] or ND_3 [27], (ii) titration with NaOH in the presence of salt [28], (iii) reaction with alkyl lithium [29], (iv) reaction with Grignard reagents [26], (v) reaction with dimethylzinc [30], (vi) reaction with diborane and organoboron reagents [22, 29] and (vii) reaction with alkali metal naphthenides [31]. Isotopic exchange seems to be the most reliable method of all for determining the concentration of the surface hydroxyl groups. These method gave a result of $8.0 \pm 1.0 \mu\text{mol}/\text{m}^2$ for a fully surface hydroxylated silica, which is considered as a physicochemical constant [22]. However, "as received" fumed silicas may contain fewer surface silanols, since the manufacture of silica involves thermal treatment. Weight loss upon ignition of the silica at 1200°C can also be used to determine the concentration of the sum of surface silanol groups [32].

One of the most informative methods of studying fumed silica has been high-resolution ^{29}Si NMR spectrometry and ^1H NMR. The use of ^{29}Si NMR, particularly with cross polarization (CP) and magic-angle spinning (MAS), was demonstrated, making use of separate signals for single and geminal silanols [33]. A comprehensive ^{29}Si NMR study was also conducted, in which CP dynamics and/or various relaxation issues were used to elucidate surface details [34]. In the computer-deconvoluted spectra three peaks attributed to the surface groups are observed at about -89, -99 and -109 ppm. The first is due to geminal silanols, referred to as Q_2 , the second to single silanol groups, Q_3 , and the third is attributed to surface siloxane groups, Q_4 , that can be cross polarized by nearby protons. High resolution ^1H NMR, especially when obtained by the CRAMPS technique [36], has also proven to be very useful in studying the surface of fumed silica [33-35]. The CRAMPS computer deconvoluted spectrum shows three major peaks between the area from about 1 to about 8 ppm, which is

assigned to silanol protons in a variety of hydrogen bonding environments. Hydrogen bonding is commonly identified with proton shifts to lower shielding, and thus, a distribution of types and strengths of hydrogen bonding should yield a distribution of isotropic chemical shifts. This broad peak significantly overlaps with the resonance intensity arising from protons of water molecules that are strongly hydrogen bonded. Thusly, the peak at 3.5 ppm is attributed to water molecules physically adsorbed on the silica surface, while the resonance at 2.0 ppm is due to protons of isolated silanols. Furthermore, a broad bump, difficult to discern, is centered around 5 ppm due to hydrogen-bonded silanols.

Infrared spectroscopy has been used to characterize fumed silica, especially in the region of 3200-3800 cm^{-1} , corresponding to the ν_{OH} stretching mode of silanols [45]. A broad band appears at around 3520 cm^{-1} due to hydrogen-bonded silanol. The appearance of another band at around 3715 cm^{-1} suggests the presence of isolated silanols, which behave as proton acceptors and have their own protons free for additional hydrogen bonding. However, it is difficult to differentiate between isolated and geminal silanols because their properties are almost similar [46]. Sometimes splitting of the band is observed. Exchange studies with heavy water have shown that internal silanols, absorbing in the range of 3650-3670 cm^{-1} , are not accessible to water molecules.

Table 2. IR spectral characteristics of silica.

Frequency (cm^{-1})	Position assignment	References
465-475	Si-O bond rocking	[37]
800-870	OH bending (silanol)	[38-40]
935-980	Si-OH bond stretching	[37-40]
1050-1150	Asymmetric Si-O-Si stretching in SiO_4 tetrahedron	[41-43]
1625	O-H bending (molecular water)	[44]
3000-3800	O-H stretching and adsorbed water	[44]
3740-3750	OH stretching	[38, 39]

When dry silica was immersed in organic solvents the 3750 cm^{-1} band due to OH stretching was found to shift to lower wavenumbers, in particular to 3705 cm^{-1} in heptane or 2,2,4-trimethyl pentane [47]. The magnitude of shifting varied for different liquids and thus can be a measure of the interaction's strength between isolated surface OH groups and organic molecules present on the surface. Lateral hydrogen bonding interactions of adjacent silanols can broaden and shift the absorption maximum to lower wavenumbers. Estimation of the

surface area was also used by McCool [48], comparing the integrated area of the band due to isolated groups. An accuracy of about 7% was obtained when compared to the surface area computed by BET nitrogen adsorption techniques. The advantage of this method is that it enables surface area measurements of silica films on porous supports. Furthermore, IR is very often used for a characterization of modification reactions proceeding on the silica surface. Observation of silanol absorption bands changing upon modification permit a better understanding of the reactions and the properties of the modified silicas.

Near infrared transmission (NIR) was successfully applied for quantitative surface silanol measurements [58]. NIR has the advantage over fundamental IR of providing a clear separation of silanol and water absorption bands [59]. The suitability of photoacoustic NIR for the observation of the silanol groups was also demonstrated [60].

Electron microscopy has been used extensively to study the dispersion and agglomeration of fillers of colloidal dimensions in polymers. Unfortunately, due to the small particle sizes and fine structure of the fillers, ultra-thin sectioning is required and it is very difficult to obtain quantitative results representative of the bulk material. Studies of the filler in fractures or other surfaces are unlikely to be representative of the bulk. However, the surface areas of fumed silicas in air and dispersed in a silicone rubber were determined by analyzing small-angle X-ray data according to the methods of Porod and Debye [57]. Broad agreement with the corresponding BET area values were obtained.

2.3 SURFACE MODIFIED FUMED SILICAS

The physical mixture of a polymer and fumed silica may not form a nanocomposite. This is analogous to polymer blends, whereat phase separation is usually observed. Poor physical interaction, which is typical to the more conventionally filled polymers, leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the filler lead to a nanometric dispersion of the inorganic phase. As a result, nanocomposites exhibit unique properties not shared by polymers filled with micro or conventional counterparts. Pristine fumed silica has a hydrophilic nature. In this state it is usually miscible with hydrophilic polymers, such as poly(vinyl pyrrolidone) and poly(ethylene oxide). To render the nanoparticles miscible with other polymer matrices the hydrophilic surface is usually converted to an organophilic one by a suitable reaction. The resulting silica is usually no longer wettable by water.

Chemical modification of oxide surfaces, immobilization of polymers on them, and addition of different surfactants or solvents to the aqueous suspensions may be responsible for alterations in the hydrogen bond network, the free energy of the interfacial layers, and the surface charge distribution. Usual reagents used for such a purpose involve chloroalkylsilanes [62], alkylsilazanes [64], alkoxyalkylsilanes [53, 62] and poly(dimethylsiloxane).

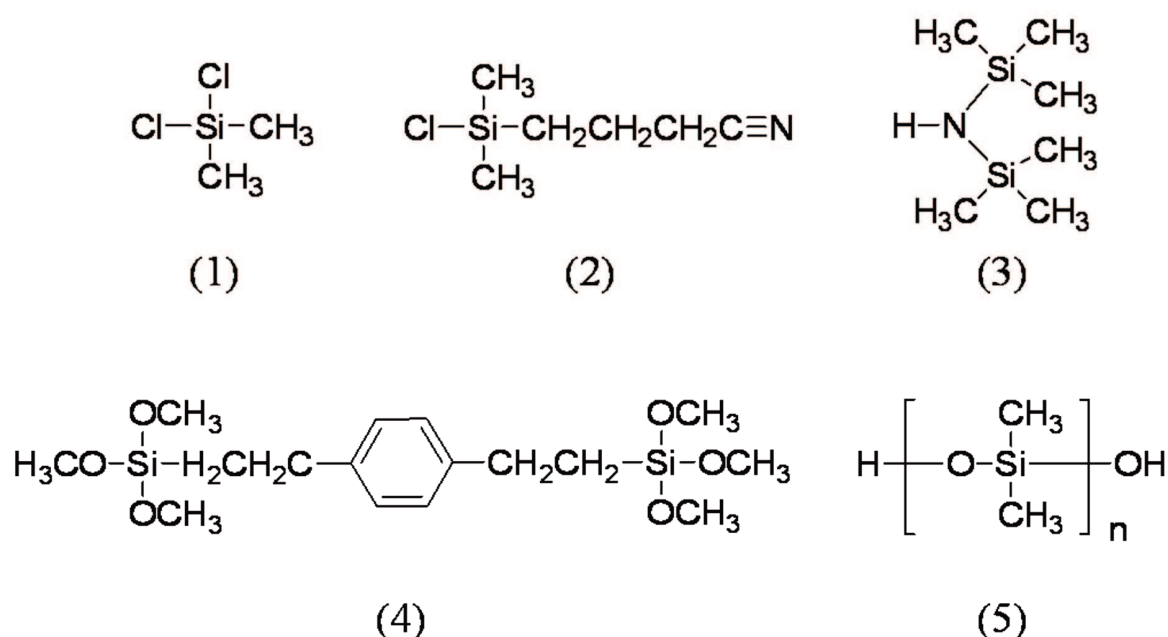


Fig. 3. Various reagents used to modify the surface silanols: (1) dimethyl-dichlorosilane, (2) cyanopropyltrimethyl-chlorosilane (3) hexamethyl-disilazane, (4) *p*-bis (trimethoxysilyl)ethyl benzene, (5) poly(dimethylsiloxane).

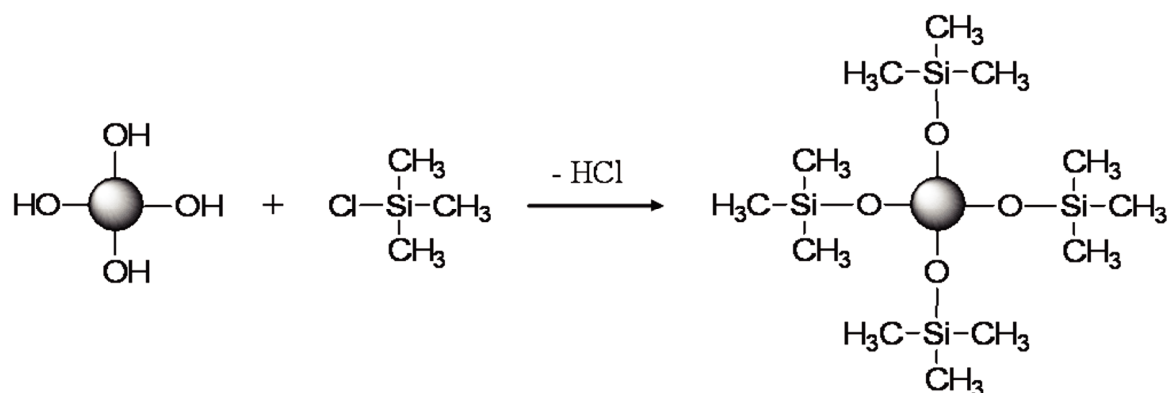
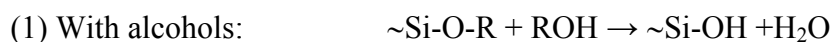


Fig. 4. Reaction between trimethyl-chlorosilane and surface silanol groups of fumed silica.

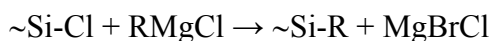
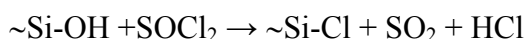
Alkoxyalkylsilanes coupling agents are mostly preferred, since they have been found to make SiO_2 nanoparticles form fine and stable dispersions in many organic solvents as well as in many polymers. In this case, surface modification of nano- SiO_2 takes place in two distinct steps. Firstly, the coupling agent is hydrolyzed, usually in acidic conditions, with the disappearance of the absorption band in IR spectra at 1080 cm^{-1} confirming the disappearance of the Si-O-C bond. Secondly, the surface hydroxyl groups of SiO_2 react with the terminal hydroxyl groups of the hydrolyzed coupling agent through a condensation process [53]. Organofunctional groups can also be anchored on the surface of fumed silicas through the use of silanes. This form of modification is commonly carried out on a large scale for

[55]. In a case, the silanol groups can participate in addition reactions with the glycidyl group in the presence of an appropriate catalyst.

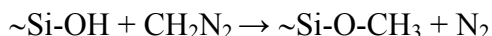
Other functional groups can be introduced on the surface of fumed silica through various acid-specific reactions of the silanol group [22].



(2) Chlorination and reaction with Grignard reagent:



(3) Esterifications with diazoalkanes:



3. THERMOPLASTIC POLYMERIC MATRICES

3.1 POLYESTERS

3.1.1 POLY(ETHYLENE TEREPHTHALATE)

Poly(ethylene terephthalate) (PET), due to its excellent combination of chemical, physical and thermal properties, is widely used as a packaging material for water, juice and mainly for carbonated drinks. In recent years further applications, such as for oxygen sensitive products like beer and tea, have been extensively investigated but without much success. PET, even at a high molecular weight, performs insufficient in packaging applications for alcoholic beverages and other oxygen sensitive drinks. PET bottles are permeable to carbon dioxide and it is estimated that 1.5-2 % of CO₂ is lost every week. The addition of nanoparticles is one of the most promising techniques since nanoparticles usually enhance the gas barrier properties of polymers. Just recently the addition of SiO₂ was mentioned to serve such an association for PET bottles [65].

The addition of SiO₂ nanoparticles into a PET matrix can take place by in situ polymerization or by simple melt mixing. However, in both cases the achieved PET performance is mainly depended by the silica distribution in the PET matrix. PET/silica nanocomposites were prepared by direct polymerization of terephthalic acid and ethylene glycol, wherein organically modified silica nanoparticles were dispersed by ultrasonic irradiation [66-68]. Strong interactions between the nanoparticles and the polymer chains resulted in an average particle size ranging between 10-60 nm. While no direct effect on the polymerization reaction

was observed, glass transition temperature, crystallization rate and temperature and the melting point, as well as thermal stability, were increased at higher filler loadings, while crystallization activation energy decreased. The increased melting temperature was attributed to hindrance to the PET chains caused by the nanoparticles at the beginning of the melting process and the formation of more perfect crystals, due to the higher crystallization temperature and lower activation energy. The crystallization process, analyzed by the Avrami method, differed between pure PET and its nanocomposites, the former being fitted for athermal nucleation and three-dimensional spherical growth in the whole process, while the latter exhibited two stages. The first corresponded to athermal nucleation and three-dimensional spherical growth and the second to recrystallization caused by the earlier spherulite impingement.

The increased crystallinity and strong interactions between the nanoparticles and the macromolecular chains resulted in higher tenacity and modulus values of melt spun and drawn nanocomposite fibers compared to the pure PET fiber, while the heat shrinkage was lowered. Alkaline hydrolysis of such a nanocomposite fibers showed greater degree of weight loss compared to pure PET fibers [69]. More and tougher superfine structures, such as cracks, craters and cavities were introduced, which would facilitate certain applications, such as deep dying. Tensile strength was also increased at low filler concentrations and the nanocomposite fibers exhibited much higher tensile strength drop rates during alkaline hydrolysis.

Using the same preparatory procedure, but dimethylterephthalate instead of the acid, nanocomposites were prepared in situ with hydrophilic and organically modified, with trimethylsilyl groups ($\text{Si}(\text{CH}_3)_3$), fumed silica [70]. In situ polymerization was found to be more effective than direct melt compounding at dispersing the nanoparticles in the polymeric matrix, with the organically modified fumed silica being dispersed more homogeneously in the PET matrix. The incorporation of fumed silica increased the intrinsic viscosity of the matrix, while the melt viscosity of the nanocomposites was increased, due to particle-particle interactions of fumed silica. Contrarily to other studies, crystallization rates were found to be retarded, this tendency being related to the improvement of dispersability of the nanofiller. Toughness was increased remarkably, especially at low concentrations and regardless of the filler type, thus improving the processability of PET.

Bikiaris et al. [86] recently prepared poly(ethylene terephthalate)/fumed silica nanocomposites by melt-mixing. The dispersion of the nanoparticles in the PET matrix was examined with SEM and TEM. Silica particles were spherical in shape, detected as white spots in the SEM micrographs, with a diameter depending on the SiO_2 concentration. For very low silica contents (up to 0.5 wt% SiO_2) the sizes were found to range between 60-100 nm while for compositions 1 and 2.5 wt%, the particle sizes ranged between 100-160 nm and 120-220 nm respectively. Fumed silica created agglomerates, since, according to the supplier, fumed silica of primary particle size of 12 nm was used. Thus, by further increasing the silica

content up to 5 wt% the detected particle sizes became larger, between 130 and 250 nm. This was clearly shown in the TEM micrographs of the same nanoparticles (Fig. 7), since SEM is insufficiently informative due to the detection limits of the instrument. Inside the aggregates the individual SiO_2 nanoparticles were well detected, with average primary particle size diameter close to that reported by the provider.

The agglomerates were in the nanoscale level, consisted by clusters of smaller silica particles, not exceeding 300 nm. These results were in good agreement with previous findings in isotactic polypropylene/ SiO_2 nanocomposites, where it was also found that increasing the content of untreated fumed silica larger agglomerates were found [71] and only when a compatibilizer like PP-g-MA was used, these agglomerates could be decreased in size [72]. Just recently it was mentioned that the nano-silica dispersion could be promoted using a polymerizable additive grafted onto nanoparticles [73].

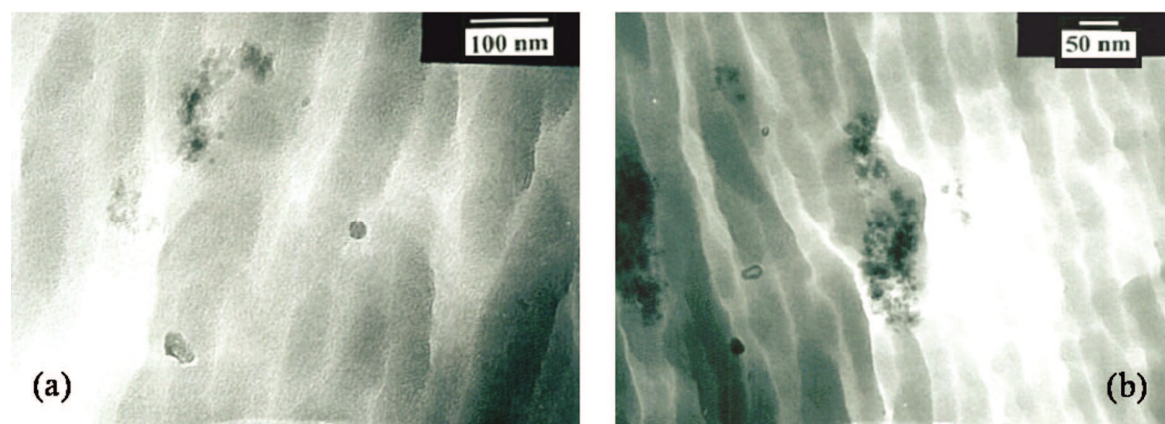


Fig. 7. TEM microphotographs of PET/ SiO_2 nanocomposites at different magnifications containing (a) 0.5 wt% SiO_2 and (b) 2.5 wt% SiO_2 [86].

The production of PET begins with an esterification step where the terephthalic acid or its dimethyl ester is slurried in ethylene glycol and heated to produce a mixture of oligomers of a low degree of polymerization. The polymer at the end of the oligomers' polycondensation exhibits relatively low and heterogeneous intrinsic viscosity (IV) value, generally in the range of 0.4 to 0.65 dL/g. This corresponds to a molecular weight too low for injection or blow molding applications, such as the production of bottles. Thus, a subsequent post-polymerization process in the solid state is required, in order to obtain IV values greater than 0.80 dL/g [74-76]. During this process, the PET granules are heated to a temperature higher than the glass transition temperature (T_g), but lower than the onset of melting (T_m), so as to make the end groups mobile enough to react and the byproducts are removed by passing inert gas through the reacting mass or by maintaining reduced pressure.

As was mentioned SSP is a requisite procedure in order to achieve a high molecular weight polyester. The reactions of PET during SSP are controlled by many parameters while its kinetics have been investigated in connection with the initial molecular weight, the levels of crystallinity and the carboxyl and hydroxyl end groups [74-85]. The catalyst effect is also important not only in the polycondensation stage but also in SSP [75].

The intrinsic viscosity of PET/fumed silica nanocomposites prepared by melt-mixing and subjected to SSP procedure, using different temperatures and heating times, was measured [86]. As can be seen in Fig. 8 the increase of intrinsic viscosity of pure PET depended on time as well as temperature and high molecular weights could be achieved at higher temperatures (230 and 240°C) and heating times (8h). A similar trend was also observed for the sample containing silica and the intrinsic viscosity increase was directly depended by the temperature. Furthermore, this increase was completely affected by the added silica. At low silica content up to 0.25 and 0.5 wt% the intrinsic viscosity increase was higher than the observed in pure PET in all studied temperatures. In samples containing 0.25 wt% SiO₂ the IV values were 0.74, 0.84, 1.02 and 1.24 dL/g at temperatures 200, 210, 220 and 230°C respectively, after 8h of SSP, while, for samples containing 0.5 wt% SiO₂, IV values were slightly lower from those. Thus, taking into account these data, it was concluded that at such low concentrations fumed silica promoted the reactions that took place during SSP. A similar accelerating behaviour on the SSP process was also observed in a study using activated carbon black [87].

Fumed silica contains a lot of surface hydroxyl groups which can react with alcohols [3, 5, 88]. The possibility that during the SSP process of PET/SiO₂ nanocomposites these surface hydroxyl groups of SiO₂ reacted with the end groups of PET, and more preferably with hydroxyl end groups, forming H₂O or ethylene glycol as by-products was confirmed by FTIR measurements. As can be seen in the FTIR spectrum of SiO₂ (Fig. 9) there are two characteristic peaks recorded at 3431 cm⁻¹ attributed to its hydroxyl groups and at 1111 cm⁻¹ corresponding to the Si-O-Si bonds. On the contrary PET contains a lot of peaks, while most characteristic ones are situated in the area of the hydroxyl groups 3150-3700 cm⁻¹, the carbonyl groups or ester bonds at 1721 cm⁻¹ and two peaks at the fingerprint area, the first one at 1122 cm⁻¹ and the second at 1090 cm⁻¹. From the FTIR spectrum of the insoluble fraction it was established that it consisted of PET and silica particles since all the absorbencies corresponding to PET and SiO₂ particles are discerned. However, a lot of differences were presented. The hydroxyl absorbance was recorded at 3350-3730 cm⁻¹, without exhibiting a maximum at 3431 cm⁻¹, where the hydroxyl peaks of SiO₂ are recorded. At the carbonyl peak of PET no clear differentiation was found and the carbonyl absorbance was recorded at 1724 cm⁻¹. However a clear shift was recorded in the area of Si-O bond absorbance. In the insoluble fraction two peaks were recorded at 1117 and 1099 cm⁻¹ in completely different positions from SiO₂ or pure PET, indicating strong interactions. Furthermore, in the insoluble fraction a shoulder was recorded at 1042 cm⁻¹, which was

attributed to the new formed Si-O-C bond from the cross-linking reactions. Furthermore, as can be seen, the absorption of silanol -OH (bending) at 807 cm^{-1} was shifted to a considerably lower wavenumber, at 801 cm^{-1} , which proved that these groups strongly reacted with the end groups of PET.

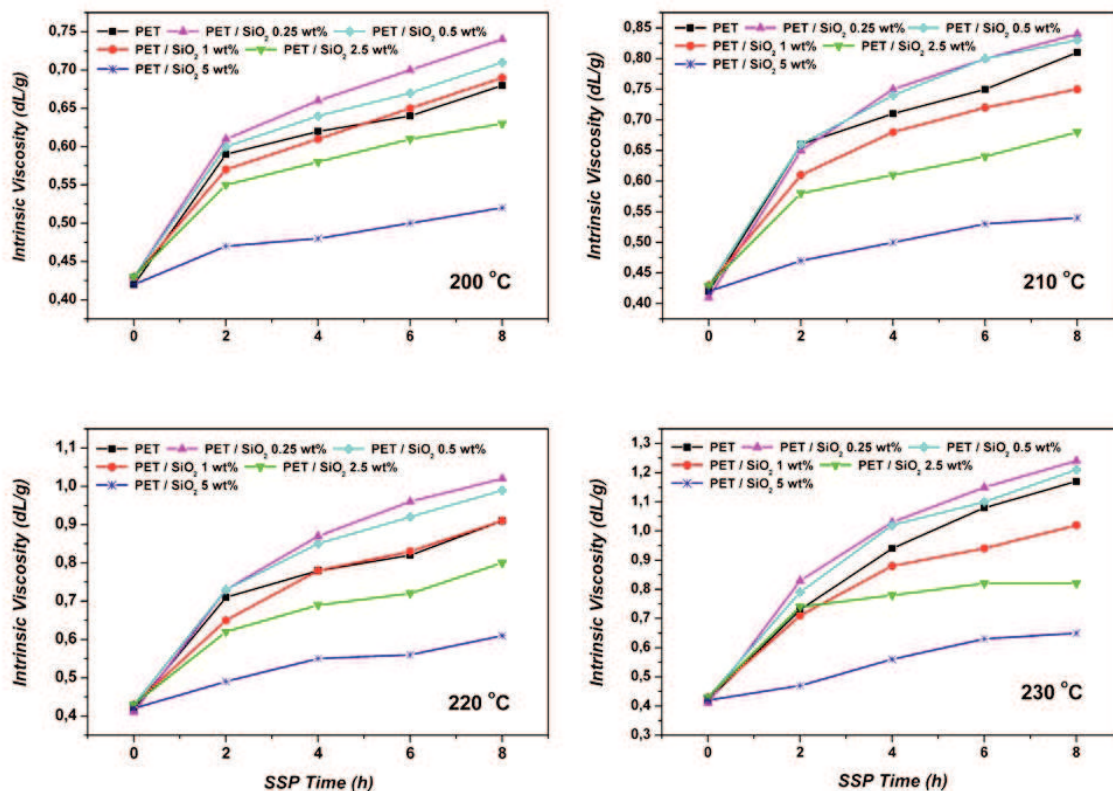


Fig. 8. Variation of intrinsic viscosity of PET/SiO₂ nanocomposites during SSP for different heating times and temperatures [86].

In the literature there are a lot of studies discussing the reaction between hydroxyl groups of different compounds with silanol groups, but only few studies reported that carboxylic acids could react with surface hydroxyl groups of SiO₂ forming ester bond [89, 90]. Furthermore, in the preparation of poly(acrylic acid) nanocomposites with TiO₂, which also has surface hydroxyl groups as SiO₂, it was reported that the carboxylic acids of PAA could form hydrogen bonds or react with the surface hydroxyl groups [91]. The broad band recorded at 3449 cm^{-1} in neat TiO₂ was shifted to 3437 cm^{-1} , while the characteristic bands due to the stretching of -COO^- , at 1575 and 1388 cm^{-1} in the case of free PAA, were shifted to higher wavenumbers in the nanocomposites, at 1580 and 1395 cm^{-1} respectively. These shifts are indicative of the interaction of -COO^- with the titanium dioxide surface.

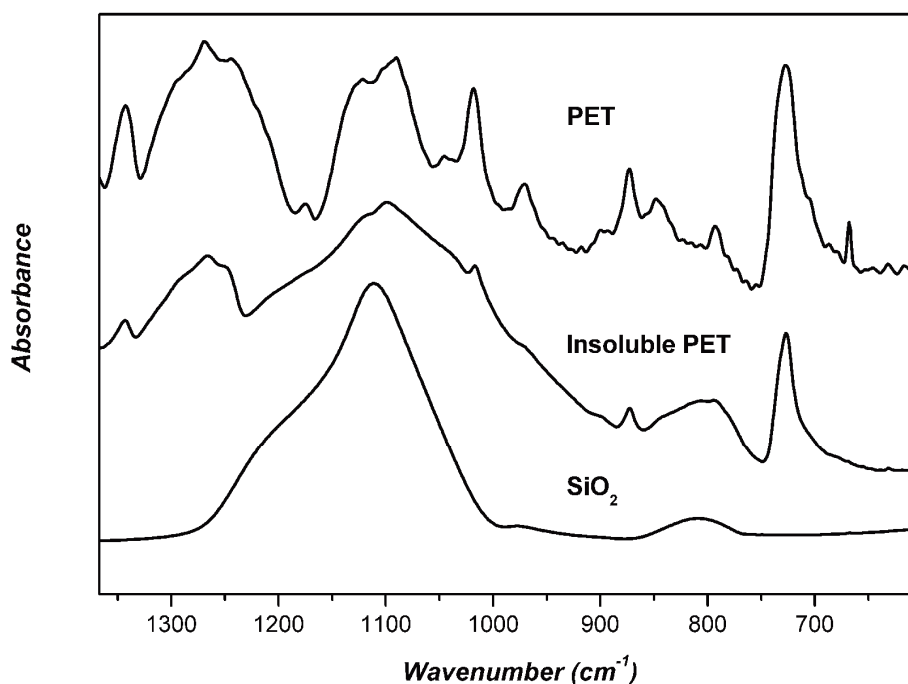


Fig. 9. FTIR spectra of pure PET, SiO_2 and the insoluble fraction which was isolated from the PET/ SiO_2 sample containing 5 wt% SiO_2 [86].

From the already reported studies in literature, concerning SSP of PET, an optimum carboxyl end group and an optimum ratio between carboxyl/hydroxyl groups of PET prepolymer are essential, in order to achieved high molecular weights during SSP [85]. This $[\text{COOH}]/[\text{OH}]$ ratio for PET prepolymers must lie between 0.3 and 1. The optimum end group concentrations for reactions controlling the SSP process exists only if $k_2/k_1 > 2$, where k_2 and k_1 are the forward reactions rate constants of esterification and transesterification, respectively [83, 84]. According to these reports, in the studied PET/ SiO_2 nanocomposites it seems that this optimum ratio was achieved by adding small amounts of SiO_2 (≤ 0.5 wt%). Furthermore, fumed silica provided additional reactive groups acting, at such low concentrations, as chain extender joining the PET macromolecules together (Fig. 10). Thus, the increase of molecular weight was much higher than in neat PET.

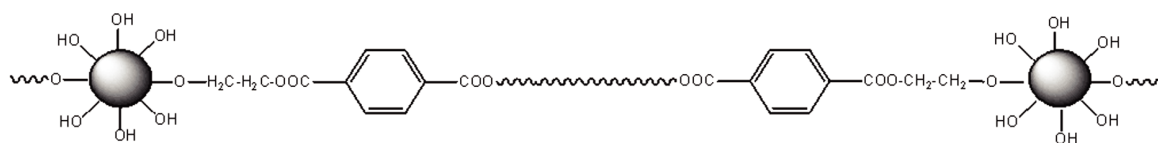


Fig. 10. Schematic representation of PET- SiO_2 reactions taking place during the SSP process into nanocomposites containing low concentrations of SiO_2 nanoparticles (up to 0.5 wt%) and leads to extended macromolecules.

Increasing the SiO₂ concentration in the nanocomposite did not lead to a further increase of IV, as was expected due to SiO₂ acting as chain extenders. For samples containing SiO₂ more than 1 wt% the observed increase of IV was lower compared to the corresponding value for neat PET, at all studied temperatures, while the sample containing 5 wt% exhibited the smallest IV increase. Many reasons could have been the cause of such an effect. It was possible that the nanoparticles hindered the diffusion of the reaction by-products during SSP (water and ethylene glycol) from the esterification and transesterification. It is well known that nanocomposites have lower permeability to gases such as hydrogen, oxygen and carbon dioxide, for which the mean molecular diameters are in the range of a few Å, this having been proven in i-PP/SiO₂ nanocomposites [92]. Water and ethylene glycol are larger molecules and thus their removal is much more difficult from the PET matrix and as the amount of SiO₂ increases the barrier properties of PET nanocomposites will be further enhanced. However, this speculation is in disagreement with a recent study where montmorillonite was used for the preparation of PET nanocomposites. During the SSP procedure it was found that montmorillonite could accelerate the intrinsic viscosity increase, acting as co-catalyst [93]. Additionally, such a difficulty of diffusion would also exist in samples containing 0.25 and 0.5 wt% SiO₂ and higher IV values from the neat PET samples should not have been obtained.

Another observation that led to the conclusion that something else was concurrently occurring that obstructed the IV increase was the presence of an insoluble residue in the sample containing 5 wt% SiO₂, which exhibited the lowest intrinsic viscosity values over all the reaction temperatures and times examined. Such an insoluble residue could only be found in cases where multifunctional monomers like trimethyl trimellitate or others additives such as diepoxides or dianhydrides are used [94-100]. The SiO₂ nanoparticles acted as multifunctional additives leading to the production of branched macromolecules and, above a certain concentration, to insoluble cross-linked macromolecules. It is well known that polycondensation reactions with multifunctional comonomers can form extensive branching or gel, above a critical concentration of the comonomer or at high conversion degrees. The critical extent of a reaction (α_c) at which a polymer is predicted to form a gel is given from the following equation and is dependent by the degree of functionality and the concentration of the multifunctional ($f > 2$) branching agent: $\alpha_c = 1/[r + rp(f-2)]^{1/2}$, where r is the ratio between A bifunctional and B multifunctional groups and p is the ratio of functional groups with $f > 2$ to the total number of A groups. The added SiO₂ at 5 wt% constituted such a critical concentration for gelation. Unfortunately, in the case of SiO₂ it was not possible to exactly measure its functionality and to predict the exact concentration that gelation would occur using the Flory theory [101]. However, from the experimental data it was realized that this concentration lied between 2.5 and 5 wt% silica content. The insoluble PET content % of each PET/SiO₂ sample containing 5 wt% SiO₂ for temperatures 200, 210, 220 and 230°C is presented in Fig. 11.

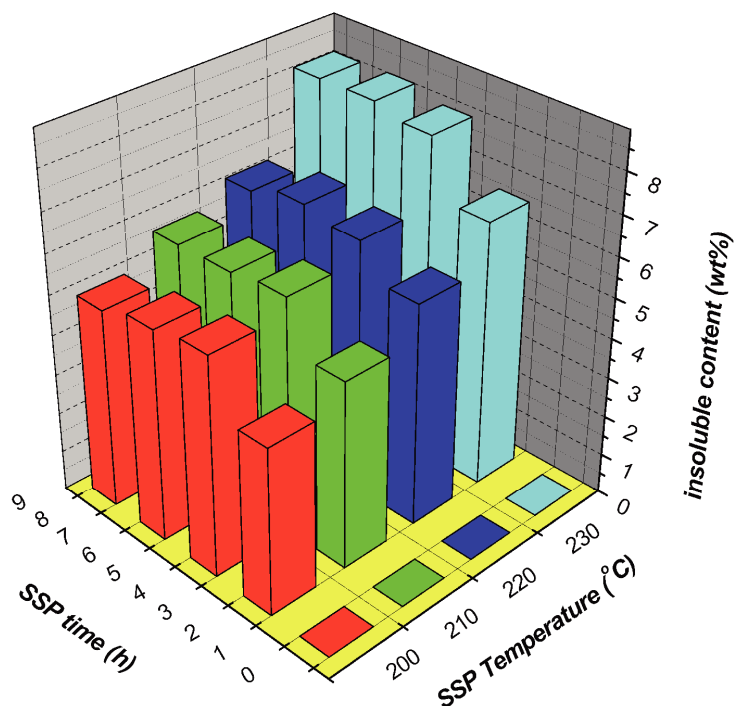


Fig. 11. Insoluble gel content of PET/SiO₂ containing 5 wt% SiO₂ during SSP for different heating times and temperatures.

As can be seen the insoluble content was temperature depended and increased at higher temperatures. At 230°C the insoluble fraction was almost 8.2 wt% after 8 h of SSP while at 200°C it was close to 5 wt% for the same reaction time. Besides, at all SSP temperatures most of the insoluble fraction was formed at the first 2h of post-polycondensation. After 4 h the insoluble fraction reached a plateau and remained almost constant until the end of the SSP process. This is an indication that the insoluble fraction may have formed by the reaction between the carboxyl and most preferable between the hydroxyl end groups of PET with the surface hydroxyl groups of SiO₂. Since the reactive groups, mainly from the PET resin, were consumed, it was not possible for the reaction to proceed further. This is the main reason that during SSP the molecular weight did not increase linearly but reached a maximum value after a certain time. The macromolecular chains have restricted mobility when at the solid state and thus it is difficult for two distant end groups to come close enough to react, increasing the molecular weight. According to the comparative elemental analysis, recorded with EDS-SEM, the insoluble fraction of the sample after 8 h at 230°C, which was separated after filtration, consisted of high silica content. From TGA analysis it was found that almost half of the insoluble fraction was consisted by SiO₂. This was further verified by EDS-SEM analysis since, as can be seen in Fig. 12, the ratio between Si/O elements was higher in the insoluble

material. The concentration of silicon element was very high in the insoluble material compared to that of the PET/SiO₂ nanocomposite containing 5% wt% SiO₂.

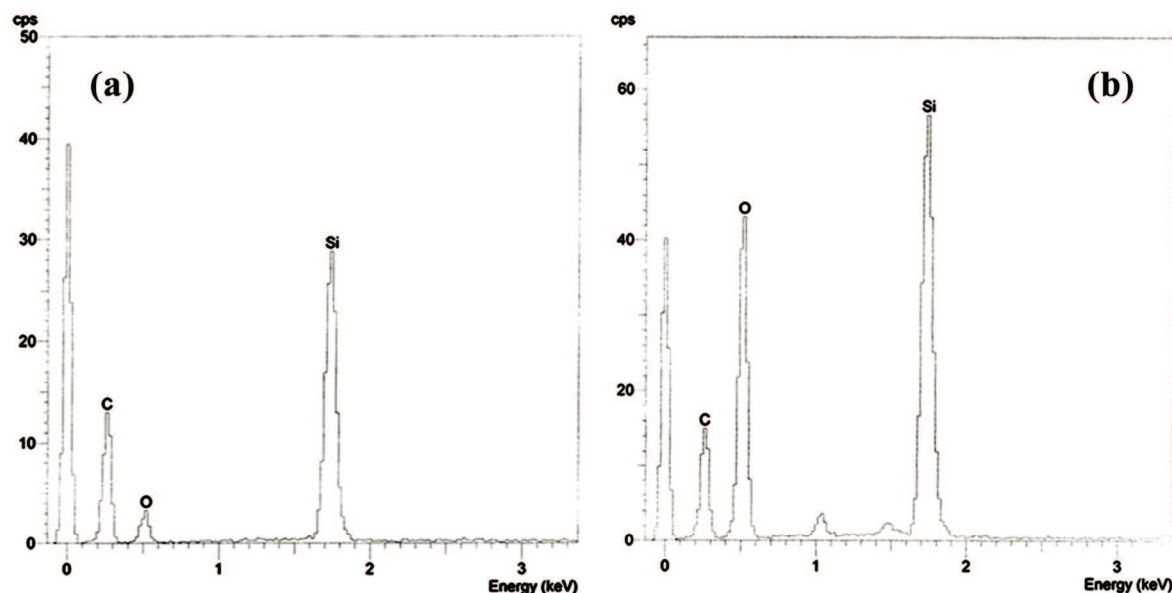


Fig. 12. EDS-SEM analysis of (a) PET/SiO₂ nanocomposite containing 5 wt% SiO₂ and (b) insoluble gel content of PET/SiO₂ nanocomposite containing 5 wt% SiO₂ after SSP for 8h at 230 °C.

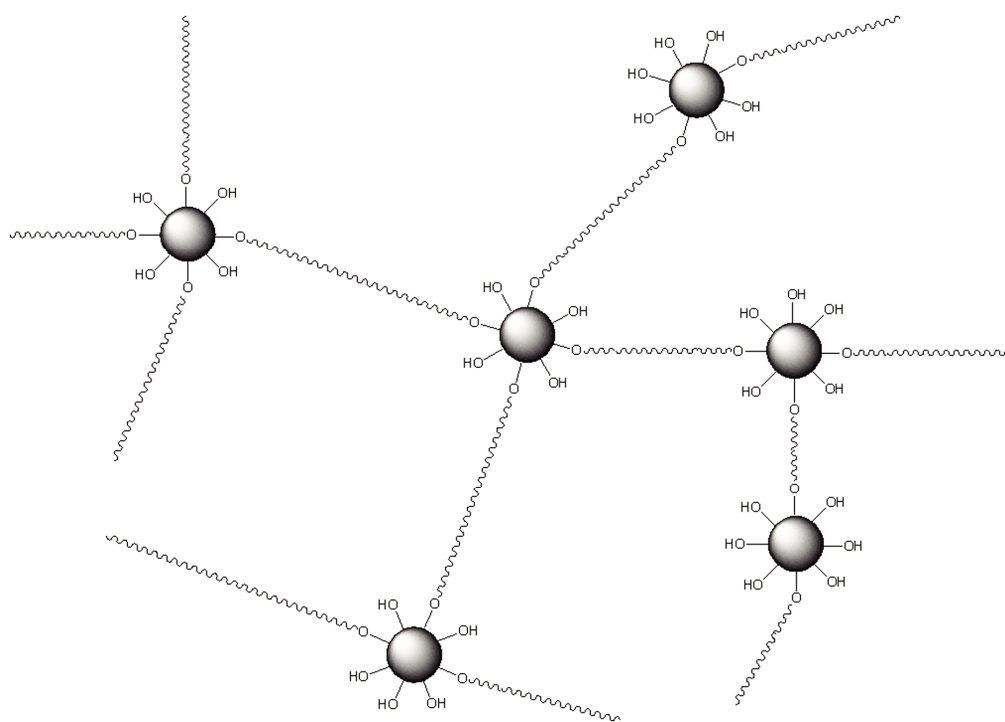


Fig. 13. Schematic representation of PET-SiO₂ reactions taking place during the SSP process in nanocomposites containing high concentrations of SiO₂ nanoparticles (1 up to 5 wt%) and leading to branched or cross-linked macromolecular structures.

All these differences proved that the surface hydroxyl groups of SiO_2 reacted with the end groups of PET macromolecules, leading to the formation of higher molecular weight macromolecules at concentrations up to 0.5 wt%, acting as chain extender. At higher concentrations (1 and 2.5 wt%) these reactions led to the formation of branched or cross-linked macromolecules in the case of extended reactions at a concentration of 5 wt% silica, particularly (Fig. 13). Consequently, the extend of branching or cross-linking could be fully controlled using the appropriate amount of fumed silica.

3.1.2 POLY(ϵ -CAPROLACTONE)

Poly(ϵ -caprolactone) (PCL) is a semi-crystalline polymer, with a crystallinity degree around 50%, exhibiting a glass transition temperature at about -60°C and, depending upon its crystalline nature, a melting point ranging between 59 and 64°C . Being fully biodegradable, biocompatible and non-toxic, it has been approved by the Food and Drug Administration (FDA) as a material for use in the human body as, for example, suture filaments, drug delivery device or tissue scaffold. It is thermodynamically miscible with many polymers, such as PVC, SAN and ABS, with which it is blended to improve their processing characteristics and their end-use properties, such as the stress crack resistance. Research has been aimed at exploring its uses in biodegradable packaging materials [102], in pharmaceutical controlled release systems for nanoparticles formulations and in other medical applications [103]. However, disadvantages such as its low melting temperature, low modulus and abrasion resistance, low heat distortion temperature and its poor barrier properties have hindered its extended commercial usage.

Coating of fumed nanoparticles with poly(ϵ -caprolactone) was performed in situ by the ring opening polymerization of the cyclic monomer with aluminium, yttrium and tin alkoxides as catalysts [104]. Alcohol groups, able to initiate the polymerization of ϵ -caprolactone through a catalytic process in the presence of either Al, Y or Sn alkoxide, were first introduced on the surface to ensure the formation of a non-hydrolyzable bond between SiO_2 and the polymer. As a result both non-grafted and grafted polymer chains were formed. Graft density was dependent on the metal and the metal-to-OH ratio; the more active the catalyst the smaller the grafting efficiency and polymer content.

PCL nanocomposites with fumed silica nanoparticles, organically modified with dimethyldichlorosilane, were prepared by the in situ technique [105, 106]. For the preparation of PCL/ SiO_2 nanocomposites the filler amount was introduced and dispersed in the monomer prior to polymerization. The presence of the filler in the bulk polymerization mixture affected the final viscosity average molecular weight of the polymer; an affect more pronounced as the filler's concentration increased (Table 3).

Table 3. Viscosity average molecular weights and mechanical properties of PCL/SiO₂ nanocomposites [105, 106].

SiO ₂ wt%	[η] (dL/g)	M _v (g/mol)	Young's Modulus (MPa)	Tensile stress at yield (MPa)	Tensile stress at break (MPa)	Elongation at break (%)
0	0,96	83224	342	10.1	28.3	872
0.5	0,94	80808	373	11.1	35.2	912
1	0,91	77593	413	12.4	37.4	922
2.5	0,77	62814	449	12.9	33.0	869
5	0,65	50186	499	13.4	29.0	835
7.5	0,53	38445	526	14.4	16.7	471

Possible explanations for this loss of reactivity were either a detrimental hydrolysis of the titanium alkoxide functions by residual water or trapping of the active species in an heterogeneous exchange reaction between the titanium tetrabutoxide functions and the nanoparticles' surface silanol groups (Figure 14b). Further intensive drying of the nanoparticles under vacuum did not improve the polymerization rate while increasing the initiator's concentration did produce a small effect. Trapping of the active species by a strong interaction with the surface silanol groups and a very slow exchange reaction between them, similar to an alcohol-alkoxide exchange reaction was suspected [107]. In contemplating such a reaction it is noteworthy to also consider the greater acidity demonstrated by silanols compared to the corresponding organic alcohols, due to electron back donation from oxygen through (p→d orbital) π bond. Indeed, the concurrent presence of silanol functions with titanium alkoxide results in an alkoxide-silanol exchange as presented in Fig. 14b. It was observed that the monomer wasn't inserted in the Si-O-Ti bond and this inactivity of the oxygen lone pair was probably due to its overlapping with silicon's d-orbitals. Thus, the propagating species (metal alkoxide) are converted into dormant hydroxyls and vice versa. This equilibrium between active and dormant species (reversible chain transfer), which is however shifted to the right due to the high concentration of silanol groups, which further increases with larger amounts of silica nanoparticles added, reduces the final concentration of the initiator which leads to reduced final molecular weights since it deviates from the optimum amount [108]. However, the occurrence of intramolecular transesterification reactions leading to the formation of cyclic poly(ϵ -caprolactone) chains soluble in toluene cannot be precluded. Titanium tetrabutoxide has been proven to promote such back-biting reactions [109].

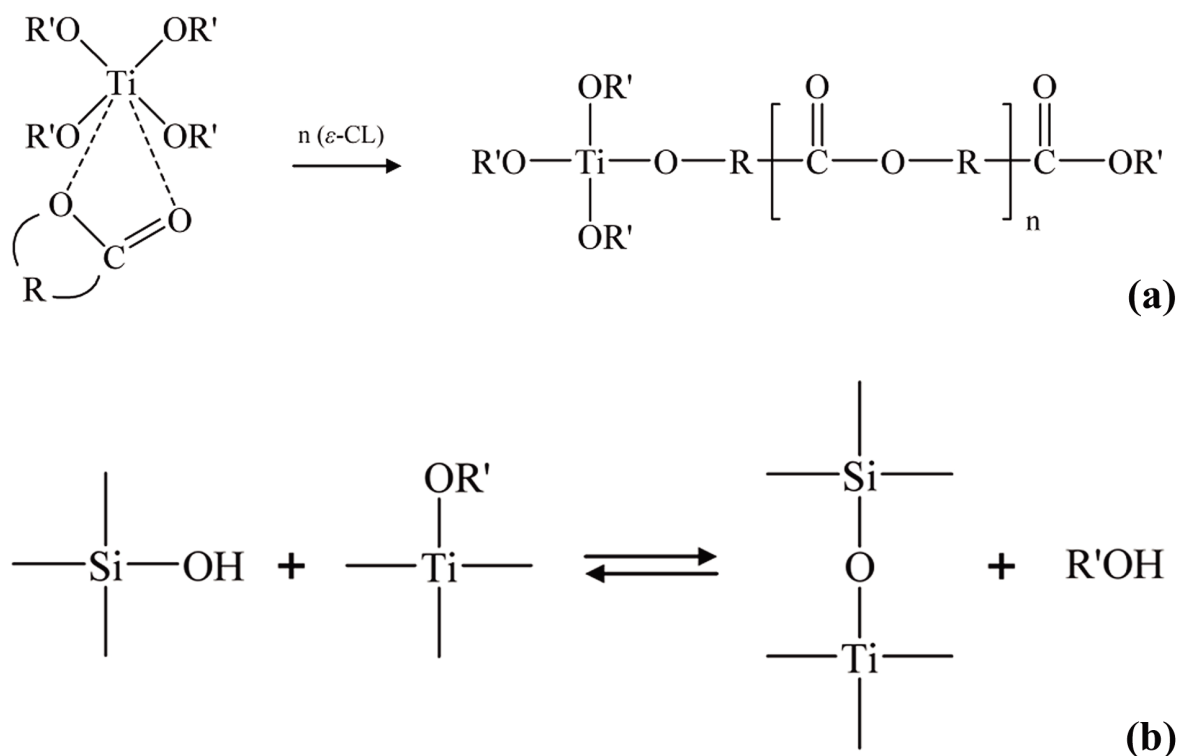


Fig. 14. (a) Polymerization reaction of ϵ -caprolactone initiated by titanium alkoxides and (b) exchange reaction between surface silanol groups and titanium tetrabutoxide [105].

TEM micrographs showed that even by using such a procedure a significant amount of the silica nanoparticles formed aggregates, as was previously discussed in the PET/SiO₂ nanocomposites, dependent on the silica content and increasing as the content of silica increases. This reflected on the mechanical properties of the prepared materials, with increased agglomeration resulting in reduced stress and elongation at the break point (Table 3). All stress-strain curves exhibited the same pattern, similar to that of neat PCL and materials characterized as hard and tough.

Polarized light microscopy tests in PCL/SiO₂ nanocomposites revealed that the nanoparticles in the polymer matrix acted as nucleating agent, enhancing its crystallization rate. In all nanocomposites during cooling from the melt PCL spherulites appeared at higher temperatures, compared to pure PCL. Additionally these spherulites were somewhat larger in diameter compared to those of the pure resin (Fig. 15).

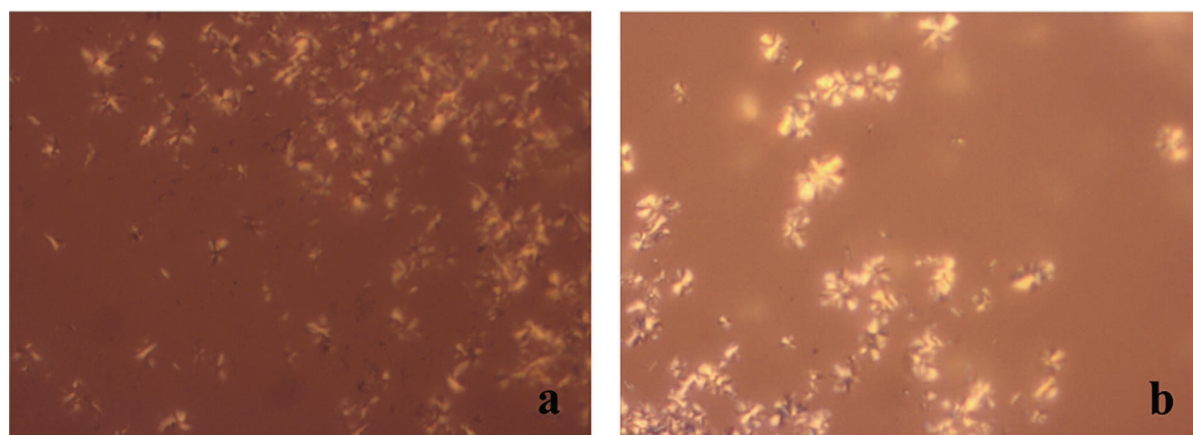


Fig. 15. PLM photographs taken during cooling by $1^{\circ}\text{C}/\text{min}$ for (a) pure PCL and (b) PCL/SiO₂ 2.5wt % nanocomposite [105].

Non-isothermal crystallizations by cooling at various rates proved that the crystallization peak temperature for a given cooling rate increased with silica content showing a nucleation effect of the nanoparticles (Fig. 16).

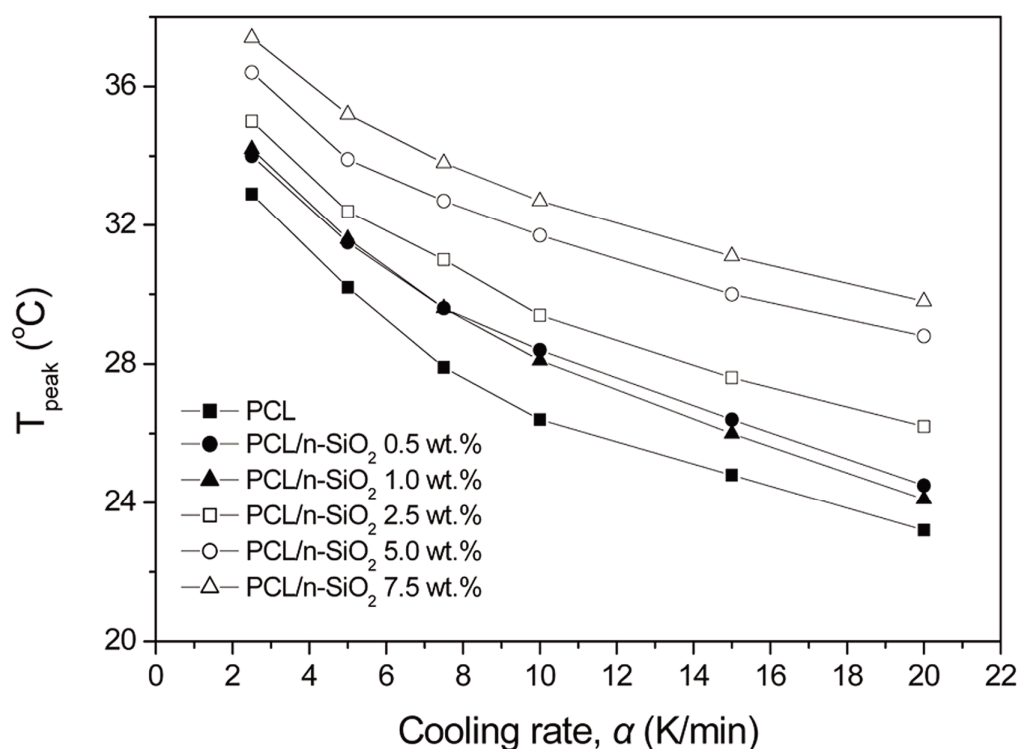


Fig. 16. Crystallization peak temperature against cooling rate for the PCL/SiO₂ nanocomposites [105].

The nucleation activity of the filler was estimated using the method developed by Dobрева et al. [110]. Nucleation activity (ϕ) is a factor by which the work of three-dimensional nucleation decreases with the addition of a foreign substrate. If the foreign substrate is extremely active, ϕ approaches 0, while for inert particles, ϕ approaches 1. The effect of the amount of the nano-SiO₂ on the activity is presented in Fig. 17.

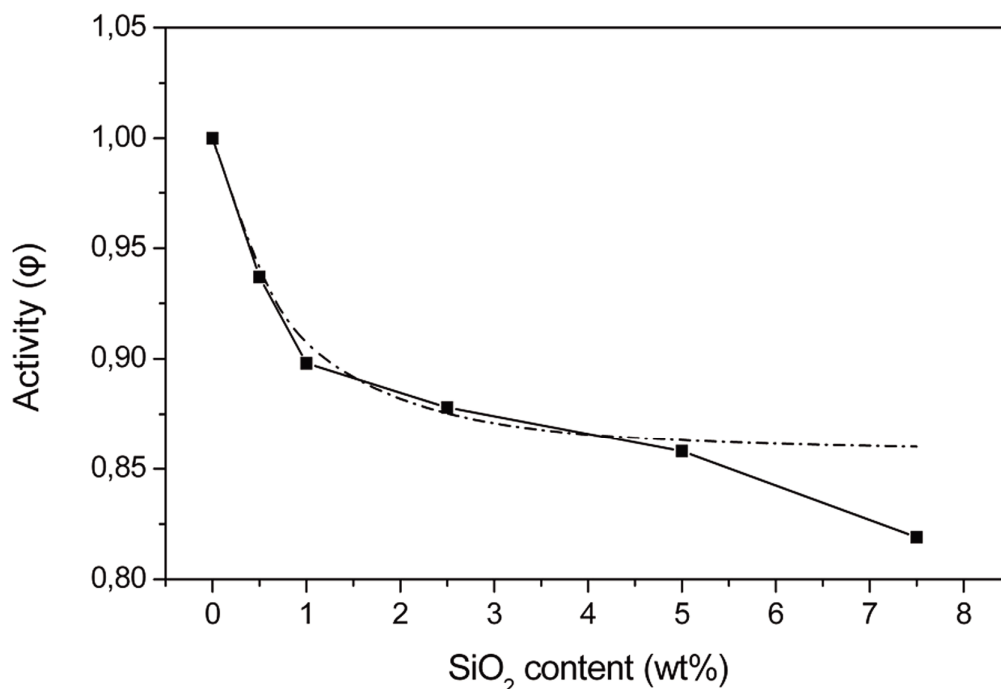


Fig. 17. Variation of the nucleation activity (ϕ) with silica content, for the PCL/SiO₂ nanocomposites. The dash-dot continuous line represents the suggested trend [105].

The nucleation effect increased with increasing SiO₂ content, indicating that fumed silica was acting effectively as a nucleation agent in the PCL matrix. It was noted at this point that for a 5 or 7.5 wt% silica content the decrease in the molecular weight of the PCL may have also caused an acceleration of the crystallization of the polymer. Thus, the trend for the nucleation activity might have been a little different for such high nanoparticles content from that shown in Fig. 17. A plateau would probably have appeared for a SiO₂ content exceeding 2.5 wt% (indicated with a continuous dash-dot line), in the case of constant molecular weight. This was reasonable because the nanoparticles showed an increased tendency to form aggregates in the case of high filler content in the nanocomposites.

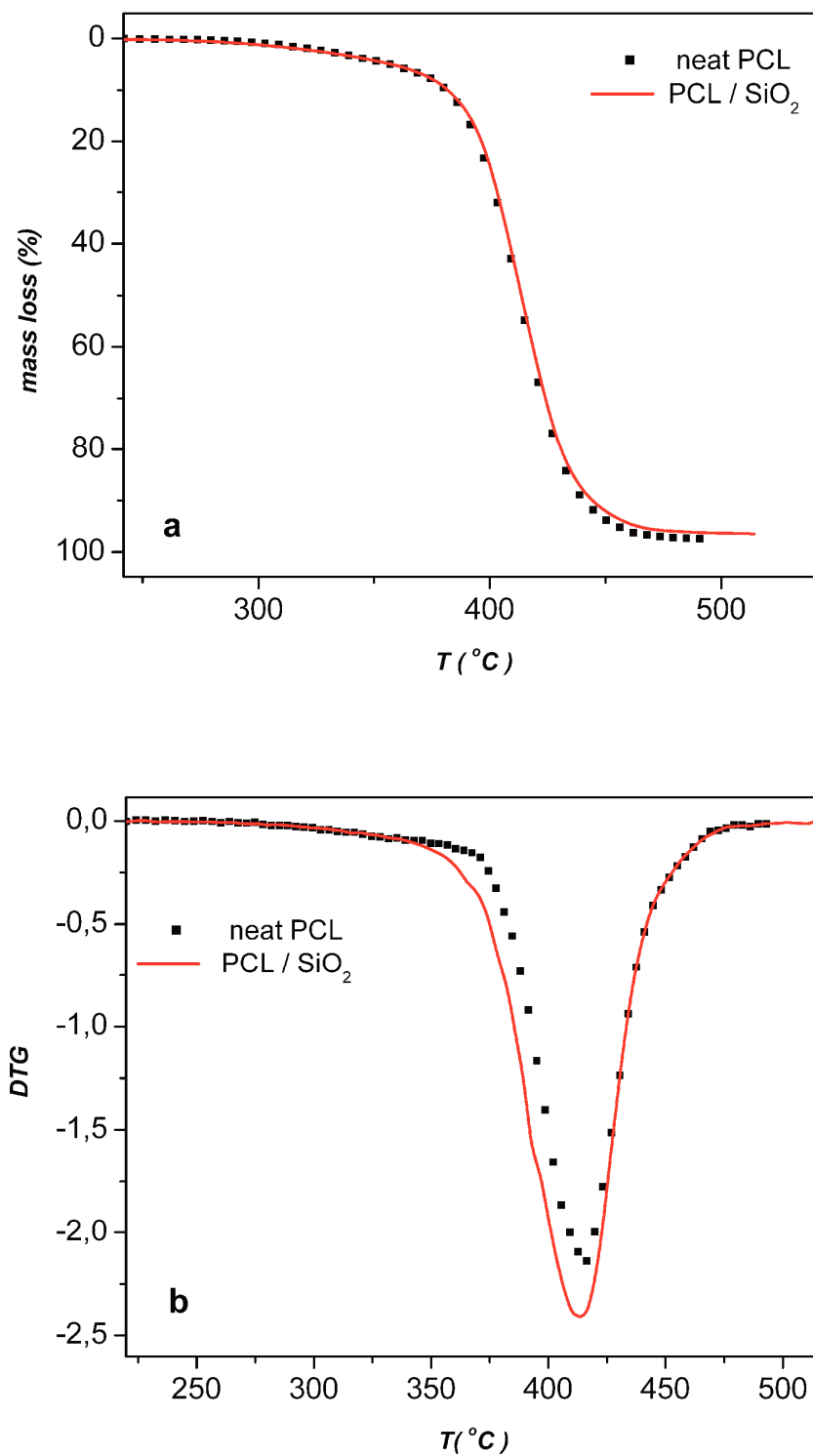


Fig. 18. a) Mass loss (TG%) versus temperature and b) Derivative mass loss (DTG) versus temperature with a heating rate $\beta=10^{\circ}\text{C}/\text{min}$ for all the studied samples [106].

Although a lot of work has been done for the synthesis and properties' characterization of various PCL nanocomposites, little attention has been directed towards the effect of the nano-filler on the thermal degradation mechanism of PCL [106]. For this reason thermogravimetric analysis was carried out in N_2 . Thermal degradation of PCL/SiO₂ nanocomposite was studied by determining its mass loss during heating. In Fig. 18 the mass loss (TG %) and the derivative mass loss (DTG) curves of PCL/fumed silica nanocomposite containing 2.5 wt% silica is presented at a heating rate of 10°C/min. From the thermogravimetric curve it was observed that PCL and its nanocomposite presented a relative good thermostability, since no remarkable weight loss occurred up to 275 °C. The temperature at which the PCL decomposition rate was highest was at $T_p=415.3$ °C, for a heating rate of 10 °C/min. This temperature is almost identical with the decomposition temperature of similar biodegradable aliphatic polyesters [111-113] and very close to that of alipharomatic polyesters [114, 115]. The same temperature was at $T_p=413.7\pm0.6$ °C for the PCL/SiO₂ nanocomposite, which was somewhat lower than the respective temperature of neat PCL. So it seems that SiO₂ had a small accelerating effect on the thermal degradation mechanism of PCL.

In order to analyze more thoroughly the effect of SiO₂ nanoparticles on the degradation mechanism of PCL it was important that the kinetic parameters (activation energy E and pre-exponential factor A) and the conversion function $f(\alpha)$ were evaluated. For the calculation of the activation energies all heating rates were used and they were estimated using the Ozawa, Flynn and Wall (OFW) and Friedman methods for comparison reasons [166-168].

As can be seen form Fig. 19 the activation energy for PLC/SiO₂ nanocomposite was at all degrees of conversion always lower than the corresponding for neat PCL. This proves that silica nanoparticles had a small accelerating effect on PCL's degradation. Additionally, it was educed that the dependence of E on α value could be separated in three distinct regions in both samples. The first for values of α up to 0.1, in which E presents a rapid increase, the second ($0.1 < \alpha < 0.8$) in which E presents a slight increase and the third one for $\alpha > 0.8$. This dependence of E on α was an indication of a complex reaction with the participation of at least two different mechanisms, from which one had quite a small effect on mass loss. For the determination of the first stage mechanism for neat PCL as well as for its nanocomposites, the following were assumed: a) the two mechanisms are consecutive or parallel, b) this mechanism, which we try to identify, corresponds to a small mass loss, according to the experimental results. The fitting with two parallel mechanisms on PCL did not lead to sufficient results while the consideration of two consecutive mechanisms led to a remarkable improvement in the fitting of the experimental results with the theoretical ones (Fig. 20). Similar were the results obtained for the PCL/SiO₂ nanocomposite.

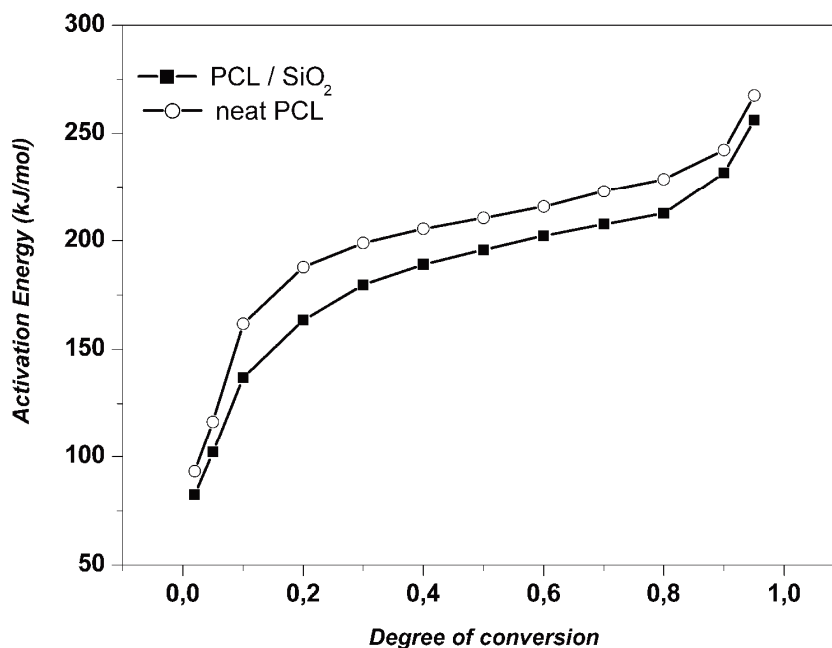


Fig. 19. Dependence of the Activation Energy (E) on the degree of the conversion (α) of the mass loss, as calculated with Ozawa's method for the different nanocomposites [106].

The form of the conversion function, obtained by the best fitting, with a correlation factor 0.99991, was the mechanism of autocatalysis n -order $f(\alpha) = (1-\alpha)^n(1+K_{cat}X)$ for the studied samples. As can be seen the parameters of the mechanisms for neat PCL were: the pre-exponential factor $\log A \text{ (s}^{-1}\text{)} = 8.6$, the activation energy $E = 130.0 \text{ kJ/mol}$, the exponent value $n = 1.07$ for the first one, and the pre-exponential factor $\log A \text{ (s}^{-1}\text{)} = 14.47$, the activation energy $E = 220.2 \text{ kJ/mol}$, the exponent value $n = 1.78$ for the second one. The corresponding values for PCL/SiO₂ nanocomposite were: the pre-exponential factor $\log A \text{ (s}^{-1}\text{)} = 4.7$, the activation energy $E = 84.8 \text{ kJ/mol}$, the exponent value $n = 0.40$ for the first one, and the pre-exponential factor $\log A \text{ (s}^{-1}\text{)} = 13.2$, the activation energy $E = 203.2 \text{ kJ/mol}$, the exponent value $n = 1.70$ for the second one. It was concluded that in order to describe the thermal degradation of poly(ϵ -caprolactone) and its nanocomposite with hydrophobic fumed silica, which had an identical degradation mechanism, two consecutive mechanisms of n^{th} -order autocatalysis had to be considered.

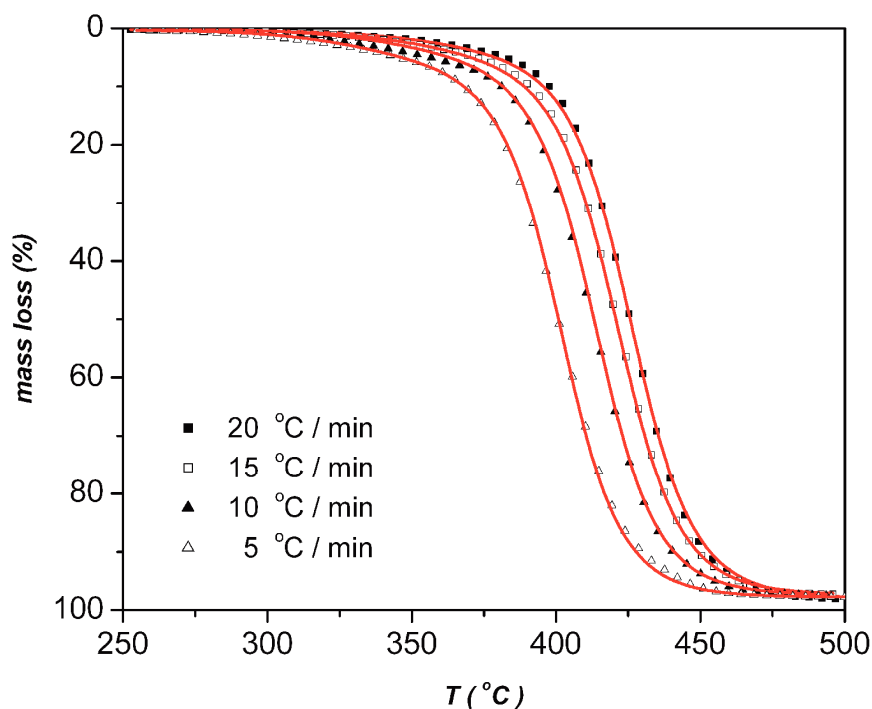


Fig. 20. Mass loss experimental data of neat PCL samples and fitting curves for different heating rates $\beta=5, 10, 15, 20$ °C/min and for a two consecutive reactions mechanism [106].

3.2 POLYOLEFINS

3.2.1 ISOTACTIC POLYPROPYLENE

Isotactic polypropylene has become one of the most interesting commodity thermoplastic, due to its low price and balanced properties, mainly used for fiber production in the textile industry, as film for food packaging, in bottle production, in tubes, etc. The worldwide production of iPP has grown very fast and there is a tendency to replace with it some of the more conventionally used polymers, especially poly(vinyl chloride) and poly(styrene), in many of their applications. However, despite of these advantages, the widespread application of iPP is hindered by one drawback. Although its resistance to crack initiation is very high, its crack propagation resistance is very low, and when a crack or mechanical failure exists in the iPP matrix, it breaks very easily, especially at low temperatures. In recent years much effort has been aimed at overcoming this drawback and enhancing its properties through the preparation of nanocomposites with various nanoparticles, such as clay, calcium carbonate, calcium phosphate, silver and SiO_2 .

Nanocomposites of isotactic polypropylene and untreated and surface treated (with dimethyldichlorosilane) were prepared by melt-mixing in a twin-screw co-rotating extruder [71, 116]. All nanocomposites retained the transparent properties of pure iPP, indicating a fine dispersion of the silica nanoparticles into the iPP matrix. Tensile and impact strength were found to increase and to be mainly effected by the type and content of the silica nanoparticles. Maximum enhancement was observed at a concentration of 2.5 wt%. TEM and SEM observations revealed that at higher concentrations large aggregates of fumed silica were formed, which explain the aforementioned behavior. Surface-treated nanoparticles produced larger agglomerates compared to the untreated, despite the increased adhesion to the iPP matrix, as was postulated from the yield strength values. The critical interparticle distance theory for rubber and composite toughening was successfully implemented on the prepared materials. Both fillers acted as effective nucleating agents, increasing the crystallization rate and degree of crystallinity of iPP. Similar behaviour was observed when a novel surface treatment method, which uses a combination of dispersant and a coupling agent, was developed and used to treat fumed silica nanoparticles, which were then uniformly dispersed into the iPP matrix [117]. However, finer dispersion resulted in the tensile strength at break reaching a maximum at a concentration of 4 wt% and the notched impact toughness at 5 wt% fumed silica.

Isothermal and non-isothermal crystallization kinetics of the samples containing the surface treated fumed silica were extensively studied [118]. Isothermal crystallization was characterized by faster rates as the silica amount increased. The Ozawa analysis of the non-isothermal crystallization was found inapplicable. However, the modified Avrami method and the method proposed by Mo et al. [169] gave satisfactory correlation with the experimental results. Using the isoconversional analysis of the calorimetric data the effective energy barrier for non-isothermal crystallization was found to vary with the degree of conversion, as well as with the presence of the filler. The nucleation activity of the nanoparticles reached a maximum at a concentration of 7.5 wt%, without further significant improvement being observed at higher filler loadings.

The compatibility of the two different phases, iPP and untreated fumed silica, was improved by the addition of maleic anhydride grafted polypropylene (PP-g-MA) during melt compounding in the extruder [72, 92, 119]. Evidently the surface silica hydroxyl groups of SiO₂ nanoparticles reacted with the maleic anhydride groups of PP-g-MA, leading to a finer distribution of individual SiO₂ nanoparticles in the iPP matrix, as was confirmed by SEM and TEM micrographs (Fig. 21).

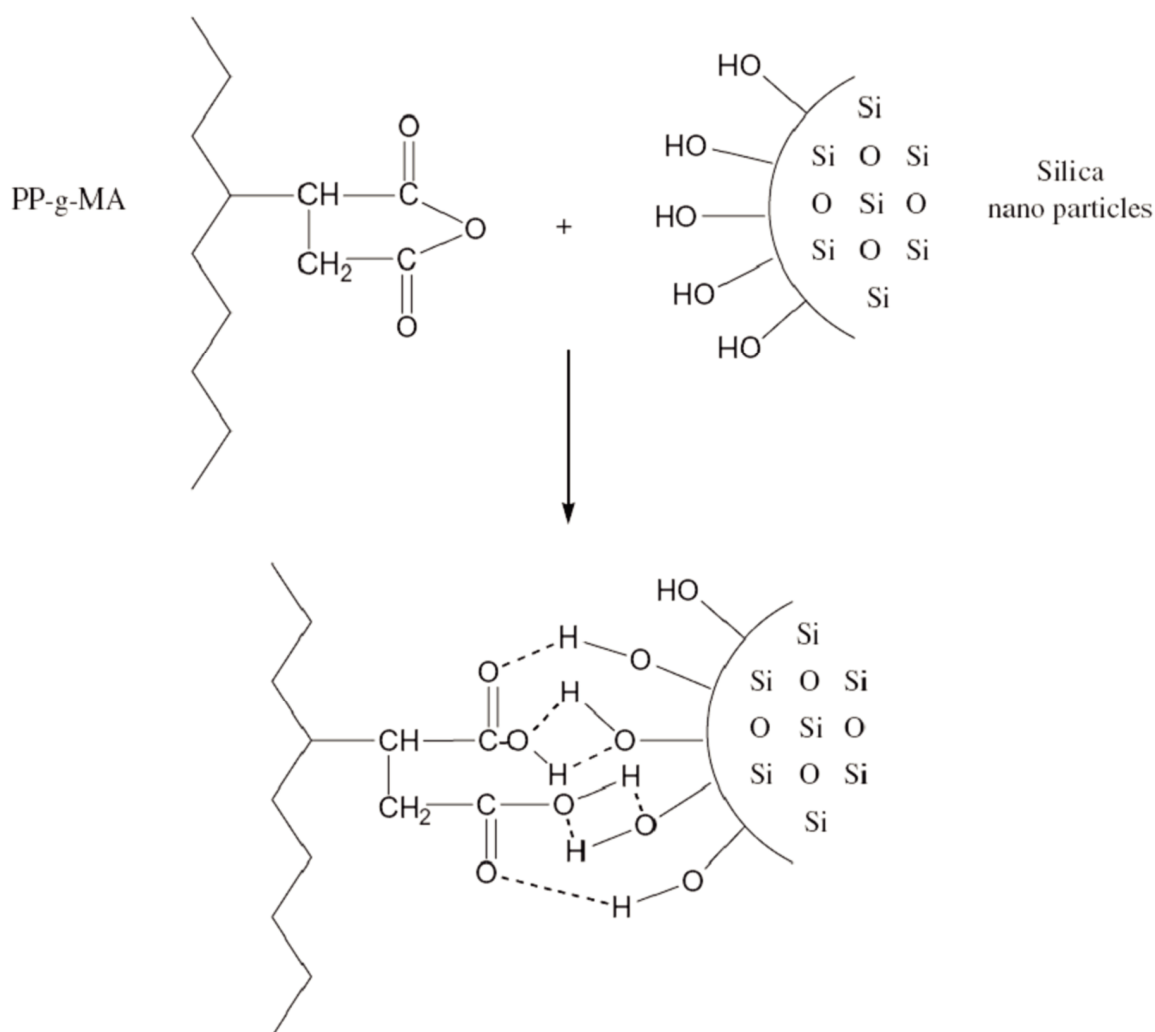


Fig. 21. Reaction between the surface silanol groups of fumed silica and the maleic anhydride groups of PP-g-MA [72].

Thus, mechanical properties were significantly improved with increasing compatibilizer amounts, in the concentration range studied. The enhanced adhesion between the two materials was validated by applying various theoretical models. However, as the concentration of fumed silica increased so did the average size of the agglomerated silica particles in the iPP matrix. Storage modulus values were sensitive to the microstructure of the material, with higher values observed for higher silica and PP-g-MA contents. Crystallisation rates were increased not only at higher fumed silica concentrations, but also at higher PP-g-MA contents, reaching a maximum at 7.5 wt% SiO₂ for a given amount of PP-g-MA. Permeability rates of O₂ and N₂ decreased with increasing silica concentration, due to the more tortuous path needed to be covered by the gas molecules as they pass through the material, since silica nanoparticles are considered impenetrable by them.

Various commercial monomers, i.e. styrene, methyl methacrylate, ethyl acrylate and butyl acrylate, were grafted on nano-SiO₂. This was accomplished through free radical polymerization reactions, after double bonds were introduced onto the surface of the nanoparticles using γ -methacryloxypropyl trimethoxy silane. After extraction of the homopolymers formed the prepared grafted nanoparticles were melt-compounded with isotactic polypropylene to the desired filler loading. Subsequently, the interfacial effects and interactions in such nanocomposites were extensively analyzed [120, 121]. The grafting percentage was varied for each monomer. All thus treated nanoparticles resulted in much higher impact strength of the corresponding nanocomposite compared with the value obtained for the untreated fumed silica. The greatest contribution was found at a low grafting percentage. Treated fumed silica also provided iPP with stiffening, strengthening and toughening effects at a rather low filler content (0.8 vol%), due to the enhanced interfacial adhesion resulting from molecular entanglement and interdiffusion between the grafted polymers and the matrix macromolecules, thus providing the means of a tailorable interphase. A hard interphase was beneficial to stress transfer, whereas a soft one hindered the development of cavities in the matrix. This could be adjusted by choosing the appropriate grafting monomer and its grafting percentage. A number of models dealing with the static and dynamic mechanical behavior of the particulate composites were applied. It was found that stronger interfacial interactions existed in the grafted fumed silica polypropylene composites compared to the composites with untreated silica. This interaction was greatest in the case of low silica concentration and low percentage grafting. Increased grafting percentages resulted in increased interphase thickness, but interfacial interactions and tensile performance of the nanocomposites were not necessarily improved, since the agglomeration structure of the nanoparticles and the miscibility between the components played a key role.

Similarly, nanosilica particles were treated by irradiation grafting polymerization with styrene before melt compounding with isotactic polypropylene [122]. The prepared materials were studied using atomic force microscopy. The loose agglomerates of the untreated SiO₂ became more compact, due to the linkage between the nanoparticles offered by the grafted polymer. The macromolecules of polypropylene were able to diffuse into the agglomerates during the melt compounding. Thus, entanglement between the molecules of the grafted polymer and the matrix facilitated a strong particle-matrix interaction. A double percolation of yielded zones was furthermore presented to explain the specific influence generated by the nano-SiO₂ particles at low-filler loadings [123].

Finally, the phase structure and toughening mechanism in iPP/EPDM/SiO₂ ternary composites was studied [124]. Two kinds of SiO₂ particles were used (hydrophilic and hydrophobic) as well as two processing methods; a one-step or a two-step method, whereat the elastomer and the filler were premixed in a two-roll mill. A unique structure was observed, with the majority of the EPDM particles surrounded by silica nanoparticles, in the sample where hydrophilic fumed silica and the two step processing method were used, which

resulted in a dramatic increase of Izod impact strength when the rubber content was in the range of brittle-ductile transition (15-20 wt%). The significant increase could be tentatively attributed to the overlap of the stress volume between EPDM and silica particles, due to the formation of the aforementioned unique structure.

3.2.2 LINEAR LOW DENSITY POLYETHYLENE

Thermo-mechanical properties of two series of linear low density polyethylene (LLDPE) nanocomposites with hydrophobic fumed silica (treated with dimethyldichlorosilane) were studied [125]. The first series was comprised by LLDPE prepared by a metallocene catalyst (mLLDPE) and the other by a traditional Ziegler-Natta catalyst (zLLDPE). The secondary transitions were affected by the filler presence, while the tensile properties were reinforced with varying the nanoparticles' weight fraction. The elastic modulus and tensile strength of mLLDPE were increased and accompanied by an unusual dramatic increase of the elongation at break. The same trend but to a lesser extent was observed for the corresponding zLLDPE samples. The optimum silica content was found at ~ 4 wt%. Silica contents above 8 wt% were detrimental to the properties of the composites. Three micromechanical models previously developed were used in an attempt to simulate the increment of the nanocomposites' elastic modulus. Best fitting with the experimental data of the mLLDPE nanocomposites were provided by the model which assumed an effective interface between the matrix and the nanoparticles. Thusly, the nanofiller not only increased the stiffness of the polymers, but also modified their morphology, as well as introduced new energy-dissipation mechanisms, enhancing the toughness of the prepared nanocomposites.

3.3 POLYAMIDES

Nylon 11 coatings filled with hydrophilic and hydrophobic fumed silica nanoparticles using a high velocity oxy-fuel combustion spray deposition process were prepared [126, 127]. The hydrophobic fumed silica's surface chemistry was further modified using γ -aminopropyltriethoxy silane. The filler was found to agglomerate at the splat boundaries in the final coating microstructures. Aggregates of silanated silica were of the order of 50 nm in size, whereas the aggregates of untreated and hydrophilic silica were of the order of 100 nm. The morphology of the polymer and the microstructure of the coating depended on the filler surface chemistry and the volume fraction of the filler, as well as the initial nylon 11 particle sizes. All filled coatings had higher crystallinities compared to corresponding pure nylon 11 coatings, with the filler acting as a nucleation site. Coatings with hydrophobic silica exhibited higher crystallinity compare to coating with hydrophilic silica. Smaller starting polymer particle size resulted in coatings exhibiting improved spatial distribution of the silica in the matrix, lower crystallinity, higher density and lower porosity.

Improvements of up to 35% in scratch and 67% in wear resistance were obtained for coatings with 15 vol% hydrophobic silica. This increase was primarily attributed to filler addition and

the increased matrix crystallinity. Particle surface chemistry, distribution and dispersion also contributed to the observed difference in performance. The largest increase of storage modulus was measured for coatings containing hydrophobic fumed silica (205%), which was shown to be a function of both surface chemistry and amount of reinforcement. At temperatures above the glass transition temperature the storage modulus was improved by a maximum of 195%. Water vapor transmission rate through the reinforced coatings were also decreased by up to 50%, again for coatings containing hydrophobic fumed silica. Crystallinity and filler content seemed to have a dominating effect on the mechanical properties, whereas coating density dominated the permeation behaviour of the nanoreinforced coatings.

In situ polymerization was used for the preparation of nylon 6 nanocomposites with hydrophilic and hydrophobic fumed silica, surface modified with dimethyldichlorosilane, and the mechanical properties were examined [128]. Tensile strength, elongation at break and impact strength of the nanocomposites with hydrophobic silica exhibited a tendency to up and down with increasing silica content, with a maximum observed for 5 wt% filler, while those with unmodified fumed silica gradually decreased. Increased aggregation of the silica nanoparticles was observed with increasing filler concentration. Thus, using the critical matrix ligament thickness theory of polymer toughening the exhibited behavior was interpreted.

4. THERMOSET POLYMERIC MATRICES

Epoxy resins are used in a variety of applications since their properties, such as thermal stability, mechanical response, low density and electrical resistance can be varied considerably. Important factors influencing their performance are the molecular architecture, curing conditions and the ratio of the epoxy resin and curing agent(s). The use of an additional phase (e.g. inorganic fillers) to strengthen the properties of the epoxy resin has been a common practice. Nanoparticles, especially, can fill up the weak microregions of resins to boost the interaction forces at the polymer-filler interfaces. Fumed silicon dioxide nanoparticles have already been used for a long time in epoxides [129]. They are mainly used to prepare thixotropic formulations and the effects are observed with filler contents in the lower percent range. The achieved changes of the rheological properties are caused by the interaction of the nanoparticles and this is the cause for the restricted maximum amounts of filler in epoxides [130]. To use fumed silicas in fields where high amounts of filler or not interacting particles are required, a deaggregation is necessary.

Three different approaches were followed to disperse the nanoparticles in the epoxy resin (CYD-128) prior to curing [131]. These included simple ultrasonic irradiation, ultrasonic irradiation and treatment of the filler with a coupling agent, and ultrasonic irradiation of pretreated nanoparticles followed by mechanical mixing in a high speed homogenizer. The

introduction of the nanoparticles had a dramatic effect on the nanocomposites. Uniform dispersion was critical to the morphological structure of the nanocomposites, which in turn affected the impact strength of the nanocomposite. Although agglomerations on the surface of the specimen cast with the first approach were observed, the coupling agent was quite useful in sufficiently dispersing the nanoparticles in the epoxy and breaking up these agglomerates. With the further assistance of the high speed homogenizer, a relative uniform distribution of the nanoparticles was achieved. Enhancements on tensile strength, tensile modulus and impact strength reached up to 114%, 12.6% and 56% respectively, in comparison to the pure epoxy resin. Using positron annihilation lifetime spectroscopy, the free volume parameters (τ_3 and I_3) of the nanocomposites were found to change with the addition of the nanoparticles.

DGEBA-based epoxy nanocomposites filled with various amounts of untreated fumed silica were prepared by a solvent assisted dispersion procedure [132]. Thermo-mechanical properties were found to decrease for 6.3 and 11.8 wt% filled samples, while a trend inversion was observed for 16.7 wt% filled samples. The reduction in properties such as glass transition temperature, dynamic storage and tensile modulus was explained by postulating the presence of polymer-filler interactions limiting the cross-linking degree attained by the polymer matrix during curing. The inversion at higher filler content was supposed to be due to the enhanced physical immobilization effects experienced by the polymeric matrix near the percolation threshold of the filler. SEM inspection suggested the existence of strong polymer-filler interactions in the case of 16.7 wt% filled samples. The obtained results pointed out the key-role of matrix-filler interactions in determining the whole composite performances of the studied system.

Fracture surfaces, from single edge notched bend specimens of the aforementioned DGEBA-based epoxy nanocomposites, prepared and deformed to failure in three-point bending configuration, were examined by atomic force acoustic microscopy. This was done in order to obtain information about the local elastic modulus of the surface at high spatial resolution [133]. The decrease in thermo-mechanical properties was found to correspond to highly heterogeneous fracture surfaces presenting a broad distribution of elastic modulus values. These heterogeneities were interpreted as representative of different degrees of filler exposure on the fracture surface and, also, of localized cavitation effects involved in crack propagation, both phenomena accounting for the effective plasticizing effect induced by silica amount of 6.3 and 11.8 wt%. A substantial reduction of the exposure probability of silica nanoparticles on fracture surfaces was found for the sample containing 16.7 wt% fumed silica, corresponding to an improvement of the observed mechanical and dynamic-mechanical properties. This latter feature was tentatively attributed to the physical immobilization of polymer chains at the polymer-matrix interface.

5. BIOCOMPOSITES

5.1 CHITOSAN

Chitosan, poly-D-glucosamine, is a polysaccharide obtained by the deacetylation of chitin (poly-N-acetyl-D-glucosamine), manufactured from shrimp or crab shells, with concentrated alkali and high temperature treatment (30-40 % NaOH, 110-115°C). While chitin is insoluble in common solvents, chitosan is completely soluble in slightly acid solutions and even in water, depending from its molecular weight and degree of deacetylation. It is a tractable, inexpensive, non-toxic, hydrophilic, biocompatible and biodegradable material with a large number of applications such as in pharmaceutical technology, agriculture, biomedical, waste water treatments, fiber industry etc.

To improve the effectiveness of chitosan and, mainly, its mechanical and physical properties, cross-linking is conveniently and effectively carried out for many of its applications. The most common cross-linking reagent used is glutaraldehyde, which, however, has the great disadvantage of being highly toxic and cannot be used in pharmaceutical technologies. As an alternative way γ -glycidoxypropyltrimethoxysilane (GPTMS) has been used [134]. Cross-linked chitosan/silica hybrid membranes were in situ prepared by a simple way. In the first stage chitosan amino groups reacted with the epoxy groups of GPTMS via an acid catalyzed addition reaction, incorporating the silane groups into the chitosan backbone. Simultaneously, the methoxysilane groups of incorporated GPTMS were hydrolyzed to form silanol groups, which easily participate in condensation reactions. At the end of this procedure Si-O-Si linkages were formed from these condensation reactions and the inter-chain covalent bonds resulted in a crosslinking structure.

In a similar way crosslinked chitosan was prepared using 3-(trimethoxysilyl) propyl methacrylate (TMSPM) instead of γ -glycidoxypropyltrimethoxysilane [135]. In the acidic aqueous solution of chitosan TMSPM was quickly hydrolysed forming silanol groups and dispersed in an aqueous solution. After *tert*-butyl hydroperoxide addition, radicals were generated on the nitrogen atoms of chitosan's $-NH_2$ groups, and the silanols with the active vinyl groups were grafted onto the chitosan chains (Fig. 22). The side silanol groups could participate in the condensation reactions and a microgel was formed. The preparation of a chitosan macroporous layer coated non-porous silica gel was reported as a support for metal chelate affinity chromatographic adsorbent [136]. The adsorption capacity of Cu^{2+} on the chitosan-SiO₂ support was increased. In all of the above articles no reaction between the silanol groups and the amino or hydroxyl groups of chitosan was mentioned. Finally, sulfonic acid groups were introduced on the surface of nanosized silica particles, which were then utilized as an ionic cross-linker for chitosan, forming a series of chitosan-silica nanocomposite membranes [137]. This led to an increase of permselectivity in pervaporation dehydration of an ethanol-water mixture, while the addition of the silica particles provided

extra free volumes in the polymeric matrix for water permeation, resulting in high permeation for the complex membrane.

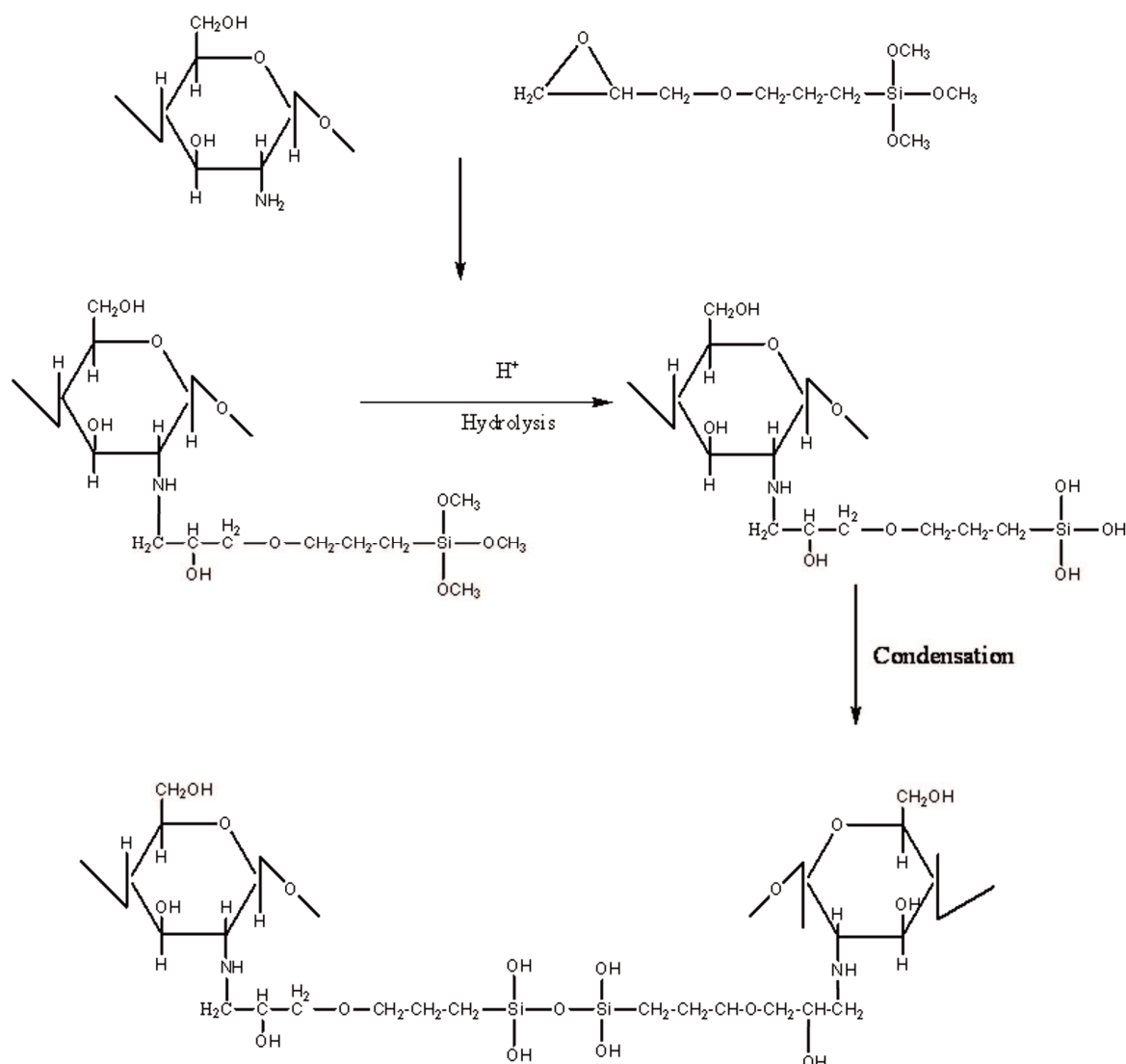


Fig. 22. Chitosan crosslinking using γ -glycidoxypropyltrimethoxysilane.

Chitosan/fumed silica nanocomposites can be prepared by dissolving the proper amount of chitosan in water containing 2 wt% acetic acid, while fumed silica is dispersed in water producing a slightly viscous transparent dispersion. Upon addition to the chitosan solution the final viscosity is increased but the solution remains transparent, in agreement with previous studies where it was found that polysaccharides containing cationic charged groups can form transparent or opalescent monolith hydrogels [138]. After solvent evaporation, the prepared chitosan/SiO₂ nanocomposite films are also transparent, which indicates that fumed silica is well dispersed in the chitosan matrix, due to the evolved interactions between the reactive groups of the polymer and silica's hydroxyls. It is well known that fumed silica

contains a lot of surface hydroxyl groups. Thus, three possible ways exist for the fumed silica particles to interact with the chitosan macromolecules; (i) hydrogen bonds between the amino or hydroxyl groups, (ii) formation of covalent bonds by condensation reactions with subsequently water evolution and (iii) electrostatic attraction between the slightly negative charges ($\sim\text{SiO}^-$) on silica particles and positive charges ($-\text{NH}_3^+$) on the chitosan macromolecules. Only in the case when fumed silica was used at higher than 15 wt% concentration a slightly opalescence was observed.

Fourier transform infrared spectroscopy (FTIR) is a versatile technique for studying specific interactions between reactive groups in polymer nanocomposites. In the case when intermolecular reactions are very strong the spectral differences are very clear, mainly in the position of the characteristic bands of the groups involved in the interactions. However, when the intermolecular forces are rather weak, the subtracted spectrum is ideal at giving information about the interactions that take place. Consequently, in the prepared chitosan/ SiO_2 nanocomposites it is expected that intermolecular hydrogen bonding between the surface hydroxyl groups of SiO_2 and amide groups of chitosan probably exist. Thus, to gain a deeper understanding of the hydrogen-bonding interactions in chitosan/ SiO_2 nanocomposites, their FTIR spectra were studied.

In the chitosan spectrum the peaks at 3418 and 3271 cm^{-1} are attributed to the $-\text{OH}$ and $-\text{NH}_2$ groups respectively, while other characteristic absorbencies are that of $>\text{N-H}$ group (in-plane bending) which is recorded at 1562 cm^{-1} (Fig. 23a). In the chitosan/ SiO_2 nanocomposites these bands are shifted to 3421 and 3262 cm^{-1} respectively for nanocomposites containing up to 10 wt% of SiO_2 . Additionally the absorption band at 1562 cm^{-1} was shifted at 1565 cm^{-1} , indicating that the $-\text{NH}_2$ groups of chitosan are involved in grafting reactions [135]. Furthermore, its absorption at 1652 cm^{-1} attributed to the $>\text{C=O}$ group was shifted to 1658 cm^{-1} in the nanocomposites, which indicates that the remaining carbonyl groups of chitosan can also participate in hydrogen bond reactions with surface hydroxyl groups of SiO_2 . However, the most remarkable shift was recorded on the silanol groups of SiO_2 , which shifted from 809 cm^{-1} to 801 cm^{-1} (Fig. 23b). These shifts indicate strong interactions between the reactive groups of chitosan and surface silanols of fumed silica and can be attributed to condensation reactions, leading to graft macromolecules, and strong hydrogen bond interactions.

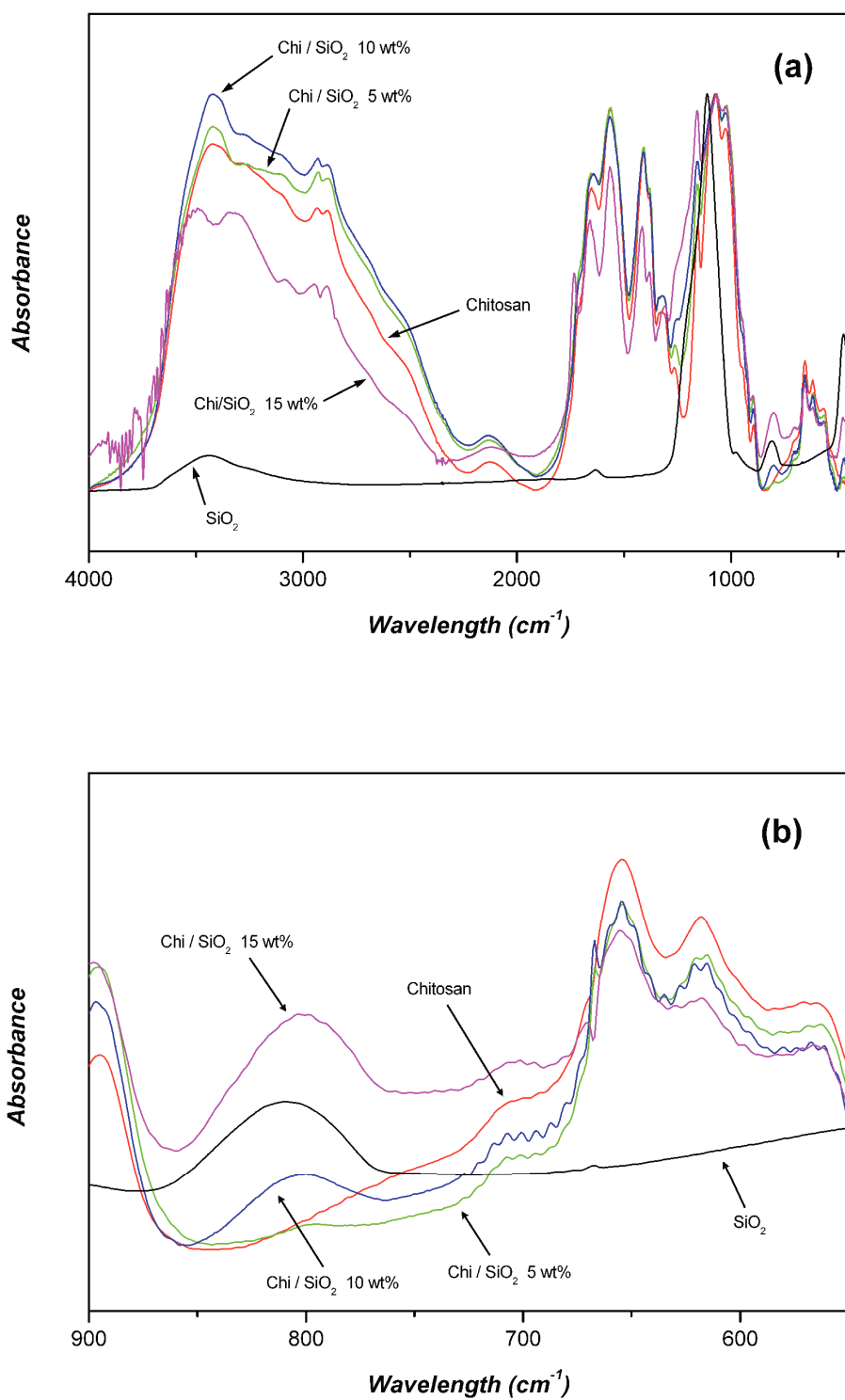


Fig. 23. FTIR spectra of Chitosan / SiO_2 nanocomposites containing different silica content.

From the dissolution tests at 90°C of chitosan/SiO₂ nanocomposites membranes, which were prepared after water evaporation at 60°C, unexpected insoluble particles were detected. This fraction remained insoluble, even after heating at the same conditions using water/acetic acid 80/20 w/w solvent. Additionally, as can be seen, the insoluble fraction increased by increasing the fumed silica concentration (Fig. 24).

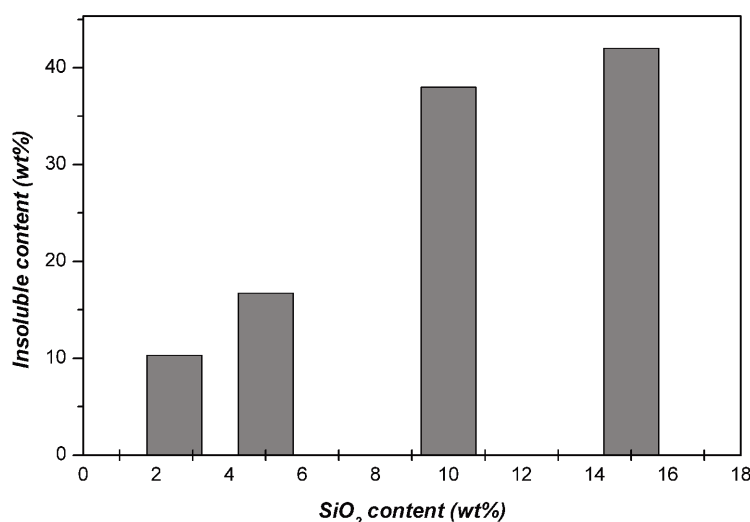
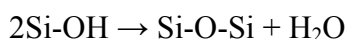


Fig. 24. Insoluble content of Chitosan/SiO₂ nanocomposites containing different silica content.

In the literature cases were reported of crosslinked chitosan treated either with γ -glycidoxypolytrimethoxysilane (GPTMS) or with 3-(trimethoxysilyl)propyl methacrylate (TMSPM), through different mechanisms [135, 139]. In both cases GPTMS or TMSPM were grafted onto silica macromolecules and in the second stage silane compounds were hydrolyzed into silanols. These groups are known to produce siloxan bridges after thermal condensation at elevated temperatures, according to the following reaction, which is accelerated at acid conditions.



However, such reactions can not form insoluble content in the present chitosan/SiO₂ nanocomposites. This insoluble fraction indicates that some interactions between the surface hydroxyl group of SiO₂ and amide groups of chitosan have taken place. The only case of such a possibility is the amide or hydroxyl groups of chitosan participating in condensation reactions with the surface hydroxyl groups of SiO₂. These reactions can be seen in Fig. 25

and are affirmed by the FTIR spectra, since the characteristic absorbance of amide groups of chitosan at 1562 cm^{-1} was shifted to 1665 cm^{-1} after chitosan treatment with SiO_2 , indicating the grafting reaction of $-\text{NH}_2$ groups. Additionally, from FTIR studies on the adsorption of small organic molecules containing $>\text{NH}$ groups like piperidine, it was found that piperidine molecules are strongly chemisorbed onto the SiO_2 surface through the protonation of $>\text{NH}$ groups by surface silanol $-\text{OH}$ groups [140]. However, it is well known that chitosan is insoluble at pH 7 and becomes soluble in acidic aqueous solutions, due to the protonation of the amine groups. Thus, the only possible route for the formation of insoluble molecules is the condensation reactions between the amide groups of chitosan and the silanol $-\text{OH}$ groups of SiO_2 .

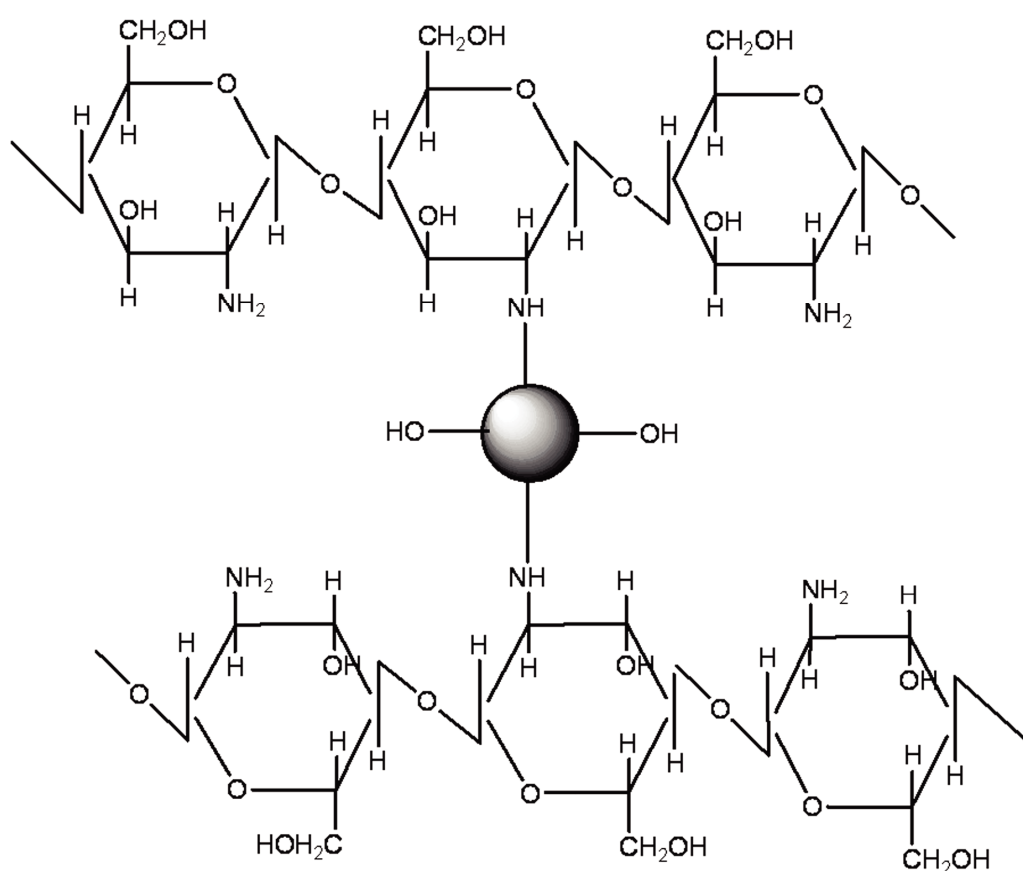


Fig. 25. Possible condensation reactions between chitosan and SiO_2 nanoparticles participating in the formation of chitosan crosslinked macromolecules.

Concerning the rheological properties of chitosan solutions containing different amounts of fumed silica, it was reported that with the addition of small silica amounts (up to 2%) the viscosity decreased [141]. This was attributed to the decrease of chitosan concentration in the dispersed medium, because of the adsorption of chitosan on the silica aggregates [142]. Furthermore, the amount of adsorbed chitosan decreased with increasing silica volume fractions, indicating a significant decrease of the silica aggregate surface accessibility, when

the silica content was increased. Thus, for silica volume fractions greater than 2%, addition of chitosan in the semidilute regime led to rheological properties attributed to the formation of a colloidal suspension of percolating silica aggregates that interacted through hydrogen bonds, mediated by silica and adsorbed chitosan. At such high silica fractions the Newtonian plateau was difficult to obtain experimentally.

The recorded T_g of chitosan is at 137°C , as can be seen from the $\tan\delta$ curves (Fig. 26), and is very close to that mentioned in the literature (140 – 150°C), which was determined using four different techniques [143]. However, it should be mentioned that there are major arguments as far as the accurate determination of the T_g is concerned and completely different values have been reported [144]. This is something that should not be considered incorrect since there is a strong dependency from the deacetylation degree, molecular mass and degree of crystallinity [145].

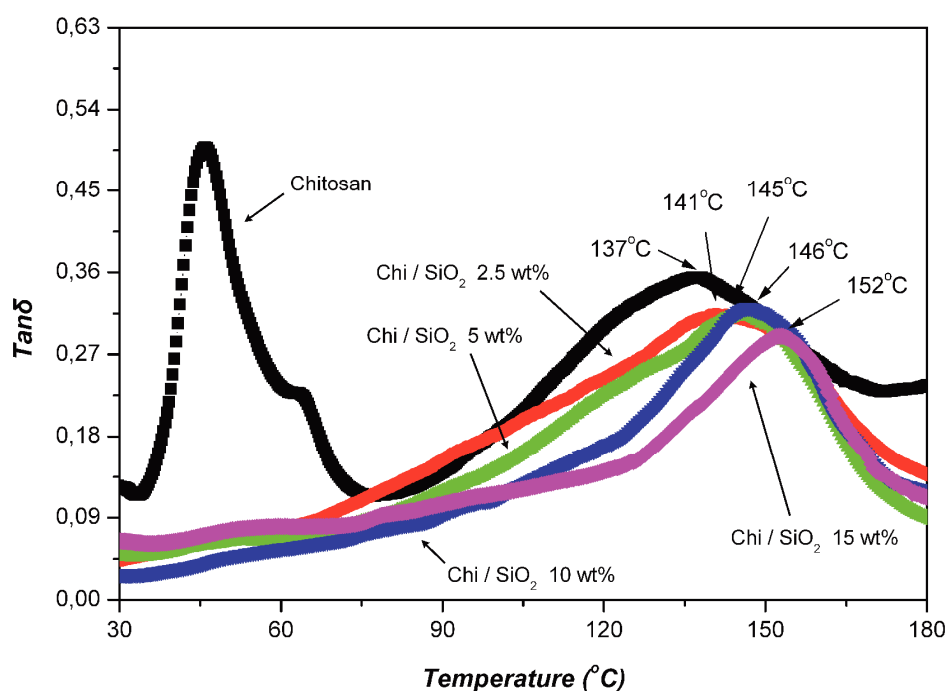


Fig. 26. $\tan\delta$ variation of chitosan/SiO₂ nanocomposites.

It is remarkable that in all nanocomposites the T_g is shifted progressively to higher temperatures by increasing the silica content in the nanocomposite. These differences indicate that the movements of certain macromolecular groups or spaces have become more difficult and higher energy is required. The cross-linked macromolecules may contribute to this shift.

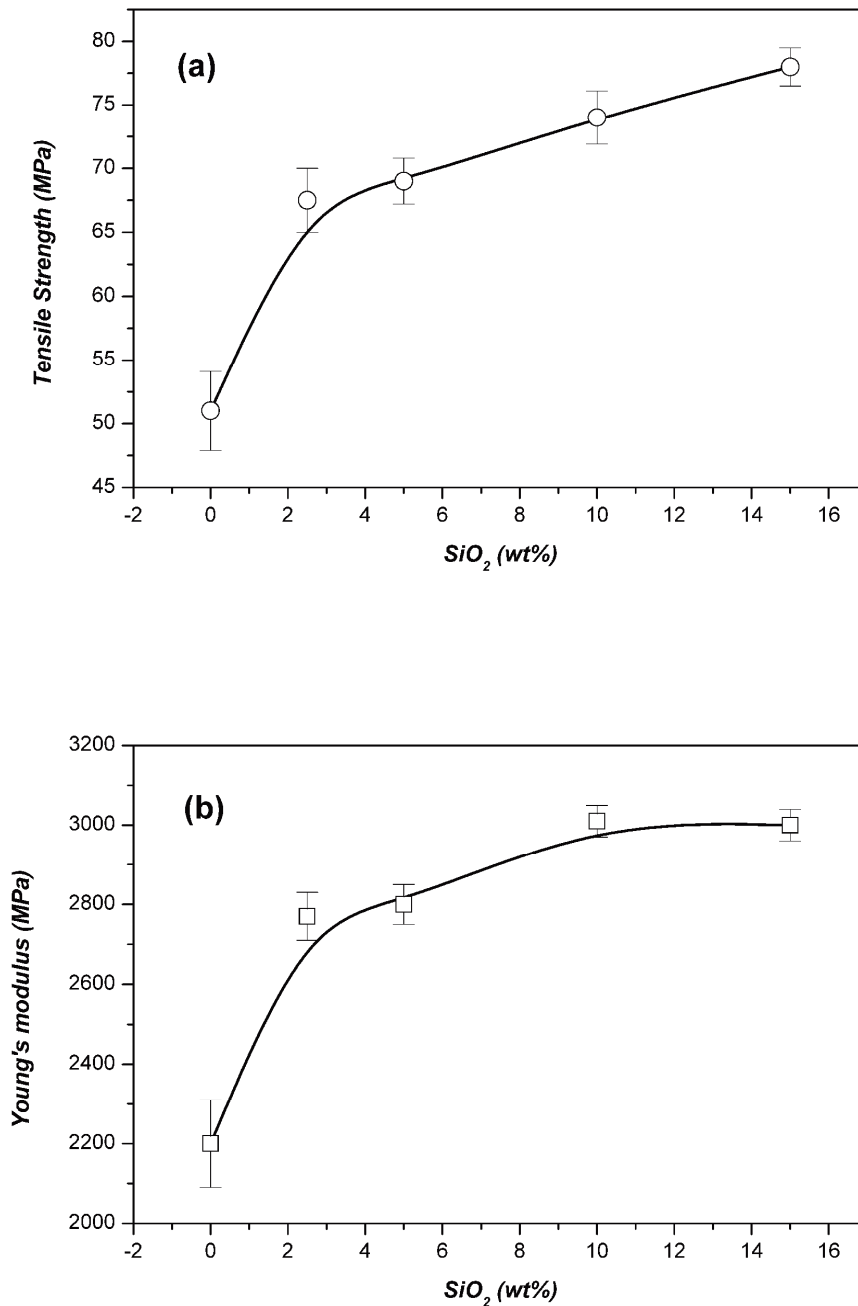


Fig. 27. Variation of mechanical properties of chitosan/SiO₂ nanocomposites containing different SiO₂ content. (a) Tensile strength and (b) Young's modulus.

Tensile properties were measured to evaluate the reinforcing effect of the nanoparticles on the chitosan matrix. Since nanoparticles have very high surface area in the Chitosan/SiO₂ nanocomposites, it is expected the applied stress can be easily transferred from the matrix onto the silica particles and the mechanical properties be enhanced. The samples extended at 50 mm/min showed superior mechanical properties (Fig. 27). As can be seen, dry neat

chitosan has a tensile strength of 51 MPa and breaks before yield point, since it is a very brittle material, with an elongation at break of 5%. After the addition of SiO₂ nanoparticles the tensile strength increases remarkably, even for nanocomposites containing only 2.5 wt% SiO₂, whereat tensile strength climbed to 67.5 MPa. In most studied nanocomposites at such nanoparticles load usually the maximum tensile strength, or better, the maximum mechanical properties' enhancement can be achieved. At higher loadings fumed silica nanoparticles tend to form extended aggregates, which result in a deterioration of the mechanical properties. However, in the studied chitosan/SiO₂ nanocomposites such behaviour was not observed. On the contrary, a further increase of the tensile strength was observed. For nanocomposites containing 10 and 15 wt%, which are considered a very high loading for nanocomposites, tensile strength achieved its highest values, 74 and 78 MPa respectively. Young's modulus also increased considerably, up to 50%, by the addition of 10 or 15 wt% SiO₂.

The thermal stability of chitosan and its nanocomposites with SiO₂ have been investigated by TG using 10°C/min heating rate under nitrogen flow. From the recorded thermogravimetric curves (Fig. 28), it is clear that the decomposition mechanism of the nanocomposites is similar to that of pure chitosan. In both cases there are three well distinguished degradation steps, which are more obvious from the DTG curves. The first step recorded at the temperature range 100-180°C, corresponding to a mass loss of 8-10 wt%, is associated with the loss of water, while the second step, which is the main decomposition step (mass loss 50-55 wt%), is recorded at the temperature range 180-340°C and corresponds to the degradation of chitosan. The third step takes place mainly at the temperature range between 340-410°C, corresponding to a very small mass loss (5-10 wt%) and is associated with chitosan deacetylation.

In the chitosan nanocomposites containing 2.5 and 5 wt% of SiO₂ the maximum decomposition temperature is observed at 1 and 2°C lower temperatures (261 and 260°C respectively), compared to that recorded for neat chitosan ($T_d = 262^\circ\text{C}$). A similar behaviour was also found in a study concerning the degradation mechanism of poly(ϵ -caprolactone)/SiO₂ nanocomposites [106]. However a significant shift of this temperature at higher values was recorded for nanocomposites containing 10 and 15 wt% SiO₂, at 266 and 268°C respectively. This is an indication that the addition of silica nanoparticles at such a high amount promotes chitosan stabilization, probably due to the formation of the cross-linked structure and a shielding effect of the fumed silica nanoparticles. Furthermore, as can be seen from the TG curves, the remaining char progressively increases, since SiO₂ is not degraded at such low temperatures.

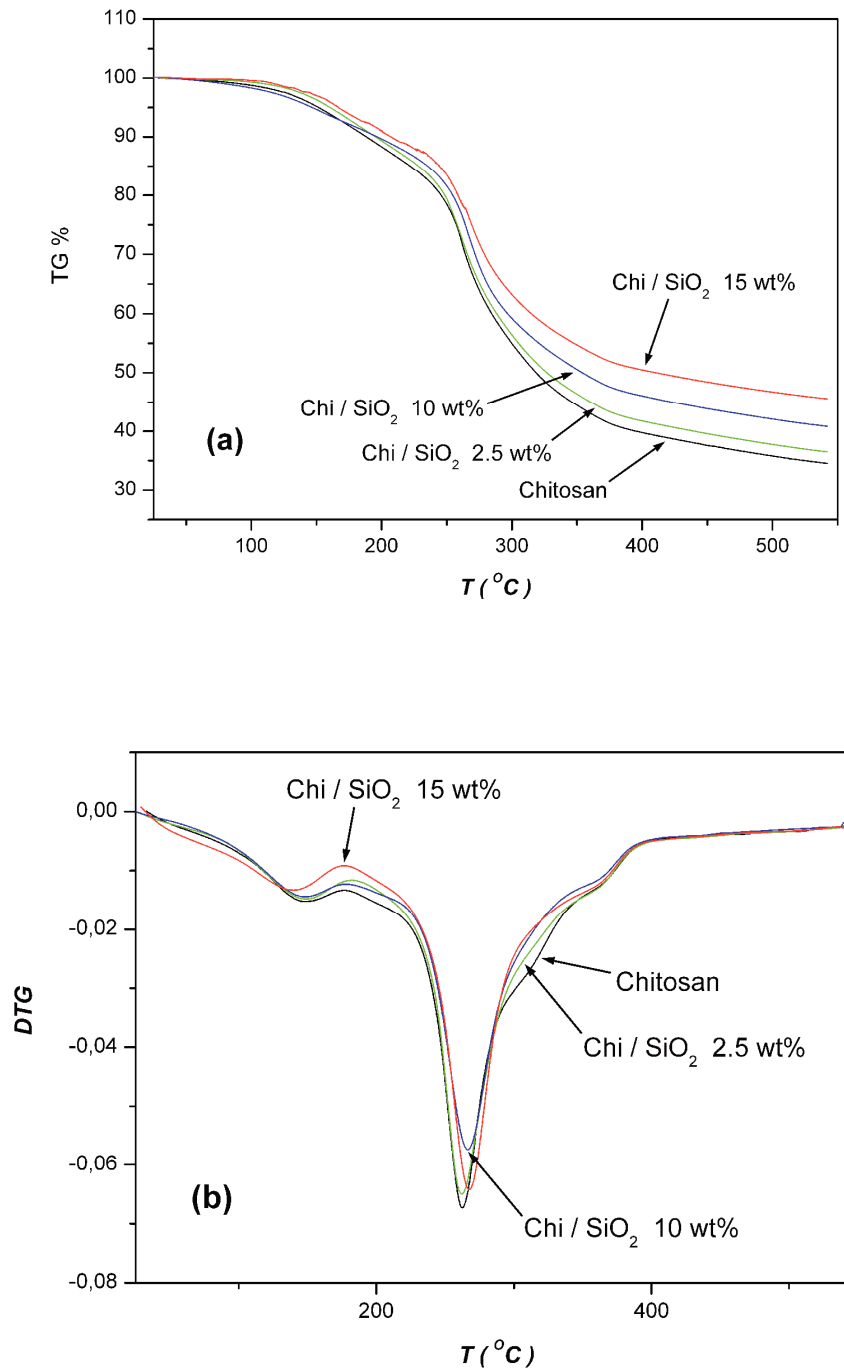


Fig. 28. (a) Mass loss (TG%) versus temperature of chitosan/SiO₂ nanocomposites and (b) derivative mass loss (DTG) versus temperature of chitosan/SiO₂ nanocomposites (heating rate $\beta = 10^\circ\text{C/min}$).

5.2 POLY(N-VINYL PYRROLIDONE)

Poly(n-vinylpyrrolidone) (PVP) is a readily water soluble macromolecular compound, as well as in most common polar organic solvents, such as alcohols, amines, acids, and chlorinated hydrocarbons, exhibiting exceptional low toxicity and high biocompatibility. It is found as a white powder. The glass transition temperature depends on the water content, which when completely dry is given at 175 °C. It is highly hygroscopic, absorbing about 30% water at 60% humidity. Aqueous solutions of PVP are stable to electrolyte addition and the viscosity of the solution decreases with increasing temperature and with strong shearing. It is insoluble in esters, ethers, ketones, and hydrocarbons. Completely anhydrous PVP is also soluble in toluene. It is highly compatible with numerous film forming polymers, water-soluble binders, and plasticizers. On solution casting, a clear, high-gloss, hard film is formed. The polymer is chemically inert. The lactam group is saponified only by the action of concentrated acids, with the formation of poly[vinyl(g-amino)butyric acid]. In cosmetics, PVP is used as film former in setting lotions and hairsprays and as a thickening agent and protective colloid in cosmetic emulsions. In pharmacy, PVP has a wide spectrum of applications; as a solubilizer, as a crystallization retarder, for detoxification, for reducing the irritant action and toxicity of certain substances, as a tablet binding and coating agent, as a suspension stabilizer, and as a dispersant for pigments in tablet-coating suspensions. The PVP complex with iodine is used as a disinfectant. It is also used for the clarification of beer and other beverages. PVP forms hard, transparent, strongly adherent films on glass, metal, plastics, and cellulose, and is used in the adhesives industry as a binder and water-soluble hot-melt adhesive. Polyvinylpyrrolidone is also used as an auxiliary in textile finishes, as a dye acceptor for synthetic fibers, as a leveling and stripping agent for dyes, as a thickener for printing inks and latex paints, as a dispersant in laundry detergents, as a protective colloid in the emulsion and suspension polymerization of many polymers, and as a water-binding agent for the concentration of protein solutions.

Its nanocomposites with fumed SiO₂ are transparent, which is an indication that nanoparticles are finely dispersed in polymer matrix. The prepared nanocomposite with SiO₂, even at high silica loading (15 wt%) remain very brittle and thus it wasn't possible to measure their mechanical properties with high accuracy. However, from DMA studies it was revealed that as the amount of silica nanoparticles increased the material became stiffer. As can be seen in Fig. 29, storage modulus in all nanocomposites, at low as well as at high temperatures, is much higher than the storage modulus of the pure PVP. The T_g is often designated by either the temperature at which the dynamic loss modulus is at a peak height or the temperature at which the loss tangent $\tan \delta$ (E''/E') exhibits a peak. As can be seen from $\tan \delta$ variation there is a shift of only 1-2°C of T_g in higher temperatures. Such an increase in the glass transition temperature of polymer nanocomposites is very common due to the formed interphase between nanoparticles and polymer matrix. Macromolecules placed at this interphase have lower mobility, especially when interactions develop between the components, resulting in an

increase of the rigidity of the nanocomposites. However, this increase is very small, indicating that the evolved interactions are weak rather than strong.

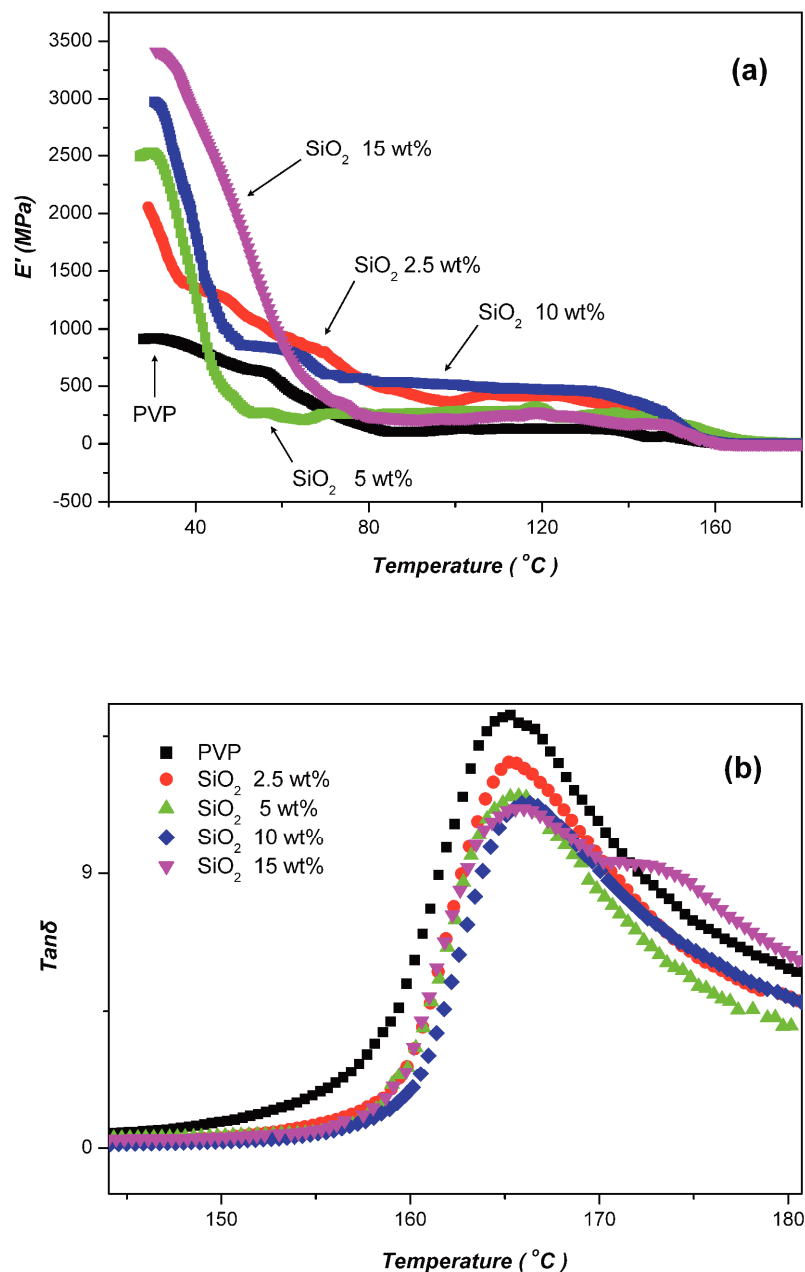


Fig. 29. Dynamic mechanical scans of PVP/SiO₂ nanocomposites as function of temperature (a) storage modulus and (b) $\tan \delta$.

In order to evaluate the effect of hydrogen bonding between PVP and SiO₂ their spectra were collected. From all spectrum areas three regions are of great importance. The area between 800-1200 cm⁻¹, where the silicate groups are absorb, the carbonyl group area, ranged between 1600-1750 cm⁻¹ and the respective of hydroxyl groups at 3350-3700 cm⁻¹, where the

hydrogen bonding takes place (Fig. 30). In the PVP spectrum the characteristic peaks are at 1662 cm^{-1} and at 1291 cm^{-1} attributed to the stretching of amide $>\text{C}=\text{O}$ and $>\text{N}-\text{C}$ groups respectively. Since PVP is very hydroscopic, to avoid any plasticizing effect of the presence of water, the sample was extensively dried for 24 h at 130°C . The relatively low frequency of PVP carbonyl group compared to the usual carbonyl frequencies can be explained by the contributions of the $>\text{N}-\text{C}$ adjacent group and to the resonance effect that lowers the wavenumber of stretching vibration. The $-\text{OH}$ stretching vibration of hydrogen bonded silanol groups can be observed at 3438 cm^{-1} , while this corresponding to the free hydroxyl groups at 3747 cm^{-1} is very weak and hardly detectable. However, the most intense peak of SiO_2 is that corresponding to $\text{Si}-\text{O}-\text{Si}$ groups recorded in FTIR spectrum at 1111 cm^{-1} . The intensity and the position of these characteristic peaks of both compounds allow us the easy interpretation of the kind of the formed interactions.

From the FTIR spectra of the prepared nanocomposites it is obvious that the characteristic peaks of $\text{Si}-\text{O}-\text{Si}$ remained unaffected and are recorded at the same wavenumber as in pure SiO_2 , while from the $\text{Si}-\text{O}$ absorbance at 3438 cm^{-1} there is no clear shift since in this area PVP also has a strong peak. However, it was reported that a complete disappearance of the free hydroxyl groups at 3737 cm^{-1} for $C_{\text{PVP}}/C_{\text{SiO}_2} \approx 0.2$ is due to the formed hydrogen bonds between the carbonyl groups of PVP and the surface hydroxyl groups of SiO_2 . At such ratio a PVP monolayer or slightly greater coverage was formed on the silica surface [146] while for a concentration ratio of $C_{\text{PVP}}/C_{\text{SiO}_2} \leq 0.1$ an irreversible adsorption of PVP into SiO_2 particles was observed since PVP is not washed from silica [147]. A large number ($\sim 100/\text{PVP}$ molecule) of polar electron-donor $\text{N}-\text{C}=\text{O}$ bonds that are between the pyrrolidone rings may be responsible for practically irreversible adsorption of the polymer molecules on silica.

PVP molecules are not washed from the silica surfaces at $C_{\text{PVP}}/C_{\text{SiO}_2} \leq 0.1$ because of bonding in multicentered adsorption complexes, and approximately two-thirds of $\text{C}=\text{O}$ groups at $\theta < 1$ form hydrogen bonds with silanols, as simultaneous breaking of all these bonds is unlikely. These wavenumber shifts indicate that α PVP/ SiO_2 hybrid material is created due to the hydrogen bonds formation between the carbonyl groups of PVP and surface hydroxyl groups of SiO_2 [148]. The energy of these hydrogen bonds as calculated according to Kitaura-Morokuma method is $\Delta E_{\text{HF}} = -41\text{ kJ/mol}$, which is significant higher from the interaction energy between the PVP molecules (-7 kJ/mol) [149]. To calculate the ΔH value for PVP interacting with the surface silanols, the following equation is used [150]:

$$-\Delta H = 1.9 \Delta_{\text{VOH}} + K$$

where ΔH denotes the enthalpy in kJ/mol, Δ_{vOH} the IR wavenumber displacement from the surface silanols in cm^{-1} , and K is a constant (12.6 kJ/mol). This estimation gives $-\Delta H=48$ kJ/mol.

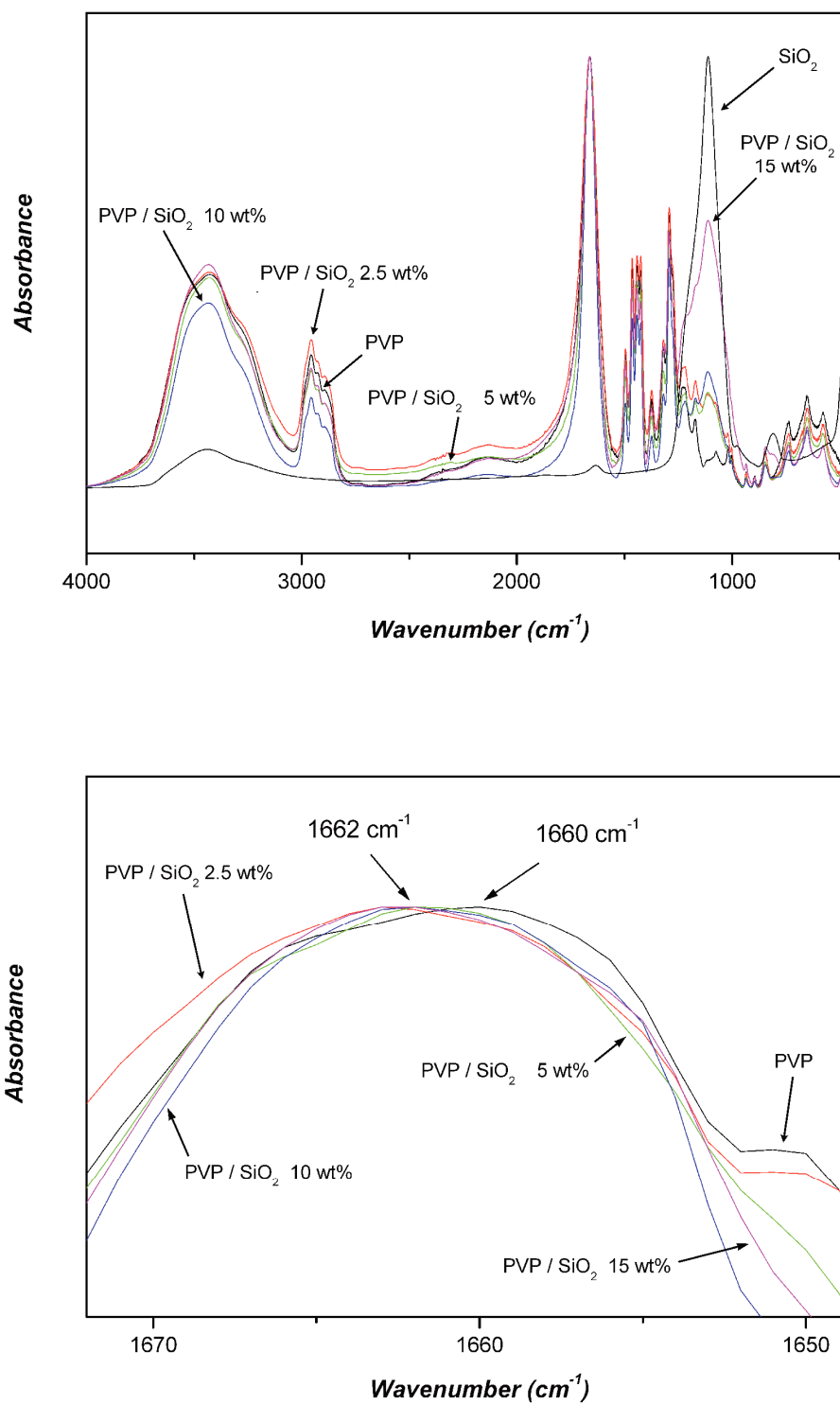


Fig. 30. FTIR spectra of PVP/SiO₂ nanocomposites.

In the studied PVP nanocomposites with fumed silica the only shifts that were observed are in the wavenumber of the carbonyl groups of PVP to slightly higher positions, from 1660 to 1662 cm^{-1} (Fig. 30). This shift is evidence that carbonyl groups of PVP participated in hydrogen bonds with the reactive groups of SiO_2 . However, since the difference between the absorbance in neat PVP and its nanocomposites is very small, it must be supposed that these interactions are of low intense. This is in accordance with DMA results where only a small shift was observed on the nanocomposites' T_g .

These hydrogen bonds between the carbonyl groups of PVP and hydroxyl groups of SiO_2 may affected the silica dispersion on the PVP matrix. From SEM micrographs of PVP/ SiO_2 nanocomposites it was obvious that some silica particles, spherical in shape, could be detected in the PVP surface (Fig. 31). Their diameter seemed to be independed from the SiO_2 content and in all nanocomposites it ranged between 80-150 nm. From these micrographs it can be concluded that fumed silica creates small agglomerates. It seems that the involved interactions break the large silica agglomerates that were reported in other nanocomposites like PP/ SiO_2 , [72] into smaller particles. The only difference between the nanocomposites containing different amounts of silica nanoparticles is that increasing the SiO_2 content more silica nanoparticles can be observed. Low amounts of water or ethanol (30 wt% with respect to the silica content) promote the finer distribution of the silica particles in PVP.

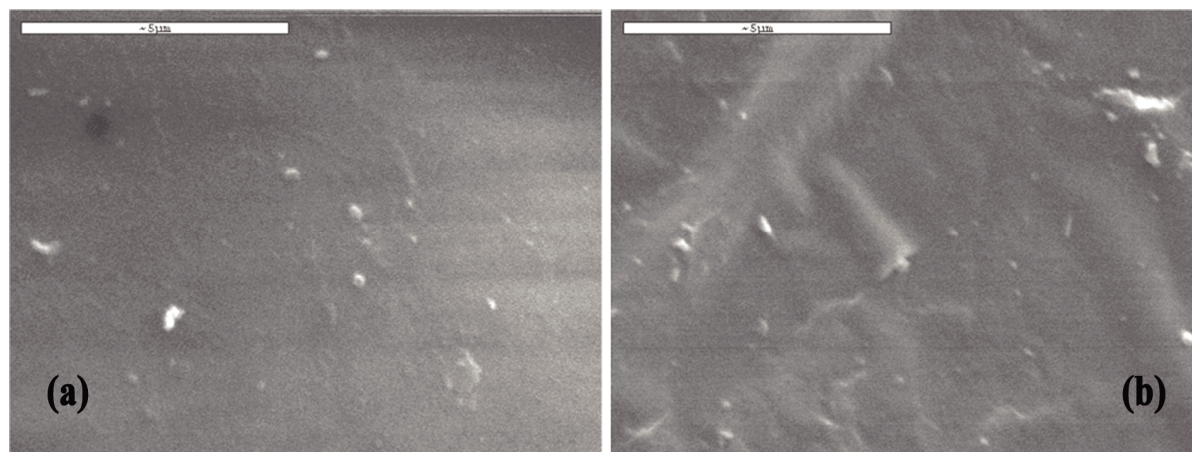


Fig. 31. SEM micrographs of PVP/ SiO_2 nanocomposites containing (a) 5 and (a) 15 wt% SiO_2 .

Thermal degradation of PVP/ SiO_2 nanocomposites was studied by determining their mass loss during heating. In Fig. 32 and 33 are presented the mass loss (TG %) and the derivative mass loss (DTG) curves at heating rate 10°C/min for all nanocomposites in comparison with neat PVP. In both thermograms two stages of mass loss can be followed. The first one is taking place at low temperatures (up to 200 °C) where the absorbed water from PVP is evaporated. This mass loss corresponds of about 5 wt% of the initial weight. The second

mass loss, which corresponds to the main decomposition stage of PVP, takes place at temperatures up to 450 °C, where about 90 wt% of the polymer is degraded. The temperature at which the maximum decomposition rate takes place is recorded at 436°C. From the TG curve it can be seen that PVP presents a relatively good thermostability, since no significant weight loss occurred up to 300°C, ignoring the water loss. A temperature $T_d(-2 \text{ wt}\%)$, at which 2.0 wt% of the neat PVP sample has already been thermally degraded and lost, was hereby taken as index to express its thermal stability. This temperature is close to 320°C. The thermal behaviour of PVP/SiO₂ nanocomposites is identical with that discussed for neat PVP, with the most significant difference being the remaining char. Since SiO₂ is not degraded at such low temperatures, by increasing its content in the PVP matrix the remaining char is higher and proportional to the added amount of SiO₂. Furthermore, examining more carefully the DTG curves in the main decomposition stage, it can be seen that the temperature where the maximum rate of decomposition takes place is shifted to slightly higher temperatures. Thus, for nanocomposites containing 10 and 15 wt% these temperatures are recorded at 439 and 441°C respectively, while for nanocomposites containing lower SiO₂ content this shift is only 1°C at higher temperatures. This shifts reveal that nanocomposites formation can increase the thermal stability of PVP, which is a common phenomenon in nanocomposites. It is well known that when an inorganic particle is dispersed in a polymer matrix, the dispersed layers are impermeable towards small molecules –gases or volatile liquids- that are generated during decomposition and a much longer route around the nanoparticles is needed for their removal from the decomposed matrix. Thus, improved thermal stability of these nanocomposites can be attributed to the shielding effect of these nanoparticles.

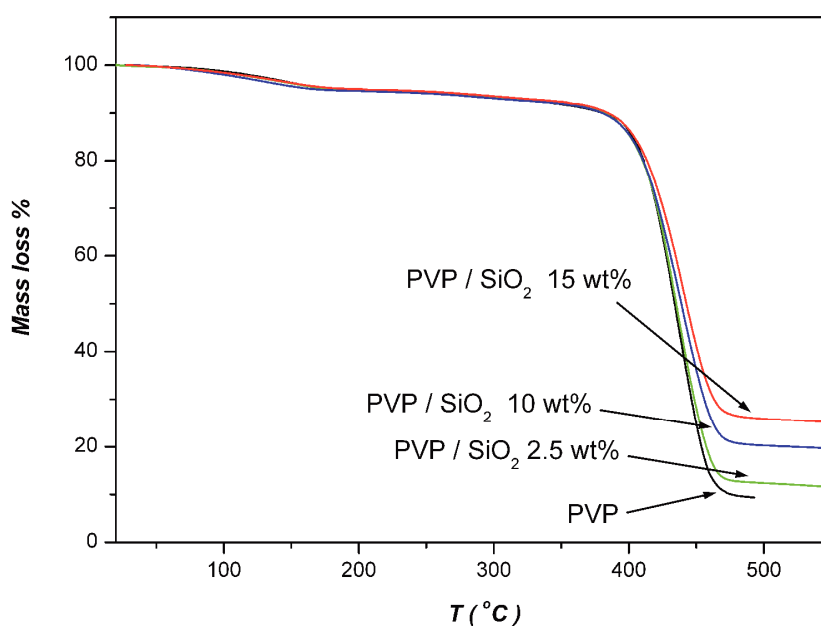


Fig. 32. Mass loss (TG%) versus temperature of PVP/SiO₂ nanocomposites with heating rate $\beta=10^\circ\text{C}/\text{min}$.

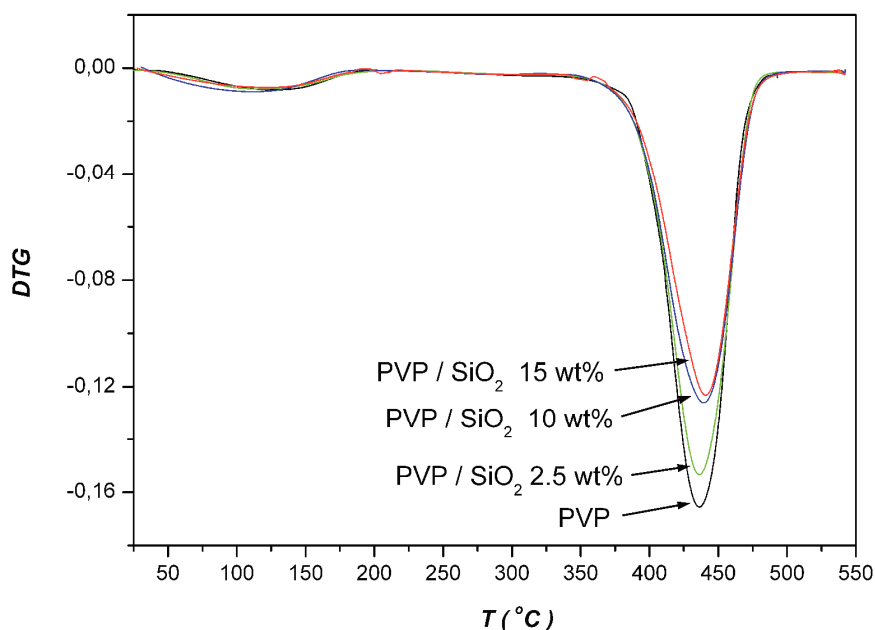


Fig. 33. Derivative mass loss (DTG) versus temperature of PVP/SiO₂ nanocomposites with heating rate $\beta=10^{\circ}\text{C}/\text{min}$.

5.3 POLY(VINYL ALCOHOL)

Commercial poly(vinyl alcohol) (PVA) is a hydrophilic polymer containing pendant hydroxyl groups. It cannot be prepared by the direct polymerization of vinyl alcohol and thus it is derived from the hydrolysis of poly(vinyl acetate) (PVAc). Its aqueous solution can form transparent films. However, it is not soluble in cold water and must be heated at temperatures higher than 90°C, whereat the strong hydrogen bonds are weakened. It is used mainly in paper and textile sizing, for preparation of desalination and pervaporation membranes, as oxygen barrier additive, in food wrappings, etc. PVA/SiO₂ membranes have recently gained increased interest for fuel cell applications, since the incorporation of silica particles in the PVA matrix reduces the free water ratio of the membranes and results in a remarkably reduction of methanol permeability [151-153]. In the case of PVA/SiO₂ nanocomposites, most of the used silica nanoparticles have been prepared by the sol-gel technique using tetraethoxysilane as precursor [151, 154-160]. Nanocomposites prepared using fumed silica nanoparticles are limited, without any extensive study having been carried over the effect of silica nanoparticles on physical and thermal properties [161, 162]. In order to improve the thermal and electrochemical performance of PVA membranes, usually crosslinking is necessary by the addition of glutaraldehyde. Although the addition of inorganic particles can increase the mechanical properties of a polymer matrix and reduce its permeability, just recently a combinatory procedure for crosslinking and silica addition was reported [163]. For

this reason γ -glycidoxypyrtrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) were used simultaneously. The crosslinked PVA macromolecules were prepared by a combination of addition reactions of PVA's hydroxyl groups with the glycidyl groups of GPTMS and the condensation reactions of silanol groups produced after hydrolysis of GPTMS and TEOS.

PVA/SiO₂ films using fumed silica nanoparticles can be prepared by a simple casting procedure from aqueous solutions. PVA was dissolved at 95°C while fumed silica was dispersed in water. Both PVA solution and silica dispersion were mixed under sonication and the solutions were maintained at 50°C for water evaporation. SEM micrographs of PVA/SiO₂ nanocomposites demonstrated the existence of silica aggregated particles in the range of 100-150 nm, along with some fine fumed silica dispersed particles. Additional morphological differences of PVA/SiO₂ films with the pure PVA films were not detected. The film's surface in all samples was almost identical.

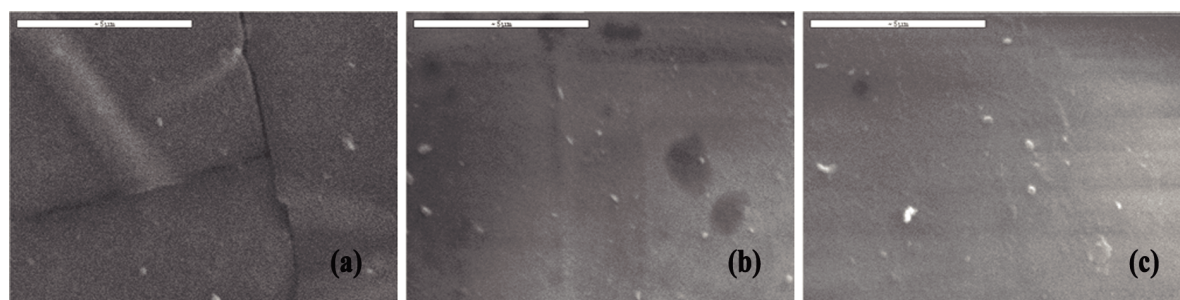


Fig. 34. SEM micrographs of PVA/SiO₂ nanocomposites containing (a) 2.5, (b) 5 and (c) 15 wt% SiO₂.

It is well known that filler dispersion and adhesion with the polymer matrix are of great importance for improving the mechanical behaviour of composites. Fine control of the interface morphology of polymer nanocomposites is one of the most critical parameters to impart desired mechanical properties to such materials. Stress-strain curves of PVA/SiO₂ nanocomposites revealed that these materials have a very high tensile strength, which is directly related to the silica nanoparticles' content. As can be seen in Table 4, tensile strength increases with increasing SiO₂ content, reaching its maximum (about 68 MPa) at 15 wt% SiO₂ loading. This value corresponds to a more than 30% increase, compared with the tensile strength of neat PVA, and is unusual for such thermoplastic nanocomposites. In most of them a maximum increase was achieved for nanoparticles' loading up to 2.5-5 wt%, while after this content a decrease is recorded. Young's modulus also increases with SiO₂ content, in agreement with tensile strength increase, indicating that the nanocomposites became progressively harder. Mechanical properties of the polymer nanocomposites result from the rich interplay between the polymer matrix and inorganic nanoparticles, which is greatly influenced by the length scale of the different component phases as well as from their

interfacial interactions. This increase must be attributed to the silica nanoparticles which are stiffer than the PVA matrix, as well as from the evolved interactions that take place between the reactive groups. On the contrary a substantial decrease is calculated for the elongation at break, which is directly related to the SiO₂ content, because the mobility of PVA chains is depressed by the presence of silica nanoparticles. However, even at 15 wt% SiO₂ the elongation at break remains at an acceptable value.

Table 4. Mechanical properties of PVA/SiO₂ nanocomposites.

PVA/SiO ₂	Tensile strength at break (MPa)	Young's Modulus (MPa)	Elongation at break (%)
100.0/0.0	51 ± 2.3	926 ± 30	520 ± 30
97.5/2.5	60 ± 1.5	897 ± 40	423 ± 50
95.0/5.0	62 ± 3.1	940 ± 35	375 ± 40
90.0/10.0	64 ± 2.1	966 ± 35	355 ± 63
85.5/15.0	68 ± 1.6	1078 ± 40	294 ± 35

FTIR spectrum of PVA reveals the characteristic peaks of PVA at 3490 cm⁻¹ (O-H stretching), at 2980 and 2850 cm⁻¹ (-CH₂ stretching), at 1425 cm⁻¹ (-CH₃/O-H bending), and 1095 cm⁻¹ (C-OH stretching). It was reported that PVA can form strong hydrogen bonds with the surface hydroxyl groups of SiO₂ [164]. In the recorded FTIR spectra of PVA/SiO₂ nanocomposites there are many shifts of the characteristic peaks (Fig. 35). As can be seen there is a shift to lower wavenumbers of the C-OH stretching from 1095 to 1089 cm⁻¹, indicating that the hydroxyl groups of PVA participate in such hydrogen bonds. Furthermore, in the area of 3100-3700 cm⁻¹ the peaks recorded in neat PVA at 3485 and 3296 cm⁻¹ are shifted; the first one at higher wavenumbers 3498-3536 cm⁻¹, depending by the silica amount, and the second one from 3294 at lower wavenumbers, such as 3287 cm⁻¹. Some shifts, but in lower extent, are also visible in the peak of the carbonyl group at 1007 cm⁻¹, which is shifted to 1011 cm⁻¹. This is an indication that except for the hydroxyl groups of PVA, the carbonyls of the remaining un-hydrolyzed acetate groups of PVA can also participate in hydrogen bonding (Fig. 36).

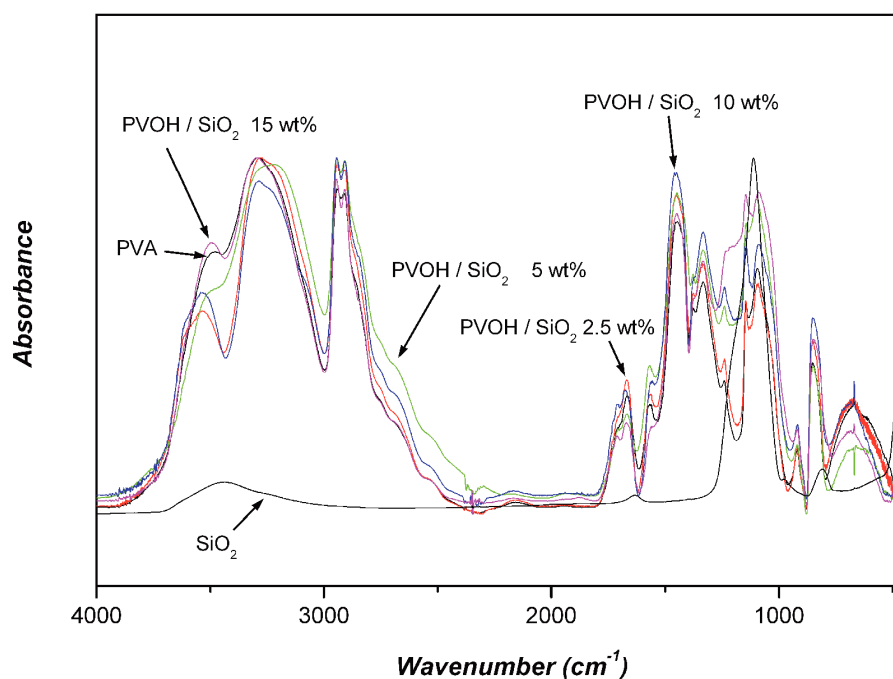


Fig. 35. FTIR spectra of PVA/SiO₂ nanocomposites containing different silica content.

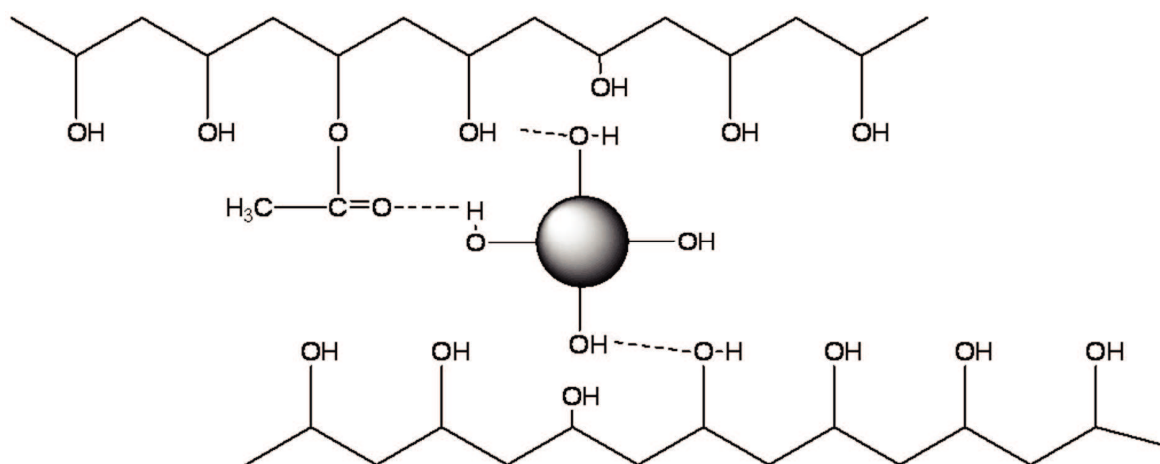


Fig. 36. Interactions between PVA and SiO₂ nanoparticles.

WAXD patterns of neat PVA exhibits a strong peak at $2\theta=19.5^\circ$ (Fig. 37), corresponding to the (101) plane of PVA crystals, as well as to two additional peaks with low intensity at $2\theta=11.4$ and 40.8° . The intensity of these peaks becomes progressively lower by increasing the silica content in the nanocomposites, but the position of the peaks remains unchanged. It

was found that the peak at $2\theta=19.5^\circ$ was markedly broadened due to the addition of silica nanoparticles for concentrations higher than 30 wt%, which is an indication that the crystal growth was inhibited from the addition of SiO_2 [160]. However, such effect was not observed in our nanocomposites, probably because the silica content is much lower than in the reported study.

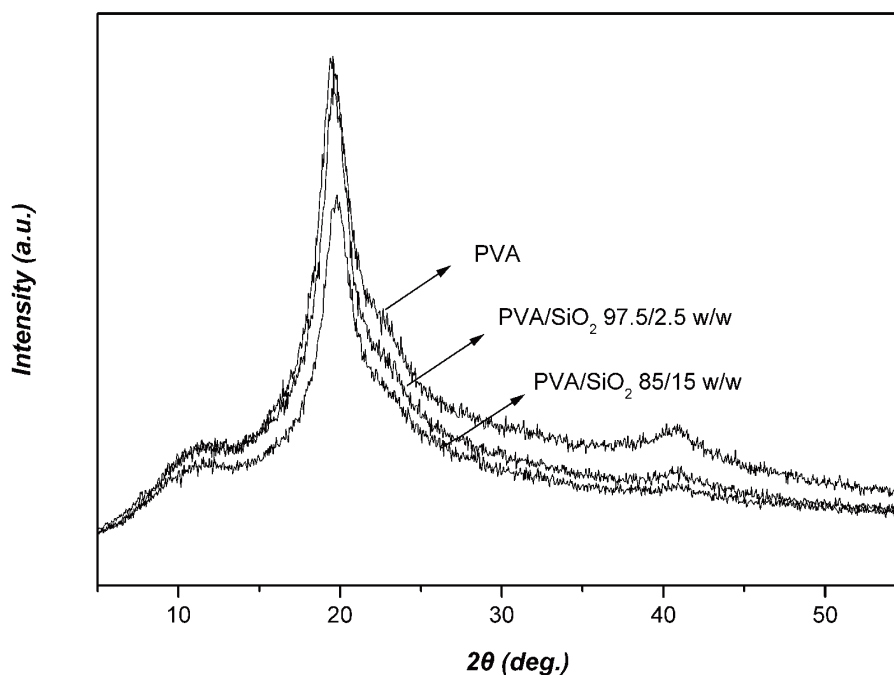


Fig. 37. WAXD patterns of PVA/SiO₂ nanocomposites containing different silica content.

Fig. 38 demonstrates the representative storage modulus, loss modulus and $\tan\delta$ of PVA/SiO₂ nanocomposites, as recorded from dynamic mechanical analysis in the temperature range of 25-150°C. From the storage modulus (E') curves it can be seen that there is a sharp decrease from temperature 25°C up to 50°C and after that temperature E' remains practically stable. Additionally, at low temperatures it is obvious that, as the amount of silica increases, storage modulus obtains higher values. Loss modulus (E'') at this temperature area is recorded as a peak whose intensity and position differs and is related to the added silica content in the nanocomposites.

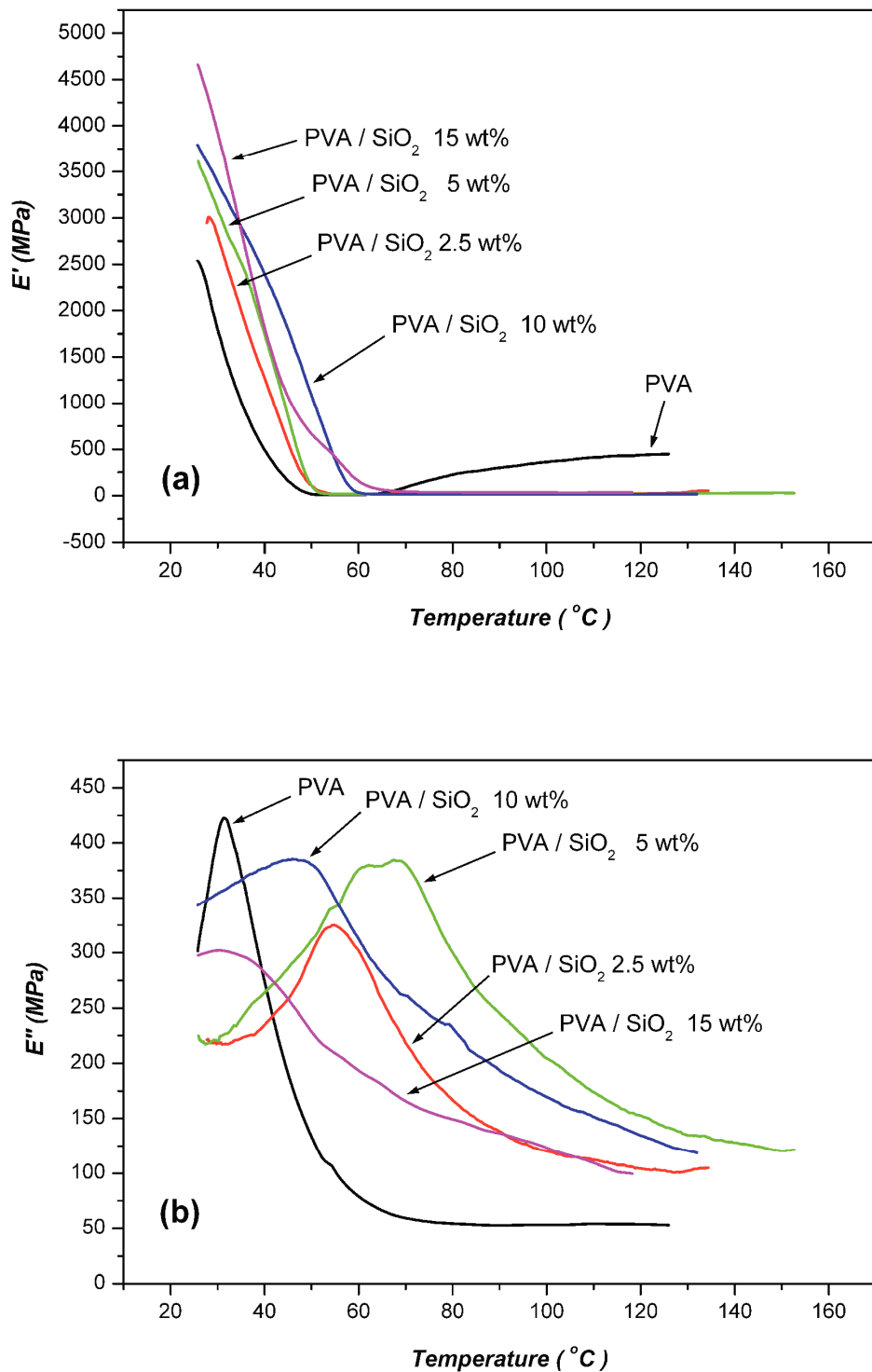


Fig. 38. Dynamic mechanical measurements of PVA/SiO₂ nanocomposites as function of temperature. (a) Storage modulus and (b) loss modulus.

Molecular motions of polymeric materials are usually evaluated by the dynamic viscoelastic measurements. $\tan\delta$, which directly corresponded to the T_g of a polymer, can give much more information about the effect of SiO_2 on the PVA matrix. As can be seen in Fig. 39, PVA has a glass temperature transition at 53.3 °C. This temperature shifts to higher values by increasing the silica content, specifically to 58.7, 62.8, 71.0, 76.1 °C for nanocomposites containing 2.5, 5, 10 and 15 wt% SiO_2 . Furthermore, the intensity of the $\tan\delta$ peak is lowered with higher SiO_2 contents. This behaviour proves that SiO_2 interacts quite strongly with the reactive groups of the polymer, as already verified by FTIR measurements, and restricts the motion of the PVA macromolecules. Hydrogen bonds formed between fumed silica and PVA act as physical cross-links. Furthermore, in a recent study it was reported that some cross-links can be generated by heating PVA and silica nanoparticles at elevated temperatures [165]. So this possibility should not be excluded in such samples.

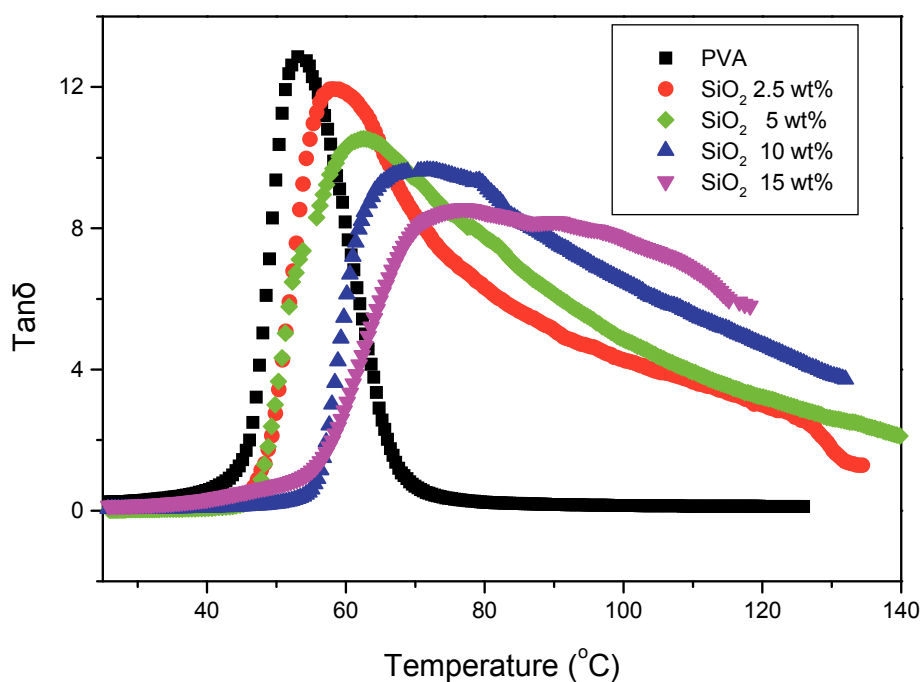


Fig. 39. $\tan\delta$ of PVA/ SiO_2 nanocomposites containing different SiO_2 content as a function of temperature.

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CHAPTER 5

Hard and Tough Nanocomposite Coatings: Design, Synthesis and Characterization

Sam Zhang*, Hui Li Wang

School of Mechanical and Aerospace Engineering,
Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798, Republic of Singapore

*email address: msyzhang@ntu.edu.sg

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1. INTRODUCTION

Nanocomposite solids represent the subject of rapidly growing fundamental and applied efforts by researchers and engineers because of their outstanding physical, mechanical, chemical and other properties. These outstanding properties are due to the interface and nanoscale effects associated with structural peculiarities, where the volume fraction of the interfacial phases is extremely high, and the crystallite size does not exceed 100 nm. Of special importance from both fundamental and applied aspects are the unique mechanical properties of nanocomposite materials. Nanocomposite coatings exhibit the outstandingly high hardness, good toughness and enhanced tribological characteristics, highly desirable for applications. Composite materials such as multilayer coatings and isotropic nanocomposite coatings, having structures in the nanometer range, can even show properties which can not be obtained by a single coating material. Nanocomposite single layer coatings being composed of nanocrystalline hard materials and amorphous phases are the subject of intensive Research & Development efforts towards the design of new improved wear resistance, good high-temperature stability, and improved friction properties are important characteristics for use in applications such as cutting tools. These nanocomposite coatings are far superior to their constituent phases. First of all, the hardness can be enhanced due to the hindering of dislocation motion at interfaces. Besides, the toughness can be improved since their architecture favors the hindering of crack development and propagation and enhancement ductility by grain boundary sliding and atomic diffusion. Of course there will be some other significant contributions (for example, electrical and optical properties), however in this chapter, the main focus is the hardness and toughness of hard coatings. This approach of using nanocomposites is an alternative to using specific alloying elements in single-phase coating materials (to improve properties such as hardness and toughness) and provides far better flexibility in tailoring multifunctional coatings.

2. CLASSIFICATION

Hard coatings can be classified in four separate groups: (I) intrinsically superhard materials such as diamond, diamond-like carbon (DLC), and cubic boron nitride (c-BN); (II) coatings in which the hardness is due to a complex, synergistic effect of ion bombardment during their deposition by plasma chemical or physical vapor deposition (PECVD or PVD); (III) nanocomposite coatings which require thermodynamically driven phase segregation; and (IV) multilayer structures.

(I) The first group has been studied extensively by many researchers who utilize high temperatures and high pressure as well as PCVD and PVD techniques and are not outside the scope of this study.

(II) The second group includes coatings prepared under bombardment of energetic ions during their growth and displaying hardness enhancement and nano-grain development. This ion bombardment which renders densification and high compressive stresses, can lead to

improved hardness, morphology, structure and nanostructure. A number of researchers including Hoffman and Gaerttner [1], Sundgren [2] and Musil [3] have studied and reviewed the effects of ion bombardment on the film properties.

(III) The third group includes nanostructure superhard materials originating from “thermodynamically driven segregation”.

(IV) The fourth group includes heterostructures consisting of alternating layers of transition-metal nitrides and nanocomposites consisting of transition-metal nitride nanocrystals embedded within an amorphous structure of covalent nitride.

Coatings can be differentiated by their hardness, H , into three main categories: hard with $H < 40$ GPa; superhard with $H > 40$ GPa; and ultrahard coatings with $H > 80$ GPa. Due to the scarcity of ultrahardness, we will focus on hard and superhard coatings.

3 DESIGN METHODOLOGY FOR NANOCOMPOSITE COATINGS

3.1 MATERIALS SELECTION

The selection of materials to be combined in such a multiphase structure should refer to their phase relations in the corresponding phase diagram. The design of nanocomposite coatings can not be doubted for the usage of hard phase as a base. Most hard coating are composed of ceramic compounds such as oxides, carbides, nitrides, ceramic alloys, cermets, metastable materials such as diamond, and cubic boron nitride. The hardness and toughness of some popular bulk materials are listed in table 1. The bulk hardness and toughness can be selected as a reference although the counterparts for coatings may differ greatly. The toughness and hardness will depend on the composition, stoichiometry, impurities, microstructure, imperfections, and in the case of coatings, the preferred orientation (texture). Diamond, diamond-like carbon (DLC), cubic boron nitride, and the new class of nanocomposites are currently referred to as superhard materials.

3.2 MICROSTRUCTURE DESIGN

The aim of developing a new material is to achieve unique or enhanced mechanical, physical or chemical properties through creating a particular microstructure. This means that the development of a new material requires aspects of materials design. The resulting microstructure and property profile of a multiphase or nanocomposite coating is clearly determined by the plasma process parameters and by the kinetics of the deposition and growth process. These can be completely different by either fine-tuning the ratio of the volume fraction of the nanocrystalline and of the amorphous phases, or, by fine-tuning the crystallite sizes [4, 5]. Consequently, the properties of nanocomposite coatings are dominated by the grain boundaries and interfaces [6, 7].

Table 1. Vickers microhardness (H_V) and fracture toughness of some hard bulk materials

Materials	H_V [8]	K_{IC} (MPa m ^{1/2})
Diamond	96±5	3.4 [9]
B ₄ C	63±5	2.8 [10]
AlB ₂	37±2	NA
B ₆ O	35±5	<1 [11]
WB	35±3	2.5-6.4 [12]
TiB ₂	33±2	3.3 [13]
SiO ₂ (stishovite)	33±2	NA
Ta ₃ B ₄	33±2	NA
TiC	20-32	1.5-3.6 [14]
β -Si ₃ N ₄	30±2	4.1-6.0 [9]
CeB ₂	30±2	NA
ZrB ₂	30±2	4-5 [15]
VC	29±2	NA
ZrN	27±2	3.7-6.2 [16]
SiC	26±2	3.3 [17]
TiN	20±2	3.4-5.5 [18]
Al ₂ O ₃	20±2	4.2-5.9 [9]
ZrO ₂	11-12	7.0-12.0 [9]
WC	17±2	7.5-8.9 [19]

Related to nanometer-scale multilayered coatings are nanocomposite thin coatings with hardness approaching to that of the diamond. These coatings usually have nanocrystalline grains of transition-metal nitrides or carbides surrounded by amorphous hard nitrides. The immiscibility of the amorphous phase and nanocrystalline transition-metal nitrides is the key to developing this structure. The hardness enhancement is due to restricted dislocation movement, as it is with nanometer-scale multilayered coatings because the small grains hinder dislocation formation and movement, and the well-defined interface hinders grain boundary sliding.

Another type of coating system is metal carbide/ductile metal because the carbide phase provides hardness and the metal provides toughness. For example, composites such as WC/Co, WC/TiC/Co are commonly used in cutting and forming tool applications, and these can be synthesized by various routes. These nanocomposites, in which the particle or grain sizes of the component phases are in the nanometer range, have much better mechanical properties (strength, hardness and toughness).

It is well established that the production of high quality thin coatings made by physical vapor deposition requires ion bombardment, suggesting the importance both of processing variables and of the microstructure of the coating. Ion bombardment produces a range of effects. These include breaking up of the nuclei on the substrate so that layer by layer growth occurs, forming denser microstructures. Atomic displacement causes the formation of vacancies and interstitials. As the coating is constrained by the substrate, this leads to the development of compressive stresses in the coating. Some ion bombardment always occurs in sputtering processes but it can be greatly increased by applying a bias voltage to the substrate on which the sample is supported and by placing a radio frequency coil in the region between the magnetron and the substrate to develop additional plasma. The flux of bombarding ions is controlled by the r.f. power density, their energy by the substrate bias.

It is also possible to fabricate isotropic nanocomposite coatings consisting of crystallites embedded in an amorphous matrix, with grain sizes in the nanometer range. These coatings generally have one phase that is hard (load bearing; e.g., transition metal carbides and nitrides) and a second phase that acts as a binder and provides structural flexibility (amorphous silicon nitride, amorphous carbon). The formation of these composite structures involves phase separation between two materials (which show complete immiscibility in solid solution), which are often co-deposited, for example, by sputtering or plasma deposition. Unlike in multilayer composite systems, the possible material compositions and particle sizes in nanocomposite coatings are restricted by material properties and deposition conditions.

The danger of catastrophic fracture can be considerably reduced if the coating is hard and elastic at normal operating loads, and plastically compliant at higher or extreme loads. The change of behavior from elastic to plastic can provide stress relaxation and distribute the localized load over larger volumes.

In composites, plasticity can be introduced either by plastic deformation in one of the phases or by grain boundary deformation similar to superplasticity in nanocrystalline ceramics and oxides. According to Voevodin et al. [20] for composites consisting of hard phases, a controlled development of nanocracks and microcracks along phase boundaries can be used to obtain grain shifts and to achieve unrecoverable pseudoplasticity. This approach removes some constraints of superhard composite designs [21], which require 3-4 nm grain sizes with less than 1 nm separation. First, crystalline grains can be increased to a size, which is sufficient for dislocation formation but smaller than the critical size of a self-propagating crack at the applied stress. For a variety of wear protective coatings, contact stresses are in the

range 10^8 - 10^{10} Pa, e.g., journal and rolling bearings. If a localized stress of 1 GPa is used as an average, then a self-propagating crack from Griffith's criteria is in the range of 50-100 nm for materials with elastic moduli of 200-400 GPa and the adhesion work for crack opening is about 1 J m^{-2} .

Second, the separation of crystallites in an amorphous matrix can be increased to relax incoherence stress and to permit non-catastrophic nanocracks along grain boundaries. For most materials, incoherence stresses relax to negligible values for interface thicknesses above four to five crystal lattice periods or 1-3 nm.

4. COATING HARDNESS AND TOUGHNESS ENHANCEMENT

4.1 METHODS OF INCREASING COATING HARDNESS

Hardness is defined as the resistance of a material to plastic deformation. Plastic deformation of crystalline materials occurs predominantly by dislocation movement under applied load. It means that a material with enhanced hardness has a higher resistance to dislocation movement. Very often, several of the classical hardening or strengthening mechanisms are active in hard coatings deposited by plasma-assisted vapor deposition techniques. Such hardening mechanisms work by providing obstacles for dislocation movement, which can also be applied to some extent to hard coatings. Hindering of dislocation movement can be achieved by: (i) grain boundary hardening, (ii) solid solution hardening, (iii) age hardening and (iv) compressive stress hardening.

4.1.1 GRAIN BOUNDARY HARDENING

In a recent review [22], Veprek has analyzed the design criteria to produce superhard or even ultrahard nanocomposite coatings. From material-selection point of view, combinations of nanocrystalline transition-metal nitrides, e.g. TiN, W_2N and VN, with amorphous Si_3N_4 or BN as the grain boundary phase, have a potential to achieve coating hardness exceeding 40–50 GPa. This hardening behavior, especially in the regime where the crystallite size $d < 10$ nm, is because in case of a thin amorphous grain boundary, the tiny crystallites will restrict the grain boundary sliding [23]. Dislocation pile-up may be described by the Hall-Petch equation [24, 25]. The relationship indicates the hardness of the material is inversely proportional to the square root of the grain size. However, as grain sizes are reduced to the nanometer scale and the percentage of grain boundary atoms increases correspondingly, this traditional view of dislocation-driven plasticity in polycrystalline metals needs to be reconsidered. In a sample with grain diameters of 20 nm, about 10% of atoms are located at grain boundaries. Originally it was thought the tiny crystallites should be free of dislocation [23]. In the superhard design, dislocation sources and pileup were hardly expected to exist in such a material and deformation was believed to be carried mostly by the grain boundaries via a certain accommodation mechanism [26]. Although recent evidence for dislocation existence in

nanocrystalline [27], the main deformation mechanism is believed to be grain boundary sliding. For very small grains, the numbers of atoms at inter-granular boundaries and inside grains become comparable. In this case, softening may happen via inter-granular slip as inter-granular boundaries cease to be barriers for the motion of dislocations [28]. This behavior is called inverse Hall-Petch effect.

The search for very hard materials is coupled to the study of low-compressibility solids, which have high values of the bulk (K_b) or shear (G) modulus. Transition-metal-containing compounds have large cohesive energies and high K_b , associated with the distribution of their valence electrons between bonding and anti-bonding states within the partly filled electronic bands. Transition metal carbides, nitrides, borides, or oxides have very low compressibility and also often possess high hardness.

Based on thermodynamically driven spinodal segregation in a binary or ternary system, Veprek et al. proposed a design to achieve superhard or even ultrahard coating; a highly thermally stable nanocomposite structure with ≤ 10 nm crystallites of the transition metal nitride separated by about one monolayer of α - Si_3N_4 was synthesized (see ref. [23] and references therein). The approximately one monolayer thin tissue of Si_3N_4 acts as a 'glue' for the MeN nanocrystals, thus avoiding reverse Hall-Petch effect, to achieve an ultra-hardness. Though the original value given was 103 GPa, more recently studies show that the Fischerscope used normally gives too high a hardness values for superhard coatings [29]. Many superhard similar nanocomposites with similar design have been synthesized, but none approaches the hardness of diamond. Fig. 1 shows the hardness of nc-TiN/ α - Si_3N_4 coatings deposited by close-field unbalanced magnetron sputtering as a function of the silicon nitride fraction. Silicon-free TiN forms elongated crystallites that are several hundreds of nanometers long and tens of nanometers wide (inset A in Fig. 1) [30, 31]. TiN crystallites become very small at increased Si_3N_4 contents. At 15–20 at.% Si_3N_4 , the mean grain size of TiN does not exceed 7 nm; this size is too small for dislocation activities. Therefore, under mechanical loading, such a material can react only by grain-boundary sliding (i.e., by moving single, undeformed TiN nanocrystallites against another). This process requires more energy than deformation by dislocation movement; hence a higher hardness can be achieved for such a coating structure. Estimations of the mean grain separation at this composition show that only a few monolayers of silicon nitride separate the nanocrystallites (inset B in Fig. 1). At high silicon nitride fractions, the mean grain separation becomes so wide that ordinary crack propagation in Si_3N_4 takes place, and the hardness approaches that of Si_3N_4 (inset C in Fig. 1).

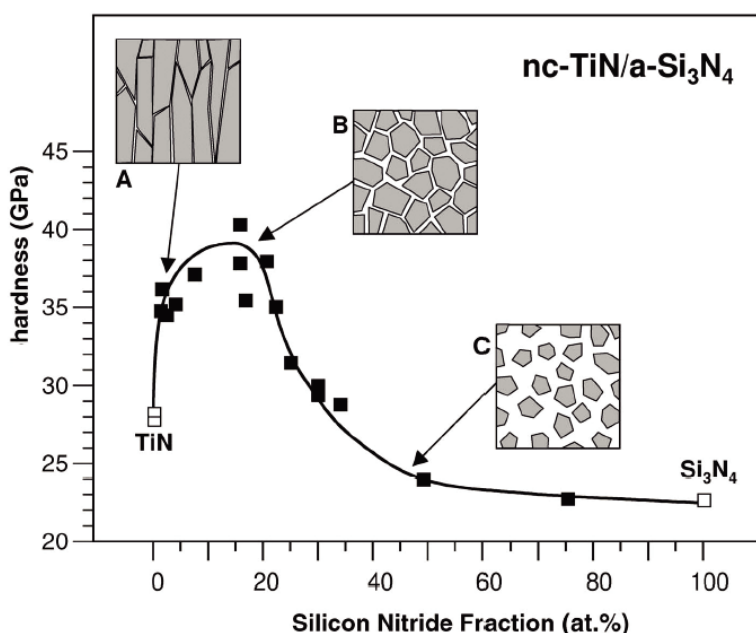


Fig. 1. Hardness of nc-TiN/a-Si₃N₄ as a function of silicon nitride fraction [30, 31]. In sets illustrate the schematic nanostructure at different compositions.

4.1.2 SOLID SOLUTION HARDENING

Solid solution hardening comes from the lattice distortion as a result of insertion of atoms of alloying element in the interstitial location or substitution for some of the host atoms. This is, perhaps, one of the oldest hardening methods in bulk materials. In coatings, the same principle works too. TiCN [2], TiAlN [32], CrAlN [33] and CrZrN [34] are a few popular examples. Formation of a non-equilibrium supersaturated solid solution of B in TiN may contribute to further strengthening of the material [35], since the gliding of dislocations eventually formed inside the crystallites is hindered by the strain exerted by insertion of B. To increase the solubility of B in TiN, non-equilibrium growth processes, such as physical vapor deposition (PVD) or plasma-assisted chemical vapor deposition (PACVD) have been used, where a maximum B solubility of 17.4 at.% has been reported for PACVD [35] with hardness up to 43 GPa. For reactive arc evaporation from Ti-B compound targets, the highly ionized flux of coating-forming species was utilized to synthesize a promising nanocrystalline metastable supersaturated solid solution of B in TiN at lower nitrogen fractions [36]. The maximum in hardness (34.5 GPa) is obtained when the crystallites are 6–8 nm in size, and are strained by the formation of a substitutional solid solution of B in TiN. The formation of a metastable solid solution was confirmed by XRD-observed widening of the lattice upon B substitution of N as compared to TiN. Therefore, the mobility of deformation-induced dislocations is hindered in these small crystallites that are initially dislocation-free. At high N₂ fractions, the substitutional B sites in the TiN crystallites are replaced with additional N to form energetically favorable unstrained TiN crystals. This unstrained TiN crystals combined with high fraction of less strongly bonded BN amorphous phase lead to a hardness drop (Fig. 2). Another example is the superhard Ti–Al–Si–N coating (maximal harness ~ 55 GPa)

synthesized by a hybrid coating system of arc ion plating and sputtering method [37]. Based on XPS and XRD results, it was suggested that the Ti–Al–Si–N coatings were a composite consisting of solid–solution (Ti,Al,Si)N crystallites and amorphous Si₃N₄. The equilibrium phase diagram for Ti–Si–N does not contain any stable ternary phases [38], but Vaz et al. found phases originating from a possible (Ti,Si)N solid solution [39]. The maximum Si content in metastable supersaturated cubic solution Ti_{1-x}Si_xN is 10–15 at.% [38]. The silicon content influenced almost linearly the coating hardness due to solid-solution hardening [40]. Kinetic limitations during coating deposition combined with ion bombardment induced collisional mixing are proposed as conditions for the growth of metastable (Ti,Si)N coatings instead of the thermodynamically stable—and widely studied TiN/Si₃N₄ system. But it should be pointed out that the metastable phase will disappear via annealing at a certain temperature so as causes the loss of solid solution hardening effect.

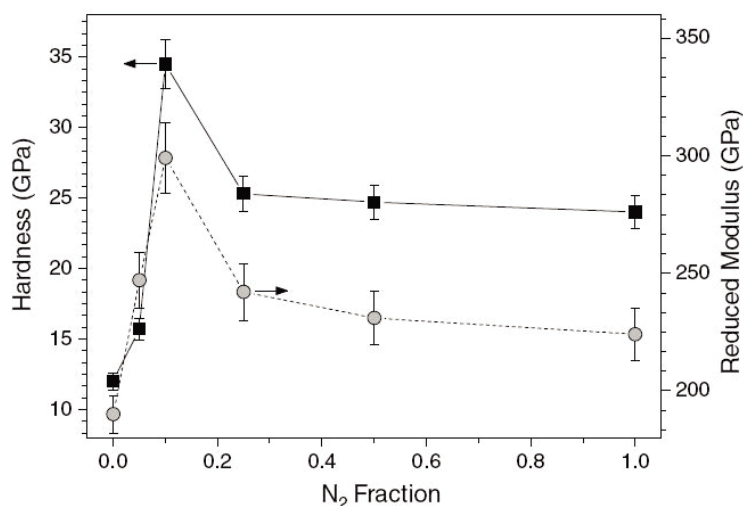


Fig. 2. Indentation hardness and reduced modulus values for Ti–B–N coatings under different N₂ fraction of mixture of N₂ and Ar gas [36].

4.1.3 AGE HARDENING

Age hardening is another convectional hardening mechanism in strengthening bulk materials (for example Al alloys and steels). Age hardening achieves higher hardness through precipitation over time of a small and uniformly distributed strengthening phase in the form of particles from a supersaturated solid solution. This works equally well in hard coatings, as demonstrated in reference [41–43]. Supersaturated phases can be easily obtained by non-equilibrium deposition techniques such as PVD or PACVD due to limited atomic kinetics during deposition. As-deposited (TiAl)N [42] and Ti(BN) [43] coatings show a dense columnar microstructure of a supersaturated NaCl structured phase based on fcc TiN whose Ti location is partly substituted by Al to form (TiAl)N, and N is partly substituted by B to form Ti(BN). During annealing, (TiAl)N and Ti(BN) coatings undergo spinodal decomposition and transform into coherent cubic-phase nanometer-size domains, resulting in an increase in the hardness.

4.1.4 COMPRESSIVE STRESS HARDENING

Hardness increases and decreases due to compressive and tensile stress, respectively, has been reported for a number of bulk materials [44]. The measured hardness enhancement (decrease) due to compressive (tensile) stress is related to the flow stress σ_{flow} under the applied stress σ_{appl} as $\sigma_{\text{flow}} = \sigma_{\text{Yield}} - \text{const.}$ (σ_{Yield} is the yield stress of unconstrained material) in experiments with bulk samples where the stress induced by bending is typically $\sigma_{\text{app}} \leq 0.3 \text{ GPa}$ [44]. For coatings, it is more complex when the compressive stress can approach to 10 GPa. Ion bombardment during deposition at low temperatures has been utilized to increase the density and modify the morphology of the coatings [45]. During growth, stresses are generally induced by energetic particle bombardment. The lattice defect arrangements induced by impinging energetic ions are responsible for the stress. As the incoming ion or knock-on atoms possess enough kinetic energy, they knock atoms out of their lattice positions and create secondary collisions which tend to cascade. The atom first knocked absorbs most of the energy. The resulting strong atomic motion along the trajectory of the ions leads to a rearrangement of the lattice atoms [46]. The hardness enhancement results from a complex synergistic effect of the decrease of crystallite size, densification of grain boundaries, and compressive stress upon ion bombardment. Musil et al. reported enhancement of hardness of TiN (up to 80 GPa) and (TiAlV)N (up to 100 GPa) during deposition by means of unbalanced magnetron sputtering at negative substrate bias [3] where a correlation between the hardness enhancement and biaxial compressive stress exists [47]. However, upon annealing at a certain temperature, when the induced defects are annealed and the compressive stress relaxes, the hardness may decrease back to “normal”. It is well known from the work of Thornton, Hoffman and others that large residual stresses can be developed in thin coatings [48, 49]. For many hard coatings (e.g., PVD deposited coatings, in which the compressive stress is typically 4 to 6 GPa or even greater than 10 GPa), the measured enhancement of the apparent hardness and elastic modulus is due to high biaxial compressive stress.

4.2 METHODS OF INCREASING COATING TOUGHNESS

In order to obtain high hardness in nanocomposite coatings, usually plastic deformation is designed to be prohibited, and dislocation movement and grain boundary sliding are prevented, thus causing a loss in ductility. Ductility is related to toughness which is very important for hard coatings to avoid catastrophic failure. Veprek [50] indented a 6-10- μm -thin coating on a soft steel substrate with a high load of 1000 mN and found no cracks. This, however, does not necessarily mean it has high “fracture toughness”: the classical definition of “fracture toughness” measures the resistance to crack propagation – a crack exists first, then how difficult it is to make the crack propagate. The coating in the above example is ‘damage tolerant’ owing to the difficulty in generating a crack (but once a crack is generated, it might propagate in a catastrophic manner and thus results in a brittle failure if it is not truly “tough”). Apart from superhardness, good mechanical properties should also include high fracture toughness due to flaw size refinery, crack deflection and crack termination [51].

However, in such superhard coatings, dislocation movement and grain boundary sliding are prevented, thus probably resulting in a loss in ductility which will often restrict the toughness. In order to improve the toughness of nanocomposite coatings, recently researchers have been working on toughening of hard coatings. It is important to study the routes to enhance the toughness of hard coatings. In bulk ceramics, various toughening methods are available: ductile phase toughening, fiber and whisker toughening, transformation toughening, microcrack toughening, etc. [52]. In hard coatings, however, investigation on toughening mechanisms lags far behind. Only limited aspects of these mechanisms have been investigated.

4.2.1 DUCTILE PHASE TOUGHENING

In order to toughen hard ceramic coatings, a straightforward method is to incorporate ductile phase. Ductile toughening may profoundly increase the toughness. Ductile phase toughening arises from two major mechanisms: relaxation of the strain field around the crack tip through ductile phase yielding and bridging of cracks by ligaments of the ductile phase. These two mechanisms can increase the work for plastic deformation. There are at least two types of microstructures: a continuous ductile phase (matrix) and isolated ductile phase. The first type has been widely explored in macrocomposites made of ceramics and metals which are known as cermets. Musil et al. is the pioneer to scale down to the nanometer level in coatings made of hard nitride and soft metal matrixes [53-55]. Zhang et al. [56] doped Al into a-C coatings by co-sputtering of graphite and Al. The composite coatings exhibit improvements in the toughness at the expense of hardness. In order to restore the hardness, nanocrystalline TiC (or nc-TiC) was embedded into the a-C matrix doped with Al to form nc-TiC/a-C(Al) nanocomposite coating. The hardness is restored to ~20 GPa, while toughness remained high (indentation plasticity of 55%) and residual stress low (only 0.5 GPa) [57]. Although toughness is not measured due to lack of proper measurement facilities for such a high toughness coating, the nc-TiC/a-C(Al) nanocomposite coating is evidently very tough: the optical comparison of scanning scratch tracks between nc-TiC/a-C (Fig. 3a) coating and nc-TiC/a-C(Al) (Fig. 3b) shows that without doping of Al, the coating basically fails in a brittle way (Fig. 3a); with doping of Al, however, the scratching tip ploughs into the coating causing the scanning amplitude to reduce along the scratch direction (Fig. 3b). Co-sputtering of Ti, TiNi and Si₃N₄ targets produced nanocomposite coatings where amorphous metallic Ni increases the toughness of nc-TiN/a-SiN_x coating [58]. Doping from 0 to ~40 at.% Ni brings about an increase in toughness from 1.15 to 2.60 MPa m^{1/2}, but at the expense of hardness from 30 to 14 GPa. Nanocomposite coatings of ZrN-Me (Me=Ag, Au, or Pd) were produced by reactive unbalanced magnetron sputtering and were found to form a dense and homogeneous microstructure whereby nanocrystals of Me are distributed evenly throughout the ZrN matrix [59]. Interestingly, the Young's modulus was found to decrease much more dramatically with the increase in metal content for the ZrN-Ag system. The properties of these materials depend on the following factors: (a) The intrinsic properties of the constituent

phases, (b) the coating architecture, and (c) the interfacial energy. It was found the grain boundary sliding responsible for the ductile behavior of the nanocomposite coatings. Grain boundary sliding is defined to be the relative displacement of two neighboring constituent grains in a direction parallel to the boundary interface [60]. Preparation of $\text{Al}_2\text{O}_3/\text{DLC}/\text{Au}/\text{MoS}_2$ chameleon coatings for space and ambient environments is targeted for the material system of interest included alumina (Al_2O_3) in an Au matrix with diamond-like carbon (DLC) and MoS_2 nanoparticle inclusions using a hybrid magnetron assisted pulsed laser deposition (MSPLD) process [61].

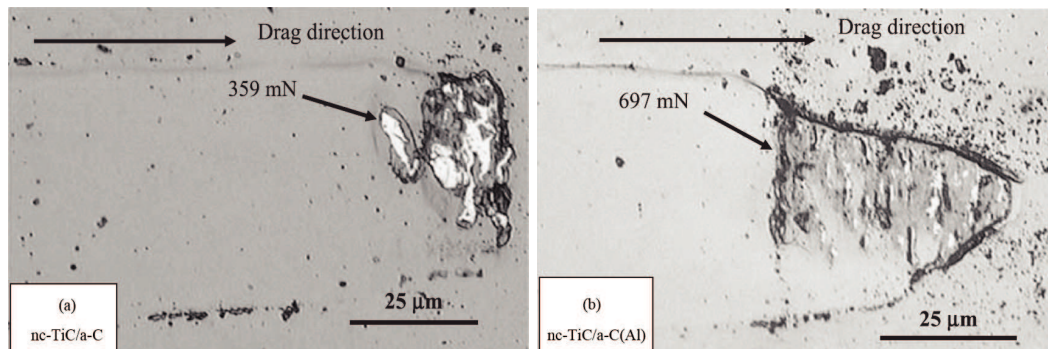


Fig. 3. Optical image of scratch tracks on coatings: (a) nc-TiC/a-C and (b) nc-TiC/a-C(Al) [57].

4.2.2 PHASE TRANSFORMATION TOUGHENING

Some phase transformation occurs under stress and is accompanied by absorption of large quantity of energy, thus could be used to toughen a material. Transformation from tetragonal to the monoclinic phase takes place under stress. The process occurs in the stress field around the tip of the crack and is accompanied by a volume increase of about 4%. The resultant strain during the transformation relieves the stress field and absorbs the fracture energy, whereby toughens the material. One example is ZrO_2 toughened ZrB_2 composite [62]. In order to facilitate the phase transformation, retention of the high-temperature tetragonal phase is the key, which can be easily realized during deposition. Sprio et al. [63] deposited thin zirconium oxide coatings by radiofrequency (RF) magnetron sputtering. The coatings have a mixture of tetragonal and monoclinic zirconia phases. It was shown that increasing substrate bias power disrupted columnar grain growth. TEM confirmed a reduction in intergranular porosity but also an increase in lateral defects [64]. These defects are hypothesized to be stress-induced microcracks caused by a tetragonal to monoclinic phase transformation. Tetrahedral zirconia has a high toughness and is proposed to increase properties of brittle substrates [65]. Trinh et al. [66] prepared $\gamma\text{-Al}_2\text{O}_3\text{-ZrO}_2$ coatings by RF magnetron sputtering with hardness up to 30 GPa. However, owing to the lack of proper toughness measurement instrumentation, toughness was not measured.

4.2.3 COMPRESSIVE STRESS TOUGHENING

Generally cracking is initiated by tensile stress, thus compressive residual stress has to be overcome first before a crack is initiated in tension. When a coating has a high compressive residual stress to start with, the coating will be able to take more tensile strain before fracture, as is demonstrated in Zr-Cu-O coatings (see Fig. 4) [67]. Although certain level of compressive stress can increase toughness, excessively large compressive stress can cause coating delamination or cracking [68].

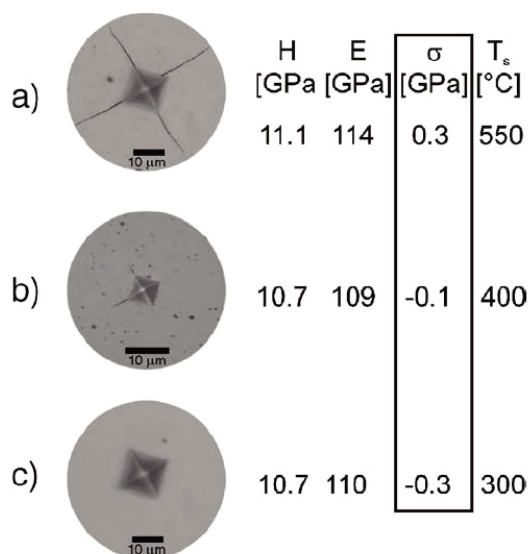


Fig. 4. Comparison of Vicker's indenter impressions into Zr-Cu-O with different residual stress (a) 0.3 GPa (b) -0.1 GPa (c) -0.3 GPa [67].

4.2.4 NANOTUBE TOUGHENING

The discovery of carbon nanotube (CNTs) has opened up new avenues in producing unique carbon-based materials. The simplest version of the carbon nanotube, a cylindrically rolled sheet of hexagonally arrayed carbon atoms, or single-walled nanotubes (SWNTs), has been produced in strands of macroscopic length [69], and micrometer-long crystals consisting of ordered arrays of aligned SWNTs have also been produced [70]. Novel mechanical tests on individual CNTs [71-73] and atomistic calculations [74-77] suggest that CNTs have ultra-high elastic moduli of approaching 1 TPa, and exceptional tensile strengths, in the range of 20-100 GPa. Due to their outstanding properties, carbon nanotubes have attracted growing interest and are considered to be the most promising materials for applications in the nanoengineering field [78-85]. Toughness enhancement can be obtained through crack deflection, crack bridging and CNT pull-out. CNT toughened bulk ceramics are attractive and outstanding results have been successfully achieved, for instance, in Al_2O_3 matrix [85] and BaTiO_3 matrix [86]. Composite materials with a nanocrystalline Al_2O_3 matrix and reinforcement by ropes of SWNTs that form a network at the grain boundaries have recently been fabricated by ball-milling to mix the Al_2O_3 powders and nanotubes, followed by consolidation using the low-temperature spark plasma sintering process [85]. The best of

these composites, fully dense with 10 vol.% SWNTs, had a fracture toughness of $9.7 \text{ MPa m}^{1/2}$, almost three times that of pure Al_2O_3 of the same grain size. Peigney [87] suggests that the high toughness of these Al_2O_3 -carbon nanotube composites results from the combination of high-quality starting materials, homogeneous dispersion without damaging the nanotubes, and the relatively short time and low temperature required for spark plasma sintering. This work demonstrates that carbon nanotubes can be used as reinforcement for ceramic matrix composites.

However, nanotube toughened coatings is yet to be realized, due to difficulties in controlled alignment, interface reaction and reasonable volume fractions. Xia et al. [83, 88] anodized aluminum to obtain an amorphous alumina matrix having pores in 30-40 μm diameters in which multiwall carbon nanotubes were grown by CVD to realize CNT/alumina composite layer of 20 to 90 μm in thickness. Crack deflection at the CNT/matrix interface (Fig. 5a), crack bridging by CNT (Fig. 5b), CNT pull-out (Fig. 5c) are all observed.

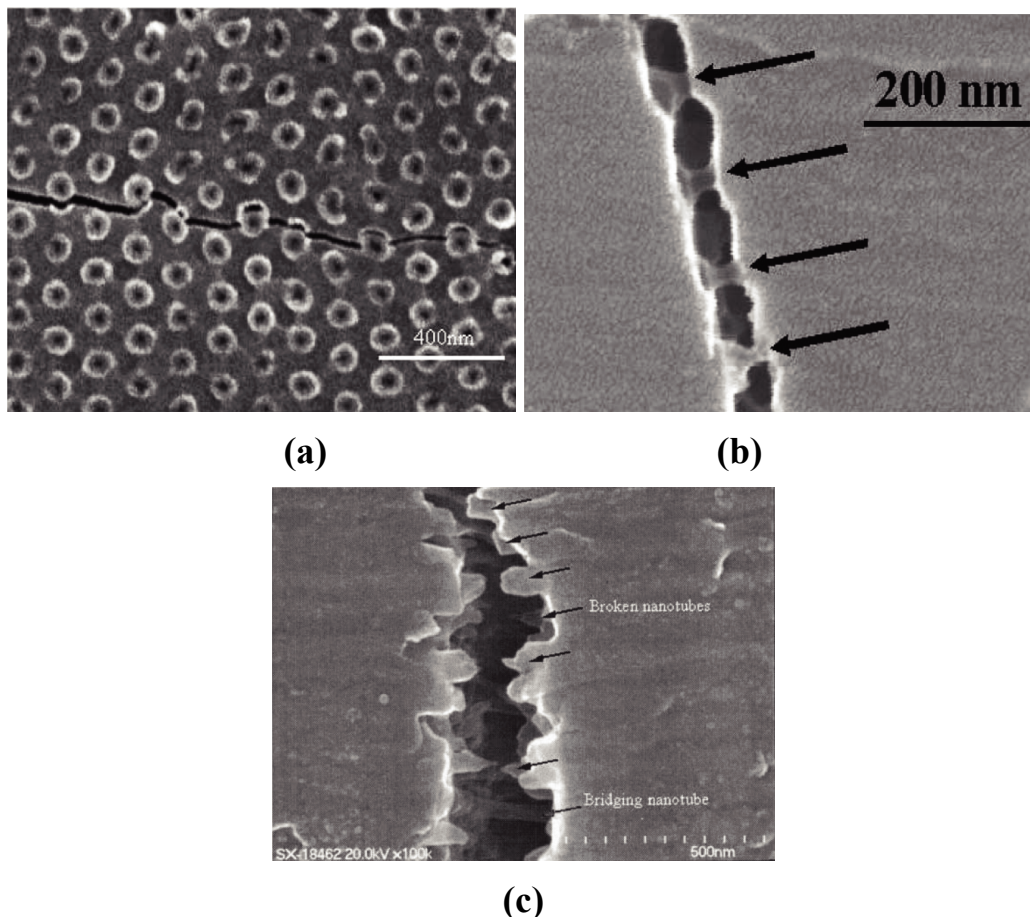


Fig. 5. Micrographs of deformation in CNT-alumina composites fabricated using ordered porous alumina templates (a) transverse crack deflection at the CNT/matrix interface (b) CNTs bridging longitudinal matrix cracks (c) nanotube pullout, and subsurface nanotube bridging [83, 88].

4.2.5 COMPOSITION OR STRUCTURE GRADING TOUGHENING

Graded inter-layering is a well known and effective method to reduce crack concentration and enhance adhesion between coating and substrate. In gradient design, the substrate is first coated with a high adhesion layer, and then the coating constituents are allowed to vary homogeneously or heterogeneously while the coating thickness builds up. With biased graded (varying substrate bias voltage while coating thickness builds up) in magnetron sputtering, Zhang et al. [89] prepared 1.5 μm a-C gradient coating on tool steels with moderately high hardness (25 GPa) but very high toughness (plasticity 57.6%). During deposition, substrate bias gradually increased from -20 to -150 V during deposition, and a graded sp^2/sp^3 was achieved through coating thickness. The bottom layer has the highest sp^2 fraction for high adhesion whereas the top layer possesses the highest sp^3 fraction to render high hardness. Bias-graded coating design enhances the toughness and the adhesion of the coating on tool steel (Fig. 6). The adhesion strength increased more than two times as compared to the same coating deposited at constant bias (-150 V).

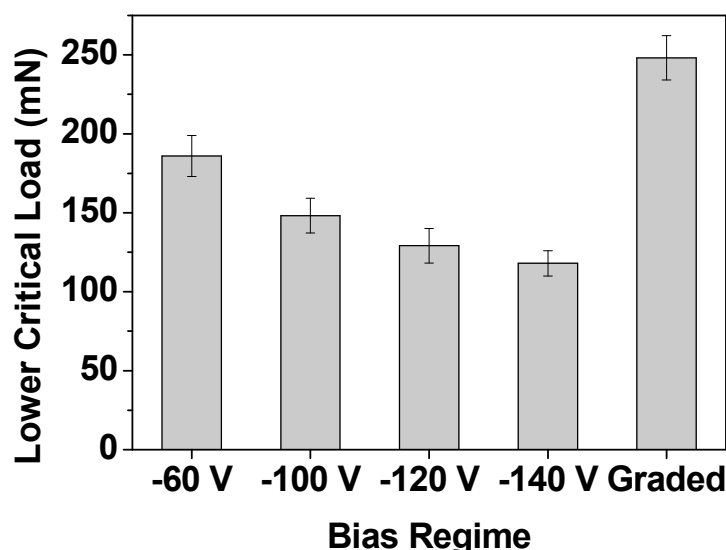


Fig. 6. Scratch adhesion strength of the non-hydrogenated DLC deposited under various constant bias or bias-graded conditions [89].

5. DEPOSITION TECHNIQUES

Methods applied successfully for the deposition of various nanocomposite coatings include magnetron-sputtering, either reactively or non-reactively, arc deposition, laser ablation, plasma assisted CVD, as well as non-reactive PVD hybrid deposition techniques or PVD-CVD hybrid deposition techniques using reactive atmospheres (see Table 2). But most popular techniques are magnetron sputtering and chemical vapor deposition. High deposition rate and uniform deposition without line-of-sight drawback are the advantages of CVD method compared to sputtering. The main concern is the environmental impact. Besides, a

relatively high deposition temperature is often required which will cause thermal stress due to the coefficient thermal expansion (CTE) mismatch between coating and substrate. If a low deposition temperature is required, the first choice is to use PVD for example magnetron sputtering. At present, much effort is devoted to synthesize nanocomposite coatings using reactive magnetron sputtering or co-sputtering which is low temperature (which may produce hard metastable phases) and flexible. Therefore, these coatings still are subject to optimization and scale-up activities. Just a few coatings are available commercially today, for example WC–C coatings are used in combination with (Ti, Al)N coatings for tool applications. Precision control of grain size and grain boundary fraction is vital for nanocomposite coatings. In magnetron sputtering process, many basic process parameters affect the grain size of the coatings including substrate temperature, substrate ion current density or substrate bias voltage, partial pressure of reactive gas. Even if much progress in the development of such coatings was achieved in the past decades on the laboratory scale, the correlation between the kinetics of the deposition and growth, the microstructure and constitution, and the properties and performance of these coatings is not yet fully understood.

The last type of deposition techniques is Sol-gel (SG) technology which has enjoyed success in the last 20 years, for deposition of coatings of relatively hard, corrosion resistant single phase ceramics (e.g. SiO_2 , ZrO_2 , Al_2O_3 [90]) for sensors, membranes, etc. The sols used for these investigations are made from alkoxides, and their stability was obtained by controlling the electric charges on the sol particles, which, in general, are in the range of several nanometers in diameter. The formation of these entities either in form of macromolecules or in form of spherical or non-spherical particles follow the established rules for nucleation and growth. For stabilization of the sols, the pH value is established in a range aside from the point of zero charge. The resulting surface charges reduce the particle to particle interaction to a level that no aggregation or agglomeration takes place. Thus, gelation can be prevented. Gelation takes place if the surface charges are decreased, for example, by pH change or if the particle to-particle distance is reduced below the repulsing level, for example, by solvent evaporation, and the repulsion turns into attraction. If the particles grow too large, precipitation takes place. In sol-gel systems based on oxides, the particle-to-particle interaction is strong (oxide bridges accompanied by hydrogen bridges) so that, especially after drying, the agglomeration is irreversible.

Hard coatings for the improvement of wear properties of metallic tools can be obtained by traditional PVD and CVD processes, however these technologies demand cost intensive equipment. Sol–gel processing can be a cost-effective alternative to vacuum and vapor phase coating methods for the application of wear resistance coatings. Another benefit for SG is its ability to deposit the coating onto polymeric substrates. The key challenge for hard coatings is to densify the coating at low temperature. Since ceramic coatings require high temperatures for densification, it may be applicable to use nanoparticulate systems and surface-limited firing methods. So far, only a few studies have researched on SG hard nanocomposite coatings. Recently, Krzyzak et al. synthesized $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-TiO}_2\text{-ZrO}_2$ coatings by the

dip coating method [91]. Choudhury et al reported the synthesis of nano-structured boride metal matrix composite (MMC) coatings obtained by laser melting of a pre-placed mixture of B_4C +Ti-6Al-4V powders and sol-gel derived nano-particulate $Ti(OH)_4$ [92]. The resulting nano-composite coatings have micro-level FeB phases and nanoparticulate TiB phases in a (Fe+Fe₂B) matrix on a mild steel substrate. It was envisaged that while B_4C would act as the boron donor for boride formation, Ti-6Al-4V powder could act as a soft binder phase within the hard boride structure to enhance the toughness while nano-particulate $Ti(OH)_4$ would react with B_4C to produce a uniform dispersion of hard nano-phases (such as TiB) throughout the metal matrix and act as a strengthening component in the MMC. The hardness is up to about 14 GPa. A higher hardness will be achieved by further investigation. SG has been widely researched in conventional ceramic or polymer based composite. However applications of SG methods for hard nanocomposite coatings are still far from well understood and require further investigation. In our viewpoint, it is hopeful to realize hard and tough CNT/ceramic nanocomposite coatings if only the porosity is minimized and interfacial strength between CNT and ceramic phase is optimized.

Table 2. Classification of deposition techniques

Group	Sub-group	Methods
Physical deposition (PVD)	vapor	Pulsed laser deposition (PLD) Electron beam deposition (EB-PVD)
		Sputter deposition Ion beam sputtering
	vapor	Arc deposition Filtered arc deposition
		Ion implantation Ion beam deposition (IBD)
Chemical deposition (CVD)	vapor	Plasma enhanced CVD (PECVD) Plasma assistant CVD (PACVD) Electron cyclotron resonance CVD (ECR-CVD)
Sol-gel		Dipping Spinning spraying

6. MICROSTRUCTURES OF HARD AND TOUGH NANOCOMPOSITE COATINGS

6.1 FACTORS INFLUENCING THE HARDNESS AND TOUGHNESS

The factors governing the mechanical properties and the toughening mechanisms in nanocomposite microstructures include the properties of the reinforcing phases, such as their elastic properties; their yield strength and ductility for enhancing the load transfer from the matrix to the reinforcing phase(s); and the properties of the interface between the second phase and the matrix in terms of bonding strength and wettability, together with the volume fraction, size, and morphology of the second phases.

- (1) Grain size
- (2) Grain boundary/crystalline fraction

There is an essential role of the interplay between discrete (crystalline) intragranular and continuous (often amorphous) intergranular in determining mechanical properties [93].

- (3) Interfacial region

In the last decades, nanocomposite protective coatings have gained popularity among researchers because of their superior mechanical properties compared to the traditional single-phase coatings. Most of the work, however, concentrated on the synthesis and characterization of these materials. For example, no systematic investigation has been carried out to understand the role of the interface in influencing the mechanical properties of these materials. From an experimental perspective, current understanding of the interface and of the phenomena that occur during loading is very limited. Interfaces have much greater complexity and are much more difficult to study experimentally. Recent simulation shows the smallest maximum energy variation during sliding occurs for the ZrN-Ag material and the largest for the ZrN-Pd case. These results are in agreement with experimental findings confirming that grain boundary sliding occurs more readily in the ZrN-Ag system when compared to ZrN-Pd [93]. Process parameters are altered in order to adjust the grain size and crystalline spacing (interface thickness).

6.2 PROCESS PARAMETER EFFECTS ON NANOCOMPOSITE MICROSTRUCTURE

The resulting microstructure and property profile of a nanocomposite coating is clearly determined by the process parameters and the kinetics of the deposition and growth process. These can be achieved by either fine-tuning the ratio of the volume fraction of the nanocrystalline and of the amorphous phases, or, by fine-tuning the crystallite sizes [5, 94]. It is well known that many process parameters including power density, substrate bias voltage, deposition temperature, process pressure, and etc can affect the as-deposited coating microstructures.

6.2.1 POWER DENSITY

It is straightforward to apply different power density of the targets during magnetron sputtering process to tune the composition and microstructure of as-deposited coatings. Fig. 7 shows the microstructure evolution of these coatings dependent on the carbon contents. For a low carbon concentration of up to approximately 8 at.%, the carbon is fully solved in the nanocrystalline fcc (Ti,Al)N phase resulting in the growth of a metastable solid solution, single-phase fcc (Ti, Al)(N, C) microstructure. For carbon contents between 8 at.% and 16.5 at.%, the carbon starts to build isolated nanoclusters or agglomerates at grain boundaries of the (Ti, Al)(N, C) phase. For even higher carbon concentrations (up to 28 at.%), the simultaneous growth of a metastable, nanocrystalline fcc (Ti, Al)(N, C) phase and a continuous amorphous carbon grain boundary phase was observed. Due to an appropriate choice of the deposition conditions, the stability of the quickly forming fcc (Ti, Al)(N, C) phase seems to be very high: the basic constitution of the coatings, indicated by the $Ti/(Ti+Al)$ and the $N/(Ti+Al)$ ratios, in general does not change by continuously increasing the carbon concentration, even above the maximum solubility of carbon in the first substoichiometric fcc (Ti, Al)N phase. On the basis of a critical evaluation of these results on the microstructural evolution of these coatings dependent on the carbon content, a five-step growth model for reactively magnetron-sputtered (Ti, Al)(N, C)/a-C nanocomposite coatings is suggested: (1) the growth of these nanocomposite coatings starts from a sub-stoichiometric (Ti, Al) N_{1-x} phase with a significant N-deficiency; (2) all N-vacancies of this substoichiometric lattice are filled first by carbon atoms; (3) once the N-vacancies are filled, regular N positions can be substituted by carbon atoms; 4) if the maximum solubility for carbon in the nanoscale fcc lattice is achieved, the carbon starts to build nanoclusters or agglomerates at grain boundaries of the (Ti, Al)(N, C) lattice; (5) increasing the carbon content further, the carbon builds an amorphous grain boundary phase or even an amorphous carbon matrix.

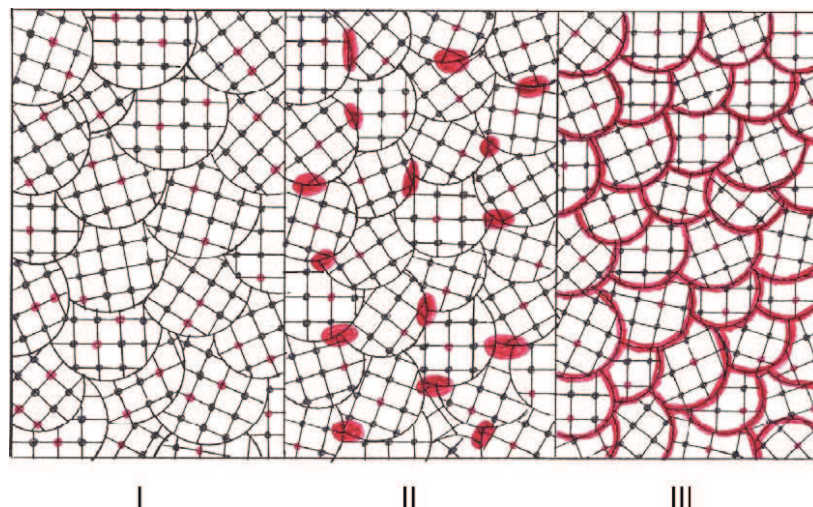


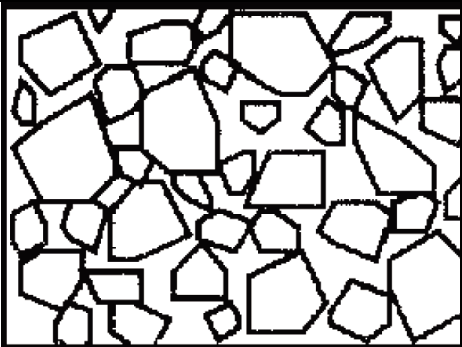
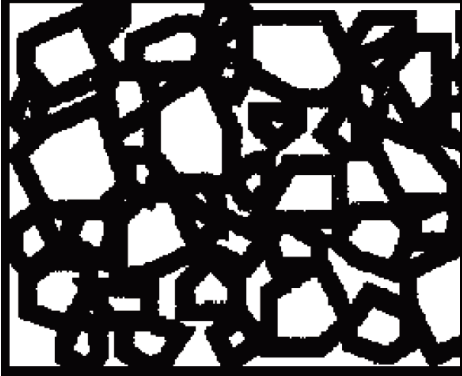
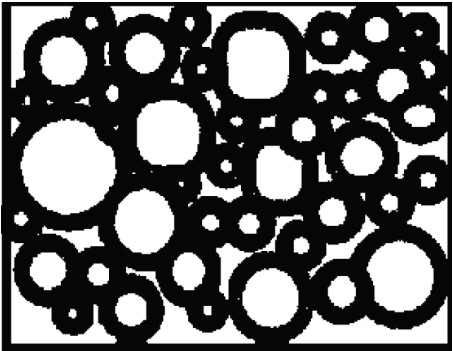
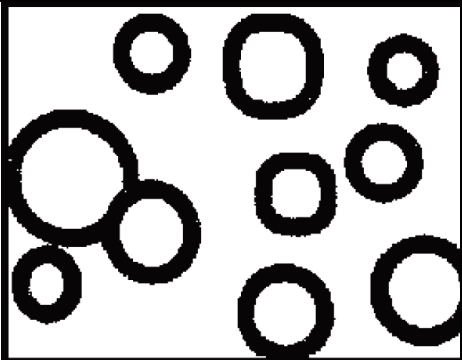
Fig. 7. Evolution of the microstructure of reactively sputtered Ti–Al–N–C coatings dependent on the carbon concentration (schematically) [95].

Studies have shown that the addition of Si to TiN coatings results in a nanocomposite structure consisting of TiN crystallites (nc-TiN) surrounded by an amorphous Si_3N_4 (a- Si_3N_4) matrix [96-101]. The addition of small amounts of Si leads to a rapid decrease in the grain size and the usual $\langle 111 \rangle$ texture of pure TiN disappears with additions of less than 3 at.% Si [102]. A large increase in the hardness is also noted. With increasing Si content, the grain size continues to decrease and the hardness continues to increase to a critical point, where the grain size reaches a minimum and the hardness reaches a maximum. However, with the further addition of Si, the hardness suddenly drops rapidly, although the TiN crystals remain close to the size noted at the peak hardness. Veprek and co-workers have demonstrated that the critical point (i.e. the highest hardness) occurs when the silicon nitride content corresponds to a calculated percolation threshold in a three-dimensional network, where the surfaces of the TiN nanocrystals are just covered by approximately 1 to 4 monolayers of Si_3N_4 [50, 103-106]. This observation was shown to be true for coatings of varying crystallite size. The coverage was calculated from the crystallite size (determined using X-ray diffraction (XRD)) and the known fraction of a- Si_3N_4 .

It is similar for TiC/a-C nanocomposite coatings. As we can see in Table 3, the C content greatly affects the microstructures of TiC/a-C nanocomposite coatings prepared by magnetron sputtering-assisted pulsed-laser deposition (MSPLD) [107]. The a-C phase volume and a-C interface thickness increases but crystallite size of TiC drops as the carbon content increases. At high carbon content, the formation of a-C suppresses the growth of TiC crystals, encapsulates TiC grains and, eventually, reduces the number of TiC grains, providing their rounded appearance and less dense packing.

For another example, ZrN/Ni nanocomposite coatings [21], the grain size was deduced from the width of the XRD peaks using the Scherrer formula and was found to decrease with the increase in nickel content. Similarly, Fig. 8 shows the dependence of mean grain size of the nanocrystallite on the B content in nc-Ti(N,B)/a-(TiB_2 ,BN) coatings [108]. The value of mean grain size was obtained by averaging the grain size values calculated from (111) and (200) XRD peaks using the Scherrer equation. This result qualitatively indicates that the grain size of the coatings decreases with increasing B content, and the same trend was also observed by TEM. It is believed that the decrease of grain size with increasing B content is related to the segregation of boron along grain boundaries after nc-Ti(N,B) was initially formed. During the deposition the excessive B is presumed to be continually excluded during nucleation and growth of nc-Ti(N,B), and segregated along grain boundaries, and hence hindered grain growth. Thus, the addition of B decreased the grain size, and at the same time it also accelerated the occurrence of twinning deformations under the compression residual stress.

Table 3. Carbon content effect on structural characterizations of TiC-a-C composites [107]

Carbon content (at.%)	Structure (schematic)	Composite description	TiC crystal size (nm)	a-C phase volume (%)	a-C interface thickness (nm)
55-65		Consists of TiC grains with a minor amount of secondary a-C phase	10-70	5-20	1-2
65-70		Significant amount of a-C phase formed between TiC crystallites	10-50	20-30	2-5
70-80		Densely packed TiC grains encapsulated in a-C, providing grains of spherical shape	20-90	30-60	5-12
80-100		Random inclusion of TiC grains encapsulated into an a-C matrix	20-100	60-100	>12

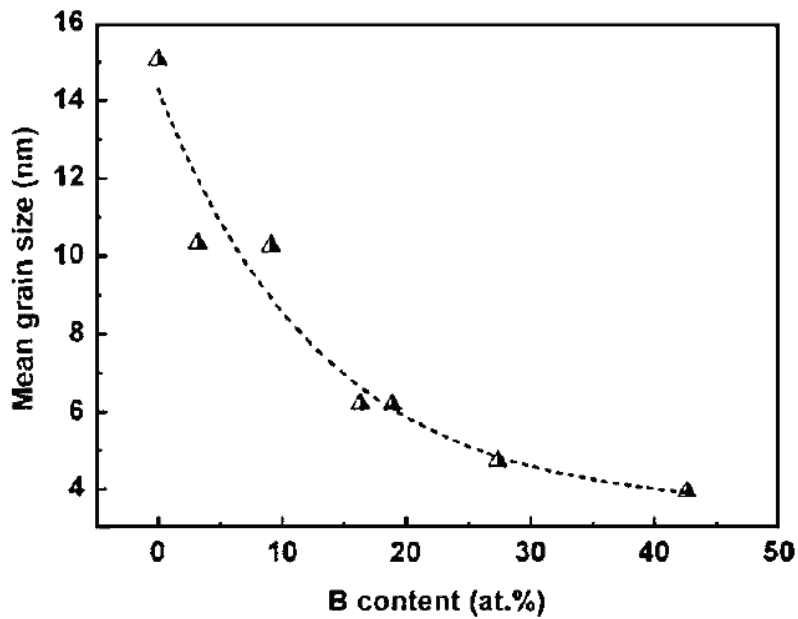


Fig. 8. Mean grain size as a function of B content in nc-Ti(N,B)/a-(TiB₂,BN) coatings [108].

6.2.2 SUBSTRATE BIAS

For single phase hard coatings, for example the reactively sputtered TiC or TiN, the substrate bias effect on grain size was studied many years ago [109]. It was found the substrate bias strongly affected the composition and grain sizes. An increase in bias increases both the carbon and the nitrogen contents in substoichiometric coatings. However, when stoichiometric TiN is formed no further change in the composition occurs. For TiC coatings an increase in the carbon-to-titanium ratio above 1.0 is possible. The structure is also affected by the bias voltage. For example the grain size of TiN has a maximum at a bias of - 200 V. A possible explanation is the dual influence of the ion bombardment. At low voltages, the adatom mobility is enhanced and the grain size increases but as the bias increases resputtering of species from the growing coating surface becomes increasingly important and the grain size decreases. It is evidently shown it is complicate for substrate bias effect on the grain size because the substrate bias may affect the composition and as a result, the composition change will the grain size. It is possibly much more complex for nanocomposite. The substrate bias affects the chemical composition of Cu/ZrN coating greatly (see Fig. 9 [53]). The content of Cu in the coating decreases from 43 at.% to 0.2 at.% due to preferential resputtering of Cu from the coating when substrate bias increases up to - 700 V. The content of ZrN increases as the substrate bias increase. The grain size of ZrN increases correspondingly.

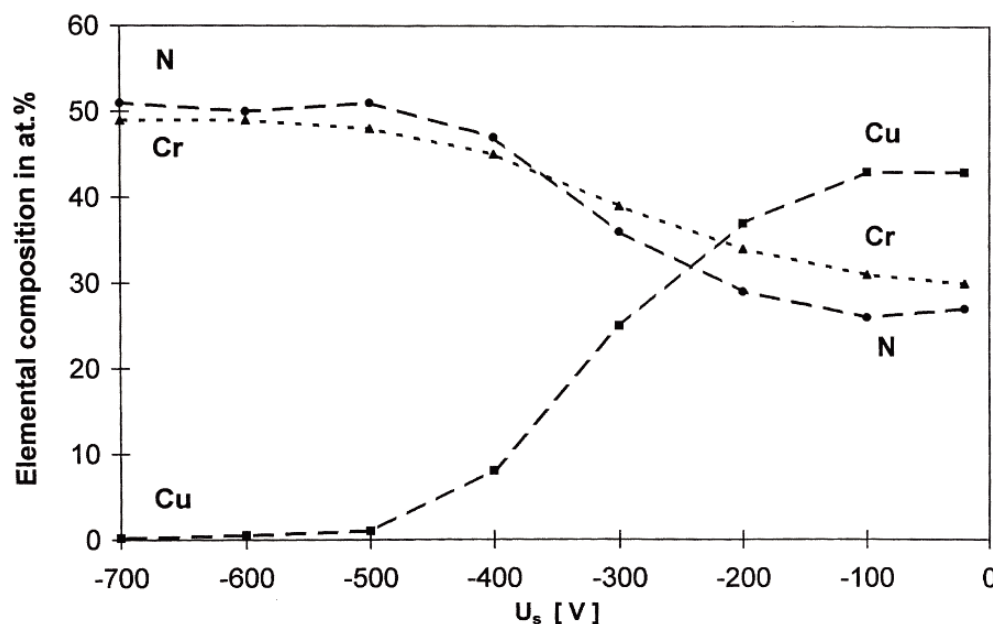


Fig. 9. Elemental depth profile of the CrCu–N coating as a function of the substrate bias [53].

Pei et al. [110, 111] adjusted the substrate bias to study the effect on the microstructure of nc-TiC/a-C:H coatings prepared by close field unbalanced magnetron sputtering. Increasing bias resulted in a clear transition from columnar to glassy microstructure in coating (Fig. 10). Substrate bias also simultaneously and greatly enhanced coating hardness, toughness and adhesive strength. The coating with glassy microstructure exhibits substantial toughening (however, a word of caution on the actual toughness value given in the paper – the value – in few tens of $\text{MPa}\cdot\text{m}^{1/2}$ – is unbelievably high, as also pointed out by the authors, due to experimental limitation). Ion bombardment can densify the structure and prevent the formation of columns which are detrimental in terms of microcrack initiation and propagation under load. The induced residual stresses grow as the bias voltage increases.

6.2.3 DEPOSITION TEMPERATURE

Deposition temperature affects the crystallization of crystalline phases and phase separation. Musil et al. [55] studied deposition temperature effect on ZrN/Cu coatings and found that addition of nitrogen to the ZrCu coatings converted the nanocrystalline coating to a nanocomposite and to separate clearly individual phases of this nanocomposite, its substrate needed heating. But the deposition temperature did not affect the microhardness of the as-deposited coatings. For TiN/Ni coating, the size of both TiN and nickel grains increases with increasing T_s (the substrate temperature) in the range 270–430 °C, see Fig. 11 [112].

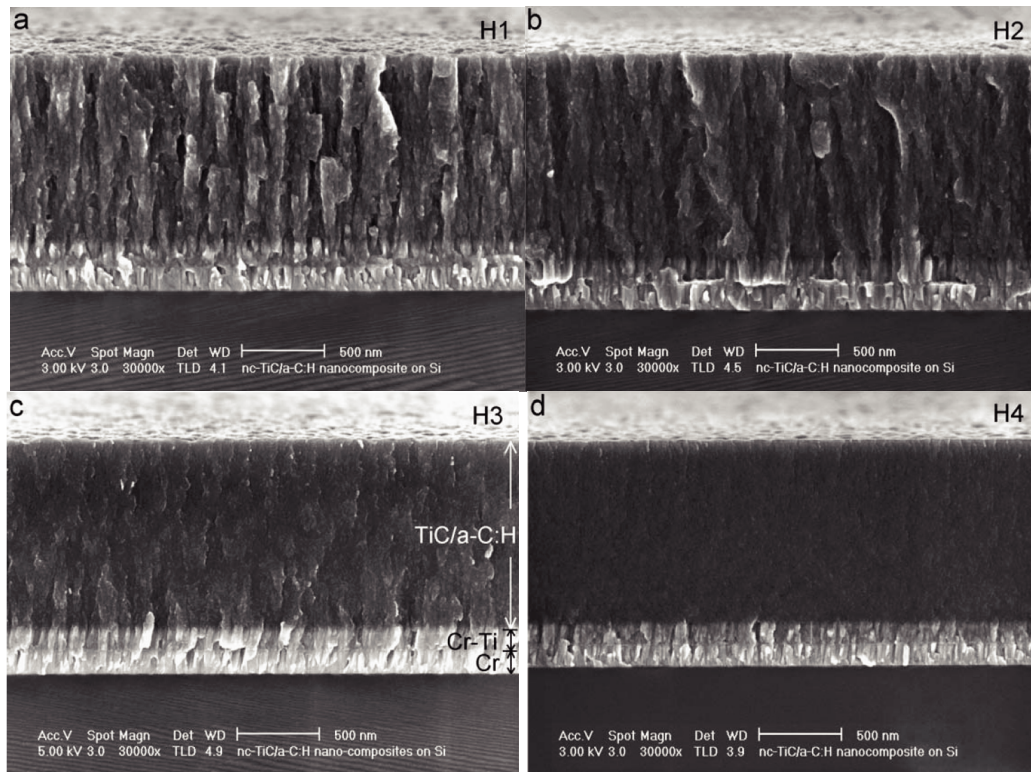


Fig. 10. SEM micrographs showing the fractured cross-sections of nanocomposite coatings deposited at different substrate bias: (a) floating, (b) $-60V$, (c) $-100V$ and (d) $-150V$ [110].

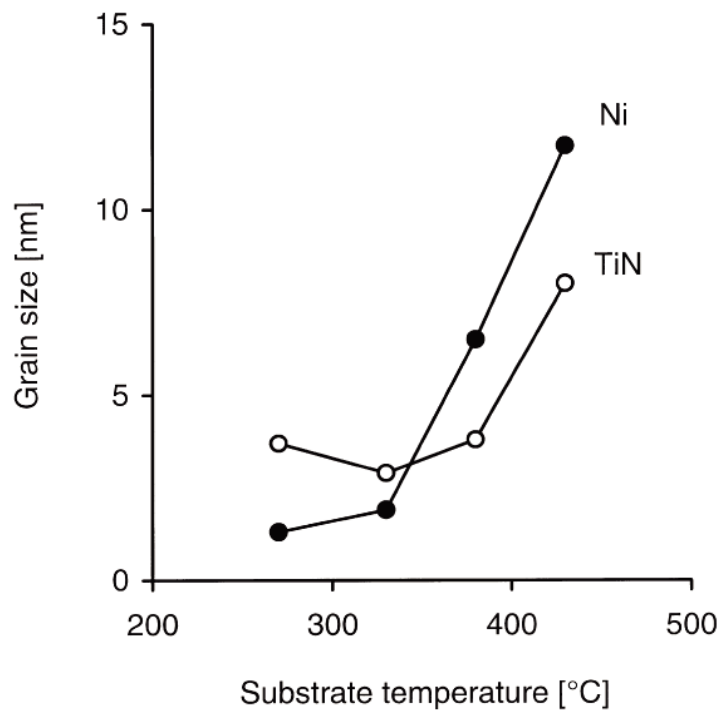


Fig. 11. Grain size of TiN and nickel as a function of substrate temperature [112].

7. CHARACTERIZATION OF COATING HARDNESS AND TOUGHNESS

7.1 HARDNESS

In terms of hardness, it is useful to consider the types of structure changes that a material can undergo under load. These changes can be divided into elastic (reversible) and plastic (irreversible) deformations. A material is considered stiff if it is difficult to compress elastically. Such a material has a large bulk modulus (it is resistant to volume compression) and/or Young's modulus (it is resistant to linear compression). Elastic deformation in a direction different from that of the applied load results in shape rather than volume changes; these motions are measured by the shear modulus. In all elastic distortions, the basic relations between atoms do not change. A material is considered hard if it resists plastic deformation. In contrast to elastic deformation, plastic deformation usually involves irreversible motion of the atoms with respect to each other, often via the creation and movement of dislocations [113].

Microindentation or nanoindentation is a standard technique to measure the coating hardness. A hardness value is the ratio between an indenter load divided by the projected contact area of the indentation formed. In order to determine the projected contact areas of micro- and nano- indentations, it is more appropriate to image the indentations using a well-calibrated atomic force microscope than to use the unloading curves obtained from the Nanoindentation machine [114]. As a precaution, the maximum indenter load should be chosen carefully so that there is no cracking around the indentation formed. Many debates are ongoing whether there is a material harder than diamond (80-120 GPa) [115, 116]. Understanding the plastic deformation of nanoscale crystalline materials is a longstanding challenge in materials science – a challenge that is not only of scientific interest but has implications for constructing materials with specific mechanical properties [117]. Since the 1930s, it has been known that the key to unlocking the secrets of plastic deformation lies in the behavior of dislocations – line defects in the crystalline lattice. The intricate interplay between dislocation and grain boundaries has a new twist for nanocrystalline materials, where the small grains put severe limitations on the dislocation behavior. Because of the difficulty of directly observing grain boundary and dislocation processes in such small grains, the exact role of grain boundaries in the deformation behavior of nanocrystalline materials has remained an open question. The interactions between grain boundaries dislocations need to be extensively examined for the purpose of controlling the dislocation thereby the mechanical properties. The improved understanding of the interactions dislocations and grain boundaries in materials may lead to new possibilities grain boundary engineering at the nanoscale. Although it is almost mature in hardness measurement, there is a deep understanding of the mechanics of elastic-plastic contact. For the most recent advances in hardness measurement, there are some detailed reviews [29, 118, 119].

7.2 TOUGHNESS

The toughness of a material is a measure of the energy necessary for fracture initiation and propagation. The ability of a material to deform plastically and to absorb energy in the process before fracture is termed toughness. The emphasis of this definition should be placed on the ability to absorb energy before fracture. In fracture, energy is adsorbed in the material and at the propagating crack tip, by elastic deformation, plastic deformation, generation of defects, phase changes and the generation of new surfaces. For bulk materials and some thick coatings, toughness can be easily measured according to ASTM standards [120, 121] which are based on the formation of well-developed cracks. For coatings, fracture toughness measurement is difficult or tedious due to the thickness limitation. Although many proposed methods can be used in some cases, there is no standard procedure or widely accepted methodology. Qualitatively, the toughness can be simply estimated by plasticity [122, 123], MDP (microhardness dissipation parameter) [124, 125], and scratch toughness [126, 127].

The plasticity or MDP measured as the ratio of the plastic displacement or work over the total displacement or work, is the parameter showing to what extent the coating can deform plastically without any crack during the indentation. The easier the stress relaxation proceeds, the larger plasticity is inherent. Hence two parameters can be considered as the first approximation of the coating toughness. The scratch crack propagation resistance parameter, or *CPR* ($CPR = L_{c1}(L_{c2} - L_{c1})$, L_{c1} : the lower critical load meaning cohesive failure load, L_{c2} : the upper critical load meaning adhesive failure load) could be a measure of adhesion toughness of the coating indicating the scratch resistance crack initiation and propagation.

To quantitatively describe coating toughness, researchers developed bending, buckling, indentation and tensile methods. Further details can be found in a recent review paper [127]. The most widely used in assessment of coating toughness is indentation. There are two categories: stress approach and energy approach.

The fist type was initially developed from monolithic bulk materials tested by microindentation for well-developed radial cracks. During indentation, when the stress exceeds a critical value, a crack or spallation will be generated. Failure of the coating is manifested by the formation of a kink or plateau in the load–displacement curve or crack formation in the indent impression. The length c of radial cracks is related to the fracture toughness K_{IC} through [128]:

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (1)$$

where P is the applied indentation load; E and H are the elastic modulus and hardness of the coating, respectively. δ is an empirical constant which depends on the geometry of the indenter (for Vickers or Berkovich indenter $\delta = 0.016$ and for cube corner indenter $\delta = 0.032$). c is the crack length (Fig. 12 [127]) which can be measured by scanning electron microscopy. The criterion for a well-defined crack will be that $c \geq 2a$. This method has been extended to

coated systems with radial cracks (e.g. [129, 130]). The problems include crack formation threshold and crack length measurement. This traditional method will be invalid when the cracks are confined to the indentation impression and coated systems which consists of a harder coating on softer substrate. The radial cracks which run along the indenter edges in hard coatings on softer substrates are generally confined within the indentation impression provided that the substrate is not sufficiently brittle that coating cracks can propagate into it. Therefore, the conventional indentation method will render the measured toughness invalid.

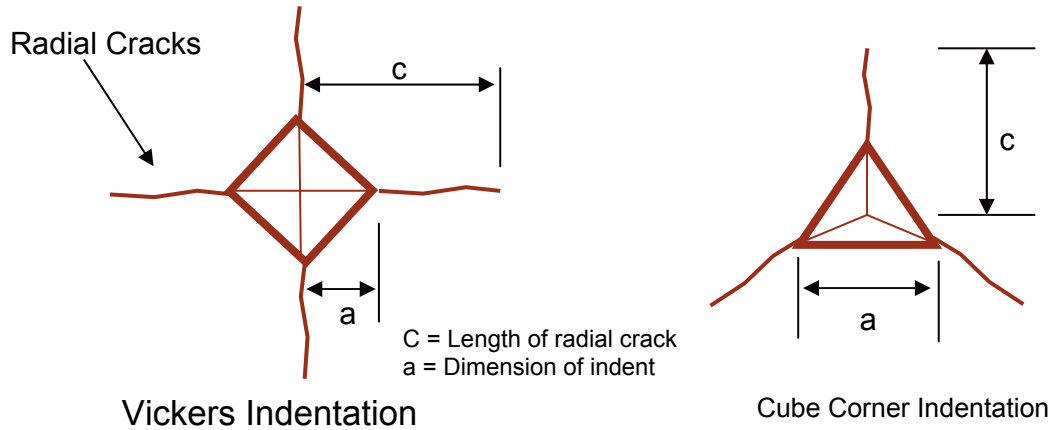


Fig. 12. Schematic illustration of the determination of crack length and indent dimension for Vickers indentation and Berkovich indentation [127].

Another approach based on indentation is through determining the fracture energy. The energy difference before and after through-thickness cracking is assumed responsible for the coating fracture. The fracture toughness of the coating can be calculated by

$$K_{IC} = \left(\frac{E}{(1-\nu_f^2)2\pi L_{\text{crack}}} \frac{\Delta U}{t} \right)^{1/2} \quad (2)$$

Where E is the elastic modulus of the coating, ν_f the Poisson's ratio of the coating, L_{crack} the planar crack perimeter, t the coating thickness, and ΔU is the strain energy difference responsible for the cracking. Li et al. [131, 132] used the step in the nanoindentation load-displacement curve obtained under load control which is associated with chipping. In this model the load-displacement curve is extrapolated from the step start point to its end point. This is illustrated in Fig. 13, where the curve OABD is the measured loading curve and OAB is the extrapolated loading curve from the initial loading part OA where no cracks occur. The fracture dissipated energy is assumed to equal to the difference between the extrapolated curve and the actual curve (i.e. area ABC in Fig. 13).

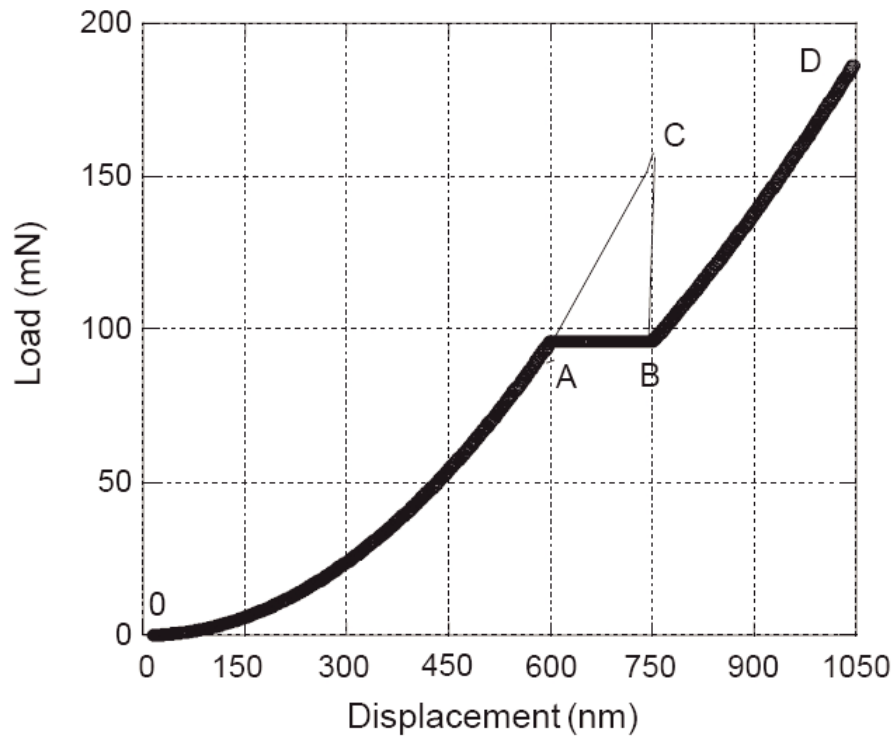


Fig. 13. Schematic of load-displacement curve, showing a step during the loading cycle and associated energy release [131].

However, this method completely ignores the change in the elastic-plastic behavior of the coating system when fracture occurs. Toonder et al. [129] also argued that the area ABC was not the actual energy dissipated by fracture. The author proposed a bound model to calculate the lower limit and upper limit for the toughness by assuming a fully elastic behavior or fully irreversible deformation during chipping (see Fig. 14(a)(b) [129]).

The energy dissipated during fracture can be obtain through

$$2/3P_{cp}(h_{cp}-h_0) \leq U_{fr} \leq P_{cp}(h_{cp} - h_0) \quad (3)$$

where P_{cp} is the indentation load at which the chipping occurs, U_{fr} the fracture energy, while h_0 and h_{cp} are the indentation depths before and after the fracture event, respectively.

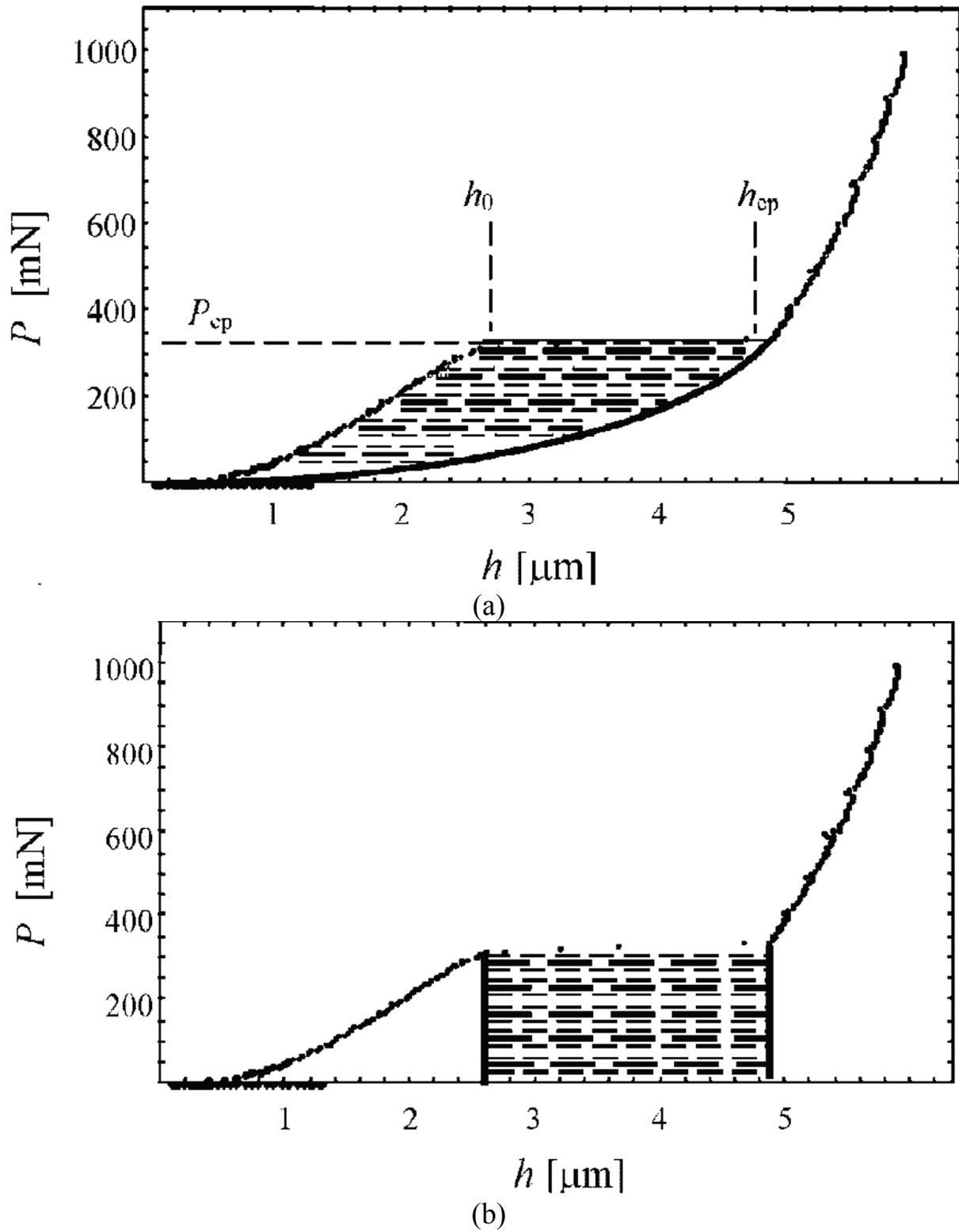


Fig. 14. Indentation load-displacement curves, showing the upper or lower bounds of the energy dissipated in the chipping during load-controlled experiment [129].

To eliminate the elastic-plastic deformation influence from substrate, Chen et al. performed small indentations in thin coating and examined the ultra small crack by atomic force

microscopy to calculate the toughness [133, 134]. The authors also proposed to calculate the energy for fracture based on extrapolating the total work vs. displacement curve at a load where cracking occurs. A possible cause of the overestimation of K_{IC} by energy approach comes from the occurrence of additional energy dissipation that cannot be separated from the energy for the fracture. This may be due to energy dissipation for plastic deformation of the coating due to buckling, substrate plastic deformation, or a contribution of interfacial fracture. Whilst Michel et al. calculated the fracture energy by subtracting the system load-displacement curve by the substrate Si load-displacement curve. In Fig. 15, the segment (GB) represents a partial loading curve of the Si substrate after chipping. The segment (GB) represents a partial loading curve of the Si substrate after chipping. The dotted area (ABEF) represents the energy under the step. The gray area 1 (ABH) indicated represents the energy released on chipping, while that area 2 (BEF), represents the energy of Si deformation.

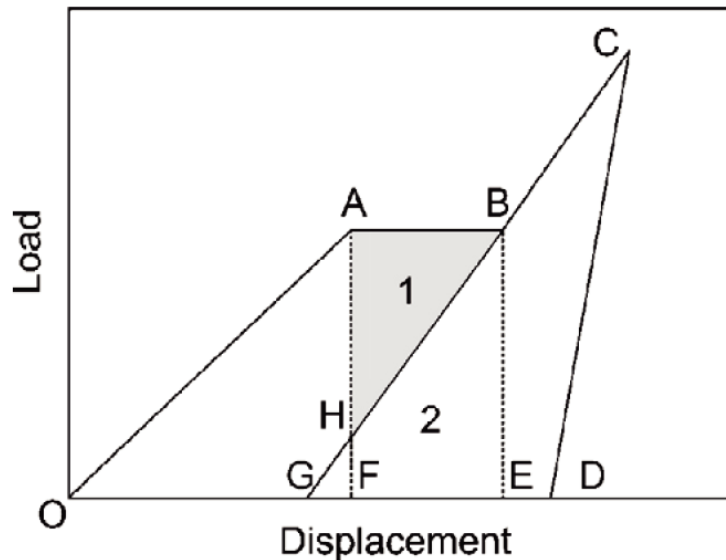


Fig. 15. Michel model schematic drawing representing load-unloading curve of nanoindentation in a coating after chipping [135].

Tensile testing of free-standing thin films with precrack induced by indentation recently was used to measure the toughness of 0.52 and 1 μm tetrahedral amorphous diamond-like carbon (ta-C) [136]. But this method needs wet etch the 2 μm SiO_2 interlayer between the coating and silicon substrate and post annealing which may affect the coating fracture behavior. It is difficult to widely apply such method due to difficulties in obtaining freestanding film without curling, precrack sharpness and accurate measurement of the precrack dimension. A simple two-step tensile method [137], it is based on strain energy difference between two tensile processes. A nc-TiN/a-SiN_x nanocomposite with thickness of 3.0 μm gives a toughness value of 2.6 $\text{MPa m}^{1/2}$. The drawback of the method involves the elastic deformation and perfect adhesion between coating and substrate.

Due to the unavailability of standard toughness database for the coatings, it is extremely difficult or even possible to determine the best method from those described in earlier sections. For comparison, the researchers should consider the availability and feasibility for their special coating systems.

Currently, there are relatively few toughness data available for thin nanocomposite coatings due to the difficulties in forming a sensible crack while reducing the substrate effect in the coatings. Toughness values of some nanocomposite are listed in table 4..

Table 4. Toughness values of some hard coatings

Materials	Toughness (MPa m ^{1/2})	Evaluation Method	Reference
TiC _x N _y /SiCN	1.0	Indentation	[138]
TiN/SiN _x	1.15	Indentation	[58]
Ni-doped nc-TiN/a-SiN _x	2.60	Two-step tensile test	[137]
YSZ/Au	1.6	Indentation	[139]
Nanolayered Cr/a-C	1.81-3.49	Indentation	[140]
Ni/Al ₂ O ₃	2.4	Indentation	[141]
ta-C	4.25~4.4	Tensile with precrack	[136]

8. CONCLUDING REMARKS

A variety of possibilities to deliberately improve the mechanical properties of hard coatings have been presented. Especially the hardness and toughness are of prime interest for many applications. The most important characteristics for the successful use of a hard coating are the tribological properties, hardness and toughness. While the high hardness has been continuously surveyed by many researchers, their toughness studies lagged behind due to the difficulties of quantifying the toughness values of the coatings. Systematical investigations of toughening mechanisms in hard nanocomposite coatings are in urgent need and so as the toughness characterization techniques.

Hard coatings development in the decades led to the appearance of a limited choice of coatings which were used for wide range of applications. This is especially true for the single-phase materials TiN, TiCN, and TiC. Future new coatings will have to compete against their

successful predecessors and therefore new hard coatings with synergetic combination of properties will occupy niches where no existing product can satisfy the requirements. Another incentive for the development of new performance-improved coatings is the scientific curiosity of materials scientists. Based on prediction rules and theoretical models, which emerged over the last two decades, the behavior of materials, the interaction between different phases, especially in the nanometer range, is fairly well understood. This knowledge will lead to the appearance of new coatings, which may have superior properties compared to those currently available.

A sensible route is to toughen superhard coatings to achieve what we call “hard yet tough” coatings. In principle, all toughening mechanisms can be applied to toughening of ceramic coatings, the real challenge lies in the implementation. Super hard nanocrystalline phases including diamond, carbon nitride, boron nitride, and some new oxides [142] will be incorporated into coatings to supply superhardness while an effective toughening agent will be used to toughen the brittle hard phases. One perspective will use CNT as a toughening agent. In-situ synthesis of carbon nanotube-imbedded nanocomposite (such as nc-TiC/a-C(CNT) or nc-TiN/a-Si₃N₄(CNT)) or nanocrystals imbedded in a complete matrix of carbon nanotubes (for instance, nc-TiAlN/CNT, or even nc-Diamond/CNT) may hold the key (at least, one of the keys) to this ideal “hard yet tough” coating, where the CNT-imbedded matrix or the CNT matrix provides the ultimate toughness to stop or block crack propagations and the nanocrystalline phase provides the superior hardness.

There is a widely accepted methodology to measure the coating hardness. In toughness measurement, however, the lack of a universally accepted toughness measurement methodology and instrumentation for coating has effectively hindered the progress of the research. It is anticipated that a universally accepted methodology will be developed in near future.

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CHAPTER 6

Plasma Enhanced Magnetron Sputter (PEMS) Deposition of Thick Nanocomposite Coatings for Erosion Protection

Ronghua Wei

Institute Scientist, Southwest Research Institute, 6220 Culebra Road
San Antonio, Texas 78238, USA

rwei@swri.org

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1. INTRODUCTION

Hard nitride coatings such as TiN prepared using Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD) technologies have been widely used for cutting tools to improve tribological properties and household appliances for both tribological and aesthetic purposes [1-5]. In this chapter, we will discuss another application of hard nitrides, and specifically nanocomposite coatings, in rotary machinery such as gas turbines against solid particle erosion (SPE) and steam turbines against liquid droplet erosion (LDE).

Erosion damage to the blades reduces engine efficiency and reliability [6,7]. Various coatings have been applied to combat erosion including soft materials such as polyurethane and epoxy to the hardest known material - diamond [8,9]. However, the most commonly used coatings are nitride or carbide coatings including single layered TiN, ZrN, CrN and TiAlN; multilayered Cr/CrN, Ti/TiN, TiN/TaN, W/WC and W/WN; and superlattice CrN/NbN [7,10-18]. Conventional PVD including magnetron sputtering and arc evaporation is commonly used method for the deposition of these coatings. CVD has been used to prepare coating such as boron carbide [8], boron phosphide (BP) [19] and TiC [20].

In recent years, Ti-Si-N based nanocomposite coatings (mainly nanocrystalline TiN in a matrix of amorphous Si₃N₄ or nc-TiN/a-Si₃N₄) have been actively studied by a number of research groups worldwide using mainly CVD and sometimes PVD (in particular, magnetron sputtering) [21-27]. These coatings are super hard and have shown high wear resistance in laboratory experiments. Therefore, it is believed that these coatings should also exhibit superb erosion resistance. For cutting applications, thin coatings of 2-5 μm are commonly used. However, relatively thick coatings (~15 μm) are normally required for erosion protection. To explore the possibility of using nanocomposite coatings for gas turbine compressor blades, preliminary studies were carried out which clearly demonstrated that nanocomposite coatings (Ti-Si-C-N) outperformed CrN, ZrN and TiN and dramatically reduced erosion of turbine materials [28-30].

In this chapter, the erosion mechanisms will be discussed with reference to a newly developed plasma enhanced magnetron sputter deposition technology. The emphasis will be specifically on nanocomposite coatings, i.e., Ti-Si-C-N. The preparation, characterization and evaluation of the these coatings will be discussed. The erosion resistance of these coatings will be compared with single-phased nitrides such as CrN, ZrN and TiN. The effect of processing parameters on the micro-nano structure, hardness, coating adhesion and erosion resistance will also be discussed. Furthermore, the coating properties will be correlated with the erosion behaviour. Finally, future research possibilities in this area will be discussed.

2. EROSION OF MATERIALS

Material removal from a solid surface due to successive impacts of solid particles or liquid droplets will eventually lead to the loss of usefulness of the component. The study of erosion

damage and its protection becomes important especially in aerospace and energy industries for turbines and offshore oil and gas production equipment [7,12,31-38]. Occasionally, erosion of a component occurs in a very complex manner and both SPE and LDE can be observed such as in oil or hydrocarbon transport equipment. Corrosion may also have to be considered in some applications [12,38,39]. The simultaneous erosion and corrosion can accelerate the degradation of materials. In this section the mechanisms of SPE and LDE will be reviewed. The main purpose of the discussion is to present information leading to the selection of protective coatings.

2.1. SOLID PARTICLE EROSION (SPE)

It has been observed that erosion is strongly influenced by the incident angle between the incident beam and the solid material surface. The erosion rate is commonly defined as the volume of the solid material removed per unit mass of incident particles. Depending on the nature of the material being eroded, the erosion rate of ductile materials such as metals peaks at about 15°-30°, while the erosion rate of brittle materials such as ceramics peaks at 90°, shown in Figure 1 [6,8,20,31,37]. For materials with both brittle-ductile characteristics, a combined erosion rate can be used [11,18].

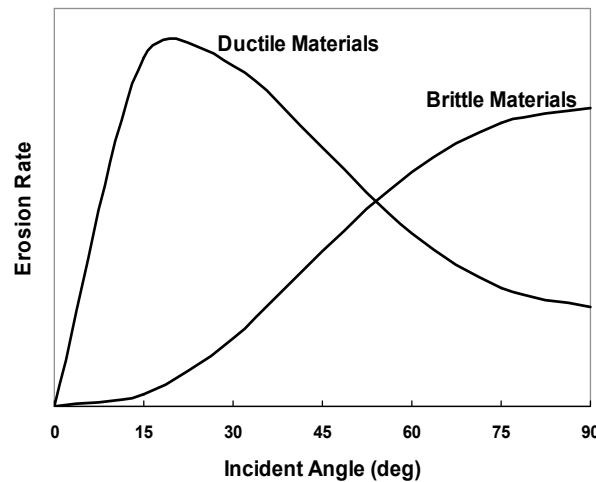


Fig. 1. Erosion rate of materials.

The erosion rate can be expressed as:

$$\varepsilon(\theta) = \varepsilon_{\perp} f(\sin \theta), \quad (1)$$

where $\varepsilon_{\perp}$ is the erosion rate at 90°, while $f(\sin \theta)$ can be written as $\sin^m \theta$ in one model [11], where m is determined by experiments, or

$$f(\sin \theta) = (\sin \theta)_{n_1} (1 + H(1 - \sin \theta))_{n_2} \quad (2)$$

in another model [40], where H is the hardness of the target material and n_1 and n_2 are constants determined by experiments.

For brittle materials, which is of most interest because bulk ceramic or coatings are widely used, using dynamic and quasistatic models [41,42], $\varepsilon_{\perp}$ can be written as:

$$\varepsilon_{\perp} = V^m R^n \rho^l K_c^{\alpha} H^{\beta} \quad (3)$$

where V , R and ρ are the velocity, radius and density of the incident particles, respectively, while K_c and H are the solid material fracture toughness and hardness, respectively. The exponent constants (m , n , l , α , β) are 3.2, 3.7, 0.25, -1.3, -0.25 and 2.4, 3.7, 1.2, -1.3, 0.11 in the dynamic model and quasistatic model, respectively [41,42].

From materials selection point of view, K_c and H are the two most important parameters. It is understood that a material with higher fracture toughness has a higher tolerance to crack initiation and growth, or it is less prone to chipping due to particle impact. In a comparative study of these two models, K_c was found to be -1.9, indicating the importance of the materials fracture toughness [43]. In contrast, the weak, positive dependence of erosion on hardness is counter intuitive. This is because in the quasistatic model for a fixed impact energy the maximum impact load increases as the hardness increases. Since the amount of chipping is proportional to the maximum load, the erosion rate increases as the hardness increases. However, it has been observed that diamond, the hardest material, showed the lowest erosion among a number of materials in two separate studies [8,9].

From the above discussion, one realizes that the toughness has a very strong influence on the erosion rate. Therefore, the high toughness together with the high hardness of nanocomposite coatings [44] may be more advantageous in combating erosion than single phased nitrides.

2.2. LIQUID DROPLET EROSION (LDE)

Compared to solid particle erosion, liquid droplet erosion (LDE) is much more difficult to model. It is known that the erosion rate is proportional to the impact velocity, V , and the incident angle, θ , [32,45,46]:

$$\varepsilon(\theta) \propto (V \sin \theta - V_c)^n / \sin \theta, \quad (4)$$

where V_c is the critical velocity, below which erosion will not occur. It is noted the incident angle used here is in consistent with the definition in SPE, which is the angle between the incident stream and the solid material. For materials selection, a relationship between erosion and the materials properties given in Eq. (3) would be useful. Unfortunately, no such a relationship could be established even after many years of research effort by the LDE researchers [32]. Although the erosion resistance was found to be proportional to $H^{8/3}$, the scatter from the results was very wide [47] and we can only use this as a general guideline.

In addition to hardness of a material, there is a good correlation between the strain energy and erosion resistance except for a few materials [48,49]. Even though an analytical expression to correlate the materials properties with the erosion rate, as in SPE, is required a high toughness and a high hardness are desirable.

3. PLASMA ENHANCED MAGNETRON SPUTTER DEPOSITION

Hard coatings such as TiAlN, CrN and ZrN have been studied for erosion protection. They are prepared using physical vapor deposition (PVD) processes, in particular, magnetron sputtering. In this section, we will introduce a new technology – plasma enhanced magnetron sputter deposition.

3.1. PRINCIPLE OF PEMS

Plasma enhanced magnetron sputter (PEMS) deposition is an improved version of conventional magnetron sputtering. Figure 2 shows a schematic of the PEMS process. The PEMS technique introduces an electron source such as a hot filament or a hollow cathode to generate electrons. When the DC power supply (discharge) applied between the electron source and the chamber wall, the electrons are accelerated toward the wall. The presence of the gas(es) in the vacuum chamber causes electron-neutral collisions resulting in ionization of the gas(es) and hence generating plasma.

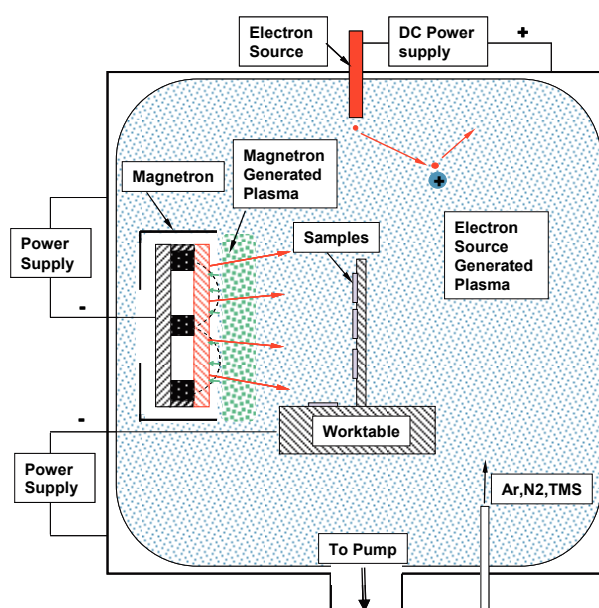


Fig. 2. PEMS schematic.

3.2. COMPARISON WITH CONVENTIONAL MAGNETRON SPUTTERING

There are a few, but significant, advantages of the PEMS process for preparing a coating. Almost all PVD processes aim to achieve adherent and dense coatings. Prior to deposition, sample cleaning is a crucial stage to obtaining an adherent coating. During deposition, adequate ion bombardment of the growing coating is very important to achieve a dense coating. The PEMS technology provides the means for both thorough sample cleaning and intense ion bombardment in both stages.

In conventional magnetron sputtering (CMS), during the cleaning stage, sometimes the magnetron is turned on at a low power to generate the plasma. The substrate is then biased at a high voltage to achieve sputter cleaning of the substrate. Even when the magnetron is at low power, inevitably some of the target material will be sputtered off and hence deposited on the samples even before they are cleaned. In other cases, the magnetron is not turned on but a glow discharge is generated by using a high pressure in the chamber and a high bias voltage. When the cleaning process is finished, the chamber is evacuated to a low pressure under which the magnetron can be turned on for the film deposition. Due to the transition, ion bombardment of the sample surface will be interrupted. As a result, the surface can be re-oxidized due to the presence of residual water vapor in the vacuum chamber. The oxidation process can occur quickly because the surface now is fresh, free from the native oxide barrier, and the water molecules are energetic in the plasma environment.

For the PEMS process, as can be seen from Figure 2, the electron source generated plasma is independent of the magnetron plasma. Therefore, during the sputter cleaning, the magnetron remains off. The electron source-generated plasma is sufficient for the cleaning. After the sputter cleaning, the magnetron is turned on while the electron source remains on. Hence, there is no interruption during the transition from sputter cleaning to deposition. During the deposition, in addition to the magnetron plasma, the electron source-generated plasma provides much more intensive ion bombardment and up to 25 times the ion current density was measured. Furthermore, since the electron source-generated plasma is controlled by the electron emission independently, nearly any ion-to-atom ratio, an important parameter for PVD processes, can be achieved. This is quite different from CMS, in which increasing the magnetron power to increase the ion-to-atom ratio also increases the neutral flux of the target material. As a result, the net ion-to-atom ratio barely changes.

To show the advantages of the PEMS process, Cr coatings were prepared using both the CMS and the PEMS processes under similar conditions as shown in Table 1. Figure 3 shows the morphological and cross-sectional SEM images of the coatings. As can be seen, the CMS deposited coating structure is a typical columnar structure and very loose. In contrast, the PEMS deposited coating is nearly featureless and very dense. This coating falls in the zone “T” in the Thornton structure zone model [50,51] due to the intensive ion bombardment (not the pressure), which was explained by Messier et al. [52]. It is particularly noted from Table

1 that the current density on the sample obtained by the PEMS process is increased by a factor of 16.5. For the same deposition time, the PEMS deposited coating is notably thinner due to the intense ion bombardment that both densifies and sputters the coating shown in Figure 3.

The PEMS technology thus produces much better TiN coatings for cutting tool applications [53,54] and the superior performance may be attributed to the very fine (~ 60 nm) TiN microstructure that is formed due to the heavy ion bombardment [55].

Table 1. Deposition parameters for CMS and PEMS deposited Cr on Si.

Deposition Method	Pressure (mTorr)	Mag Power (W)	Disch Voltage (V)	Disch Current (A)	Sample Bias (V)	Bias Current (A)	Bias Current Density (mA/cm ²)	Sample-Target Distance (mm)	Deposit Time (hrs)
CMS	2.3	500	-	-	-40	0.01	0.2	100	3
PEMS	2.3	500	120	9	-40	0.19	3.3	100	3

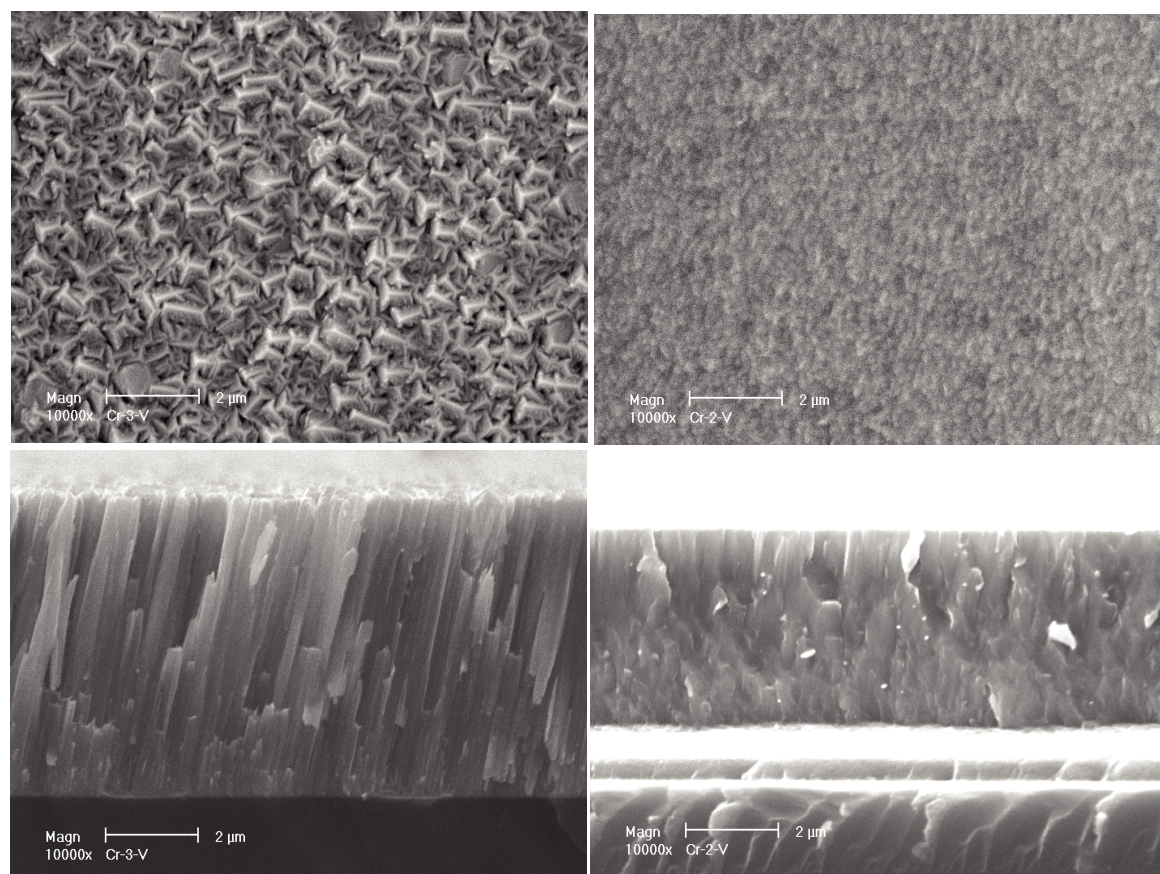


Fig. 3. Morphological (top) and cross-sectional (bottom) SEM images of CMS (left) and PEMS (right) deposited Cr on Si.

3.3. FILM PREPARATION

The preparation process in the PEMS technology is similar to that in the CMS technologies. As shown in Figure 2, normally samples are placed on the worktable. The vacuum chamber is pumped down to about 10^{-6} torr and Ar is then fed into the chamber to a pressure of about 2-5 millitorr. The electrons are generated using the electron source. By applying a negative voltage, typically about 120 V, to the electron source with respect to the vacuum chamber, electrons are attracted to the chamber. By adjusting the electron emission, a desired discharge current is obtained. After that, the worktable is biased with a DC power supply to about 100-150 V, so that an ion current can be obtained and ion sputter cleaning begins. In the PEMS process, no external heater is required and the sample heating, water vapor outgassing and ion sputter cleaning are accomplished mostly by the ion bombardment power alone (ion current density times the ion energy).

Once the samples are cleaned and the prescribed processing temperature is reached, after about 30-60 minutes, sputter deposition of a hard coating begins by turning on the magnetron power and bleeding nitrogen at a predetermined flow rate for nitride formation or acetylene for carbide formation. Meanwhile, the bias voltage on the worktable is reduced to -40 V to minimize heavy sputtering of the as-deposited film and internal stress. The current density is adjusted to the required level by only changing the electron emission. It should be pointed out that multi magnetrons and multi electron sources can be used for high volume production purposes.

The next section considers the effects of the deposition parameters on the properties of hard nitrides and superhard nanocomposite coatings using the PEMS process. This will be followed by a discussion of the film characterization and the erosion resistance of various coatings.

3.4. DEPOSITION OF NITRIDE AND NANOCOMPOSITE COATINGS

As mentioned in the earlier sections, materials with both high hardness and high toughness are desirable for increased erosion resistance. Nanocomposite coatings have been found to be both hard and tough due to their unique composite structure [22,24,44,56-59]. In particular, nc-TiN/a-Si₃N₄ (nanocrystalline TiN in an amorphous Si₃N₄ matrix) coatings have attracted considerable interest for a wide range of applications [60-65]. In order to demonstrate the superior erosion resistance of nanocomposite coatings, various nitrides (TiN, CrN and ZrN) were also prepared. In preparing these nitrides, besides the selection of the target materials, the partial pressure of nitrogen was slightly different for each nitride coating. Other ion sputter cleaning and deposition parameters were kept almost identical. In preparing the nanocomposite coatings, in addition to N₂ feed gas for the nitride formation, trimethylsilane ((CH₃)₃SiH or TMS) was also used as the precursor, while pure Ti (or Zr) were sputtered to form TiSi_xC_yN_z (or ZrSi_xC_yN_z).

It should be pointed out that using the TMS precursor for Si is advantageous over magnetron sputtering from a solid Si target or using a silane precursor (SiH_4). If Si is sputtered from a solid target, unless a composite target of Ti-Si is used, it is difficult to use two separate targets of Ti and Si to obtain homogeneous coatings in a large vacuum chamber. The sputtering rate of Si is usually low because it is a semiconductor compared to Ti. Besides, the rate control for Si is difficult especially in a N_2 environment. Certainly, a composite target of Ti-Si may solve the uniformity issue; however, not only is the target costly, but also many targets with various compositions have to be prepared before an optimized composition can be determined. SiH_4 is undesirable because it is a pyrophoric gas and requires special gas handling equipment for safe use and requires training for the operators. Even though it is commonly used in semiconductor industry or in research environments, for commercial tribological coatings, it is rarely used. In contrast, TMS is flammable but not pyrophoric and can be handled in a similar way as many other flammable gases. It should be pointed out that Ti-Si-C-N has been prepared using CVD processes [66-70], but both TiCl_4 and SiCl_4 were used in all of these studies. TMS is much safer and easier and should not cause severe corrosion to the vacuum chamber and pumps.

3.5. COMPARISON OF SINGLE PHASED NITRIDE COATINGS WITH NANOCOMPOSITE COATINGS

In order to demonstrate the advantages of the nanocomposite coatings using the PEMS process, we conducted a comparative study in which both single phased nitride coatings and nanocomposite coatings were deposited and erosion tested. All samples were made of Ti-6Al-4V material to 25 mm in diameter and 3 mm thick. The substrates were polished to a surface roughness of about 10 nm Ra, and then CrN, ZrN, TiN, $\text{ZrSi}_x\text{C}_y\text{N}_z$ and $\text{TiSi}_x\text{C}_y\text{N}_z$ coatings were deposited. For simplicity, we will use ZrSiCN and TiSiCN to represent the $\text{ZrSi}_x\text{C}_y\text{N}_z$ and $\text{TiSi}_x\text{C}_y\text{N}_z$ coatings in the rest of this chapter.

3.5.1. DEPOSITION CONDITIONS

Table 2 shows the deposition parameters used for the selected coatings. Column 1 shows the coatings. Columns 3 and 4 are the magnetron power. It is noted in some tests two magnetrons were used. Based on the magnetron surface area, the power density is calculated and listed in column 5. Column 6 shows the nitrogen flow rate in sccm (standard cubic centimeter per minute), while Column 7 the TMS flow rate. Column 8 shows the bias current density calculated from the total ion current obtained on the worktable. The bias voltage during the deposition, not listed in the table, was -40 V for all the tests. Listed in the last column is the coating thickness. It is also noted that no single layered ZrSiCN coatings are listed in the table. This is because the single layered ZrSiCN coatings, deposited under various conditions, were all cracked or flaked off due to the high internal stress. Therefore, a multilayer coating, ZrSiCN/Zr was prepared to minimize the stress. TiN/Ti is also a multilayered coating. This sample was used because multilayered TiN/Ti is commonly used

in commercial erosion resistant coatings. The coating of this sample is very thick. This is to study the thickness effect on the durability in the erosive environment.

Table 2. Deposition parameters of nitride and nanocomposite coatings for comparison.

Base Material/ Coating	Sample	Mag 1 Power (W)	Mag 2 Power (W)	Mag Power Density (W/cm ²)	Flow Rate N ₂ (sccm)	Flow Rate TMS (sccm)	Bias Current Density (mA/cm ²)	Coating Thick- ness (μm)
Ti-6Al-4V		-	-	-	-	-	-	-
CrN		2	-	8.7	25	-	4.0	16.6
ZrN	1	4	-	17.3	22	-	2.9	7.5
ZrN	2	4	-	17.3	25	-	1.9	10.0
ZrN	3	2	2	8.7	31	-	3.1	22.0
ZrSiCN/Zr*		4	-	17.3	0/25	-	2.9	26.0
TiN		4	-	17.3	23	-	2.9	18.8
TiN/Ti*		3	3	13.0	0/40	-	3.1	43.0
TiSiCN	1	4	-	17.3	23	3.0	1.7	18.1
TiSiCN	2	3	3	13.0	35	3.5	3.1	33.0
TiSiCN	3	4	-	17.3	23	3.0	2.5	26.0

* Multilayer

3.5.2. EROSION TEST

After the deposition, we conducted sand erosion tests using the following parameters: erodent – 50 μm Al₂O₃ at 80 psi back pressure; incident angle – 30°; nozzle diameter – 1.5 mm; and distance between nozzle and sample surface – 20 mm. To minimize the pressure drop in prolonged blasting, pulsing of the air pressure was used. In each test, the pulse was on for a period of 10 seconds and off for 10 seconds. A total of 10 pulses, which constituted a test cycle, were performed before the sample was cleaned and weighed using a balance with an accuracy of 10⁻⁵ g to measure the weight loss. The volume loss was then calculated using the published density data for uncoated Ti-6Al-4V, CrN, ZrN and TiN (4.43, 5.9, 7.09, 5.43 g/cm³, respectively). For ZrSiCN and TiSiCN, the bulk densities of ZrN and TiN were used since no data on ZrSiCN and TiSiCN were available. In addition the Si concentration was measured to be small. The erodent consumed during the spray was measured several times using a container which was carefully sealed, and the mass was weighed using a micro balance. The average value was used in calculating the erodent mass consumption.

Figure 4 shows the cumulative volume loss as a function of the erodent for the coatings given in Table 2. Uncoated Ti-6Al-4V is used as the baseline. As can be seen, all nitride and nanocomposite coatings reduce erosion from the baseline Ti-6Al-4V. Ranked from the worst to the best in erosion resistance are the coatings of CrN, ZrN, ZrSiCN, TiN and TiSiCN. It is also noted that the volume loss for all the TiSiCN coatings is nearly zero even at the end of the test. Another feature of the data is the linearity. From the data, we can see that the

erosion rate is nearly constant for all the coatings except one TiN coating. In later sections, we will use erosion rate (coating volume loss/erodent mass in mm^3/g).

It is evident that TiN has a much better erosion resistance than both CrN and ZrN which is inconsistent with the published data [11], in which ZrN showed lower erosion rates.

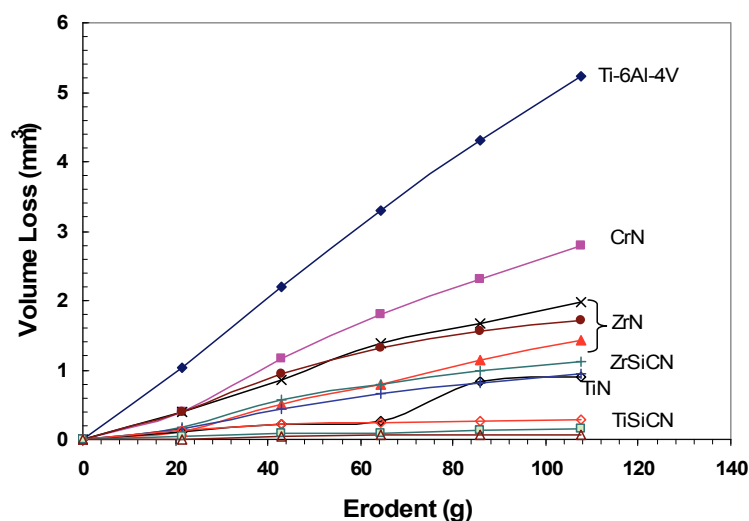


Fig. 4. Erosion resistance of various nitride and nanocomposite coatings.

3.5.3. NANO HARDNESS

The nanohardness and elastic modulus were measured using a nanoindenter and the results are presented in Table 3. As can be seen, CrN has the lowest hardness amongst of all the coatings studied. The hardness for ZrN, ZrSiCN and TiN is around 30 GPa. In contrast, the hardness of TiSiCN is in excess of 42 GPa, which is in the “superhard” range defined by the hard coating research community [24, 71-74].

Table 3. Nanohardness and elastic modulus of nitride and nanocomposite coatings.

	Nano Hardness (GPa)	Elastic Modulus (GPa)	H/E	H ³ /E ²
CrN	24.5	278.0	0.09	0.19
ZrN	33.8	317.3	0.11	0.38
ZrSiCN	29.6	241.2	0.12	0.45
TiN	31.7	333.7	0.09	0.28
TiSiCN	42.4	299.7	0.14	0.85

Table 3 also shows the values of H/E and H^3/E^2 . As discussed extensively by Musil et al., H/E is strongly related to the mechanical response, while H^3/E^2 represents toughness, or resistance to crack formation and propagation [24,44,75]. TiSiCN has the highest H^3/E^2 value among all the coatings studied and it has the highest erosion resistance. Hence, a high value of H^3/E^2 is believed to be the key characteristic of the tough and strong nanocomposite coatings.

3.5.4. MICRO-NANO STRUCTURES

The micro-nano structure analyses of the coatings were studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The detailed results can be found in Refs. [28-30]. In brief, for single phase nitrides (CrN, ZrN and TiN), the XRD major peaks are similar to the published data but the grain sizes are less than 100 nm due to the high current density of the PEM process. For TiSiCN coatings, TiN and/or $\text{TiC}_{0.3}\text{N}_{0.7}$ are the major XRD peaks. The grain size is much smaller, about 10 nm while no SiC_xN_y is present. This is in agreement with the nc-TiN/a- Si_3N_4 studies where Si_3N_4 is XRD transparent.

4. PARAMETRIC STUDY OF NANOCOMPOSITE COATINGS USING THE PEMS PROCESS

To better understand the TiSiCN nanocomposite coatings, a series of tests were designed and conducted. Based on the thick nitride coating studies [28-30], it was concluded that the partial pressures of N_2 and TMS are important for good micro-nanostructure formation and erosion resistance. Therefore, both N_2 and TMS flow rates were varied systematically, while other deposition parameters were held constant. A total of ten tests were conducted and in each test, a number of samples were deposited for various characterization tests including the erosion test.

4.1. EXPERIMENT DESIGN

In this series of study, Ti-6Al-4V was used as the substrate and the samples were prepared by the process discussed earlier. The deposition parameters are listed in Table 4. There are 10 tests in this series and they are divided into 5 groups. In the first group (sample numbers TiSiCN1 and 2), the TMS flow is 0 sccm, while N_2 flow rate varies from 25 to 50 sccm. The coatings thus formed are TiN. In the second group (sample numbers TiSiCN3-5), the N_2 flow is 50 sccm, while the TMS flow rate varies from 3 to 9 sccm. In the third group (samples TiSiCN6-8), the N_2 flow rate is decreased to 25 sccm, while the TMS flow rate varies from 3 to 9 sccm. With the addition of TMS, the coating thus formed is a composite coating TiSiCN. In the fourth group (sample TiSiCN9), no nitrogen was used. The coating thus formed is in the form of TiSiC. In the last group, a thicker coating was deposited using the same recipe as for sample TiSiCN6. The other deposition parameters are shown in the footnotes of the table. The analytical data obtained from these coatings are shown from

columns 4 through 8 while the erosion data are listed in the last three columns. The discussion for the results follows.

Table 4. Deposition parameters used and results of nanocomposite coatings.

Sample No.	Film Deposition			Results						
	N ₂ Flow Rate (sccm)	TMS Flow Rate (sccm)	Coating Thick (μm)	XRD Major Peaks	Average Grain Size (nm)	Micro-structure Ranking	Rc Adhesion Ranking	Erosion Rate (mm ³ /g)		
								30°	90°	Average
Group 1 TiN										
TiSiCN1	25	0	25.0	TiN	9.5	2	1	0.00209	0.01968	0.01089
TiSiCN2	50	0	11.9	TiN, Ti	>100	2	1	0.00523	0.02282	0.01402
Group 2 TiSiCN										
TiSiCN3	50	3	9.8	TiN, TiCN, Ti	5.8	1	1	0.00017	0.00755	0.00386
TiSiCN4	50	6	9.3	TiN, TiCN, Ti ₄ N ₃	5.2	1	2	0.00017	0.00435	0.00226
TiSiCN5	50	9	9.0	TiN, TiCN, Ti	5.0	1	5	0.00017	0.00186	0.00101
Group 3 TiSiCN										
TiSiCN6	25	3	23.0	TiN, TiCN	15.2	2	3	0.00412	0.00859	0.00636
TiSiCN7	25	6	21.4	TiN, TiCN	57.7	3	2	0.02352	0.02706	0.02529
TiSiCN8	25	9	19.2	TiN, TiCN	10.2	3	1	0.01765	0.02497	0.02131
Group 4 TiSiC										
TiSiCN9	0	6	29.8	Ti	10.6	1	6	0.03130	0.02154	0.02642
Group 5 Thick TiSiCN										
TiSiCN10	25	3	26.7			4	6	0.01214	0.01521	0.01367
Base material										
Ti-6Al-4V	-	-	-	-		-	-	0.04520	0.02399	0.03459

Sputter cleaning at 120V, 10A discharge for 90 min.
Two magnetrons, 4kW each, Ar flow rate = 150 sccm
Microstructure ranking: 1 - best, 4 - worst.
Rc Adhesion Ranking: 1 - best, 6 - worst.

4.2. SEM STUDY

Figure 5 shows the SEM images of a few selected samples showing the effect of N₂ and TMS flow rates. Figures 5a and 5b show morphological (left) and cross-sectional (right) SEM images of TiSiCN1 and TiSiCN2, both of which are TiN. The difference between them is the effect of the partial pressure of N₂. As for TiSiCN9 (Figure 5c), no N₂ was used so it should be in the form of TiSiC.

From the cross-sectional micrographs of Figures 5a and 5b, sample TiSiCN1 seems to have denser structure than that of TiSiCN2, which is a typical columnar structure. However, the topological graph of TiSiCN1 indicates the coating is still loose. In contrast, sample TiSiCN9 (Figure 5c) looks amorphous and quite dense.

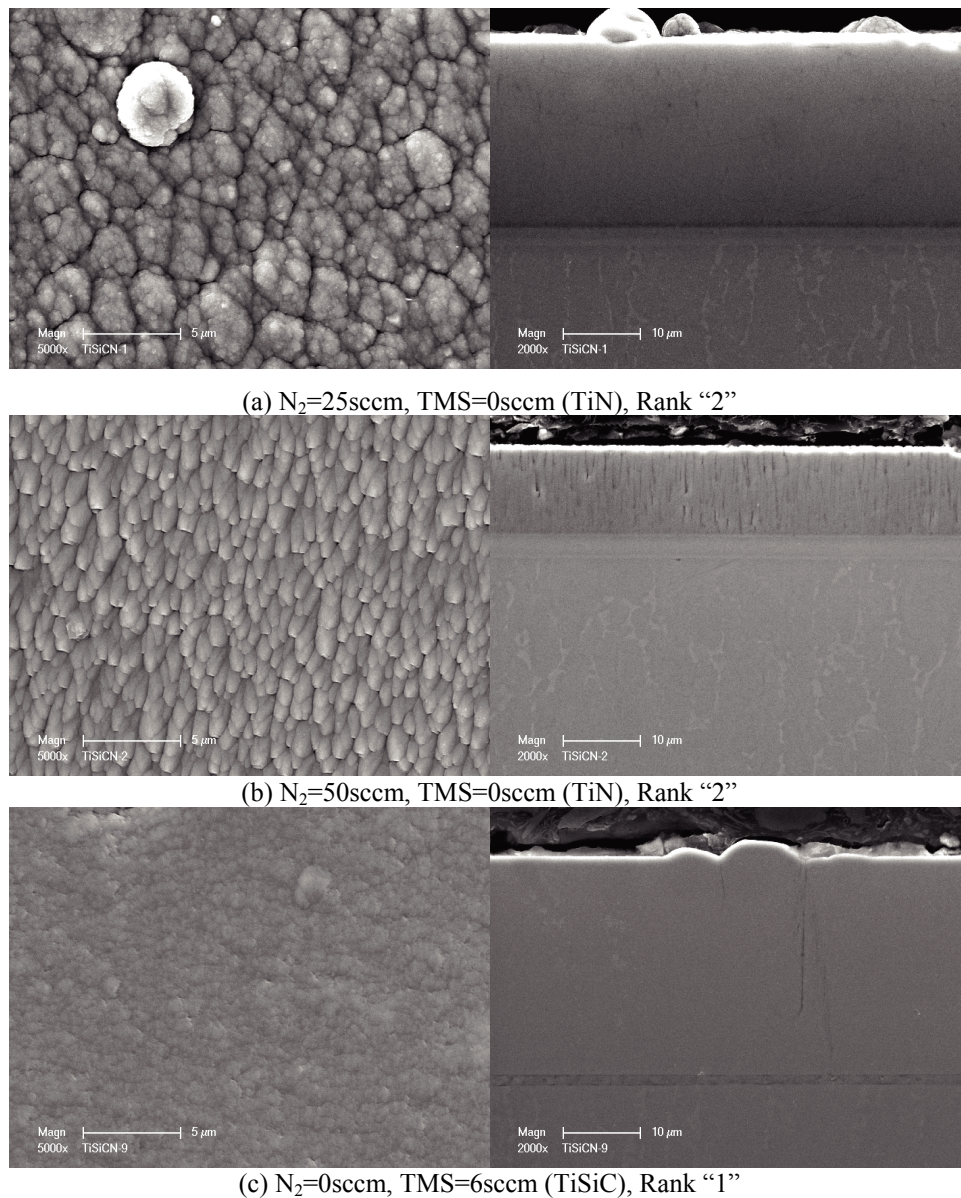


Fig. 5. Effect of N_2 and TMS on morphology (left) and microstructure (right) of various coatings.

Rockwell C scale indentation is one method that has been widely accepted in evaluating coating adhesion [76-78]. In this method after indentation, the crack pattern of the coating is examined and the adhesion is ranked from "1" through "6". Detailed results on coating adhesion will be discussed in the next section. By mimicking the adhesion ranking method, we ranked the coating microstructure from "1" to "4" with "1" being the best (dense, few inclusions, less columnar structure, etc), and "4" being the worst (loose, many inclusions, clear columnar structure, etc). The microstructure ranking for the samples shown in Figure 5 is given under the graphs and also listed in Table 4. Clearly, sample TiSiCN9 is superior to

samples TiSiCN1 and 2. However, one may have to consider other factors including the adhesion and erosion resistance, which will be discussed in later sections.

Figure 6 shows the effect of TMS and N_2 flow rates on the morphology and microstructure of TiSiCN coated samples. For sample TiSiCN6 ($N_2=25$ sccm, TMS=3 sccm) the coating is smooth and featureless (Figure 6a) but at a higher TMS flow rate (TMS=6) the coating becomes more crystalline or columnar (Figure 6b). The micrographs for TMS=9 sccm are similar to those shown in Figure 6b. Shown in Figure 6c are the micrographs for flow rates of $N_2=50$ sccm and TMS=3 sccm. It is clear that under these conditions, the coating becomes very dense and smooth. As for the other two samples in this group (TMS=6 and 9 sccm), the micrographs are nearly identical to those shown in Figure 6c. Using the same microstructure evaluation method, the ranking for all samples is listed in Table 4. To illustrate the “worst” coating microstructure, the SEM images of sample TiSiCN10 are shown in Figure 7.

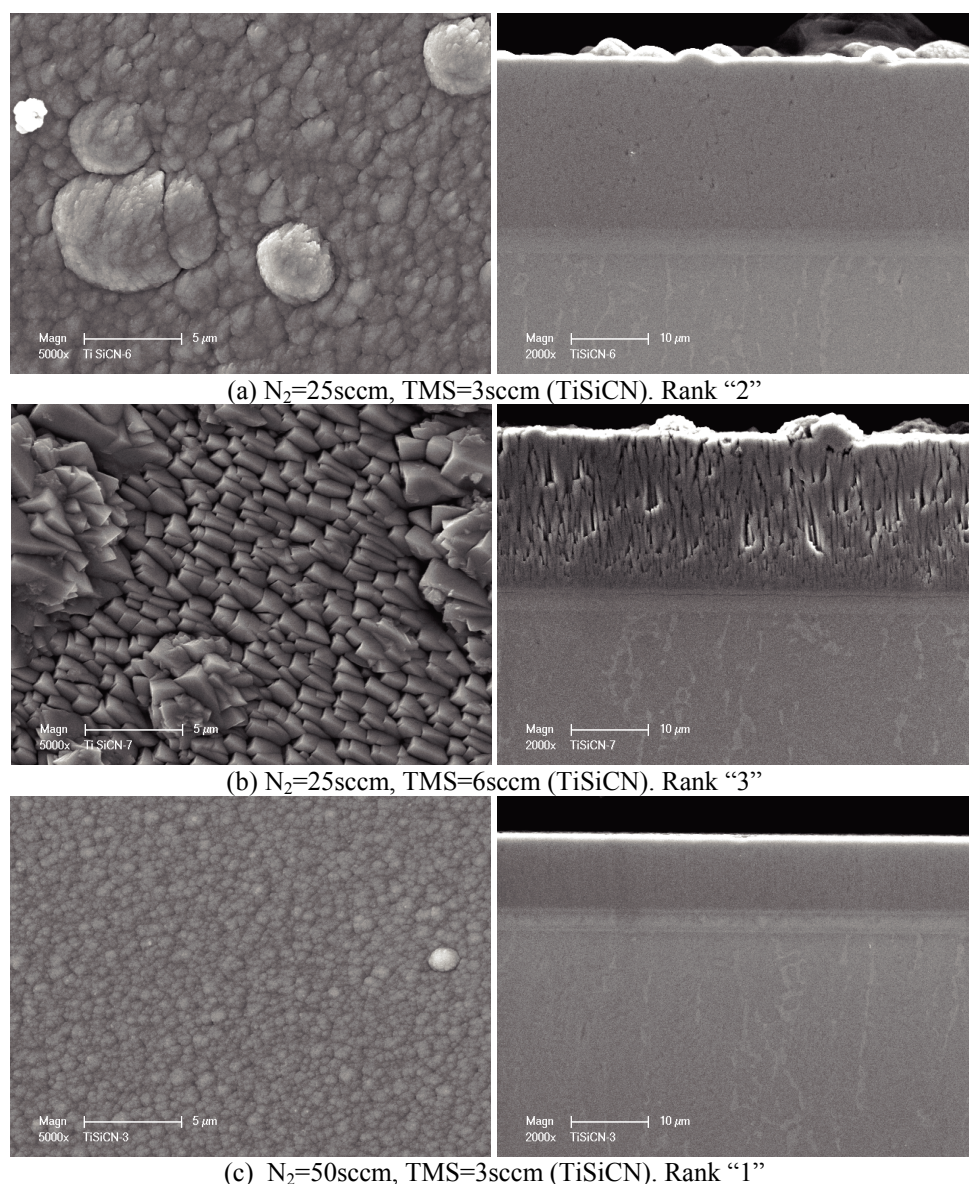


Fig. 6. Effect of TMS and N_2 flow rates on morphology (left) and microstructure (right).

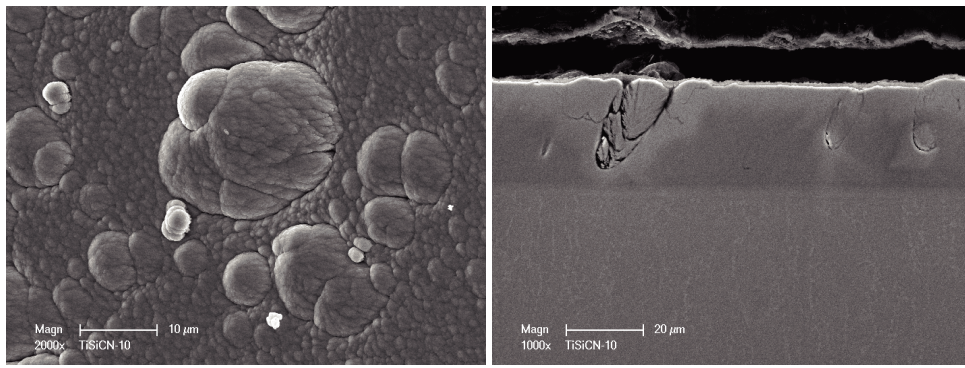


Fig. 7. Morphology and cross-section structure of sample TiSiCN10. Rank “4”.

4.3. ADHESION TEST BY ROCKWELL C INDENTATION

Coating adhesion can be evaluated using a number of methods including scratch test [79-80] and Rc indentation [76-78]. In Rc tests, by examining the crack patterning and assigning the adhesion ranks from “1” through “6”, one can obtain the coating quality. Figure 8 shows SEM images of TiSiCN1, TiSiCN2, TiSiCN9 and TiSiCN10. Sample TiSiCN2 (higher N_2 flow rate) looks smoother but many small cracks form after the indentation. However, no delamination can be observed. For sample TiSiCN9, the adhesion of the TiSiC coating is very poor and the coating delaminated all around the indent. Similarly, the thick TiSiCN coating (sample TiSiCN10) also failed after indentation. Using the Rc adhesion ranking, the numbers for each coating are given in the figure and in Table 4.

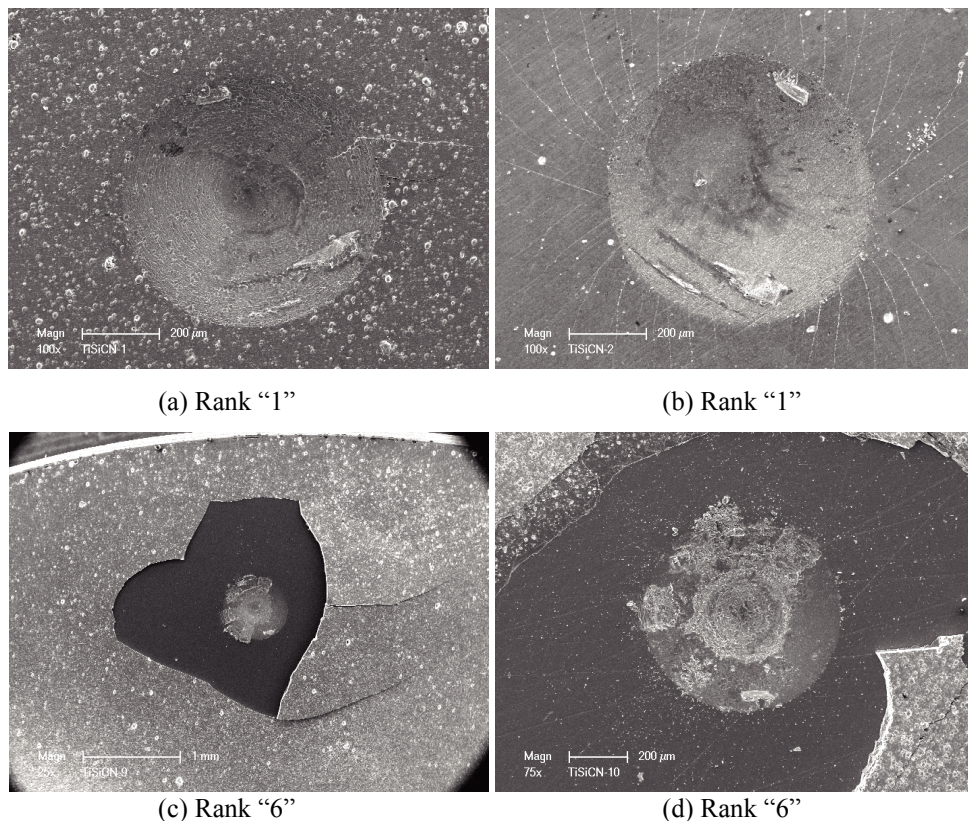


Fig. 8. SEM images of indents of (a) TiSiCN1 ($N_2=25\text{sccm}$, $TMS=0$) and (b) TiSiCN2 ($N_2=50\text{sccm}$, $TMS=0$), (c) TiSiCN9 (TiSiC) and TiSiCN10 (thick TiSiCN).

Figure 9 shows SEM images of various coatings indented with an Rc load of 150 kg and Figure 9a is a SEM of the sample of TiSiCN6 ($N_2=25$ sccm, TMS=3 sccm). No cracks are evident around the indentation. Hence its Rc adhesion rank is “1”. This sample structure looks loose and a high magnification of the surface is shown in Figure 6a. As for other samples coated with the N_2 flow rate of 25 sccm (TiSiCN7 and TiSiCN8), the Rc indentation looks the same as TiSiCN6. Figure 9b shows sample TiSiCN3 ($N_2=50$ sccm, TMS=3 sccm) and some cracks can be observed. However, no delamination of the coating has occurred. The coating is very dense, which can also be seen in Figure 6c. Further increase in the TMS flow rate results in more cracks near the indentation and some spallation (Figures 9c and 9d). Therefore, it can be concluded that the coating surfaces prepared with the flow rate of 25 sccm N_2 are rougher than those prepared at 50 sccm N_2 ; however, the coatings deposited at the low N_2 flow rate are more crack tolerant. At the 50 sccm N_2 flow rate, the higher the TMS flow rate, more cracks formed after Rc indentation. In some areas delamination occurred. Cracking and delamination of the coating in service can be detrimental because it may become the site for fatigue cracks. Although further more detailed studies are required, it may be postulated that the coatings deposited with a N_2 flow rate of 50 sccm may have the lowest fatigue resistance. The Rc indentation adhesion ranking for all samples is given in Table 4.

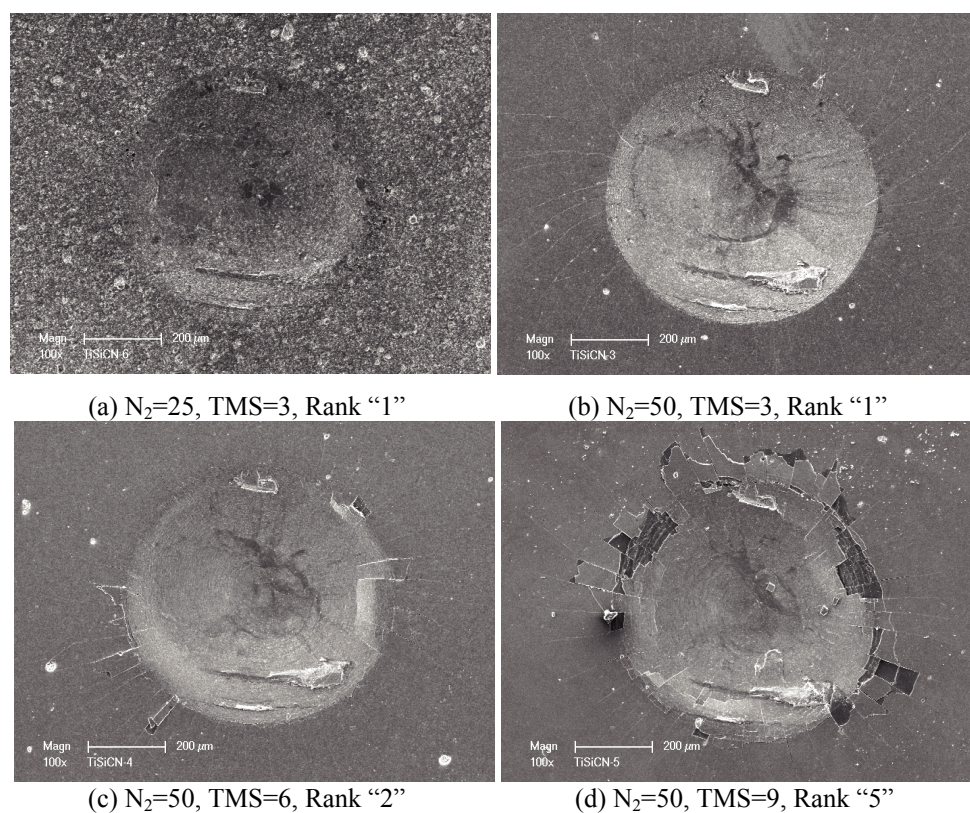


Fig. 9. Effect of flow rates in sccm of N_2 and TMS on coating adhesion.

4.4. MICROHARDNESS MEASUREMENT

The microhardness of selected samples was measured using a Vicker's indenter with a wide range of loads, and the data are plotted in Figure 10. It is evident that, due to the limited thickness of the coating, the hardness at a high load is influenced by the substrate, while the hardness at the lowest load may represent the coating hardness. In addition to the samples listed in Table 4, we plotted the hardness for sample TiSiCN23, which was deposited at a N_2 flow rate of 23 sccm and a TMS flow rate of 3 sccm using only one magnetron of 4 kW, and a multilayered TiSiCN/Ti coating.

From Figure 10, it can be seen that the hardness of sample TiSiCN1 is much higher than that of sample TiSiCN2, especially at high loads. This can be attributed to the coating thickness. As shown in Table 4, TiSiCN1 is over twice as thick as TiSiCN2. Figure 10 clearly shows that TiSiCN3 has a higher hardness, especially at low loads, than that of TiSiCN2. This is due to the addition of TMS. As discussed before, TiSiCN2 is actually a TiN coating while TiSiCN3 is a nanocomposite coating. As the load increases, the hardness difference between these two coatings decreases because both coatings are fairly thin and the substrate effect becomes relatively more pronounced.

Sample TiSiCN6 has the same coating hardness as TiSiCN3, but it is much thicker than TiSiCN3. Therefore, even at a very high load, its hardness is still quite high. Although TiSiCN10 is only a few micrometers thicker than TiSiCN6, the hardness increases even further at high loads. At the lowest load (<100 g load), no clear indentation was distinguishable. And therefore, no data were obtained.

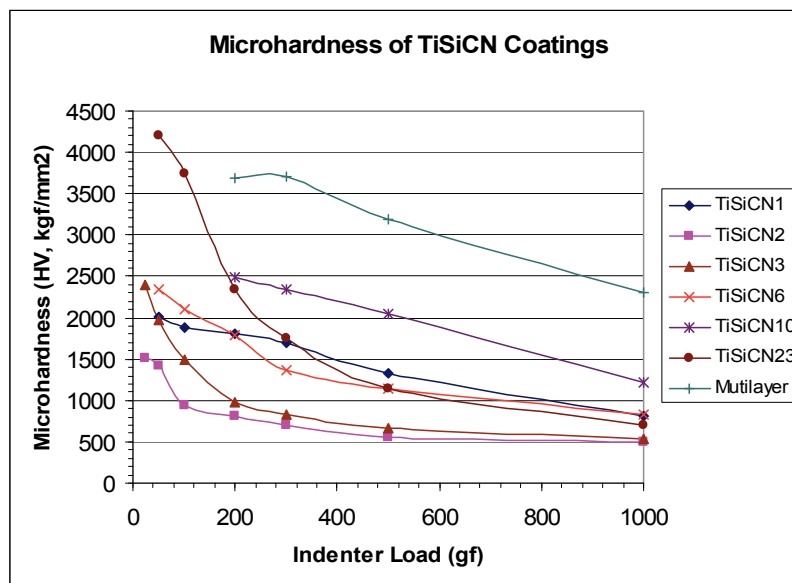


Fig. 10. Microhardness of selected TiSiCN coatings.

A multilayer coating of TiSiCN/Ti was prepared to further improve the mechanical properties of the nanocomposite coatings such as fatigue resistance. Its hardness is shown in Figure 10. It is clear that the hardness of the multilayer coating is much higher than that of the single layered thick TiSiCN10 coating and reaches above 3500 kgf/mm^2 . It should be mentioned that sample TiSiCN23, not listed in Table 4, has a very high hardness of over 4200 kgf/mm^2 and is in the superhardness category.

4.5. X-RAY DIFFRACTION

The micro-nano structure of the TiSiCN series of samples was analyzed using X-ray diffraction and Figures 11a and 11b show the spectra for samples TiSiCN1 and TiSiCN2, respectively. Since no TMS was used during the deposition of these two samples, both of which should form TiN. As can be seen, only TiN is identified in TiSiCN1. The broad peak indicates the grain size is small with an average grain size estimated to be 9.5 nm. In contrast, the XRD peaks of TiSiCN2 are much narrower and the average grain size is $>100 \text{ nm}$. In addition to the TiN phase, TiCN and Ti have also been identified. The small peaks for TiCN are possibly from the carbon incorporation from pump oil, as discussed in the composition analysis in the next section.

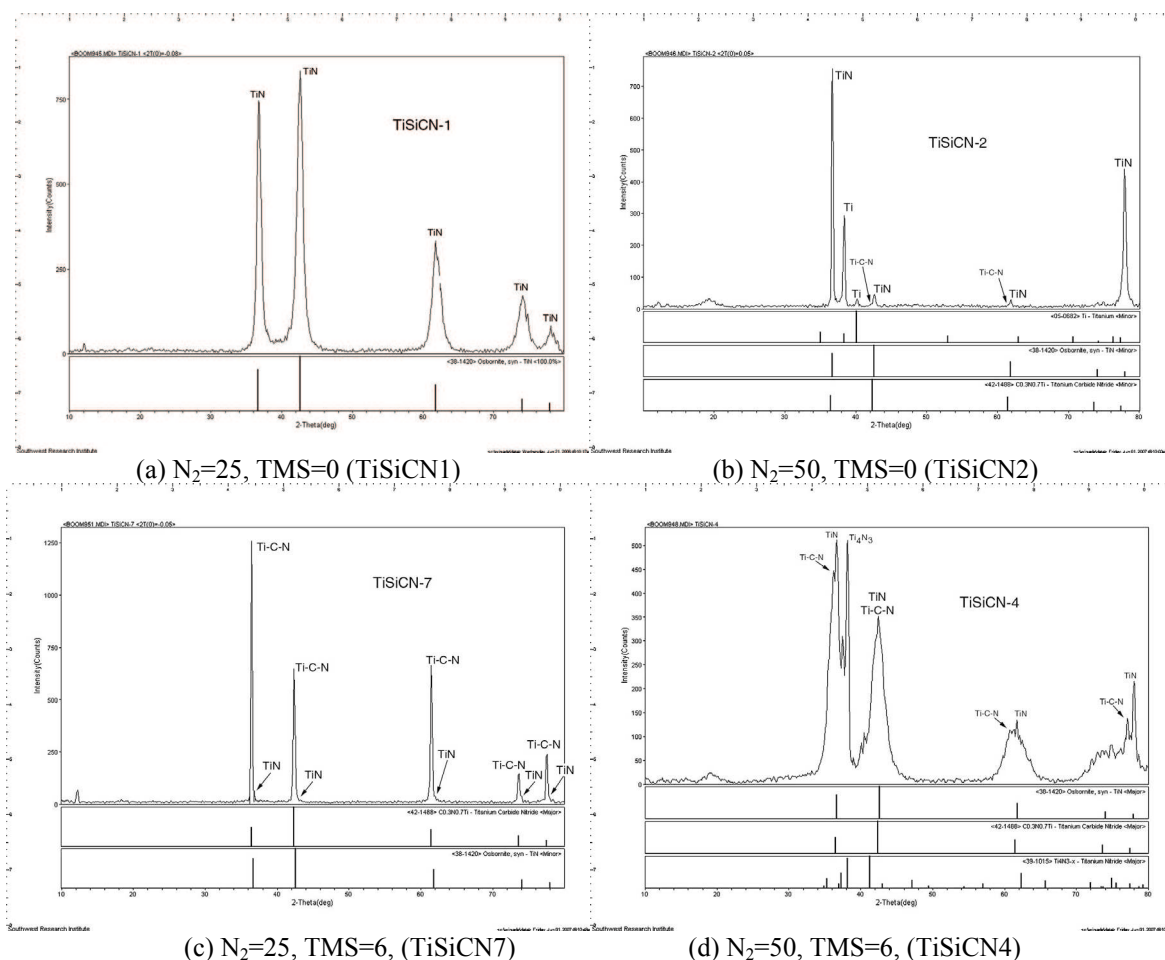


Fig. 11. XRD spectra of selected TiSiCN coatings.

As for the coatings deposited with TMS, Figure 11c is the representative XRD data for all coatings coated with 25 sccm N₂ (TiSiCN6-8), from which we observe that TiN is the dominant phase. The sharp peaks indicate that the mean grain size is large. Shown in Figure 11d represents the data for all samples coated with a high N₂ flow rate of 50 sccm (TiSiCN3-5). Comparing with Figures 11c and 11d, the higher N₂ flow rate and the addition of TMS resulted in the peak broadening, indicating that the grain size is much smaller. The dominant structure for these coatings is identified as TiC_{0.3}N_{0.7} with additional TiN, which is consistent with the previous study of the TiSiCN nanocomposite [28-30]. As observed in the nc-TiN/a-Si₃N₄ studies [81-85], crystalline Si₃N₄ does not form at the deposition temperatures in most nanocomposite film research (<500°C); therefore the coating should contain amorphous Si₃N₄. In our study, carbon was detected in the coatings; therefore, an amorphous phase of SiC_xN_y is expected.

As for sample TiSiCN9 (N₂=0 sccm), TiSiC is expected to form. The XRD data only showed the crystalline Ti peaks without any other phases. Therefore, the TiSiC phase is also amorphous.

The major peaks for all samples are identified and the mean grain size is estimated in Table 4. Clearly, most of the coatings are in the nano coating category, while the grain size for samples TiSiCN3-5 is only about 5 nm.

4.6. COMPOSITION ANALYSIS

The composition for all the samples was analyzed using energy dispersive spectroscopy (EDS) and the data is shown in Table 5. As expected, samples TiSiCN1 and TiSiCN2 have no Si. The N₂ flow rate in preparing TiSiCN2 was higher (50 sccm) than that in TiSiCN1. But only a slightly higher N concentration is observed. The carbon may originate from the vacuum pump system. In addition, analyzing low mass elements using EDS can be difficult and the uncertainty is much higher than for high mass elements.

Table 5. Composition of TiSiCN coatings.

Sample No.	Composition (at.%)			
	Ti	Si	C	N
TiSiCN1	53.9	0.0	8.9	37.2
TiSiCN2	48.2	0.0	9.7	42.1
TiSiCN3	44.3	0.7	15.9	39.1
TiSiCN4	42.0	1.4	18.1	38.4
TiSiCN5	40.3	2.1	20.8	36.8
TiSiCN6	50.8	0.4	10.8	38.0
TiSiCN7	46.3	1.0	20.4	32.3
TiSiCN8	44.0	2.0	21.7	32.4
TiSiCN9	64.7	1.5	13.9	20.0
TiSiCN10	49.6	0.6	12.9	36.9

As can be seen from Tables 4 and 5, for samples TiSiCN3-5 ($N_2=50$ sccm), both the Si and C concentrations increase as the TMS flow rate increases (from 3 to 9 sccm), while both the N and Ti concentrations decrease. As for samples TiSiCN6-8 ($N_2=25$ sccm, TMS flow rate=3 to 9 sccm), similar trends are observed. Compared with the Ti concentration, only a small amount of Si is present in all samples TiSiCN3-8. This is consistent with the nc-TiN/a-Si₃N₄ study where a small amount of Si, typically around 5-10%, is needed to form the amorphous phase to increase the hardness [22,27,84,86-90]. However, in our study, the Si concentration is lower. One of the reasons may be that in some referenced work, N was not measured due to the technique limitation, while the compositions for Ti and Si were measured and assumed $Ti_xSi_yN_{0.5}$, where $x+y=0.5$. For sample TiSiCN10, it was coated using the same parameters as for sample TiSiCN6 except that TiSiCN10 was coated longer period of time to obtain a thicker coating. Comparing both samples, TiSiCN10 has slightly higher Si and C concentrations.

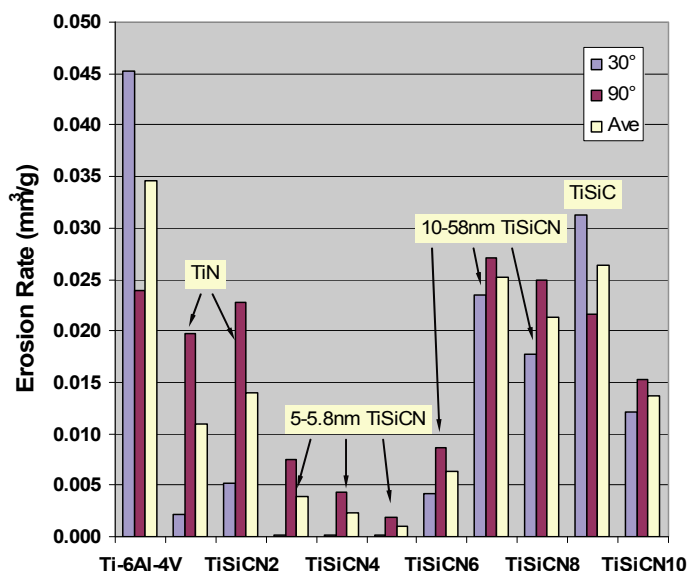


Fig. 12. Erosion rate of TiSiCN coatings.

In preparing sample TiSiCN9 no nitrogen was used, but still there is about 20% of N and this amount cannot be explained by the EDS accuracy. It is believed that during the deposition, nitrogen entrapped in the chamber wall coatings from previous depositions may be released due to the heat and the plasma desorption. As mentioned in the XRD study discussed in the previous section, no TiN or TiSiC phase was observed from this sample and only Ti was observed. Therefore, this coating may be composed of crystalline Ti in an amorphous matrix of SiC_xN_y . However, using the Si₃N₄ analogy (number of N/number of Si = $4/3 = 1.33$), sample TiSiCN9 has only 1.5% Si but the concentrations for C and N are much higher. Thus, there is an excess of C and N. So it is likely that in addition to SiC_xN_y an amorphous C_zN phase also exists. Certainly, to confirm this postulation, transmission electron microscopy (TEM) analysis is required.

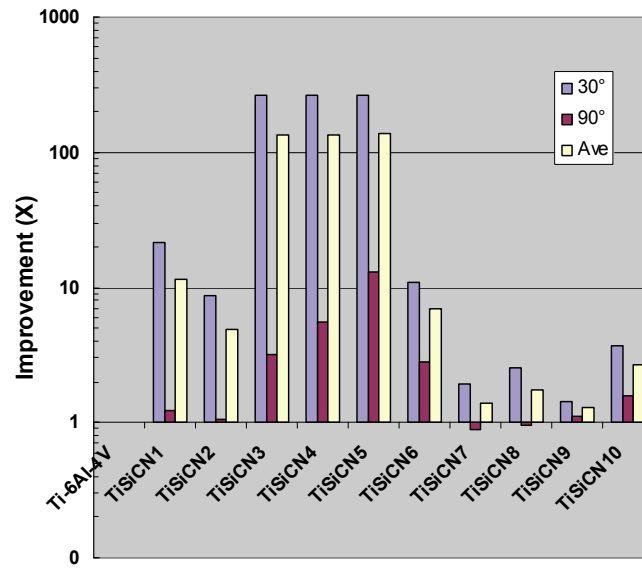


Fig. 13. Erosion resistance improvement of TiSiCN coatings.

4.7. EROSION RESISTANCE OF TiSiCN COATINGS

Erosion tests for the nanocomposite coatings shown in Table 4 were conducted using a slightly different procedure than described in the previous section. A 0.45 mm SiC nozzle was used to minimize the nozzle diameter variation due to erosion. The back pressure was set at 20 psi while the distance between the nozzle and the samples was 10 mm following the ASTM standard G76-04 [91]. The samples were eroded at two incident angles, 30° and 90°. The erosion rate was then obtained by the total mass loss of the sample divided by the total erodent (50 μm Al_2O_3) consumed. The erosion rates thus obtained for each sample are listed in the columns 8 and 9. The average erosion rate of these two was calculated and listed in the last column. The erosion rate for uncoated Ti-6Al-4V was also obtained as the baseline. It should be mentioned that for samples TiSiCN3-5, the erosion rate at 30° was basically zero. We used 0.01 mg the microbalance accuracy for their total mass loss which corresponds to an erosion rate of $1.7 \times 10^{-4} \text{ mm}^3/\text{g}$.

The erosion rate trend is plotted in Figure 12 for the 30° and 90° incidences and the average. The erosion rate for bare Ti-6Al-4V is notably higher at the lower incident angle, while the erosion rate for all coated samples except the TiSiC is higher at the higher incident angle which is in good agreement with the observations by many research groups. Ductile materials exhibit a higher erosion rate at the lower incident angles, while hard materials exhibit a higher erosion rate at higher incident angles.

Figure 12, as well as Table 4, shows most TiN and TiSiCN coatings reduced the erosion from the baseline. To clearly show the trend, the erosion resistance improvement, defined as

the erosion rate of Ti-6Al-4V divided by that of the coating, is plotted in Figure 13. It is noted that for a few samples such as TiSiCN3-5, the erosion resistance improved by over two hundred times. Even at the high incident angle 90° , the erosion resistance is still increased. This observation is very important. Based on the aero engine tests, the blades suffer much more from low angle erosion and hence significant improvement at the low angle is more important.

Finally, nanocomposite coatings (TiSiCN) with fine grains (~ 5 nm) show better erosion resistance than commonly used TiN, TiSiC, or large grain-sized TiSiCN coatings (>10 nm). This is also related to the nanohardness and toughness of the samples, which will be discussed in the next section.

4.8. NANO HARDNESS MEASUREMENT

The nanohardness and the modulus of elasticity were measured for all the samples and are given in columns 2 and 3 of Table 6. Listed in column 4 is the reduced modulus ($E^* = E/(1 - \nu^2)$ where ν is the Poisson ratio). W_p , W_e and R_e are the plastic deformation energy, elastic deformation energy and elastic recovery (elastic deformation/total deformation), respectively. The detailed discussion on these parameters can be found in Refs. [24, 44, 75]. Listed in the last column is H^3/E^{*2} , which represents the toughness of the coating, or resistance to crack formation and propagation. It seems that samples TiSiCN3-5 have high hardness H and a high value of H^3/E^{*2} , and the erosion resistances are also high.

Table 6. Composition of TiSiCN coatings.

Sample No.	H (GPa)	E (GPa)	E^* (GPa)	W_p (nJ)	W_e (nJ)	R_e (%)	H^3/E^{*2} (GPa)
TiSiCN1	28.93	321	352	2.68	3.73	52.40	0.195
TiSiCN2	23.74	353	387	3.52	2.92	38.64	0.089
TiSiCN3	38.50	406	446	2.20	3.54	54.81	0.287
TiSiCN4	26.39	286	314	2.50	3.78	50.04	0.186
TiSiCN5	29.11	300	330	2.56	3.75	49.50	0.226
TiSiCN6	27.15	376	413	3.40	3.14	43.56	0.117
TiSiCN7	9.86	306	336	6.66	2.36	25.88	0.008
TiSiCN8	10.44	218	240	6.68	3.19	33.95	0.020
TiSiCN9	10.10	146	160	5.86	3.90	33.45	0.040
TiSiCN10	32.60	448	492	2.91	3.11	48.61	0.143
TiSiCN23	34.85	352	387	2.00	3.72	54.24	0.282

5. DISCUSSION

5.1. CORRELATION OF COATING PROPERTIES WITH EROSION

As discussed earlier in this chapter, materials properties such as the hardness and the fracture toughness have a strong effect on solid particle erosion (Eq. 3.) The fracture toughness of a coating is very hard to measure and no data is available for these coatings. In contrast, H^3/E^{*2} represents the toughness of a coating resisting to fracture. The data is readily available and may be used to relate to the erosion resistance. Figures 14a and 14b show the

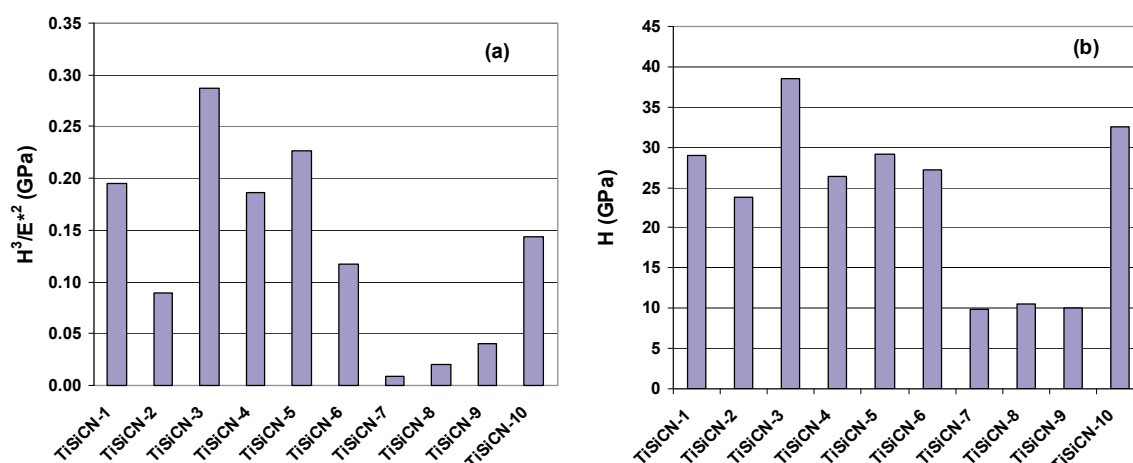


Fig. 14. (a) H^3/E^{*2} and (b) H of the TiSiCN coatings.

H^3/E^{*2} and H values for the coatings discussed in the last section (Tables 4 and 6). Comparing the erosion resistance shown in Figure 13, we can see qualitative correlations – the higher the H^3/E^{*2} , the better the erosion resistance, and the higher hardness H , the better the erosion resistance. Samples TiSiCN3-5 have the highest erosion resistance, followed by TiSiCN1, TiSiCN6, TiSiCN2 and TiSiCN10, while samples TiSiCN7-9 have the lowest erosion resistance. Similar trends can be observed from both H^3/E^{*2} and H as shown in Figures 14a and 14b. Certainly, more work is needed to quantify the relationship between the erosion and the toughness H^3/E^{*2} and hardness H .

5.2. EFFECT OF PROCESSING PARAMETERS

It is clear that the fine nanostructured composite TiSiCN coatings (~5 nm) exhibit superior erosion resistance compared to single-phase nitride coatings such as CrN, ZrN and TiN and the coarse nanostructured TiSiCN composite coatings (>10 nm). It has also been shown that for nanocomposite coatings as the grain size becomes smaller, the hardness of the coating increases. At the same time, the toughness also increases.

Selected deposition parameters (flow rates of N_2 and TMS) strongly influence the micro-nanostructure, adhesion and erosion resistance. Deposition at a low N_2 flow rate resulted in columnar, coarse microstructure with large grain sizes. The adhesion was very good, but the microstructure ranked poorly and the erosion resistance was not high. In contrast, deposition

at a high N₂ flow rate, with the addition of TMS, resulted in the formation of dense nanostructure with fine grain sizes. The coating quality (micro-nanostructure) was increased but the adhesion was reduced slightly, while the deposition rate decreased. More importantly, the erosion resistance was increased significantly. Other deposition parameters such as the ion current density and ion energy during the deposition also strongly affect the micro-nanostructure, adhesion and erosion resistance.

6. CONCLUDING REMARKS AND FUTURE OUTLOOK

A new magnetron sputtering technology – plasma enhanced magnetron sputtering (PEMS) has been discussed. The basic principles have been presented and compared with conventional magnetron sputtering (CMS). Employing the electron source-generated plasma, the ion density of the PEMS can be 10-25 times higher than that obtained in CMS. The intense ion bombardment during the ion cleaning stage ensures surface cleaning, whilst during deposition it greatly increases the coating density, reduces the grain size and increases the film adhesion. Using the PEMS technology, a method of depositing nanocomposite coatings of Ti-Si-C-N was presented using simultaneous sputtering of Ti from magnetrons in a mixture of Ar, N₂ and TMS. This method is very convenient for process control without the need for any pyrophoric or corrosive gases and produces coatings with uniform composition – a feature well suited for large scale production. The Ti-Si-C-N nanocomposite coatings were compared with single phased nitride coatings such as CrN, ZrN and TiN. Under appropriate deposition conditions, the fine-grained nanocomposite coatings (~ 5 nm) exhibited superb erosion resistance. A detailed parametric study was also conducted. Various techniques including SEM, XRD, microhardness measurement, and nanoindentation were used to determine the coating structures, and adhesion were correlated with process parameters. Over 200 fold increase in the erosion resistance was obtained for several sets of processing conditions. The erosion resistance was also related to the nanohardness data. As predicted by physical models, erosion resistance is related to H^3/E^{*2} and H , the coating toughness and hardness.

Even though the effect of the nitrogen flow rate and the TMS flow rate has been studied, the optimization of these parameters is still needed. As for other deposition parameters including the ion current density, ion energy, and the deposition temperature, a comprehensive study has yet to be conducted. In addition, the thermal stability of these coatings needs to be determined. For aero engine applications, compressor blades may experience moderate temperature up to 538 °C. Even though nanocomposites including Ti-Si-N, Zr-Si-N and more complex Ti-Si-B-N and Ti-Al-Si-B-N can be used to about 800 °C -1000 °C [82,92-96], the thermal mechanical properties of Ti-Si-C-N coatings may be different. As for liquid droplet erosion that occurs in steam turbines, these coatings have not been tested and their characteristics also need to be determined. Since these coatings exhibit superior erosion resistance, it is expected that they would also have superior wear resistance. They may also

be used for cutting tools as the next generation of coatings. Other potential applications include machinery and pipelines for offshore petroleum and gas production and transportation where severe sand abrasion occurs.

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CHAPTER 7

Synthesis of Nanowires

Y.W. Zhu^{1,2}, E.P.S. Tan³, C.H. Sow^{*,1,2} and C.T. Lim^{*,2,3,4}

¹Department of Physics, Blk S12, Faculty of Science, National University of Singapore, 2 Science Drive 3, Singapore 117542

²National University of Singapore Nanoscience and Nanotechnology Initiative, 2 Science Drive 3, Singapore 117542

³Division of Bioengineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576

⁴Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576

* physowch@nus.edu.sg, ctlim@nus.edu.sg

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1. INTRODUCTION

One-dimensional (1D) nanostructures have recently become a popular area of research. These 1D nanostructures can occur in the form of nanowires, nanorods, nanotubes or nanobelts. In this chapter, all these structures will generically be referred to as nanowires. Nanowires have been labeled as “the hottest property in nanotechnology” [1] and its popularity may be on par or even surpass that of carbon nanotubes. Nanowires are known to possess superior mechanical and electrical properties. As such, this has resulted in the development of numerous techniques to synthesize nanowires with potential applications in nanoelectronics, nanomaterials and nanocomposites among others.

Generally, two approaches are adopted to fabricate nanostructures: top-down and bottom-up methods. In the former method, the size of bulk materials is gradually reduced to the nanometer scale by using etching techniques with the help of a range of lithography techniques. The top-down method has proven to be a great success in the highly developed semiconductor industry in the last half century. However, with the requirement of minimizing the device size, the top-down route is facing major challenges. For example, to break through the wavelength limitation of conventional lithography, the technique is becoming increasingly more complex to obtain nanostructures with feature size on tens of nanometer scale [2]. Furthermore, in nanoscale fabrication process, the morphology and structure of surfaces and interfaces have important influences on the performance of nanodevices. The complicated steps in top-down technique make the precise control of these properties extremely difficult. Future applications require more rational synthesis of nanostructures, e.g. precisely controlling the position, size, surface and structures of the final nanostructures. To realize the goal, bottom-up methods appear to be more promising because they utilize the self-assembly of some basic blocks into nanostructures and such a process can be rationally controlled by the growth dynamics. It is also worth mentioning that nature utilised the bottom-up approach to the synthesis of complex biomolecules such as proteins, DNA and carbohydrates. If these methods are mimicked in the laboratory accurately and controllably, then major advances in nanotechnology will be possible. Depending on the existing form of the growth blocks, the bottom-up method can be solution-based or vapor-based and they are also two of the most commonly used methods to fabricate nanowires [3]. Here, the two routes are briefly introduced and some typical results are reviewed. We do not differentiate the morphologies of products, such as nanotubes or nanowires, because in most cases nanotubes and nanowires share similar growth mechanisms and the formation of nanotubes is often related to the layer structure of the corresponding materials. The main focus is to highlight the advantages and disadvantages of related techniques.

2. SOLUTION-BASED METHODS

In order to fabricate nanostructures with preferential growth along one specific orientation, certain procedures are often needed to break the growth symmetry. Many strategies can be realized in a solution environment, usually with the assistance of chemical reactions.

2.1 SOLVOTHERMAL METHOD

One of the commonly used solution-based fabrication techniques is the solvothermal method. A typical solvothermal process includes a mixture of precursor and a reagent for regulating or templating crystal growth like amines. Subsequent reactions are carried out under elevated temperatures and pressures. An autoclave is often used to speed up the growth and assembly. Thus if an appropriate solvent can be found for a certain material, this method may be suitable for the growth of nanostructures of many solid materials. A variety of 1D nanostructures such as Ge nanowires [4], In_2O_3 nanowires [5], CuO nanowires [6], Ga_2O_3 nanorods [7], MnO_2 nanowires [8], ZnO [9], TiO_2 nanotubes [10], CdS nanorods [11], CuS nanowires and nanotubes [12], have been successfully synthesized. Magnetic Fe_3O_4 nanowires [13], and MoO_3 nanobelts [14] have also been prepared by this method. Recently, Wang *et al.* described in detail the solution-based synthesis and rolling mechanisms of transition-metal oxide nanostructures such as MnO_2 nanowires and nanotubes [15]. It was found that by properly selecting different reaction conditions, the crystalline structure of final products can be controlled. For example, α , β and γ -phase MnO_2 have been obtained respectively, under different temperature, pressure and precursor concentrations. However, although the method is versatile, the products often suffer from low yield and low purity. Furthermore, the process may involve some solvents which are not environmentally friendly.

2.2 CAPPING REAGENTS

Capping reagents are extensively used to break the growth symmetry for obtaining 1D nanostructures. According to the existing knowledge of growth kinetics of crystals [16], the introduction of reagents can change the free energy of the crystallographic surfaces and thus their growth rates. A typical example is the synthesis of silver nanowires with high yield [17, 18], as shown in Fig. 1. In the fabrication process, poly(vinyl pyrrolidone) (PVP) was used as a polymeric capping reagent and a seeding step was introduced. When the silver nanoparticles (reduced from silver nitride) grew through the Ostwald ripening process, the presence of PVP confined and directed the growth of particles into nanowires with uniform diameters. Electron microscopy was carried out to confirm the whole process. Usually such anisotropic growth is carried out in a micro-emulsion system which is composed of oil phase, surfactant phase and aqueous phase. In order to synthesize desired products, the selection of precursor, reagents and reaction environments such as temperature, pH value and concentration is important. By choosing amines as a reagent, ZnO nanowires have also been

fabricated on a wafer scale [19]. SnO_2 [20] and NiO nanorods [21] were obtained by this route by Xu *et al.* Furthermore, PbO_2 nanorods were prepared by capping reagents assisted growth at room temperature in a rapid manner [22]. The major challenge for this method is to find a systematic way of selecting suitable capping reagents because so far most studies have been based on trial-and-error approaches.

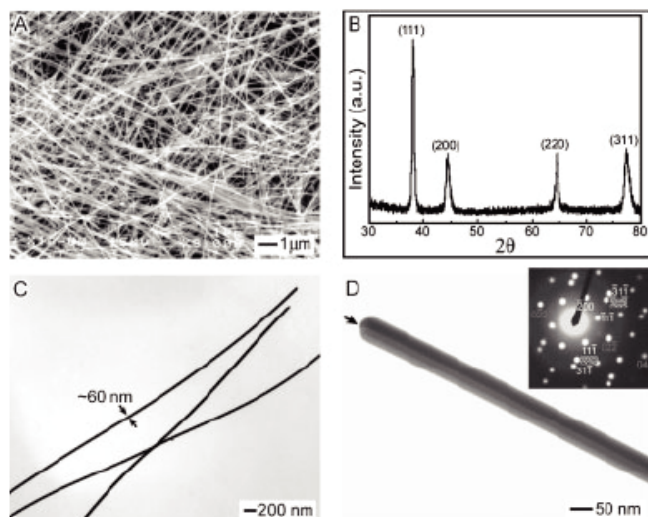


Fig. 1. (A) SEM and (C) TEM images of Ag nanowires synthesized via capping reagent method. (B) XRD pattern, indicating the fcc structure of silver. (D) TEM and diffraction pattern, showing twin structure of Ag nanowires from this synthesis. (Reprint from Ref. [17], with permission).

2.3 SONOCHEMICAL SYNTHESIS

In sonochemistry, ultrasonic wave is used to acoustically stimulate chemical reaction process in solution environments and thus stimulate the crystal growth. Usually the sonication will induce the formation, growth and collapse of many bubbles in liquid [23]. On these localized spots, temperature as high as 5000 K and pressure of 1000 atmosphere could be produced when the bubbles collapse. At the same time, the cooling rate could be higher than 10^{10} K/s. Such extreme conditions have been exploited to fabricate nanoparticles [24]. Recently, nanowires of Fe_2O_3 [25] and V_2O_5 [26] have been fabricated using this method. With the assistance of microwave heating, the formation of linked ZnO nanorods has been demonstrated [27]. ZnO nanorod/CdS nanoparticle composites have also been prepared by sonochemical synthesis [28]. However, due to the rapid reaction process, the controllability of the synthesis and the range of products still need to be improved.

2.4 SOLUTION-LIQUID-SOLID METHOD

A liquid-solid interface is often introduced in solution to create growth anisotropy, which is commonly called solution-liquid-solid (SLS) method. In a typical process, a low-melting-point metal (e.g. Bi, In or Sn) is used as a catalyst and organometallic precursors are decomposed to generate the desired nanostructures. By employing a supercritical fluid as the solvent in a SLS process, Si nanowires with uniform diameters of 4-5 nm have been successfully fabricated [29, 30]. In the synthesis, Au nanoparticles were used as catalysts and confined the growth of Si nanowires to a narrow size distribution. A variety of III-V semiconductors including InP, InAs and GaAs have also been grown in the form of nanorods at relatively low temperature (203 °C) through the SLS route [31, 32].

2.5 TEMPLATE METHOD

In addition to the use of growth kinetics, templates are extensively used to direct the growth in solution. Such a method provides a straightforward and simple route to the generation of 1D nanostructures. The capping reagent can be taken as a type of template. However, more general templates include nanoscaled channels in porous materials, steps or edges on the surface of a solid substrate, biological molecules like DNA strands or even rod-shaped viruses, and also existing nanostructures fabricated by other methods. By utilizing templates, versatile inorganic materials including elements or compounds have been obtained in the form of 1D nanostructures [33]. It is worth noting that a wide variety of metallic nanowires can be synthesized with the help of templates using sol-gel or electrochemical deposition in solution. Arrays of ferromagnetic nanowires of metals such as Ni, Co, and Fe have been prepared with distinctive magnetic behaviors [34, 35]. Moreover, various kinds of oxide nanostructures like ZnO [36], Fe₂O₃ [37], Cu₂O [38] and NiO [39], have been synthesized by electrochemical deposition in anodic aluminium oxide (AAO) arrays. In another example, SnO₂ nanowires were obtained by annealing tin metals deposited in AAO [40]. In sol-gel deposition, an AAO template is immersed into the sol suspension and the sol will aggregate on the surface of templates. After removing the gel by thermal treatment, the final products will be obtained in the templates. Nanostructures of ZnO [41], MnO₂ [42], ZrO₂ [43] and TiO₂ [44] have been fabricated by this method. However, the products from templates are often polycrystalline or amorphous structures, which may limit further application of this method.

Compared with the vapor-based method, one of the major advantages of the solution-based synthesis for fabricating metal oxide nanostructures is its low growth temperature. This renders the fabrication process readily compatible with current semiconductor processing techniques and low-melting-point polymers. However, post-treatments are usually needed to purify the products from solution, e.g., washing the products or removing the templates. Such

processes would increase the cost and contamination is often inevitable. Furthermore, environmentally friendly solvents are needed for the synthesis of many 1D nanostructures.

3. VAPOR-BASED METHODS

So far, the vapor-based route is probably the most widely adopted approach for the fabrication of nanowires and related structures. In this method, vapor is the basic element during the growth. Generally, the generation of nanostructures includes the production, transportation and deposition of vapors. The production of vapor can be realized in many ways including thermal evaporation, chemical reaction, laser ablation, arc discharge, sputtering, and so on. The precursor vapor is usually transported by a gas flow from source to the target substrate at a certain temperature and such a process is often implemented in a furnace chamber, such as a tube furnace. Various methods are used to control the supersaturation and nucleation process to realize the growth anisotropy for the synthesis of nanostructures with specific morphologies. During the synthesis, parameters such as pressure, gas flow rate and temperature gradient are varied to optimize the growth.

3.1 VAPOR-SOLID GROWTH

One of the simplest routes is the direct vapor-solid (VS) growth. The vapor is generated by evaporating source materials or decomposing precursor components, which then condenses on the target substrates at a lower temperature range. The nucleation is possibly driven by the intrinsic anisotropic growth or a screw dislocation and other defects. Although the exact mechanism for nanostructure growth is still unclear, a wide range of nanostructures have been produced by various research groups. For example, nanowires of Si_3N_4 , SiC [45] and oxides of Zn [46], Sn [47], In [48], Mg [49], Ga [50], Cd and Al [3] have been obtained by thermally evaporating commercial powders or metal solids.

Besides nanowires, Wang and co-workers achieved considerable success in synthesizing ZnO , SnO , In_2O_3 and CdO nanobelts (nanoribbons) with a rectangle cross section by evaporating the corresponding oxide powders at elevated temperatures [51]. During the synthesis, a furnace setup was used, as shown in the schematic in Fig. 2. The source material was placed in a boat and positioned at the center of the tube in the furnace. Substrates were placed downstream at lower temperature ranges to collect the oxide products. Depending on the synthesizing parameters used, the final products could be different. For example, SnO_2 nanobelts were obtained in the high-temperature region of 800-950 °C by evaporating SnO powders at 1050 °C. When the pressure was increased from 200 torr to 500-600 torr, disk-shaped SnO nanostructures were collected in the low-temperature region of 200-400 °C. Furthermore, when a layered Sn foil/ SnO mixture was used as source materials instead of SnO powders and a cold plate was introduced in the system, rutile-structured SnO_2 nanowires were collected on the cold plate (25-60 °C) [52]. PbO_2 nanobelts [53], Ga_2O_3 nanobelts and

nanosheets [54, 55], were also synthesized by thermal evaporation from VS growth. Most products produced by this method are oxide nanostructures possibly due to the inevitable presence of trace oxygen in the furnace. Although various hierarchical nanostructures have been fabricated through VS growth [56], tight control of spatial arrangement and size of nanowires still remains as a challenge.

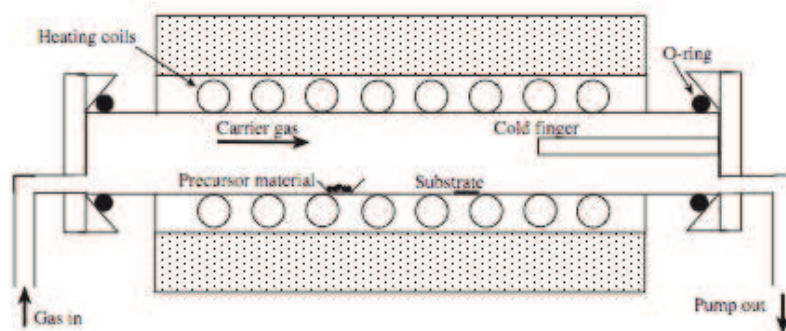


Fig. 2. A typical schematic of tube furnace for the growth of nanowires using vapor-based method.

3.2 CARBOTHERMAL REDUCTION AND OXIDE-ASSISTED METHOD

During vapor production, some precursors are often required to assist the production of desired vapors that may not be readily generated or controlled by simply heating the source materials. Carbothermal reduction and oxide-assisted method are two of the most commonly used techniques to produce vapor precursors. In the former, carbon is used to reduce oxides to the metal vapor, followed by the transportation and second-time oxidization. MgO nanowires were fabricated by Lieber and co-workers via carbothermal reduction growth [57]. Mg vapor was generated during synthesis through the reduction of MgO by carbon, transported in a flow reactor to the growth zone, and finally oxidized to form MgO again. Hydrogen gas or water can also be used instead of carbon and this method could also be extended to oxide nanowires such as Al_2O_3 [58], Ga_2O_3 [59], ZnO and SnO_2 [60, 61]. In the oxide-assisted growth, a process including oxidization followed by reduction is often introduced for the kinetic growth of nanowires. One typical example is the fabrication of Si nanowires, in which a mixture of Si and SiO_2 powders was subjected to laser ablation [62]. The authors proposed the formation process of sub oxides of Si, like Si_xO ($x > 1$) and SiO, and deduced that the subsequent decomposition played important roles in the growth of Si nanowires. The same method has been used to fabricate GaAs nanowires by using GaAs and Ga_2O_3 as precursors [63].

3.3 VAPOR-LIQUID-SOLID GROWTH

In order to create growth anisotropy, another method is to induce a liquid-solid interface in a vapor environment, which is analogous to the SLS mechanism in the solution-based route. In combination with vapor supply, vapor-liquid-solid (VLS) growth has achieved great success in the fabrication of nanostructures with high crystal quality and in large quantities. Originating from whisker growth in the 1960s [64], this method features the use of metallic catalysts which form eutectic liquids with the source materials. During growth, the precursor vapor dissolves into the liquid drops and solid nuclei precipitate after saturation for the subsequent growth of nanostructures. Thus VLS growth also produces features with catalyst particle terminator at the tip of nanostructures. The process is schematically shown in Fig. 3. Such growth process has been observed *in situ* in the transmission electron microscope (TEM) by Yang and co-workers [65]. VLS growth has been used to synthesize a rich variety of inorganic nanostructures including elemental semiconductors (Si, Ge and B) [66, 67], III-V semiconductors (GaN, GaAs, GaP, InP, InAs) [68, 69], II-VI semiconductors (ZnS, ZnSe, CdS, CdSe) [70, 71] and oxides (ZnO, MgO, SiO₂) [72] [73]. Table 1 summarizes the precursors and catalysts used for the growth of various nanowires by VLS method. One of the main merits of VLS is that the diameter and position of nanowires can be controlled by the size and position of catalysts. Thus the products can be highly uniform in diameter and readily patterned. For example, Yang and co-workers demonstrated patterned ZnO nanowire arrays by pre patterning catalytic Au films [74]. Based on the ZnO arrays, a lasing behavior was observed, which has sparked extensive interest in the fabrication of aligned and ordered ZnO nanowires or nanorods.

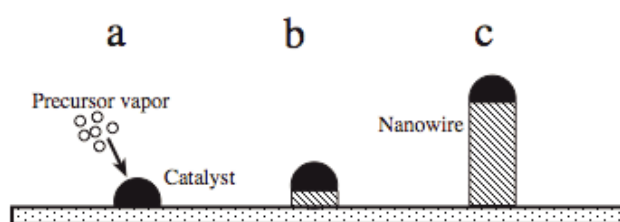


Fig. 3. A schematic showing the VLS growth mechanism. a: the precursor vapor/cluster diffuses into the melted catalyst particle; b: the precursor precipitates from the eutectic droplet and starts the growth along a preferential orientation; c: the growth continues to form a nanowire.

Table 1. Summary of nanowires grown by VLS method.

Nanowire	Precursor	Catalyst	Reference(s)
Si	SiCl ₄	Au, Ag, Cu, Pt	[64, 75]
	SiH ₄	Au	[76]
	Si ₂ H ₆	Au	[77]
	Si	Au, Ga	[78, 79]
	SiO	Au	[80]
Ge	GeH ₄	Au	[81, 82]
	Ge/Fe	Fe	[83]
	Ge/GeI ₄	Au	[66]
Si/SiGe	SiCl ₄ , Ge	Au	[84]
GaN	Ga/NH ₃	In, Co, Ni, Fe, Ni/Co, Fe/Co	[68, 85]
AlN	Al, NH ₃ , SiO ₂ , Fe ₂ O ₃ /Al ₂ O ₃	Fe	[86]
Si ₃ N ₄	Si or Si/SiO ₂ / N ₂ or NH ₃	Fe/Ni	[87]
InN	In/NH ₃ /N ₂	Au	[88]
GaP	Ga/P	Au	[89]
	GaP	Ni	[90]
InP	InP/Au	Au	[71]
GaAs	GaAs/Au	Au	[71]
	Et ₃ Ga, Bu ₃ As	Au	[91]
InAs	Trimethylindium/ AsH ₃ /H ₂	Au	[92]
GaAs/GaP	GaAs/GaP	Au	[89]
GaAs/InAs	Me ₃ As, Bu ₃ As, Me ₃ In	Au	[93]
ZnO	ZnO/C	Au	[74]
		Cu	[94]
	Zn	NiO	[95]
SiO ₂	SiH ₄ /He	Au	[96]
	Si/Ar	Ga	[97]
InO ₂	InP/O ₂	Au	[98]
	In		[99]
Ga ₂ O ₃	GaAs/Ar/O ₂	Au	[100]
TiO ₂	Ti/O ₂	Au	[101]
SnO ₂	SnO	SnO	[102]
ZnS	ZnS	Au	[103]
ZnSe	Zn/Se	GaAs	[104]
CdS	CdS	Au	[105]
CdSe	CdSe	Au	[71]
SiC	SiC	Fe	[106]

Combined with various formation methods of precursor vapor such as carbothermal reduction and metal-organic chemical vapor deposition (MOCVD), VLS growth can be very versatile. However, the choice of catalysts is mainly limited by the restrictions from the analysis of the equilibrium phase diagram of the metals and desired materials. At the same time, the catalyst metal could be a source of contamination in the as-grown nanostructures. It has been realized that gold incorporation could result in some deep-level defects near the middle band gap of semiconductors [107]. Furthermore, the existence of catalytic particles may induce an extra junction during the electronic property measurements.

4. DIRECT OXIDIZATION

4.1 HEATING METALS IN A CLOSED CHAMBER

Recently, a direct oxidization method has been developed to synthesize metal oxide nanostructures by heating the corresponding bulk metals under certain oxidizing atmospheres. Xia and co-workers fabricated CuO nanowires by heating copper substrates in a box furnace at temperatures between 400-600 °C [108]. During the synthesis, crystalline CuO nanowires can be obtained from Cu foils, transmission electron microscope (TEM) grids and Cu wires with similar quality. With the increase in heating temperature from 400 °C to 500 °C and 600 °C, the average diameter of CuO nanowires decreases from ~100 to within ~50 and ~30 nm. At the same time, the diameter distribution of nanowires becomes narrower at higher growth temperatures. It was believed that the formation of CuO is closely related to the Cu₂O precursor, which was grown from the early oxidization stages of Cu.

As compared to normal VS growth, no vapor transportation was used in such a direct oxidization method and thus the nanostructures were able to grow directly on metal substrates. Subsequently, the syntheses of ZnO nanowires [109] and nanobelts [110, 111] have been achieved by directly oxidizing Zn metals in tube furnaces. Besides ZnO, nanostructures of MgO and GeO were synthesized by heating Mg and Ge powder at 850 °C and 1000 °C respectively with a mixed gas flow of O₂ and Ar [109]. In this mechanism, melting metals play the roles of reactants and catalysts simultaneously and the growth can be regarded as a variation of conventional VLS growth. It was believed that the growth method could be extended to other low-melting-point metals such as Al, Sn and In. By heating metals in tube furnace to fabricate metal oxide nanostructures, the morphology of products was controlled mainly by the growth temperature, oxygen partial pressure and flow rate of carrier gases.

4.2 DIRECTLY HEATING METALS IN AMBIENT ENVIRONMENT

Another simpler alternative is to directly oxidize metals in air. As early as the 1950s, Pfefferkron [112] and Arnold *et al.* [113] found that various metal oxide filaments could be obtained by annealing corresponding metals in air at elevated temperatures. For example, filaments with length of several micrometers were produced in Arnold's experiments after heating Pb at 200 °C for 30 hours and Pt, Zn, Ni, Pd, Fe and Mg at 400 °C for 60 hours. During the early stages of development of this method, the covering of nanostructures on the metal surface was very low and the morphological control of the products remained a challenge.

This direct-oxidization technique has attracted much attention again due to its simplicity and low cost. Such a synthesis can be carried out on a hotplate without any flow rate or pressure control. The growth temperature is relatively lower than that used in tube furnaces. Moreover, the chamber-free approach is suitable for mass production for potential large-scale applications. This cost-effective and efficient hotplate method has already shown its preliminary success in the synthesis of Fe₂O₃ nanowalls [114].

Recently, Sow and co-workers have extended this simple method to more metal materials for the large-scale production of 1D nanostructures and investigation of their potential properties and applications. An image of a hotplate and the growth procedures are shown in Fig. 4. In a typical example, aligned CuO nanowires were fabricated by heating pure Cu (99.999%) plates on the hotplate under ambient conditions [115]. The growth temperature was about 390-430 °C and the growth durations varied from one day to three days. Fig. 5 shows the morphologies of CuO nanowires from different conditions. Depending on the heating duration, the average length, diameter and surface density of CuO nanowires could be controlled. Long nanowires have lengths that can reach 30-40 μm and the diameter falls in the range of 45-75 nm. The nanowires were characterized to be single crystalline. Nanostructures of Co₃O₄ [116] and α-Fe₂O₃ [117] have been synthesized by heating pure Co and Fe metal plates respectively. Co₃O₄ showed layer-like 2D nanowalls whereas α-Fe₂O₃ showed quasi-1D nanoflakes. The Co₃O₄ nanowalls were obtained by annealing Co foils at about 350 °C for 12 hours. It was found that both the length and the thickness of nanowalls increase with an increase in the growth temperature between 200-350 °C and the growth duration. After heating Fe foils at 300 °C for 45 minutes, nanoflakes were obtained with typical length of 1 μm and width of 100 nm at the root of the nanoflakes.

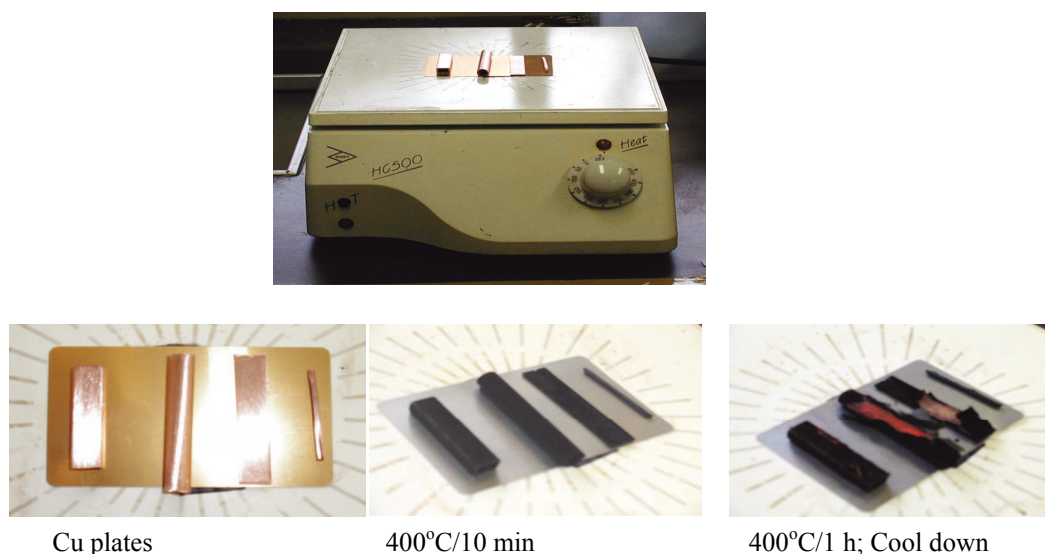


Fig. 4. Optical photos of a hotplate and growth process of CuO nanowires by heating Cu plates on it.

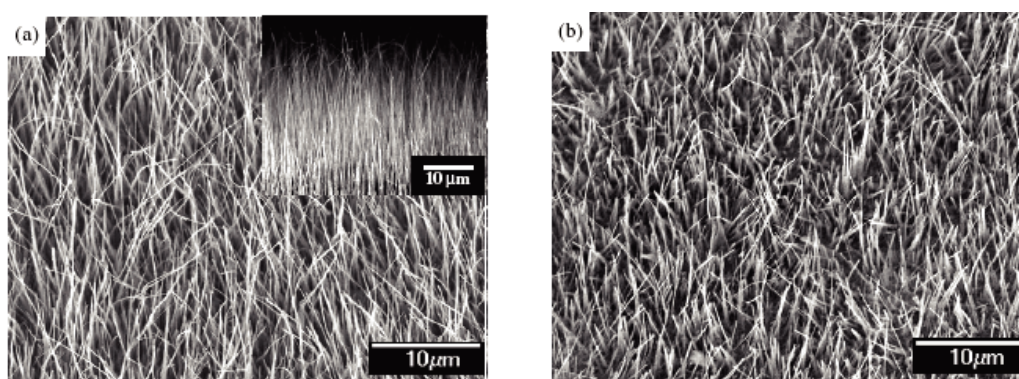


Fig. 5. SEM images of aligned CuO nanowire arrays from (a) 1 day and (b) 3 days of growth. (Reprint from Ref. [115], with permission)

By heating metal coatings on various substrates, metal oxide nanostructures can be synthesized on a wide range of substrates. Typical examples include the growth of Fe_2O_3 nanowalls and nanoflakes. In the former example, the fabrication was carried out on Cu substrates coated with FeMn films [114]. It was also found that Fe_2O_3 nanoflakes could also grow from pure Fe coatings on flat surfaces such as Si wafer, glass and quartz, rough surfaces such as microsphere and even sharp tips like atomic force microscope (AFM) tip and chemically etched tungsten tip [117]. Such a substrate-friendly growth technique renders the synthesis of metal oxide flexible and versatile. CuO nanowires have also been prepared on Si substrates and carbon papers recently.

Hybrid nanostructures can also be fabricated by using this simple oxidization method. One of the methods is to heat an alloy in ambient environment. For example, ZnO/CuO hybrid

nanostructures have been fabricated on Cu/Zn alloy (brass) substrates [118]. Depending on the Zn concentrations in the brasses, the dominant products change from CuO to ZnO, as clearly shown in the XRD patterns in Fig. 6. More interestingly, by changing the growth temperature and local Zn contents, 1D ZnO nanowires/nanoflakes, 2D ZnO nanosheets and complicated 3D ZnO networks were obtained. A relationship between the products and metal plates, growth temperature and heating duration for this hotplate method is summarized in Table 2. It is expected that this method could be extended to the fabrication and patterning of other pure/hybrid nanostructure systems.

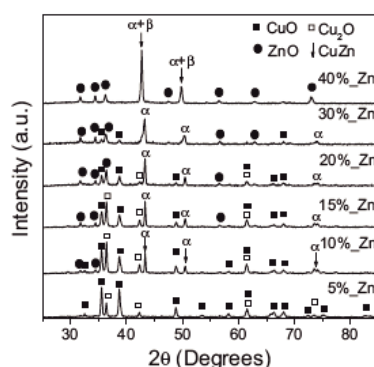


Fig. 6. XRD of products by heating brass with increase in the Zn content, showing a transition from CuO to ZnO structures. (reprint from Ref. [118], with permission).

Table 2. A collection of nanostructures by hotplate growth.

Nanostructure	Source	Heating Temperature	Heating Duration	Reference
CuO nanowires	Cu foil or Cu coating	390-430°C	3 days	[115, 119]
Co ₃ O ₄ nanowalls	Co foil	200-350°C	1min-12h	[116]
α -Fe ₂ O ₃ nanoflakes	Fe foil or Fe coating	~300°C	10min-24h	[117, 120]
α -Fe ₂ O ₃ nanowalls	FeMn alloy	300-450°C	10h	[114]
V ₂ O ₅ ·xH ₂ O nanobelts	V foil	~540°C	2 days	[121]
WO _{3-x} nanowires	W foil	~540°C	3-7days	[122]
ZnO nanowires	Zn coating	~375°C	12h	[117]
MoO ₃ micro/nanobelts	Mo foil	~540°C	2h-2days	[123]
ZnO/CuO nanohybrids	CuZn alloy (Zn 5-40 wt%)	350-540°C	2 days	[118]

4.3 GROWTH MECHANISM

Since the direct oxidization method is different from conventional VS or VLS growth, it is necessary to study the growth mechanism. In this method, no catalysts are used and no obvious terminators are observed at the end of all metal oxide nanostructures. Furthermore, there was no significant vapor transport since nanostructures were synthesized on the source substrates. Using the growth of Fe_2O_3 as an example, in order to minimize the effect of vapor transport, a very high flow rate of air ($\sim 9 \times 10^5$ sccm) was applied on the sample during synthesis. Products with similar morphologies were still obtained under this condition. This suggests that the role of vapor may not be significant to the growth. Another feature in the direct oxidization method is the existence of sub-oxides on the substrates after cooling down, e.g. Cu_2O in the growth of CuO nanowires, CoO in the growth of Co_3O_4 nanowalls and Fe_3O_4 in the growth of Fe_2O_3 nanoflakes. Evidence shows that these sub-oxides could act as precursors for the growth high of valence metal oxide nanostructures. Based on this information, a solid-liquid-solid (SLS) growth mechanism has been proposed, as schematically shown in Fig. 7. It is believed that such growth involves the melting of metal plates at elevated temperatures, preliminary oxidization of liquid metal media, further oxidization and isotropic growth of final oxide nanostructures. During the growth, the material supply may be realized by surface diffusion to the tip of the nanostructures or direct saturation at the root, depending on the material and growth conditions. The SLS mechanism can also be used to explain the formation of ZnO/CuO hybrids, except that the local Zn/Cu concentration needs to be considered as well.

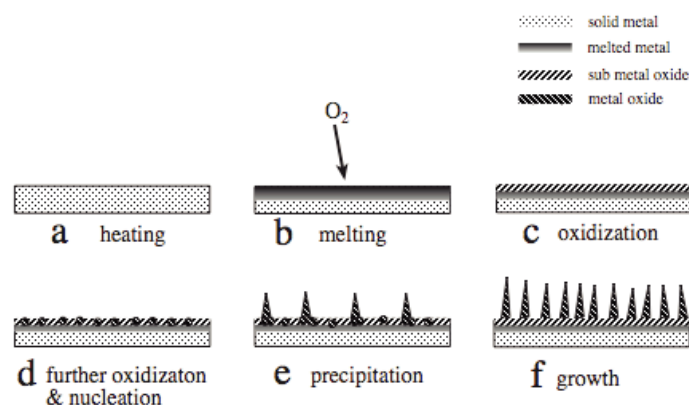


Fig. 7. A schematic showing the SLS growth mechanism of the hotplate method.

5. HYBRID NANOWIRES

In addition to chemically stoichiometric nanowires, hybrid nanowires have been fabricated from two or more different materials/structures. Hybrid nanowires have potential applications in enhanced device performance, multi-functional device, hetero-junction behavior and so on.

The routes for the synthesis of hybrid nanowires can be very versatile, including sequential growth or simultaneous fabrication. The method can be one of or combination of the growth methods mentioned in the previous section. Based on nanowire morphology, two of most important hybrid architectures are longitudinal and coaxial hybrid nanowires.

5.1 LONGITUDINAL HYBRIDS

A longitudinal hybrid nanowire is formed with different materials/structures alternately along the longitudinal direction of the 1D nanostructure. As a typical example, Yang and co-workers developed a hybrid pulse ablation/chemical vapor deposition (PLA-CVD) process in VLS growth for the synthesis of Si/SiGe longitudinally periodic nanowires [84]. During this process, Si and Ge vapor sources are independently controlled and alternately delivered to the growing end of nanowires. By a similar method, GaAs/GaP, n-Si/p-Si [89], and InAs/InP [124] hybrid nanowires have been prepared by the Lieber and Samuelson groups respectively. Atomic scale sharp interface has been observed from these junctions.

ZnSe/CdSe superlattice nanowires were reported by Solanki and co-workers [125]. By controlling the vapor supply in VLS growth, a range of longitudinal hybrid nanowires can be synthesized, as long as the different phases in hybrids share the same catalyst. In addition to the control of vapor supply, a post-reaction method has been used to generate Si/NiSi superlattice nanowires [126]. Fig. 8 shows the fabrication process, morphology and structures of Si/NiSi heterojunctions. During the fabrication, Ni was selectively coated on the as-grown Si nanowires by lithography technique, followed by heating to form NiSi. The junction has a sharp interface, based on which metal-semiconductor junction behavior has been displayed.

Besides vapor-based method, solution-based route, specifically with the assistance of templates, has also been developed for the synthesis of longitudinal hybrid nanowires. For example, striped Ag/Au [127] and Au/Co [128] nanowire superlattices have been fabricated using a sequential electrochemical method inside AAO templates. By similar routes, a wide range of multisegmented 1D hybrids has been prepared in hard templates [129]. Magnetic hybrid nanowires of Co-Cu [130], Ni-Cu [131], Fe-Cu [132] and CoNiCu-Cu [133] have been found to exhibit the giant magnetoresistance (GMR) effect. Au-polypyrrole (Ppy) nanorods have been synthesized and assembled into three-dimensional bundle- and tubular-shaped microscale architectures [134].

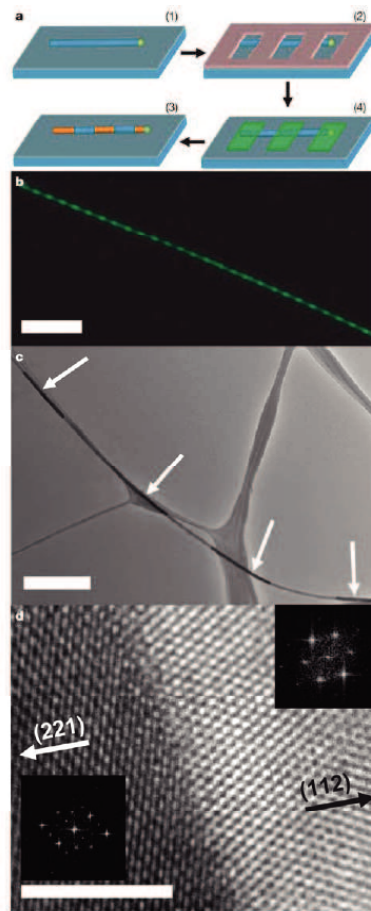


Fig. 8. Fabrication and structural characterizations of NiSi/Si nanowire heterostructures and superlattices. a, Fabrication of NiSi/Si nanowire heterostructures and superlattices. b, Dark-field optical image of a single NiSi/Si nanowire heterostructure. The bright green segments correspond to silicon and the dark segments to NiSi. Scale bar is 10 μm . c, TEM image of a NiSi/Si heterostructured nanowire. The bright segments of the nanowire correspond to silicon and the dark segments, which are highlighted with arrows, correspond to NiSi. Scale bar is 1 μm . d, HRTEM image of the junction between NiSi and Si showing an atomically abrupt interface. Scale bar is 5 nm. (Reprint from Ref. [126], with permission).

5.2 CORE-SHELL HYBRIDS

Coaxial (core-shell) nanowire is another representative type of hybrid nanostructures. In principle, core-shell structures can be fabricated by coating nanowires with a layer of a second material. The coating methods should give excellent uniformity and good control of the sheath thickness and microstructures. Thus, the formation of heterostructures from two single-crystalline semiconductor materials is of significant technological importance. GaN/Al_{0.75}Ga_{0.25}N core-sheath structures have been fabricated using a chemical vapor transport method by Yang and co-workers [135]. ZnO/GaN core-shell hybrid nanowires were grown using a MOCVD approach [136]. Recently, Lieber's group has succeeded in the

fabrication of Ge/Si [137] and GaN/AlN/AlGaIn [138] core-shell nanowires by sequential MOCVD method. As shown in Fig. 9, a quantum well is formed due to the difference in the electronic structures of Si and Ge. Based on these hybrid structures, high-performance field-effect transistor (FET) [139] and Josephson junction behavior [140] have been demonstrated.

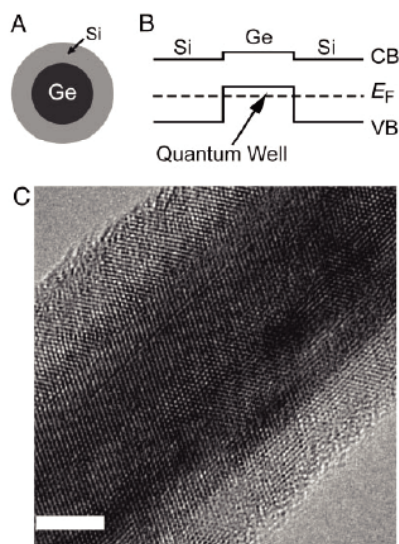


Fig. 9. Ge/Si core shell nanowires. Schematics of a cross-section through the Ge/Si core shell structure (A) and the band diagram for a Si/Ge/Si heterostructure (B). (C) HRTEM of a Ge/Si core/shell nanowire with 15-nm Ge (dark gray) core diameter and 5-nm Si (light gray) shell thickness. (Scale bar: 5 nm.) (Reprint from Ref. [137], with permission).

In a concept similar to coating a uniform layer around a nanowire, a versatile approach has been developed to carry out the second growth only along one side of the nanowire material. For example, pulsed laser deposition (PLD) was used to grow various oxides (e.g., TiO_2 , transition metal doped TiO_2 , and ZnO) on tin dioxide nanoribbons by Yang et al. [141]. Electron microscopy studies demonstrate that these functional oxides have sharp structural and compositional interfaces with nanobelt substrates. As an extension of the core-shell hybrid mentioned above, further categories of hybrids may include a nonlinear growth of sheath structure on the core structure. Such a growth could be due to the secondary growth on some specific sites with well defined orientations. As an example, from heating a mixture of In_2O_3 , ZnO , and graphite powders, faceted In_2O_3 nanowires were obtained, on which oriented shorter ZnO nanowires were crystallized [142]. Such $\text{In}_2\text{O}_3/\text{ZnO}$ hierarchical hybrid nanostructure could be used as multi-functional gas sensing devices.

6. CONCLUSIONS AND FUTURE OUTLOOK

Since C_{60} [143] and carbon nanotubes (CNTs) [144] were discovered, a great upsurge in the investigation of other 1D nanostructures has been triggered. A wide range of nanotubes, nanowires/nanorods and nanobelts have been fabricated and studied in the last decade.

Various methods, including solution-based and vapor-based routes have been developed and published extensively in the open literature. Direct oxidization of metals provides a simpler and cost-effective method for the synthesis of oxide nanostructures. Many hybrid nanowire systems have also been fabricated, for enhanced- and multiple-functional nanodevices. The challenge and future direction of the current research in the area of nanowire synthesis focuses on the rational synthesis of nanowire building blocks, integration of nanowire into more complicated functional architectures and device fabrication [145].

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CHAPTER 8

Synthesis and Applications of Inorganic–Organic Hybrid Nanostructured Materials

Martin J. Maple¹ Timothy D. Coombs² and Humphrey H. P. Yiu³

¹ School of Applied Sciences, University of Wolverhampton,
Wulfruna Street, Wolverhampton, WV1 1SB, UK

² School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland,
KY16 9ST, UK

³ Institute for Science and Technology in Medicine, University of Keele,
Thornburrow Drive, Stoke-on-Trent, ST4 7QB, UK

* H.Yiu@liverpool.ac.uk

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1. INTRODUCTION

In this chapter we review the development of selected inorganic–organic hybrid nanostructured materials. In the first part we concentrate on porous materials, before moving onto consider nanoparticles which have been modified by organic groups. In each case the origins of the hybrid solid may be traced back to an earlier, purely inorganic material, and therefore we will start with a brief description of these materials.

Nanoporous materials (both microporous and mesoporous) possess very high surface areas compared with dense solids. The modification of the inorganic pore walls, either by lining them with organic groups, or by grafting on organic linkers coupled to metal complexes or enzymes, leads to a multiplicity of novel hybrid materials. In this way the physicochemical properties of the material may be tailored to particular applications. Similarly nanoparticles have far greater surface areas than bulk solids. This affects the properties and hence the applications of both classes of material. Nanoparticles are used in areas both similar (*e.g.* catalysis, drug delivery) and dissimilar (*e.g.* diagnosis, imaging) to nanoporous solids. Their physical and chemical properties are generally rather different. Moreover, hybrids of nanoporous materials and nanoparticles have also been prepared which leads to increasingly complex systems.

2. ZEOLITE-LIKE INORGANIC-ORGANIC HYBRIDS

Microporous crystalline inorganic materials have found widespread application in industry as shape-selective catalysts, adsorbents and ion exchangers [1]. The archetypal family of such materials are the aluminosilicate zeolite minerals. These possess the general formula $[M^{m+}_{x/m}(H_2O)_n][Si_{1-x}Al_xO_2]$, where M is typically a metal cation of valence m . The framework is anionic and consists of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra (Fig. 1). The overall charge on the framework is equal to the number of tetrahedral aluminium atoms and a corresponding number of cations are required for charge balance. These cations have access to the pore system and can be exchanged. Water is present but can generally be removed and re-adsorbed without significant loss of structural integrity. It is the architectures of such materials, which contain ordered pores on the molecular length-scale, combined with exchangeable extra-framework cations and removable water molecules, which provide many opportunities for exploitation. This has inspired research to prepare synthetic zeolites, and not simply to rely on the naturally occurring mineral forms. The development of new applications has inspired much research with the aim of controlling the pore-size, shape and character (for example, relative hydrophobicity–hydrophilicity) and thus improve the processes in which they are applied.

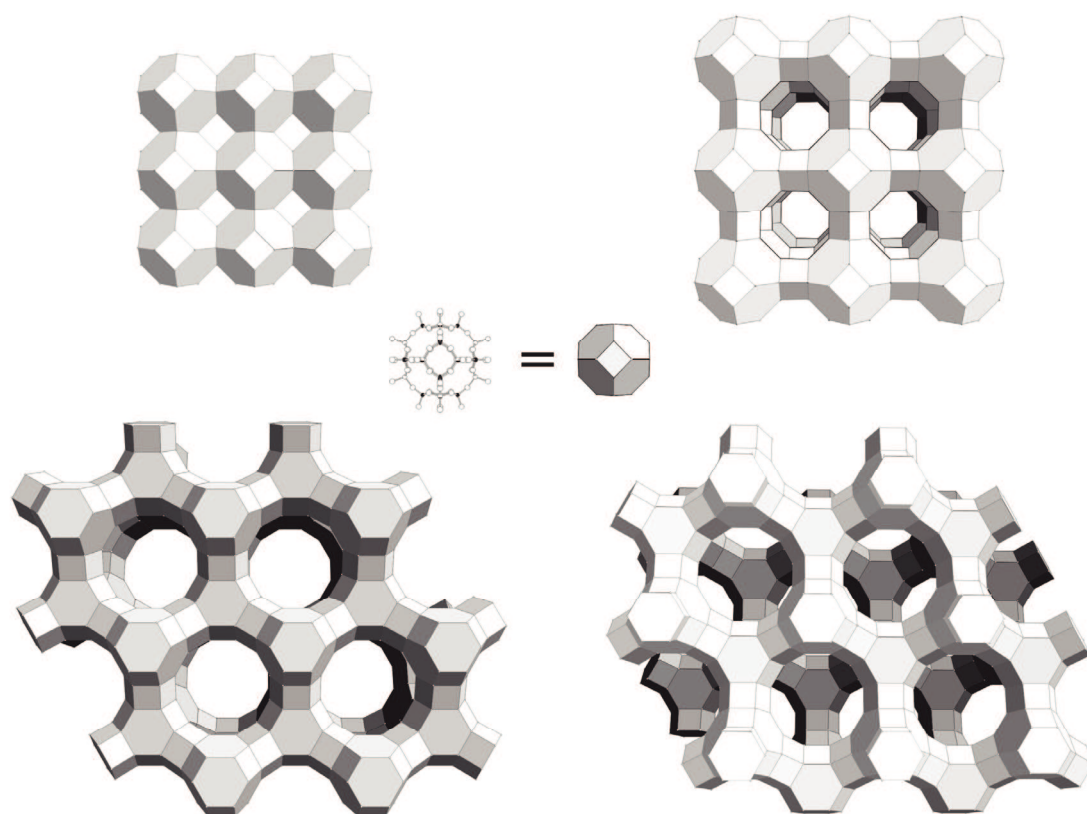


Fig. 1. Illustrative diagrams of zeolite frameworks (clockwise from top left) SOD, LTA, EMT and FAU, all constructed from the same secondary building unit, the sodalite cage (centre). The individual silica and alumina tetrahedra (centre left) are the primary building units.

Organic amines and quaternary ammonium salts have been widely applied as ‘structure directing agents’ (SDAs), or *templates*, to control the formation of the framework structure during synthesis [2]. The inorganic framework may form around an organic SDA which is occluded within the pores in the freshly prepared material. By judicious selection of novel SDA moieties over 150 different zeolite-like framework-types have been discovered [3]. Yet despite the complexity of many SDAs, and the resultant difficulty and expense in preparing them, for the majority of current applications they are removed by calcination to obtain open pores. There is no covalent bond between the inorganic framework and the organic SDA, which effectively blocks the pores and so such synthetic zeolites are not defined as hybrid solids, yet they provide a model from which to develop true inorganic-organic hybrid materials.

Recently materials have been prepared which include organic functionality covalently bonded to the inorganic framework and which exhibit novel properties; these are discussed in the sections below.

2.1 DEFINITIONS AND NOMENCLATURE

The nomenclature relating to zeolites is abstruse, and so a brief summary will be useful. When even the term ‘zeolite’ is used inconsistently in the chemical literature (to describe a range of materials with either ion-exchange or adsorption properties or both) the unwary may be caught out. The mineralogical definition is loose, yet consistent, and has been articulated by Smith as:

‘a zeolite is an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration’ [4]

‘the Al and Si atoms occupy 4-connected vertices of a three-dimensional net, and the oxygen atoms occupy 2-connected positions between the 4-connected vertices.’ [5]

A distinction is drawn between aluminosilicates that are 4;2-connected (zeolites) and others where oxygen atoms are bound either to one tetrahedral (T) atom and a hydrogen or three T atoms, or frameworks where T atoms connect to five or six oxygen neighbours.

In the chemical literature the term ‘zeolite’ is more readily used to encompass a wide range of synthetic materials. This broad definition often includes silicas such as silicalite-1, clathrasils such as sodalite, interrupted frameworks where one or more oxygens are bonded to only one T atom (such as in cloverite), and materials whose framework composition comprises elements other than aluminium, silicon and oxygen (such as the microporous aluminophosphate family of materials). In this chapter the term *zeolitic* will be applied to any ‘inorganic, three-dimensional host structure composed of fully-linked, corner-sharing tetrahedra’ [6], while *zeolite* will be reserved for silicates not containing phosphate.

The nomenclature for naming modified microporous solids and other inorganic-organic hybrid materials is far less well developed. When new microporous oxide materials have been prepared that are conceptually based on zeolites, but contain Si–C bonds, these have variously been referred to as *organic-functionalised molecular sieves* (OFMSs) or *hybrid organozeolites*. Similarly those materials which contain P–C bonds have been termed *metal phosphonates*. The family of *metal-organic frameworks* (MOFs), in which the anionic framework species is itself an organic group, will not be discussed here, but have been extensively reviewed elsewhere [7, 8, 9].

The microporous framework structures themselves may be called *hosts* and it is this that defines the pore structure that may additionally contain *guest* species. If information about the chemical composition of the host is removed the underlying framework structure represents the *topology*. Hosts may have a dimensionality of zero (finite), one (chain), two (layer), or three (framework). When the topology is of the form of a 4;2-connected regular 3-D net the International Zeolite Association (IZA) will assign a three-letter code (written in bold-face) and include a type material in the *Atlas of Zeolite Framework Types* [3]. The trivial names of

synthetic materials are given by the researchers who first prepared them, and are often abbreviations of their company or university name, followed by an integer which increases as each new material is discovered. It is often the case that materials may have different trivial names, despite being structurally or compositionally very similar.

The structures of zeolitic materials can be described in terms of composite building units (CBUs); the basic building units (BBUs) are the TO_4 tetrahedra. Rings are described by the number of tetrahedral atoms they contain (*e.g.* 4-ring, 6-ring) while pairs of rings are called double n -rings (*e.g.* double 6-ring, D6R). Polyhedra may also be identified as CBUs and described by the notation $[\text{n}_i^{\text{m}}]$, where m is the number of n -rings defining the polyhedron and $\sum \text{n}_i$ is the total number of faces (for example, a D6R would be described thus: $[4^6, 6^2]$). Some polyhedra have, however, been given additional names such as the sodalite, or β , cage, the cancrinite, or ϵ , cage and the α -cavity. In a polyhedron the n -rings are known as *windows*; polyhedra with windows too small to admit molecules larger than water (*i.e.* containing only 6-rings or smaller) are called *cages* and others *cavities*. If a cavity is infinitely extended and permits guest species to diffuse along its length it is called a *channel*.

2.2 SYNTHESIS OF HYBRID ORGANOZEOLITES

Lack of understanding of the mechanism of crystallisation means the synthesis of new materials must be carried out using empirical methods. The organic SDA is certainly the most important factor to be considered when attempting to synthesise new frameworks rationally, but the process still relies heavily on serendipity. A potentially more profitable route is to modify known materials, either by the inclusion, in framework sites, of alternative metal cations (for catalytic applications) or, as is the subject of this section, to include organic groups covalently bonded to the framework.

Microporous solids are typically synthesised solvothermally under autogeneous pressures and temperatures between 100 to 220°C. A reactive gel, containing the elements to be formed into the microporous solid, is heated with an organic SDA in a polytetrafluoroethylene (PTFE)-lined stainless steel autoclave. The solvent becomes superheated and its solvation power is greatly increased which allows the gel to mix and dissolve more effectively than in an open system. Optimising the procedure is hampered by the many variables (temperature, time, reactant source, pH, organic or inorganic cations in the gel, ageing, autoclave fill volume *etc.*) which may interact to make for extremely complex systems. The gel has high entropy (*i.e.* is more disordered) relative to the final product of crystallisation. Nevertheless zeolitic materials crystallise, the topology which does so first in any particular gel will therefore necessarily be the one with highest entropy. Microporous solids though are metastable and so may transform successively to increasingly thermodynamically stable phases. The process is encapsulated in Ostwald's law of successive transformations and is observed frequently [10]. Dense phases, such as quartz may ultimately form. Once separated from the mother liquor the metastable zeolite phase may remain unchanged almost indefinitely.

Organozeolites have been prepared by modifying procedures used to synthesise known zeolite phases. The group of Davis have created a wide range of hybrid solids by modifying zeolite- β (*BEA) by including organosilanes within the synthesis gel [11, 12, 13, 14]. Zeolite- β was chosen because it crystallises with an organic SDA (tetraethylammonium cations) that may be removed by solvent extraction. Most zeolites require calcination to burn out the SDA from within the zeolite's cavities, but this would also remove the desired organic functionality from a hybrid material. Zeolites which crystallise in the absence of organic SDAs (such as zeolite-Y) have also been suggested [11].

Davis *et al.* synthesised *BEA zeolites containing organic groups, particularly aminopropyl, phenethyl, mercaptopropyl and ethylcyclohexenyl groups (see Table 1). In most cases materials could be prepared with organosilica/silica ratios of up to 0.05 (ethylcyclohexenyl could only be included at lower levels). The functional groups within the organozeolites may be further modified using traditional synthetic organic chemical techniques. Aminopropyl may be reacted with aldehydes (*e.g.* 4-(dimethylamino)benzaldehyde and 4-dimethylamino-1-naphthaldehyde) to form imines [12]. Sulfonic acids may be formed either by reacting phenethyl with SO_3 (generated from oleum) [11, 13] or by oxidising mercaptopropyl (with H_2O_2) [14]. Such modification allows for the construction of ever more complicated hybrid materials and permits their application in catalysis (see below) [14].

The preparation of organozeolites requires extra synthetic steps, compared to classical zeolites. The general procedure follows the following steps

Step 1: crystallise the organozeolite

Step 2: extract the SDA

Step 3: further functionalise the occluded organosilanes

Between each step the solid product must be carefully washed, recovered by filtration and dried. In addition, it may be necessary to cleave organosilane groups which are bound to the outer surface of the crystals, usually before extracting the SDA. The method of extraction have been found to affect the number of defect sites within the materials' frameworks and hence their hydrophobicity.

While the preparation of crystalline materials potentially allows good control over the homogeneity of the included organic groups obtaining materials with high levels of organic groups has proved a challenge. Corma *et al.* recently reported the synthesis of hybrid organozeolites with increased levels of organic groups [15]. Differences in carbon uptake observed in different materials were attributed to differences in the parent zeolite's framework structure, but the reasons for this remain to be elucidated.

2.3 CHARACTERISATION TECHNIQUES

To characterise the hybrid organozeolite materials' structure both the parent zeolite framework and the presence of the organic group must be confirmed. This generally requires

the application of a number of complimentary analytical techniques which examine both the long and short-range structural features of the solid.

Powder X-ray diffraction (XRD) is most commonly used to confirm the bulk zeolite framework-type and crystallinity level by comparing the 'finger-print' pattern with that of a standard material. For novel materials the framework structure is most easily determined by single crystal X-ray diffraction, however for this crystals of sufficient size and quality must be available. In recent years

Table 1. A list of organosilanes tethered to zeolite framework types.

Zeolite framework type	Organosilane	Notes	Ref.
*BEA	2-cyanoethyltrimethoxysilane		[12]
*BEA	3-iodopropyltrimethoxysilane		[12]
*BEA	3-butenyltrimethoxysilane (allyltrimethoxysilane)		[12], [13]
*BEA	3-bromopropyltrimethoxysilane		[12]
*BEA	3-aminopropyltrimethoxysilane	may be further reacted <i>in situ</i> with aldehydes to form imines	[12]
*BEA	<i>N,N</i> -dimethyl-3-aminopropyl-trimethoxysilane		[12]
*BEA	phenethyltrimethoxysilane	may be sulfonated <i>in situ</i> with SO ₃ to form sulfonic acids	[11], [12], [13]
*BEA	2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane		[12]
*BEA	3-mercaptopropyltrimethoxy-silane		[12]
*BEA	2-(3-cyclohexenylethyl)tri-methoxysilane		[13]
*BEA, MFI	bis(triethoxysilyl)methane		[15]
MFI	bis(triethoxysilyl)ethane		[15]

synchrotron radiation (at X-ray wavelengths) has been used which has led to the development of microcrystal diffraction. Neutron diffraction has also been used to investigate the structure and dynamics of the organic groups found in hybrid solids [16].

To examine the environment around specific elements solid-state nuclear magnetic resonance spectroscopy (NMR) is used. ^{13}C MAS NMR will readily show whether the organic moiety has been included intact within the micropores. However, to verify that it is bonded to the inorganic framework ^{29}Si MAS NMR is applied. A signal at -60 ppm indicates the presence of Si–C bonds. ^{29}Si MAS NMR may also be used to find the number of defect sites within the framework, which influence the material's hydrophobicity.

Further characterisation may be performed to determine the stability and porosity of the hybrid solid. Thermogravimetric analysis (TGA) provides the temperature at which the material breaks down, while its pore volume and surface area may be calculated from N_2 adsorption isotherms. Scanning electron microscopy (SEM) provides images of the crystals and hence their morphology.

Researcher may use various chemical analysis techniques to establish elemental composition. The most frequently used for inorganic composition are inductively coupled plasma–atomic emission spectroscopy (ICP–AES), X-ray fluorescence spectroscopy (XRF) and energy dispersive X-ray analysis (EDX). Carbon Hydrogen Nitrogen (CHN) microanalysis is used to find the organic composition. Mass losses found from TGA may also be correlated to the loss of water and the organic to corroborate the organic compositional analysis.

2.4 APPLICATIONS OF HYBRID ORGANOZEOLITES

Hybrid organozeolites have been applied principally in catalysis. For example Davis *et al.* have found that oxidised mercaptopropyl functionalised *BEA (a supported sulfonic acid catalyst) will selectively catalyse the reaction of the carbonyl compound cyclohexanone with ethylene glycol to form a ketal [11, 14]. Unfortunately the rate of reaction was reduced, relative to commercial zeolite *BEA catalyst, organo-functionalised mesoporous solids and homogeneous acids, which was attributed to slow diffusion of the substrate within the micropores. Shape selectivity was shown since 1-pyrenecarboxaldehyde was found not to undergo reaction since it is too large to enter the micropore system and thus was unable to reach the active catalytic sites.

3. SHIP-IN-A-BOTTLE ZEOLITES

Instead of tethering organic groups on the zeolite framework, a class of inorganic-organic hybrid zeolites has their organic entities encapsulated inside the cages in the structure. Inside these hybrid materials, there is no direct bonding between the inorganic framework and the organic molecules. The organic molecules were kept inside the cages because their size is larger than the diameter of the inter-cages channels.

3.1 THE ART AND DESIGN OF MOLECULAR SHIP-IN-A-BOTTLE

The first ship-in-a-bottle zeolite was reported by Herron *et al.* [17] when iron phthalocyanines (FePc) were encapsulated inside faujasites (NaX and NaY). These hybrid zeolites were used as catalysts in the oxidation of alkanes.

To effectively produce ship-in-a-bottle zeolites, we have to consider the size of the organic entity to be used and the cage size of the zeolite to fit these organic molecules. In some cases, the inter-cage channels have to be smaller than these organic molecules but large enough for the diffusion of other molecules in the final use, e.g. the reactants and products of a catalytic reaction. Figure 2 illustrates these criterias in building a ship-in-a-bottle zeolite.

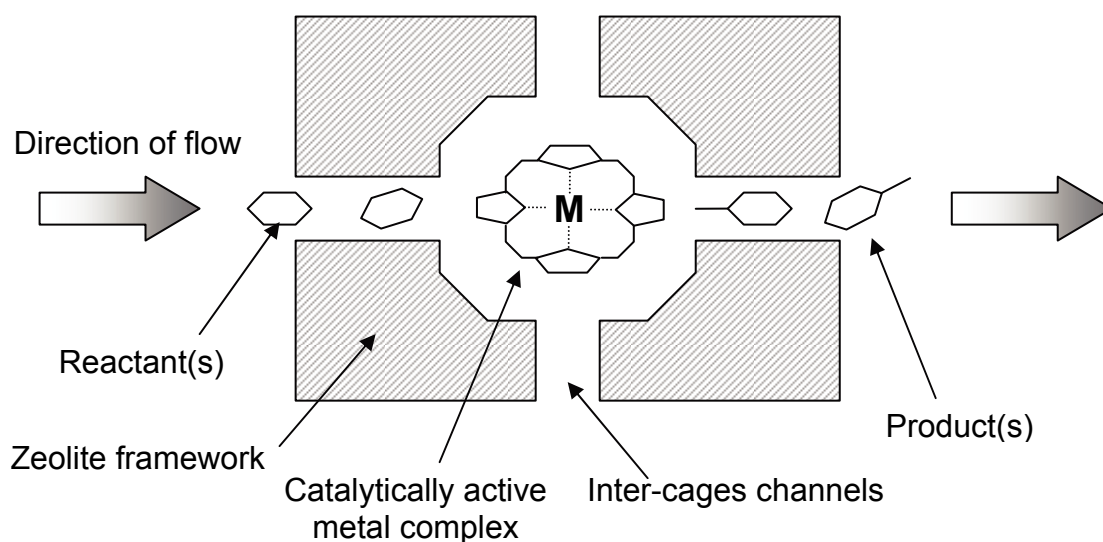


Fig. 2. A illustrated design of a ship-in-a-bottle zeolite with catalytic use.

Fajusites are among the most popular structures to encapsulate organic molecules in building these molecular ship-in-a-bottles because they possess large cages (1.2 nm in diameter) in their framework.

3.2 BUILDING THE SHIP-IN-A-BOTTLE

There are two main routes to build the ship-in-a-bottle zeolites: (1) self-assembling the organic entities inside a ready made zeolite framework (sometimes this method is termed “flexible ligands”); or (2) building zeolite framework on the functional organic template or “zeolite synthesis” method. Method (1) requires a organic molecule, which is easy to assemble from small components as these components have to “imported” through the small channels in zeolites. For example, metal bipyridine complexes $M(\text{bipy})_n$ can be encapsulated inside faujusites using this method as ligands are relatively small and linear. For method (2), since the zeolite frameworks are built in the presence of the organic molecules, these molecules have to be stable under the synthesis conditions for the zeolite. As a result, usually they are basic molecules such as macrocyclic molecules. During the synthesis, these molecules also serve as a structural directing reagent.

3.3 CATALYSIS USING SHIP-IN-A-BOTTLES

The major difference between ship-in-a-bottle catalysts and that of zeolites grafted with catalytic entities is that there is no change in the nature of the molecules while the grafting procedure usually alters the structure of the catalytic entity, and so the catalytic activity.

One of the original aims of building ship-in-a-bottle is to mimick the structure of some enzymes, particularly for redox reactions. In the structure of an enzyme, usually there is one (or sometimes more) catalytically active site, while the protein strands surrounding the active site are able to select substrates. Since the zeolite frameworks have already served as molecular sieves, by incorporating an active site into the cavity inside the framework, a enzyme mimic can be constructed.

Metal phthalocyanine complexes (MPc), such as CuPc and FePc, have been popular choices as an active site for this application. Because of the large size of MPc molecules, these ship-in-a-bottle catalysts can only be built following the “zeolite synthesis” approach [18]. These catalysts have been compared with methane monooxygenases (MMO) in methanol synthesis. A high turn over number of over 100 was achieved by faujusite encapsulated FeCl_6Pc catalysts. This family of catalysts can also mimick the activity of haloperoxidases in oxyhalogenation of aromatics [19].

Metallosalen complexes (eg. Mn(III)SalCl and CuCl_2Sal) encapsulated inside zeolites are popular examples of ship-in-a-bottle catalysts. Jacobs *et al.* [20] compared the encapsulation efficiency of both methods and found that more copper-salen complexes were encapsulated using “flexible ligands” method because of the low solubility of the complexes.

Many other examples of ship-in-a-bottle catalysts can be found in literature and reviews on ship-in-a-bottle catalysts are widely available [21, 22, 23].

3.4 OTHER APPLICATIONS OF SHIP-IN-A-BOTTLE ZEOLITES

Although the majority of ship-in-a-bottle zeolites were used as heterogeneous catalysts, using these delicate structures in other areas can also be found. One example is encapsulating fluorescent molecules inside the zeolite framework [24]. These “fluorescent zeolites” can be used in biotechnology as imaging agents. For instance, fluorescein has been assembled inside the cages of zeolite Y and the composite material was shown to be used in cellular imaging with laser confocal microscopy [25]. Unfortunately, this approach still restricts to small organic molecules which ideally can be formed by self-assembly mechanism. Other molecules may need a more spacious environment to be encapsulated.

4. MESOPOROUS SILICA WITH AN ORGANIC SURFACE

Chemists have strived to prepare materials with ever larger pores, which would enable the tethering organic groups to the pore walls allowing catalysis to be performed on larger molecules and enzymes to be supported. This has led to the development of silica-based solids containing ordered arrays of pores much larger than any found in zeolites. The Mobil M41S family (MCM-41, MCM-48 and MCM-50) [26, 27] have pore dimensions of 20 to 100 Å (or 2 to 10 nm) [28]. These materials are called *mesoporous molecular sieves* (MMS) or *ordered nanoporous materials*. The walls are amorphous silica (the thickness is approx. 1 nm) but the mesopores remain highly ordered. In this section, we will discuss mesoporous materials, concentrating on the potential of inorganic–organic hybrid silicas.

4.1 FORMATION MECHANISM OF MESOPOROUS SILICAS

Instead of simple molecular templating mechanisms, these materials are formed by a unique mechanism called *liquid crystal templating* (LCT). Figure 3 illustrates the formation of these materials. Generally, a reaction mixture including a silica source (*e.g.* tetraethylorthosilicate, TEOS), a surfactant *template* (*e.g.* cetyltrimethylammonium bromide, CTAB), a pH modifier (*e.g.* NaOH or HCl) and water. Mesoporous silicas usually form at a temperature (0 to 150°C) lower than zeolites.

Since the Mobil report, mesoporous silicas with many different pore arrays and pore dimensions have been discovered. The preparation procedures are similar and consist of several steps; solvation of surfactant template, addition of silica precursor, gel formation, hydrothermal treatment and template removal. Reviews [29, 30, 31] and books [32, 33] with details of synthetic procedures are widely available. Among the structures, 2-D hexagonal arrays (MCM-41 and SBA-15) are the most popular choice of materials for applications in catalysis, chromatography and biotechnology because of the simplicity in their 2-D structure, which makes their behaviour more predictable.

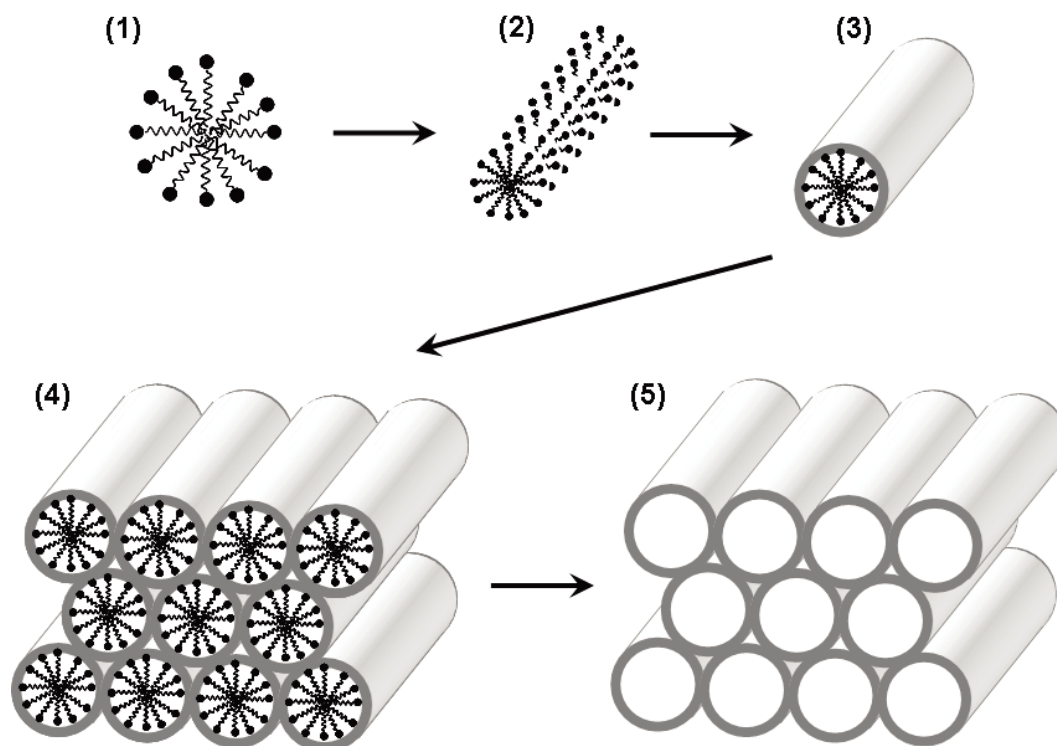


Fig. 3. Scheme illustrating the formation of mesoporous silicas through the LCT mechanism: (1) the formation of spherical micelle, (2) the formation of rod-shaped micelle at a higher surfactant concentration, (3) silica coated on the micelle surface, (4) self-assembly of silica coated micelles to form mesostructured silica, (5) removal of surfactant templates after the formation of mesoporous silicas, by either calcination or solvent extraction.

4.2 STRUCTURAL STUDIES OF MESOPOROUS SILICAS

To study the nanostructure of these mesoporous silicas, advanced analytical techniques are necessary. High resolution transmission electron microscopy (HRTEM), low-angle powder X-ray diffraction (XRD) and surface analysis using nitrogen adsorption are commonly used to examine the physical properties such as specific surface area, pore size distribution and visual images. Scanning electron microscopy (SEM) shows the morphology of the materials, which is critical particularly for chromatographic applications. Solid state nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy provides information on the surface functional groups. Literature concerning the characterisation of mesoporous silicas are widely available [34, 35].

4.3 SURFACE MODIFICATION

The original idea of surface modification was an attempt to create a mesoporous silica sample with a hydrophobic surface by tethering methyl groups. Since mesoporous silicas are chemically identical to common silica materials and procedures grafting organic groups onto silica surface have been known for many years, inorganic-organic hybrid mesoporous silicas of a wide range of surface properties became available.

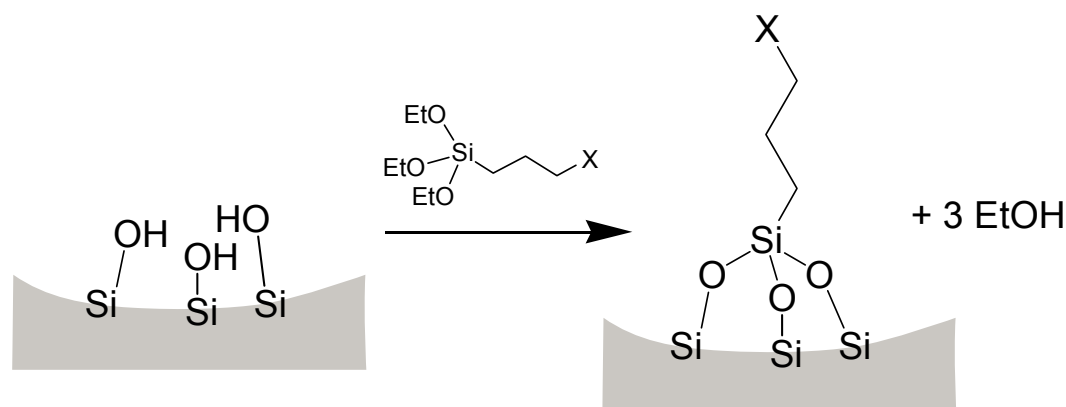


Fig. 4. Scheme illustration a typical silylation reaction for functionalising mesoporous silica using trialkoxysilane, where X may be a functional group such as Cl, CN, SH, NH₂, OH etc.

Trialkoxysilanes are commonly used in modification of silica surface. Figure 4 shows the use of triethoxysilane to modify the silica surface through hydrolysis. There are two methods of surface modification for mesoporous silicas: (1) *in situ* one-pot synthesis and (2) post-synthesis grafting. The first method involves co-condensation of trialkoxysilanes together with the silica precursors, usually tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS), during the synthesis of the mesoporous silica. It is a simple method and usually complete hydrolysis can be achieved. However, the number of functional groups is limited to approx. 10 % as a higher concentration will result in loss of structural order. Also, the surfactant template can only be removed by solvent extraction, which is not as efficient as calcination, in order to preserve the surface functionality. It is also worth noting that organic-functionalised mesoporous silicas usually have smaller pore dimensions than their pure siliceous counterparts. Depending on the nature of their tethered organic groups, a reduction of 1–2 nm in pore size is commonly observed.

4.4 CATALYTIC APPLICATIONS OF MESOPOROUS SILICAS WITH ORGANIC GROUPS

Because of their highly ordered mesopore arrays, functionalised mesoporous silicas were conjectured to have high selectivity for molecular size and shape. Together with their capability to accommodate large organic molecules, research on catalytic properties of

mesoporous silica materials flourished quickly after the discovery of the M41S series in the early 1990s.

4.4.1 SOLID ACID AND SOLID BASE

From the start chemists searched for zeolites with pores large enough for common organic reactions. Aluminosilicate zeolites are widely used in industry as solid acid catalysts and have high commercial values. As a result, the first mesoporous silica-based catalyst was aluminium-substituted MCM-41 [26]. However, the catalytic activity of these aluminosilicate mesoporous materials is poorer than that of zeolites, which is attributed to the amorphous wall structure.

Instead of aluminium substitution, mesoporous silica can carry organic acid groups such as sulfonic acid (see figure 5), which is also widely used as Brønsted acid catalysts. Sulfonic groups can be attached to the surface of mesoporous silicas by grafting thiol groups followed by oxidation using hydrogen peroxide (see figure 5). Diaz *et al.* demonstrated the use of sulfonic acid-functionalised SBA-15 in esterification of glycerol with fatty acids [36]. Mesoporous silica with higher acidity can be achieved by grafting perfluorosulfonic acid groups [37].

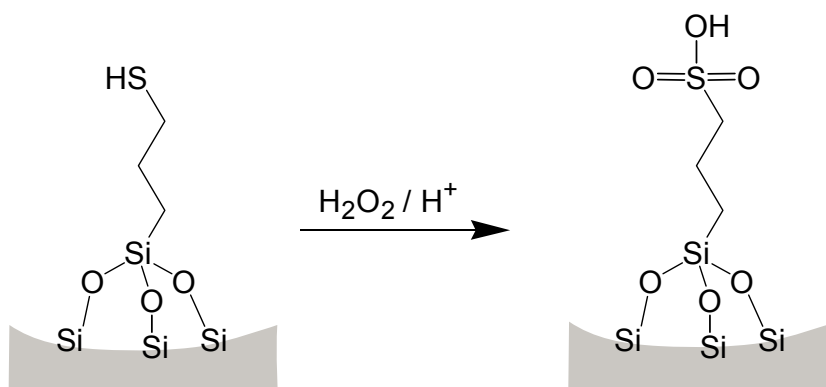


Fig. 5. Scheme for the formation of sulfonic acid groups on the silica surface through oxidation of thiol groups using H_2O_2 as oxidant.

Solid base can also be built by tethering amine or pyridine groups onto the surface of mesoporous silica. For example, the nitroaldol reaction between benzaldehyde and nitromethane can be catalysed by amine-functionalised mesoporous silica [38]. This reaction may be applied to other substituted benzaldehydes. These solid base catalysts can also be used in Knoevenagel and Michael reactions [39].

4.4.2 TRANSITION METAL COMPLEXES SUPPORTED ON MESOPOROUS SILICA

We have already discussed, in Section 3, ship-in-a-bottle catalysts which are catalytically active metal complexes encapsulated within the zeolite framework. If a reaction involves

large organic molecules, which are too large to enter micropores in zeolites, tethering the transition metal complexes on mesoporous silicas can be an option.

These catalysts can be prepared by synthesising the metal complex with a trialkoxysilane group and subsequently grafting it onto the internal silica walls of the mesoporous support. Figure 6 depicts three examples of metal complexes which can be grafted using this method. Some ligands, such as ethylenediamine with a trialkoxysilane group (*N*-[3-(trimethoxysilyl)propyl]ethylenediamine, (c) in figure 6), are commercially available. Ligands may be grafted either at *post-synthesis* or at *synthesis (in situ)* (see Section 4.3). Once grafted, the ligands are capable of binding metal ions and form active metal complexes. However, for more specific metal complexes, the first method is recommended. In many cases, grafting metal complexes onto mesoporous silica can be a multi-step process [40, 41].

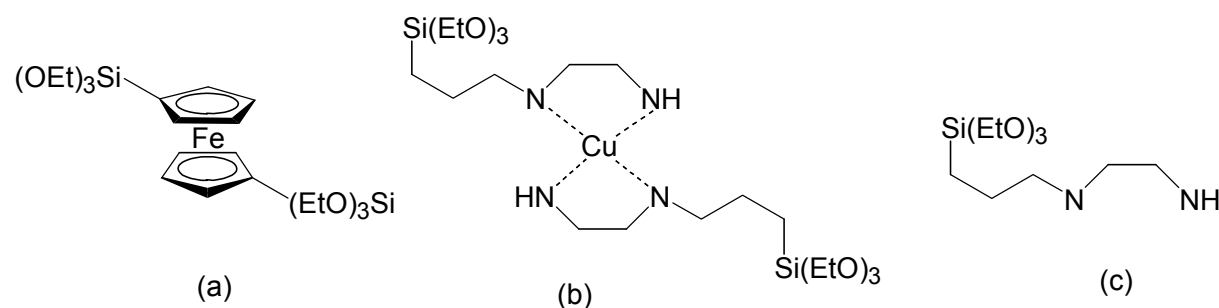


Fig. 6. Three examples of trialkoxysilane with (a) ferrocene; (b) copper(II) ethylenediamine complex and; (c) ethylenediamine ligand, which have been grafted onto the mesoporous silica.

Most of these metal complexes catalysts are used in redox reactions. For example, ferrocene supported on SBA-15 has been used in the oxidation of benzene using H_2O_2 as oxidant. Only a small loss of catalytic activity was observed after recycling the catalyst [42]. Generally these catalysts exhibit lower activity than their corresponding homogeneous catalysts because of the reduced diffusion of reactants and products. Literature reviews are available in this area of research [43, 44, 45].

4.4.3 ENZYME–MESOPOROUS SILICA HYBRIDS

Since mesoporous silicas have pore dimensions of several nanometres, it is possible to use them to support small biomolecules such as small enzymes and proteins. This idea was first suggested by Diaz and Balkus [46] who demonstrated it for cytochrome *c*, trypsin, papain and horseradish peroxidase on MCM-41. Without a strong interaction between the enzyme molecules and the silica surface, these catalysts suffered from severe leaching (where the enzyme is lost from the support during reaction). As a result the authors suggested an encapsulation approach by reducing the pore openings. However, the chemicals used during

the encapsulation process was found to denature the enzymes and hence reduce their catalytic activity.

A more successful approach to enzyme immobilisation was the chemical binding method which used mesoporous silicas grafted with organic groups (an inorganic–organic hybrid), which was first reported in 2001 [47]. In this report, thiol, alkyl chloride and carboxylic acid groups were found to be more efficient in binding the enzymes and retaining their activity than other functional groups including amine and phenyl groups. The hybrid solid remained active after recycling. Since then much research using inorganic–organic hybrid mesoporous silicas for enzyme immobilisation has been reported. Reviews are widely available in literature [48].

4.5 SEPARATIONS USING INORGANIC–ORGANIC HYBRID MESOPOROUS SILICAS

Soon after the discovery of mesoporous materials, researchers realised the potential of their high surface area by using them as stationary phases for chromatography [49, 50]. Although some success has been achieved, the major set back of using mesoporous silicas is their non-spherical morphology, which is considered to be able to withstand higher pressure. Later, this was overcome by the use of co-surfactants. However, their true potential in chromatography depends on using their unique, highly ordered pore structure (and the possible organic functionality inside mesopores) for the size exclusion of molecules with diameters of several nanometres.

Inorganic–organic hybrid mesoporous silicas for biomolecular separation were first reported in 1999. Han *et al.* demonstrated the separation of protein molecules of different sizes [51]. Yiu *et al.* studied the adsorption mechanism of protein molecules in thiol-functionalised mesopores [52]. Recently, Gao *et al.* successfully used functionalised SBA-15 in separating protein molecules with an HPLC system [53]. Although there have been some recent developments [54, 55] in applying mesoporous materials to chromatography they remain relatively underexploited.

4.6 APPLICATIONS IN DRUG DELIVERY

With a large pore volume, mesoporous silicas were thought to be suitable for carrying molecules for drug delivery. The first work applying mesoporous silicas in this area was reported in 2001 by Vallet-Regi *et al.* [56] who conducted an adsorption–desorption study of ibuprofen on purely siliceous MCM-41. This MCM-41 material carried no functional groups but is likely to be negatively charged at the surface. With no strong interaction between the drug molecule and the carrier, the majority of the ibuprofen molecules that were adsorbed were quickly released. A more controlled release regime is needed for further *in vivo* studies.

Many drugs are negatively charged, such as ibuprofen and aspirin, and can be bound to positively charged surfaces through electrostatic interaction. Therefore studies have been

carried out using amine-functionalised mesoporous silicas for drug delivery. For example, Zeng *et al.* found that the releasing profile of aspirin from amine-functionalised MCM-41 depended on the number of tethering groups on surface [57]. As the concentration of amine groups increased the carrier became more positively charged, and more aspirin could therefore be bound onto the carrier through electrostatic interaction.

Mesoporous silicas with hydrophobic surfaces were also used in drug delivery. Doadrio *et al.* [58] reported the use of SBA-15 with C₈ and C₁₈ alkyl groups tethered to the pore walls as a support for the macrolide antibiotic, erythromycin. Although nitrogen adsorption measurements suggested that there was only a slight reduction in pore size when the C₈ to C₁₈, groups were attached, there was found to be a significant reduction in diffusion rate of erythromycin, in the hybrid material compared to the unfunctionalised SBA-15. Depending on the situation of drug delivery, one may want to have a lower diffusion rate as the amount of drug released can be easily controlled. In other cases, higher diffusion rate may be necessary for fast delivery. These experiments show a simple mechanism in controlling the rate of delivery for drugs.

4.7 OTHER ADVANCED APPLICATIONS

The well-defined channels found in mesoporous silicas have been used to control the formation of specific structures. Wu and Bein demonstrated their use for growing conducting polymer filaments of polyaniline [59]. The resultant silica–conducting polymer composite materials have potential applications as electrode materials in batteries.

Inorganic–organic hybrid mesoporous silicas have also been used to stabilise semiconducting quantum dots (QDs) [60]. A thiol-functionalised mesoporous silica has been most commonly used as the host material since II-VI QDs (CdS, CdSe) readily grow on the thiol groups. Since QDs are usually unstable in ambient conditions a protective coating, the silica framework in this case, is needed to stabilize them. The mesoporous silica-hosted QDs have been used as fluorescent probes in biology [61].

Instead of inorganic QDs, organic fluorescent molecules have also been attached on the internal surface of mesoporous silica. Fluorescein isothiocyanate (FITC) can react readily with amine-functionalised mesoporous silica and these fluorescent silica particles have been used in monitoring the decomposition process of biodegradable polymers [62]. These particles have also been used as labels for tracking human stem cells [63].

5. MULTI-LAYERED NANOPARTICLES

In this section the synthesis of hybrid nanoparticles will be discussed. Nanoparticles share a high surface area with microporous and mesoporous materials, but are structurally very different. For most applications of microporous and mesoporous materials, the active sites are located inside the complex porous structures. However, in a functionalised nanoparticles, the

active sites are likely to be on the surface while the core provides an additional physical property.

5.1 THE CORE–SHELL DESIGN

Their high surface area makes nanoparticles generally more reactive than bulk materials of the same composition [64]. An inert coating is often required to protect the nanoparticles from erosion, oxidation, decomposition or solvation [65]. For biomedical applications, a layer of biocompatible materials is also necessary. These biocompatible components can be natural organic molecules such as proteins, carbohydrates and lipids. Some synthetic polymers (including polyethylene glycol (PEG) and polyethyleneimine (PEI)) are also used as the biocompatible layer. This core-shell design is illustrated in figure 7.

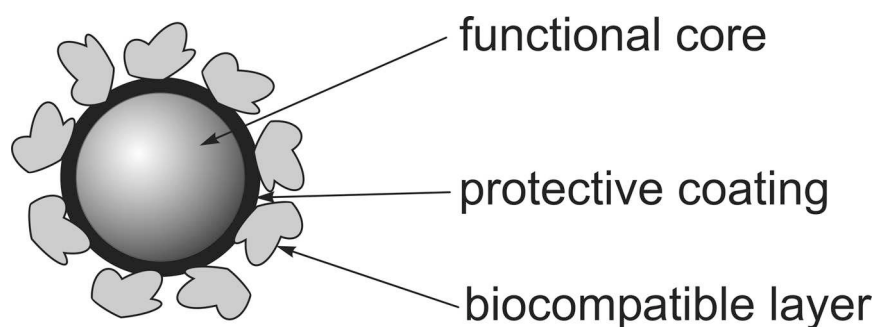


Fig. 7. A common design of a functional nanoparticle for biomedical applications.

5.2 CHOICE OF MATERIALS

5.2.1 CORE MATERIALS

The choice of materials largely depends on the nature of the application. The core material usually confers its fundamental physical properties to the whole agent. One of the common examples can be found in MRI imaging for diagnosis. Iron oxide nanoparticles may be used as a contrast agents to enhance the quality of the images (*cf.* gadolinium complexes, but these are more toxic). Iron oxide nanoparticles (mainly magnetite and maghemite) are also used for magnetic targeting delivery of drugs. These magnetic nanoparticles are designed to be able to follow an external magnetic field and travel to an infected organ and then deliver a drug. It is designed to be a highly specific therapy to minimise the side effects of the drug. In both cases, iron oxides are used as the core materials partly due to safety concerns. Other materials, such as compounds of cobalt or nickel, are also magnetic but the use of iron, which is considered to be less toxic, is preferred.

Recent developments in semiconducting quantum dots also attracted the attention of the medical community. Their unusual optical properties may be developed into a novel diagnostic technique for various diseases, usually by tagging antibodies specific to defective

organs. However, most of these quantum dots are of highly toxic, comprising elements such as cadmium and selenium, and they can be highly unstable. Research is still required before using quantum dots can be applied in medical treatments.

5.2.2 SHELL MATERIALS

Since nanoparticles are usually highly reactive, a protective, inert coating is commonly applied to them. The nature of this coating can be natural polymers, synthetic organic polymers, silica or gold. Natural polymers, including carbohydrates (dextran or agarose) [66] and proteins (collagen) [67], are one of the popular choices because of their biocompatibility. Unfortunately, they tend to be very fragile or porous, and cross-linking is often needed to prevent them from breaking down. Synthetic polymers become alternatives with improved mechanical strength. As a result, many nanoparticles are coated with synthetic polymers with PEG being the most popular choice [68]. Other synthetic polymers such as polylactic acid (PLA) and polyglycolic acid (PGA) can also be used.

Another popular choice of coating materials is silica, which offers the advantages of high mechanical strength and ease of further functionalisation [69]. The use of triethoxysilane to functionalise the silica surface has been widely applied in materials research. Nanoparticles coated with gold were also found in literature. Gold is well-known as being inert but its affinity for thiol groups ($-SH$) make gold easily functionalised [70].

5.2.3 SPECIFIC FUNCTIONALITY

On the exterior of the nanoparticles, specific entities can be attached in order to give the nanoparticles particular tailored properties. This can be a biomolecule to help target a certain organ within the body or a drug molecule that can be released only at a target organ. For example, nanoparticles tagged with biotin (or vitamin B₇) can bind to streptavidin in the body because of the strong affinity between the two [71].

5.3 APPLICATIONS

Functionalised nanoparticles have almost limitless potential. Here we introduce a few interesting examples.

5.3.1 MAGNETIC SEPARATION

The separation and purification of biological products is complicated and time consuming since the matrices used are themselves complex and the quantity of the target component is very small (microgram scale). Magnetic nanoparticles tagged with specific functional groups have been developed to isolate biomaterials, together with simple magnetic separators. For example, isolation of DNA molecules has been performed using magnetic nanoparticles with a positively charged surface, by binding the negatively charged DNA molecules through electrostatic interaction [72].

Magnetic separation of cells can also be carried out using magnetic particles coated with dextran or polyvinyl alcohol [73]. By tagging these nanoparticles with antibodies a highly immunospecific separation can be achieved, including red blood cells [74], lung cancer cells [75] and bacterial cells [76].

5.3.2 DIAGNOSIS

One of the most commonly used non-invasive diagnostic technique in medical science is magnetic resonance imaging (MRI), which is frequently used to examine tissues with elements of higher atomic number (such as calcium in bones) than the neighbouring tissues. Also, the imaging contrast can be enhanced by use of contrast agents. Traditionally, paramagnetic gadolinium (Gd) ion complexes [77] were used as MRI contrast agents but iron oxide nanoparticles have been increasingly popular in this application [78] due to their relatively lower toxicity. Usually, these iron oxide nanoparticles are coated with peptides or carbohydrate in order to make them biocompatible [79]. Usually, healthy liver tissue will retain these iron oxide nanoparticles while abnormal areas such as tumours do not.

5.3.3 DRUG DELIVERY

One of the main drawbacks of traditional chemotherapies is their non-specific nature. As a result, side-effects are difficult to avoid when the drug molecules attack healthy organs during treatment. The small size of nanoparticles means they are capable of travelling through the cell membrane and being internalised into a cell. If the nanoparticles are incorporated with a magnetic core, they may be localised by an external magnetic device. This property offers a novel mechanism for drug delivery.

The use of magnetic nanoparticles as carriers for drugs aimed at tumours in the body was reported in the late 1970s [80, 81, 82]. This strategy of drug delivery was thought to have advantages in reducing the side effects of drugs and also reducing the dosage. Generally, to prepare the hybrid drug–nanoparticle complex, a cytotoxic drug is attached to magnetic nanoparticles with a biocompatible coating. This is then injected into the patient through the circulatory system. An external, high-gradient magnetic field is used to focus the drug–nanoparticle complex onto a specified location within the body. The drug is finally released through changes in conditions such as pH or body temperature, or through enzymatic activity.

One of the major challenges in this area is to target “deep organs” where the applied magnetic field is weak and the efficiency in collecting drug–nanoparticle complexes is reduced. Present directions in research include improving the external magnetic field for focusing onto the target and improving the magnetic response of the nanoparticles.

5.3.4 CATALYSIS

Functionalised nanoparticles have been widely used in life sciences and medical research. Their applications in chemical sciences have been somewhat overshadowed by their success

in biotechnology. However, there are still some examples of functionalised nanoparticles being applied in areas such as heterogeneous catalysis.

Zheng *et al.* developed a biomimetic catalyst by supporting peptides (Asp and His) onto maghemite nanoparticles and the catalyst was found to be active in hydrolysis of paraoxon and 4-nitrophenyl acetate under mild conditions. The catalyst is recovered using an external magnetic field and recycled with no significant loss in activity after 3 months [83].

Magnetic cobalt ferrite (CoFe_2O_4) nanoparticles with diamine groups grafted on the surface have also been used in base-catalysed Knoevenagel reactions [84]. The catalysts were recovered by a magnet and shown to be reused several times without significant loss of activity.

6. CONCLUSIONS

We have introduced several families of inorganic-organic nanostructured materials and their applications. With the advance in materials engineering, the boundary between these classes is getting less distinct. For example, the pore dimension of SBA-1 (1.8 nm) is considerably too small to be classified as mesoporous materials yet its preparation procedure is remarkably similar to other mesoporous SBA materials (SBA-2, SBA-15, SBA-16), and its silica wall is fundamentally amorphous [85]. On the other hand, mesoporous silica materials have also been used as coating materials for magnetic nanoparticles [86, 87]. More complicated hybrid nanostructures will be synthesised in the near future with properties superior to any material we have seen. We shall also see major developments of using inorganic-organic nanostructured materials in nanoelectronics and nanomedicine in the next few decades.

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CHAPTER 9

Nanolayers and Nanostructured Films

Ali Shokuhfar^{1,*}, Mohammad Reza Vaezi²

¹ KN Toosi University of Technology, Faculty of Mechanical Engineering,
Tehran, Iran

² Division of Advanced Materials, Materials and Energy Research Center,
Karaj, Iran

* shokuhfar@kntu.ac.ir

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1. INTRODUCTION

The performance of materials depends on their properties. These in turn depend on the atomic structure, composition, microstructure, defects, and interfaces, which are controlled by thermodynamics and kinetics of the synthesis. A current paradigm of synthesizing and processing of advanced materials emphasizes the tailored assembly of atoms and particles, from the atomic or molecular scale to the macroscopic scale. Nanostructured materials, often characterized by a physical dimension of 1-100 nm (such as grain size) and a significant amount of surfaces and interfaces, have been attracting considerable interest because of their demonstrated or anticipated unique properties compared to conventional materials. Nanostructured materials can be made by attrition of parent coarse-grained materials using the top-down approach from the macroscale to the nanoscale, or conversely, by assembly of atoms or particles using the bottom-up approach. The control of arrangement of atoms from the nanoscale to the macroscale is indeed the strength of materials chemistry. Therefore, it is not surprising that increasing attention has been paid to the chemical synthesis and processing of nanostructured materials.

Nanostructured particles, films and coatings can be synthesized using a number of techniques including using solution chemistry. There has been a great deal of progress in chemical synthesis and processing and active multidisciplinary efforts are continually pursued. More work needs to be done in the area of processing of nanoparticles and coatings. Fundamental understanding of interfacial interactions of these high-surface materials, particularly the interfacial stability of the hybrid materials, is essential in order to design and control the properties of the materials.

Chemistry is based on the manipulations of atoms and molecules, and indeed has a very long history in the synthesis of materials comprising of nanostructures. The fields of colloids and catalysts are such examples. The recent popularity of *nanoscience* not only revitalized the use of many old chemical methods, but also motivated many new and modified ones to be continually developed for the synthesis of nanostructured materials. The scope of chemical synthesis and processing of nanostructured materials is very wide, spanning structural, optical, electronic, magnetic, biological, catalytic, and biomedical materials. In this chapter, a comprehensive review of many aspects of this field has been undertaken. An overview of synthesis and processing of nanostructured particles, films, and coatings with selected examples of metals, ceramics, and hybrid materials is presented. The chapter is organized according to the classes of materials and types of synthetic approaches. However, due to the fact that many advanced materials are hybrid consisting of several types of species and are prepared using multidisciplinary techniques, clear distinction is not always possible.

2. METALLIC NANOLAYERS

2.1 SYNTHESIS AND PROCESSING OF METALLIC NANOLAYERS

Nanostructured metal coatings can be deposited by aqueous and nonaqueous methods. Both electrolytic and electroless plating have been used.

2.1.1 AQUEOUS ELECTROPLATING

In electrodeposition, the deposition of a pure metal or alloy from an electrolyte solution occurs on the cathode when an external current is applied to the plating system. An electrically conductive substrate is required. Nanostructured metal coatings of pure metals, alloys and composites were deposited using electrodeposition. It can produce porosity-free coatings which do not require subsequent densification. Nanostructured grains were deposited when the plating variables such as bath composition, pH, temperature, and current density were controlled so that nucleation of new grains was favored over grain growth.

2.1.2 AQUEOUS ELECTROLESS DEPOSITION

In the electroless approach, electrons are generated by chemical reactions without the supply of external current as in the case of electroplating. Unlike electrodeposition, electrical conductors are not required as substrates. Electroless deposition can occur by the following mechanisms:

- 1- Deposition by ion or charge exchange
- 2- Deposition by contacting the metal to be coated
- 3- Autocatalytic deposition on catalytically active surfaces from solutions containing reducing agents

In an autocatalytic electroless process, a non-catalytic surface on which electroless metal is to be deposited is initially coated with catalyst particles. The catalyst particles are typically colloids such as Pd (with diameter ≥ 2 nm) encapsulated in a tin oxide shell. The catalyst is first adsorbed on the substrate surface, followed by chemical stripping of the protective surface oxide to expose the catalytic Pd core. Reduction of a soluble metal ion or complex by a soluble reducing agent present in the plating solution leads to deposition of metal atoms at the surface. Metal ions are reduced by electrons provided by reducing agents. Subsequently, each deposited metal layer becomes the catalyst for deposition of the next layer, hence the name *autocatalytic metallization*.

For example, electroless metallization was used to deposit nanostructured Ni-P or Ni-B coatings (phosphorous or boron was in the composition of the plating solution). Depending on factors such as post-deposition heat treatment and compositions, amorphous or crystalline structure and a range of grain sizes (2 to 100 nm) could be obtained. The control of the size of the bound catalysts is the principle determining factor in controlling the particle size of nanostructured electroless deposit. Chemical modification of the substrate surface to allow for binding smaller catalysts led to a three- to fourfold reduction in the particle size of the electroless deposit.

Using the electroless approach, nanostructured metal coatings were also deposited on self-assembled biomolecular structures. Rhapsosomes, protein tubules which are about 17 nm in diameter and 400 nm in length, were electroless metallized using molecular catalysts instead of conventional colloidal catalysts. The tubule surfaces were initially catalyzed by treating with a $(\text{PdCl}_4)^{2-}$ or $\text{Pd}(\text{Ac})_2$ solution. Several amino acids residues such as cysteine, histidine, and tyrosine could reduce the catalysts molecules to Pd crystallites (3 nm) on the rhapsosome surface. Randomly oriented nanocrystals of Ni (about 10 nm) were deposited on the surfaces by this electroless plating method. Self-assembled phospholipid hollow tubules, with an average diameter of 0.5 μm and 50 to 80 μm long, are interesting materials due to the large shape anisotropy. The tubules were metallized by electroless plating with nanoscale Ni (Fig. 1) [1]. The Ni coated tubules were magnetically aligned and cast into a polymer matrix to form a composite. The magnetic anisotropy of electroless metallized Ni or permalloy tubules (with metal grain size about 2–4 nm, depending on metallization conditions) and the alignment of metallized tubules in the magnetic tubule-polymer composite were investigated. The metallized tubules were used to fabricate an ungated vacuum field emission cathode structures for generation of a macroscopic electron beam current. The local electric field enhancement was achieved by exploiting the large aspect ratio of the metallized tubules, the radius of curvature, and the thickness of metal coatings at the edge of the metallized tubules. Selective removal of this polymer matrix resulted in a composite base template of oriented exposed metallized tubules, and subsequent surface electrical contact was achieved by a thin sputtered gold film. The resultant microstructures demonstrated vacuum field emission of current $I > 10 \mu\text{A}$ at relatively low applied macroscopic electric fields ($\sim 60\text{--}150 \text{ kV/cm}$).

2.1.3 NONAQUEOUS ELECTROLESS DEPOSITION

Aqueous electrodeposition and electroless deposition are not attractive approaches to metallization of substrates which can be detrimentally hydrolyzed or oxidized in aqueous solutions. A nonaqueous coating process capable of producing fine-grained deposits has been recently developed using the polyol method. For example, Cu coatings were deposited on AlN substrates, and Co was deposited on WC substrates. Unlike traditional aqueous electroless metallization, this process does not require the adsorption of catalysts on electrically insulating substrates to initiate metallization. A surface study of grazing

incidence asymmetric Bragg (GIAB) scattering and small angle x-ray scattering at glancing incidence revealed that the surface of Cu metal film consisted of particles with a size of 4 nm.

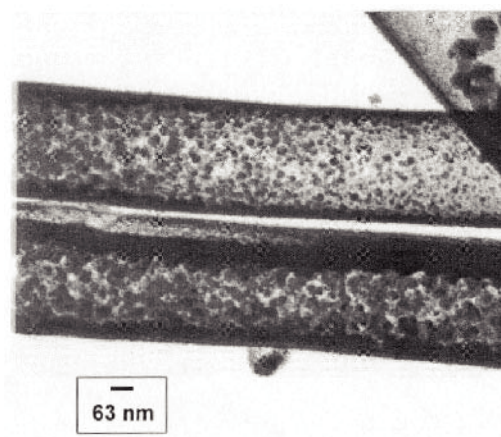


Fig. 1. TEM micrograph of Ni metallized tubes [1].

2.1.4 CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) is the process of producing a chemically reaction between a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate. High temperature CVD processes for producing nano films and coatings have found increasing applications in such diverse technologies as the fabrication of solid- state electronic devices, the manufacture of ball bearings and cutting tools, and the production of rocket engine and nuclear reactor components. In particular, the need for high quality epitaxial semiconductor films for both Si bipolar and MOS transistors, coupled with the necessity to deposit various insulating and passivating films at low temperatures, has served as a powerful impetus to spur development and implementation of CVD processing methods.

A schematic view of the MOS field effect transistor structure in Fig. 2 indicates the extent to which the technology is employed. Above the plane of the base P- Si wafer, all of the films with the exception of the gate oxide and Al metallization are deposited by some variant of CVD processing [1].

Among the reasons for the growing adoption of CVD methods is the ability to produce a large variety of nano films and coatings of metals, semiconductors and compounds in a crystalline or vitreous form, possessing high purity and desirable properties. Furthermore, the capability of controllably creating films of widely varying stoichiometry makes CVD unique amongst deposition techniques. Other advantages include relatively low cost of the equipment and operating expenses, suitability for both batch and semicontinuous operation, and compatibility with other processing steps. Hence, many variants of CVD processing have

been researched and developed in recent years, including low pressure (LPCVD), plasma enhanced (PECVD), and laser enhanced (LECVD) chemical vapor deposition. Hybrid processes combining features of both physical and chemical vapor deposition have also emerged.

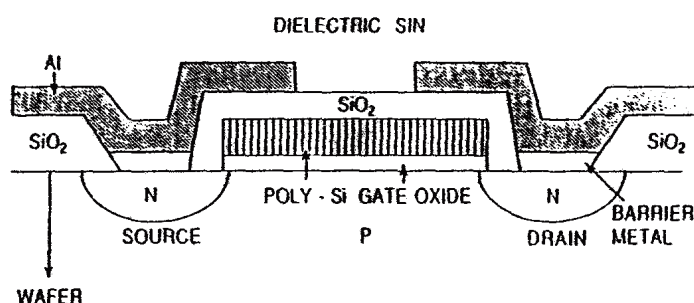


Fig. 2. Schematic view of MOS field effect transistor cross section [2].

To gain an appreciation of the scope of the subject, the various types of chemical reactions that have been employed to deposit nano films and coatings have been categorised. Corresponding examples are given for each by indicating the essential overall chemical equation and approximate reaction temperature.

2.1.4.1 REACTION TYPES

2.1.4.1.1 PYROLYSIS

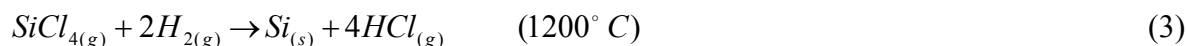
Pyrolysis involves the thermal decomposition of such gaseous species as hydrides, carbonyls, and organometallic compounds on hot substrates. Commercially important examples include the high temperature pyrolysis of silane to produce polycrystalline or amorphous silicon films, and the low temperature decomposition of nickel carbonyl to deposit nickel films.



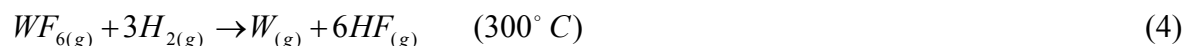
Interestingly, the latter reaction is the basis of the Mond process, which has been employed for over a century in the metallurgical refining of Ni.

2.1.4.1.2 REDUCTION

These reactions commonly employ hydrogen gas as the reducing agent to effect the reduction of such gaseous species as halides, carbonyl halides, oxyhalides, or other oxygen containing compounds. An important example is the reduction of SiCl_4 on single crystal Si wafers to produce epitaxial Si films according to the reaction:



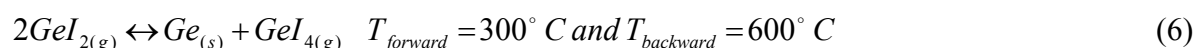
Refractory metal nano films such as W and Mo have been deposited by reducing the corresponding hexafluorides, e. g.,



Tungsten nano films deposited at low temperatures have been actively investigated as a potential replacement for aluminum contacts and interconnections in integrated circuits. Interestingly, WF_6 gas reacts directly with exposed silicon surfaces, depositing thin W films while releasing the volatile SiF_4 by- product. In this way silicon contact holes can be selectively filled with tungsten while leaving neighboring insulator surfaces uncoated.

2.1.4.1.3 DISPROPORTIONATION

Disproportionation reactions are possible when a nonvolatile metal can form volatile compounds having different degrees of stability, depending on the temperature. This manifests itself in compounds, typically halides, where the metal exists in two valence states (e.g., GeI_4 and GeI_2) such that the lower valence state is more stable at higher temperatures. As a result, the metal can be transported into the vapor phase by reacting it with its volatile, higher valence halide to produce the more stable lower valence halide. The latter disproportionation at lower temperatures to produce a deposit of metal while regenerating the higher- valence halide. This complex sequence can be simply described by the reversible reaction



and realized in systems where provision is made for mass transport between hot and cold ends. Elements that have lent themselves to this type of transport reaction include Al, B, In, Ti, Zr, Be, and Cr. Single crystal nano films of Si and Ge were grown by disproportionation

reactions in the early days of CVD experimentation on semiconductors employing reactors such as that shown in Fig. 3. The enormous progress made in this area is revealed here.

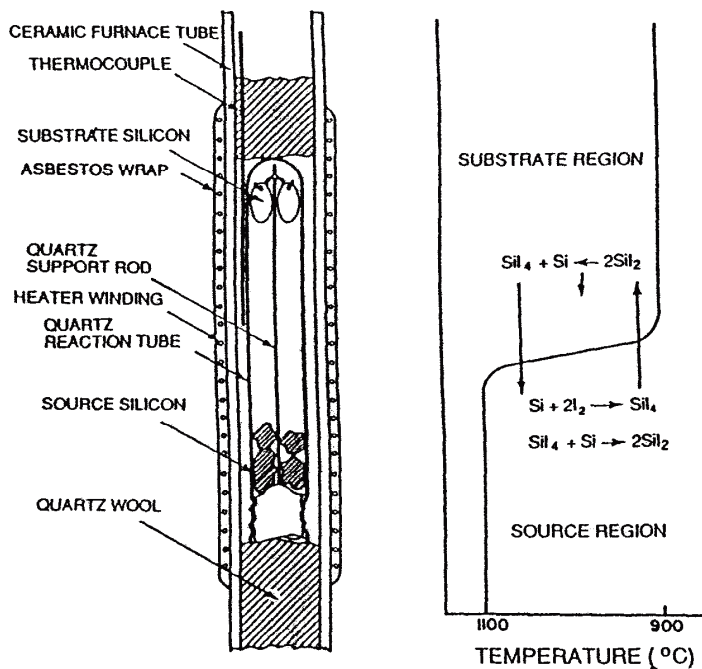


Fig. 3. Experimental reactor for epitaxial growth of Si films [2].

2.1.5 PHYSICAL VAPOR DEPOSITION, PVD

This section focuses on evaporation and sputtering, two of the most important methods for depositing thin films. The objective of these deposition processes is controlled transfer of atoms from a source to a substrate where film formation and growth proceed atomistically. In evaporation, atoms are removed from the source by thermal means, whereas in sputtering they are dislodged from solid target (source) surfaces through impact of gaseous ions.

Advances in the development of vacuum pumping equipment and the fabrication of suitable Joule heating sources, first made from Pt and then W wire, spurred the progress of evaporation technology. Scientific interest in the phenomenon of evaporation and the properties of nano metal films was soon followed by industrial production of optical components such as mirrors, beam splitters, and laser, antireflection coatings.

Up until 1960s, evaporation clearly surpassed sputtering as the preferred film deposition technique. Higher deposition rates, better vacuum, and, thus cleaner environments for film formation and growth, and general applicability to all classes of materials were some of the reasons for the ascendancy of evaporation methods. However, films used for magnetic and microelectronic applications necessitated the use of alloys, with stringent stoichiometry limits, which had to conformally cover and adhere well to substrate surfaces. These demands

plus the introduction of radio frequency (RF), bias and magnetron variants, which extended the capabilities of sputtering, and the availability of high purity targets and working gases, helped to promote the popularity of sputter deposition.

Physical vapor deposition, the term that includes both evaporation and sputtering, and chemical vapor deposition, together with all of their variant and hybrid processes, are the basic film deposition methods discussed in this chapter. Some factors that distinguish PVD from CVD are:

- 1- Reliance on solid or molten sources,
- 2- Physical mechanisms (evaporation or collisional impact) by which source atoms enter the gas phase,
- 3- Reduced pressure environment through which the gaseous species are transported,
- 4- General absence of chemical reactions in the gas phase and at the substrate surface (reactive PVD processes are exceptions).

2.1.5.1 EVAPORATION

Two modes of evaporation can be distinguished in practice, depending on whether the vapor effectively emanates from a liquid or solid source. As a rule of thumb, a melt will be required if the element in question does not achieve a vapor pressure greater than 10^{-3} mmHg at its melting point. Most metals fall into this category, and effective film deposition is attained only when the source is heated into the liquid phase. On the other hand, elements such as Cr, Ti, Mo, Fe, and Si reach sufficiently high vapor pressures below the melting point and, therefore, sublime. For example, Cr can be effectively deposited at high rates from a solid metal source because it attains vapor pressure of 10^{-2} mmHg some 500°C below the melting point. The operation of the Ti sublimation pump is based on the sublimation from heated Ti filaments. A third example is carbon, which is used to prepare replicas of the surface topography of materials for subsequent examination in the electron microscope. The carbon is sublimed from an arc struck between graphite electrodes.

2.1.5.1.1 EVAPORATION OF ALLOYS

Evaporated metal alloy nano films are widely utilized for a variety of electronic, magnetic, and optical applications as well as for decorative coating purposes. Important examples of such alloys that have been directly evaporated include Al- Cu, Permalloy (Fe- Ni), nichrome (Ni- Cr), and Co- Cr. Atoms in metals of such alloys are generally less tightly bound than those atoms in the inorganic compounds. The constituents of the alloys, therefore, evaporate nearly independently of each other and enter the vapor phase as single atoms in a manner paralleling

the behavior of pure metals. Metallic melts are solutions and as such are governed by well known thermodynamic laws.

2.1.5.2 SPUTTERING

For convenience, sputtering processes may be into four classes: (1) dc, (2) RF, (3) magnetron, (4) reactive. We recognize, however, that there are important variants within each category (e.g., dc bias) and even hybrids between categories (e.g., reactive RF). Targets of virtually all important materials are commercially available for use in these sputtering processes. A selected number of metallic target compositions representing the important classes of solids, together with typical sputtering applications for each are listed in Table 1.

In general, the metal and alloy targets are fabricated by melting either in vacuum or under protective atmospheres, followed by thermomechanical processing. Refractory alloy targets (e.g., Ti- W) are hot pressed via the powder metallurgy route. Similarly, nonmetallic targets are generally prepared by hot pressing of powders. The elemental and metal targets tend to have purities of 99.99% or better, whereas those of the nonmetals are generally less pure, with a typical upper purity limit of 99.99%. In addition, less than theoretical densities are achieved during powder processing. These metallurgical realities are sometimes reflected in emission of particulates, release of trapped gases, nonuniform target erosion, and deposited nano films of inferior quality. Targets are available in a variety of shapes (e.g., disks, toroids, plates, etc.) and sizes. Prior to use, they must be bonded to a cooled backing plate to avoid thermal cracking. Metal filled epoxy cements of high thermal conductivity are employed for this purpose.

2.1.5.3 ION PLATING

Ion plating refers to evaporated film deposition processes in which the substrate is exposed to a flux of high energy ions capable of causing appreciable sputtering before and during film formation. Since it is a hybrid system, provision must be made to sustain the plasma, cause sputtering, and heat the vapor source. Prior to deposition, the substrate, negatively biased from 2 to 5 kV, is subjected to inert gas ion bombardment at a pressure in the millitorr range for a time sufficient to sputter clean the surface and remove contaminants. Source evaporation is then begun without interrupting the sputtering; whose rate must obviously be less than that of the deposition rate. Once the interface between film and substrate has formed, ion bombardment may or may not be continued. To circumvent the relatively high system pressures associated with glow discharges, high vacuum ion plating systems have also been constructed. They rely on directed ion beams targeted at the substrate.

Table 1. Metallic targets of sputtering process.

Metals	Application
Aluminum	Metalization for integrated circuits, front surface mirrors
Chromium	Adhesion layers, resistor films, (with SiO lithography master blanks)
Germanium	Infrared filters
Gold	Contacts, reflecting films
Iron, nickel	Ferromagnetic films
Palladium, platinum	Contacts
Silver	Reflective films, contacts
Tantalum	Thin film capacitors
Tungsten	Contacts
Alloys	
Al- Cu, Al- Si, Al- Cu- Si	Metalization for integrated circuits
Co- Fe, Co- Ni, Fe- Tb	Ferromagnetic films
Fe- Ni, Co- Ni- Cr, Ni- Cr	Resistors
Ti- W	Diffusion barriers in integrated circuits
Gd- Co	Magnetic bubble memory devices

Perhaps the chief advantage of ion plating is the ability to promote extremely good adhesion between the film and substrate by the ion and particle bombardment mechanisms. A second important advantage is the high *throwing power* when compared with vacuum evaporation. These results from gas scattering, entrainment, and sputtering of the film, and enables deposition in recesses and on areas remote from the source- substrate line of sight. Relatively uniform coating of substrates with complex shapes is thus achieved. Lastly, the quality of deposited films is frequently enhanced. The continual bombardment of the growing film by high energy ions or neutral atoms and molecules serves topeen and compact it to near bulk densities. Sputtering of loosely adhering film material, increased surface diffusion, and reduced shadowing effects serve to suppress undesirable columnar growth.

A major use of ion plating has been to coat steel and other metals with very hard films for use in tools and wear resistant applications. For this purpose, metals like Ti, Zr, Cr, and Si are

electron beam evaporated through Ar plasma in the presence of reactive gases such as N_2 , O_2 , and CH_4 , which are simultaneously introduced into the system. This variant of the process is known as reactive ion plating (RIP), and coatings of nitrides, oxides, and carbides have been deposited in this manner.

2.2 CHARACTERIZATION AND PROPERTIES OF METALLIC NANOLAYERS

Scientific disciplines are identified and differentiated by the experimental equipments and measurement techniques they employ. The same is true of nano film science and technology. The role played by films was largely a utilitarian one, necessitating measurement of film thickness and optical properties. However, with the explosive growth of nanolayer utilization in microelectronics, there was an important need to understand the intrinsic nature of films. With the increasingly interdisciplinary nature of applications, new demands for film characterization and other property measurements arose. In many instances, it was a question of borrowing and modifying existing techniques employed in the study of bulk materials (e.g., X-ray diffraction, microscopy, mechanical testing) to nanolayer applications. In other cases well-known physical phenomena (e.g., electron spectroscopy, nuclear scattering, and mass spectroscopy) were exploited. A partial list of the modern techniques employed in the characterization of electronic nanolayer materials and devices is given in Table 2. Among their characteristics are the unprecedented structural resolution and chemical analysis capabilities over small lateral and depth dimensions. Some techniques only sense and provide information on the first few atomic layers of the surface. Others probe more deeply, but the depths are not much beyond a few microns accessible for analysis. Virtually all of these techniques require a high or ultrahigh vacuum ambient. Some techniques are nondestructive, others damage the sample to a varying degree. In common, they all utilize incident electron, ion, or photon beams. These interact with the surface and excite it in such a way that some combination of secondary beams of electrons, ions or photons are emitted, carrying off valuable structural and chemical information in the process. A rich collection of acronyms has emerged to differentiate the various techniques. These abbreviations are now widely employed in the nano film and surface science literature.

Table 2. Analytical techniques employed in nano film science and technology [2].

Primary Beam	Energy Range	Secondary Signal	Acronym	Technique	Application
Electron	20- 200 eV	Electron	LEED	Low energy electron diffraction	Surface structure
	300- 30000 eV	Electron	SEM	Scanning electron microscopy	Surface morphology
	1- 30 keV	X- ray	EMP (EDX)	Electron microprobe	Surface region composition
	500- 10000 eV	Electron	AES	Auger electron spectroscopy	Surface laser composition
	100- 400 keV	Electron	TEM	Transmission electron microscopy	High resolution structure
	100- 400 keV	Electron, X- ray	STEM	Scanning TEM	Imaging, X- ray analysis
	100- 400 keV	Electron	EELS	Electron energy loss spectroscopy	Local small area composition
Ion	0.5- 2 keV	Ion	ISS	Ion scattering spectroscopy	Surface composition
	1- 15 keV	Ion	SIMS	Secondary ion mass spectroscopy	Trace composition vs. depth
	1- 15 keV	Atoms	SNMS	Secondary neutral mass spectroscopy	Trace composition vs. depth
	1 keV and up	X- ray	PIXE	Particle induced X- ray emission	Trace composition
	5- 20 keV	Electron	SIM	Scanning ion microscopy	Surface characterization
	> 1 MeV	Ion	RBS	Rutherford backscattering	Composition vs. depth
	> 1 keV	X- ray	XRF	X- ray fluorescence	Composition (μm depth)
Photon	> 1 keV	X- ray	XRD	X- ray diffraction	Crystal structure
	> 1 keV	Electron	ESCA, XPS	X- ray photoelectron spectroscopy	Surface composition
	Laser	Ions	—	Laser microprobe	Composition of irradiated area
	Laser	Light	LEM	Laser emission microprobe	Trace element analysis

2.2.1 MECHANICAL PROPERTIES OF NANOLAYERS

Interest in mechanical property effects in nano films has focused on two major issues. The primary concern has been with the deleterious effects that stress causes in films. This has prompted much research to determine the type, magnitude, and origin of stress as well as means of minimizing or controlling stresses. A second important concern is related to enhancing the mechanical properties of hardness and wear resistance in assorted coating applications.

It is virtually always the case that stresses are present in nano films. What must be appreciated is that stresses exist even though films are not externally loaded. They directly affect a variety of phenomena, including adhesion, generation of crystalline defects, perfection of epitaxial deposits, and formation of film surface growths such as hillocks and whiskers. Film stresses that tend to increase with thickness are a prime limitation to the growth of very thick films because they promote film peeling. In addition, film stresses influence band gap shifts in semiconductors, transition temperatures in superconductors, and magnetic anisotropy. Substrate deformation and distortion also necessarily arise from stresses in the overlying films. In most applications, this is not a troublesome issue because substrate are usually relatively massive compared to films. In integrated circuit technology, however, even slight bowing of silicon wafers presents significant problems with regard to maintaining precise tolerances in the definition of device features.

2.2.2 ELECTRICAL AND MAGNETIC PROPERTIES OF NANOLAYERS

Electrical properties of nano films have long been of practical importance and theoretical interest. The solid state revolution has created important new roles for nano film electrical conductors, insulators, and devices. What was once accomplished with large discrete electrical components and systems is now more efficiently and reliably achieved with microscopic nano film based integrated circuits chips.

The remainder of this section is devoted to some of the ferromagnetic properties of nano films starting with the idea that magnetic phenomena have quantum mechanical origins stemming from the quantized angular momentum of orbiting and spinning atomic electrons. These circulating charges effectively establish the equivalent of microscopic bar magnets or magnetic moments. When neighboring moments due to spin spontaneously and cooperatively order in parallel alignment over macroscopic dimensions in a material to yield a large moment of magnetization (M), then we speak of ferromagnetism. The quantity M is clearly a vector with a magnitude equal to the vector sum of magnetic moments per unit volume.

Elements (e.g., Fe, Ni, Co), alloys (e.g., Fe- Ni, Co- Ni), oxide insulators (e.g., Ni- Zn ferrite, Sr ferrite) and ionic compounds (e.g., CrBr_3 , EuS, EuI_2) all exhibit ferromagnetism. Not only are all crystal structures and bonding mechanisms represented, but amorphous ferromagnets

have also been synthesized (e.g., melt-quenched Fe₈₀B₂₀ ribbons and vapor deposited Co-Gd films).

2.2.3 OPTICAL PROPERTIES OF NANOLAYERS

Nano films were first exploited practically for their optical properties. In the latter part of the nineteenth and first half of the twentieth centuries, the reflecting properties of metal films were utilized in assorted components of precision optical equipment. A noteworthy example was the Fabry- Perot interferometer developed in 1899, which required mirrors of very high reflectance or *finesse*. This instrument enabled impressive accuracy to be attained in spectroscopy, thereby greatly advancing research in this field. The utility of dielectric films in optical applications was interestingly recognized as a result of observations by early spectroscopists and microscopists, notably Lord Rayleigh and Fraunhofer. They noticed that atmospheric corrosion of the lens surfaces of their instruments actually resulted in an enhanced overall transmission rather than a deterioration of performance. Interference effects of a surface layer were quickly discovered as the cause and it was not long before this damaging effect was capitalized upon in the form of antireflection (AR) coatings. These were first produced commercially by chemical etching, a process which persisted until the 1950s. In the mid 1930s, however, AR coatings were first produced by vacuum evaporation techniques and eventually proved to be more versatile and reliable than those made by etching. Coated lenses then found rapid application in optical imaging equipment such as cameras, telescopes, binoculars, and microscopes. Similar coatings were subsequently employed in dielectric mirrors, optical filters, and selective absorbers.

3. CERAMICS NANOLAYERS

3.1 SYNTHESIS AND PROCESSING OF CERAMICS NANOLAYERS

Nanostructured ceramic coatings can be deposited by various methods. Among these methods, the chemical processing are the best methods to produce the ceramic nanolayers. In the following, we discuss these methods.

3.1.1 SOL-GEL

Nanostructured ceramic oxide films and coatings can be deposited using sol-gel type methods. These methods are especially adaptable for film formation enabling film properties to be tailored to suit specific applications. Films and coatings represent the earliest commercial use of sol-gel processing offering the following advantages: control of microstructure, pore size, and surface area. By controlling these parameters, the film properties can be tailored (Fig. 4). Thin films use very little raw materials and can be processed quickly, and very large and irregularly shaped surfaces can also be coated. Dense

pinhole-free layers can be prepared at low temperatures using sol-gel processing. Porous films can be prepared by changing the reaction conditions. This approach is particularly useful in obtaining homogeneous multicomponent coatings. To avoid cracking caused by large capillary stress during evaporation of solvent in the drying process, either slow evaporation (slow process) or supercritical drying (fast process) is used. As-deposited oxide coatings are typically amorphous. Thermal and thermochemical post-synthesis treatment can be carried out to modify the film structure and to obtain nanostructured oxide, carbide, or nitride coatings. Hybrid coatings can be fabricated by doping the sol with material of a different phase, followed by gelation and densification. For example, nanocomposite thin films for optical applications such as Ag/BaTiO₃ and Ag/PZT were prepared by spin coating the precursor solutions. The precursor solution was doped with silver ions, stabilized by adding organic chelating agents. Silver particles of 1–20 nm were formed in the ceramic matrix after heat treatment. Red shift of the optical absorption band of the metal particles was observed.

Sol-gel films can be deposited by spraying, dip coating, and spin coating. Viscosity of the sol can be increased by aging, which can affect the deposition. The amount of porosity in a sol-gel derived film can be controlled by the pH. A higher porosity is achieved when base-catalyzed sols are used. For example, nanoporous thin films of silica were prepared by dip-coating a silica sol onto a substrate and drying at or near room temperature. The film thickness followed predicted theory as a function of the dip speed. Other factors that influenced the film thickness were aging, R (H₂O/precursor), and pH. By drying the films near room temperature, the porosity of the gel was preserved. As the ratio of water to TEOS was increased under acidic conditions, there was an increase in the film thickness. This was attributed to rapid hydrolysis under acidic conditions. As the ratio, R , was varied between 2 and 6 the film thickness increased from 300 to 550 nm. Caution must be taken to not increase the R value too high, which will dilute the solution. At the lower R value, continued hydrolysis occurred in the film due to atmospheric moisture. Langmuir-Blodgett techniques can be used to prepare either closed packed or nanoporous TiO₂ thin films of a known thickness and porosity. Using successive compression and expansion cycles at different pressures, monolayers that had different average particles per area could be prepared. The porosity was controlled by controlling the average spacing between the crystallites in the monolayer.

Because the large capillary stress during solvent evaporation can cause cracking, the sol-gel process has been used traditionally for preparing thin films and coatings. To prepare thick coatings, the problems of shrinkage and cracking and the limitation of coating thickness can be mitigated by increasing particle loading in the sol-gel process. This approach involved dispersing large ceramic powders in sol-gel solution, and applying the mixture onto the substrate by various techniques such as dipping and spraying. Coatings with thicknesses of up to 200 μm were fabricated. The sol-gel film formed strong bonds to both oxide powders and substrates by interaction with functionalized surface hydroxyl groups on the oxide

powders and the oxide layer of substrates. The strong bond reduced cracking. The shrinkage problem associated with the conventional sol-gel approach was minimized due to the high loading of ceramic powders. A two dimensional sol-gel process was also used to fabricate thick films of titania. In this process, the traditional sol-gel hydrolysis and condensation reactions took place at an air-water interface. The gel films formed could then be deposited onto substrates using Langmuir Blodgett techniques.

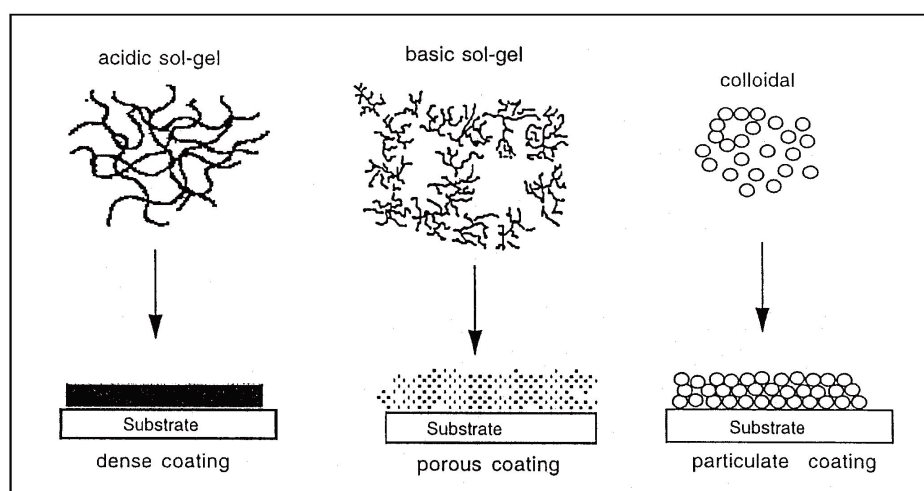
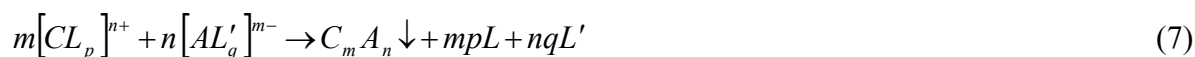


Fig. 4. An example of sol-gel processing conditions on film formation [1].

3.1.2 SUCCESSIVE IONIC- LAYER ADSORPTION AND REACTION, SILAR

This process is intended to grow polycrystalline or epitaxial nano films of water- insoluble ionic or ioncovalent compounds of the C_mA_n type by heterogeneous chemical reactions at the solid- solution interface between adsorbed cations, $[CL_p]^{n+}$ and anions, $[AL'_q]^{m-}$, following the reaction:



Here, L_p and L'_q should be different ligands, but this is not a mandatory condition.

The process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown and then in a solution containing a soluble salt of the anion of the compound to be grown. The substrate supporting the growing film is rinsed in high purity deionized water after each immersion.

In order to grow ternary or quaternary compounds, or doped compounds it is possible either to mix in solution the cations and or anion of the compounds to be grown or to introduce programmed immersions in solutions containing alternatively the cations or the anions of the compound to be grown.

Oxygen may be supplied by adsorption of hydroxyl anions as a result of immersions in alkaline solutions and subsequent deprotonation by attachment on the growing interface. The pH of the solutions can be modified by adding an acid or an alkali, but the resulting pH must be kept inside the pH domain allowing the sole deposition of the compound to be grown.

The growth mechanism involves three most important steps: (1) specific adsorption of the most strongly adsorbed ions of the compound to be grown by substrate immersion in a solution of one of its salts, (2) water rinsing of the excess solution still adhering to the substrate, and (3) chemical reaction between the most strongly specifically adsorbed ions and the less strongly adsorbed ones by the subsequent substrate immersion in a solution containing the latter, entailing the growth.

The equipment consists of four polypropylene beakers (1), of 250 ml each, containing the solutions and four rinsing vessels (2) lying in a circle on the circular PVC tray (3) of the machine (see Fig. 5). The beakers and rinsing vessels are intercalated, each rinsing vessel being placed between a beaker containing a solution of a salt of the cation and another containing a solution of a salt of the anion (both, cations and anions, yielding the compound to be deposited).

Two or four substrates (4) are attached vertically by means of polypropylene tweezers on two or four PVC arms (5) set out in line or at right angles and supported on the spindle (6). The spindle, of stainless steel, can turn and slide tightly in a Teflon bearing. It is driven by two stepping motors (7, 8). The vertical movement of the spindle is 100 mm, its rotation speed 6 rpm; the translation speed is adjustable between 1 and 2 cm/ sec.

The rinsing vessels contain transparent PVC rinsing beakers. They have a rectangular section of 20×50 mm. High purity water having a resistivity of $18 \text{ M}\Omega \cdot \text{cm}$ at room temperature supplied by a deionization station passes through four rotameters and flows upwards in a laminary state inside the rinsing beakers and finally pours into the rinsing vessels. The water that overflows the beaker walls, has a mean resistivity higher than $1 \text{ M}\Omega \cdot \text{cm}$ is trapped inside the rinsing vessels, collected, purified and recirculated.

The whole spindle with arms and substrates, beakers and rinsing vessels are all tightly enclosed by a transparent PVC bell (9). An inert gas passing through a rotameter flows inside the bell.

Conductivity cells are placed on the tubes bringing the water into and out of the rinsing vessels. Inside of each beaker containing solutions it is possible to immerse specific and reference electrodes. Sliding contacts are mounted on the spindle which allows electric

contacts to be made to each substrate. The machine is driven by means of an electronic programmer [3].

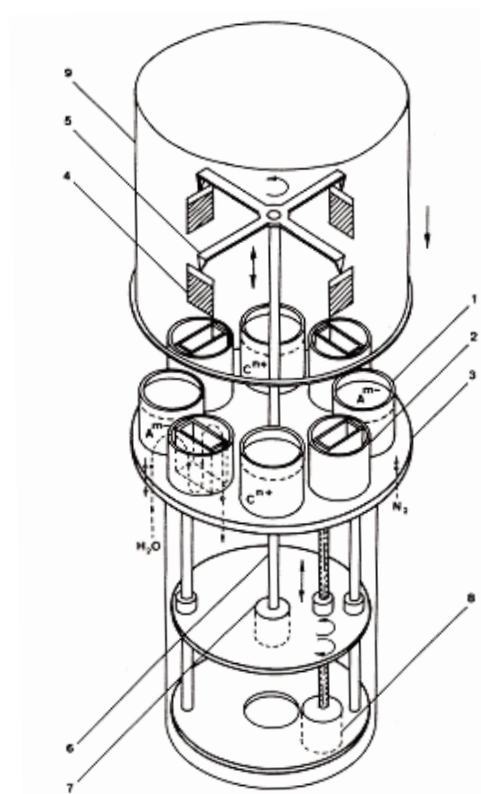


Fig. 5. Nano film deposition machine: 1- beaker, 2- rinsing vessels, 3- tray, 4- substrates, 5- arms, 6- Spindle, 7, 8- motors, 9- bell [3].

3.1.3 FLOWING LIQUID FILMS, LF

The LF method is a solution growth method, and is characterized by a simple apparatus and as a relatively low temperature process. The LF method, different from the chemical bath deposition, can prepare the films continuously, and can be easily scalable and is a low- cost technique. Fig. 6 shows the apparatus for the LF method. During the reaction for the film preparation, the temperature, the flow rate and the pH were kept constant.

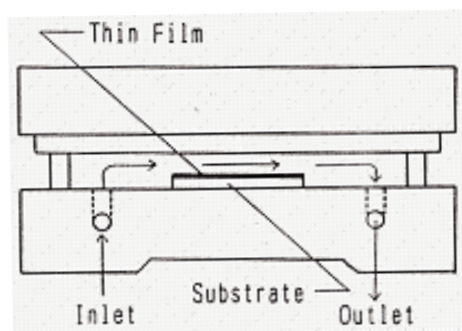


Fig. 6. Scheme of apparatus for the flowed liquid film method [4].

3.1.4 CHEMICAL BATH DEPOSITION, CBD

Compared with the technologically demanding vapor deposition techniques, the deposition of nano film from aqueous solution represents a simple and effective route. In addition, the solution growth technology is suitable for obtaining stoichiometrical oxide nano film because of its oxygen-rich deposition environment, which may be beneficial to the suppression of deep level related luminescence and the enhancement of UV emission. Among several solution growth technologies, SILAR and CBD are two methods widely used to prepare ZnO layer from aqueous solution. In SILAR method, the film is formed via the precipitation of adsorbed precursors, and is distinguished for such merits as the layer-by-layer growing feature and the separate precursor of anionic and cationic solutions. The disadvantages of SILAR include the very slow film growth rate and the difficulties involved in the deposition of oxide films. The CBD method is based on the controlled precipitation of objective material, i.e., the heterogeneous precipitation on substrate. However, the bulk precipitation in precursor solution (i.e., the homogeneous precipitation) is inevitable, which will be inevitable to impair the quality of the film obtained. Also, the presence of both anions and cations in one reaction vessel makes it difficult to precisely control the deposition process. Therefore, the development of novel solution growth techniques with higher deposition rate and better film quality is greatly stressed. In the following, a novel and simple solution growth method has been developed for the deposition of ZnO films, integrating merits of both SILAR and CBD. The underlying mechanism for the growth of ZnO film by this method will be discussed.

CBD method can be divided into two categories: (1) one- stage chemical deposition, OSCD, and (2) Two- stage chemical deposition, TSCD. OSCD method is performed to the different ways including the following:

- 1- One- stage chemical deposition without activation of substrate,
- 2- One- stage chemical deposition with activation of substrate,
- 3- One- stage chemical deposition with heat treatment.

Also, TSCD method is divided into two classes: (1) Two- stage chemical deposition without direct dipping of substrate, and (2) Two- stage chemical deposition with direct dipping of substrate.

3.1.4.1 ONE- STAGE CHEMICAL DEPOSITION

3.1.4.1.1 ONE- STAGE CHEMICAL DEPOSITION OF ZNO WITHOUT ACTIVATION OF SUBSTRATE

The ZnO:Al films were deposited on quartz glass substrate by chemical bath deposition using a beaker placed upon a heater during the growth process. Before the deposition, the substrates were cleaned in dilute HCl (1:5 by volume) for 10 min, and then rinsed in deionized water (DI). After that the glass slides were rinsed in ethanol: acetone (1:1) mixture, DI and dried in a nitrogen flux. The cleaned substrates were immersed in an aqueous solution bath for definite periods of time in order to fabricate films of desired thicknesses. The aqueous solution comprises of a mixture of 0.5 M zinc sulphate (ZnSO_4) in 40 ml of DI, 0.005–0.015 M aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$) in 10 ml of DI mixed until complete dissolution, then was added 0.5 M ethylenediamine [EN] in 100 ml and diluted to with deionized water. The pH value of the reaction bath was 9.2 and was raised to 11 by adding 4 M sodium hydroxide (NaOH). The freshly prepared solutions were mixed thoroughly until complete dissolution. The starting chemical bath prepared in the described manner initially appeared turbid before the addition of sodium hydroxide. The various baths were set up by changing the Zn:Al:[EN] ratios, by adding 100 ml of deionized water in each case. The aqueous bath for sample preparation selected has the following ratios: Zn: Al: [EN] (0.02 M: 1 mM: 0.045 M, pH = 11). The cleaned glass substrates were vertically fixed in the beaker containing the complex solution. The temperature of the cation precursor was kept at room temperature or at 60°C during the deposition. The nano films were grown for 0.5 h at 60°C. After deposition the as grown samples were rinsed in deionized water and dried in air at 150°C.

After the deposition, ZnO:Al films were subjected to rapid thermal annealing, RTA at different temperatures from 350 to 650°C, for 20 s under low vacuum (10^{-1} Pa) conditions using the RTA system schematic illustrated in Fig. 7.

An example of wafer temperature profile during 15 s processing at 650°C is shown in Fig. 8.

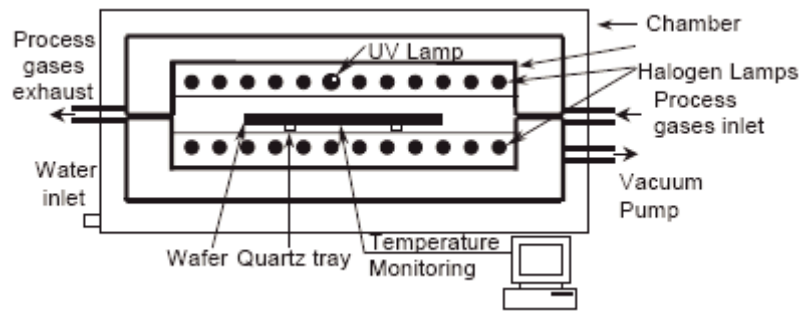


Fig. 7. Schematic illustration of the rapid thermal annealing system [5].

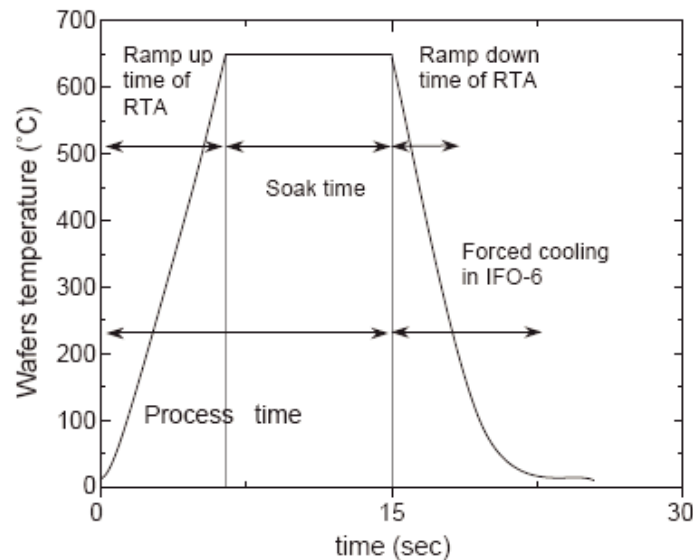


Fig. 8. The temperature profile during a 15 s, 650°C process in the RTA system [5].

Figure 9 presents the effect of RTA treatment on the surface morphology of a ZnO:Al films chemically deposited from Zn:Al:[EN] (0.02 M: 1 mM: 0.045 M, pH = 11) aqueous bath :(a) as grown without RTA and (b) treated by RTA at 650°C for 20 s .The as grown films microcrystallites mean size is 200 nm. RTA leads to a factor of two increase in the grain sizes.

The other solution used for deposition of zinc oxide without activation of substrate is the solution containing zinc acetate (0.0188 M) and ethylenediamine (0.03-0.042 M). The pH of the final bath was raised by the addition of a small quantity of 0.5 M NaOH. The reaction mixture was maintained at the desired temperature for deposition with continuous stirring. Thoroughly clean (washed with trichloroethylene, rinsed with water and acetone) glass substrate were immersed into the reaction bath. Substrates were taken out after different intervals of time, washed with distilled water and dried.

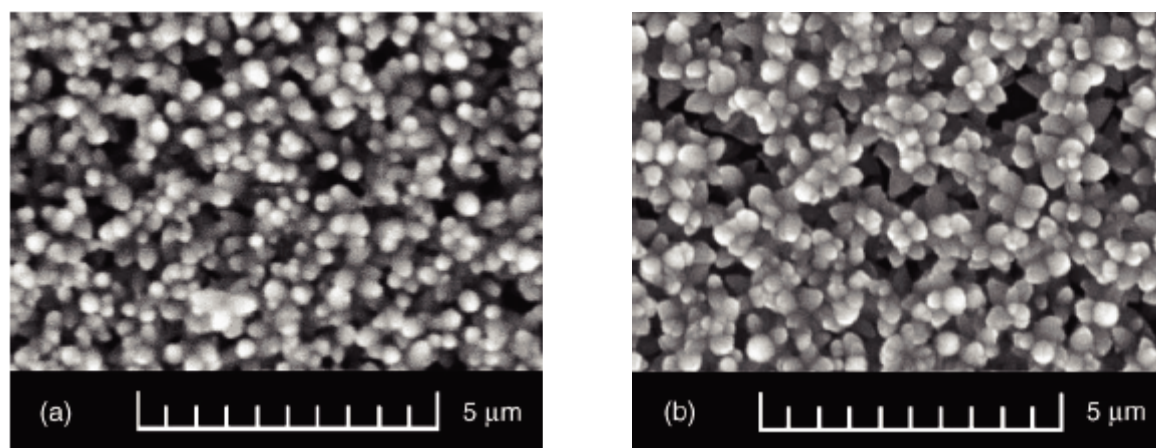


Fig. 9. SEM micrographs of ZnO: Al films. (a) as grown without RTA treatment, and (b) after RTA treatment [5].

ZnO nano films were deposited at $[\text{Zn}] = 0.0188 \text{ M}$ and for a range of ethylenediamine concentrations ($[\text{EN}] = 0.03\text{--}0.042 \text{ M}$). The best nano films were deposited with $[\text{EN}] = 0.042 \text{ M}$. The starting bath pH of 9 to 9.1, was raised to 10–11 by the addition of NaOH. The addition of base to the bath plays an important role in the deposition of good quality ZnO nano films as only poor films were grown without the addition of NaOH. The reaction bath was slightly turbid before the addition of NaOH; on the addition of NaOH, zinc hydroxides precipitates and ZnO is formed. The films grown at pH 10.5 or 11 were uniform, adherent and specular whereas films grown at pH 10 or less were powdery, spotted and non-uniform and can be easily removed by abrasion with a tissue. Details of some deposition experiments are given in Table 3.

SEM micrographs of ZnO nano films grown at different ethylenediamine concentrations and various pH values are shown in Fig. 10. At least two distinct morphologies of deposited ZnO can be identified in these micrographs. Adherent, specular films (Fig. 10a, which consist of flowers of approximately 1–2 μm diameter with well-formed triangle features, showed a central sphere. The pH values for the deposition of such films were in the range of 10.5–11 (ethylenediamine concentration of 0.042 M and zinc concentration of 0.0188 M). Such films were specularly reflecting and tightly adherent to the substrate and could not be removed by abrasion with a tissue. The morphology of a typical film obtained at an ethylenediamine concentration less than 0.376 M and pH 10 or less is shown in Fig. 10b. These films were non-uniform, powdery, and spotted and could be removed by rubbing with a tissue. Electron microscopy showed randomly rod-shaped particles up to 1 μm in length. At pH 11.5–12 the morphology was again somewhat different with clumps of sub-micron particles, similar to the spherulites in the good films but with no secondary features (Fig. 10c).

Table 3. Some deposition results for ZnO as grown onto glass substrates [6].

Ratio [Zn]/ [EN]	pH		Film quality
	starting	final	No deposition
1: 2	9	9	No deposition
1: 2	9.1	9.5	Uneven and non uniform
1: 2	9	10	Film with poor morphology
1: 2	9	10.5	Uneven and non uniform film
1: 2	9.1	11	Good film
1: 2	8.5	11.5	Uneven and non uniform film
1: 2	8.5	11.8	Uneven and non uniform film
1:2.25	9.5	9.5	No deposition
1:2.25	9.4	10	No deposition
1:2.25	9.4	10.5	Uniform, adherent and specular film
1:2.25	9.5	11	Uniform growth
1:2.25	9.5	12	Good films having poor morphology

[Zn] = 0.0188 mol/ cm³, [EN] = 0.0368 mol/ cm³,
deposition time = 1h, Temperature = 50°C.

Zinc oxide commonly exists in the hexagonal (wurtzite) form. In this section, the crystal form has been identified by X- ray diffraction (Cu K α 1.5418 Å), d- spacings were calculated for films deposited onto glass and compared with the standard values (Table 4). The data indicate that the ZnO is in the hexagonal form, (a = 3.253 Å; b = 3.253 Å; c = 5.213 Å; α = 90°; β = 90°; γ = 120°). A comparison with standard ASTM data for ZnO shows that almost all the reflections are present for a good quality film (Fig. 10a), whereas a number of reflections are absent in the poor morphology films (Fig. 10b and Fig. 10c). The XRD pattern of a specular and adherent film is shown in Fig. 11, which indicates the absence of a preferred orientation of ZnO in the deposited film.

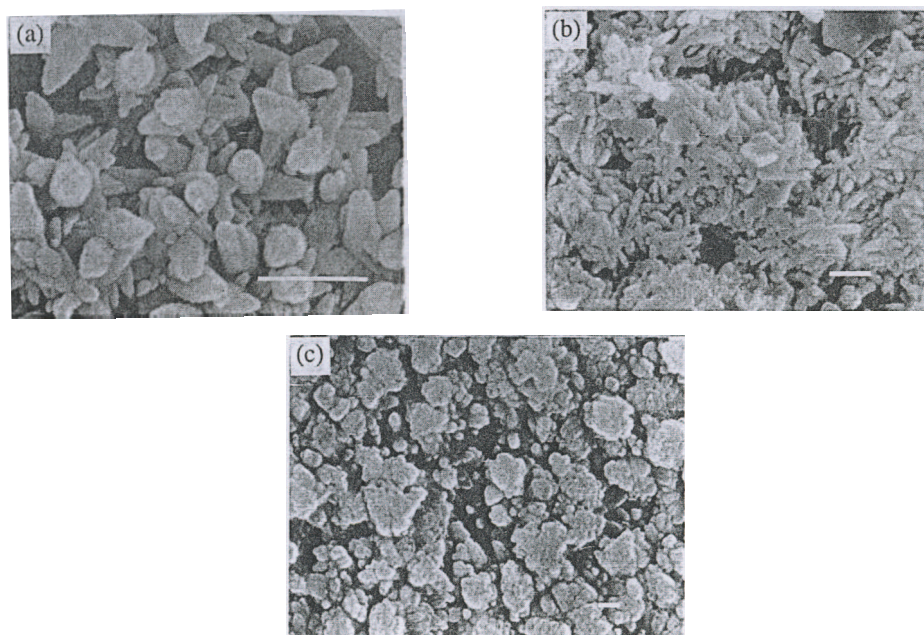


Fig. 10. SEM micrographs of ZnO films grown on glass. at $[Zn] = 0.0188 \text{ mol/cm}^3$, $T = 50^\circ\text{C}$, time = 1h. (a) $[Zn]:[EN] = 1:2.25$, $pH = 11$, (b) $[Zn]:[EN] = 1:2$, $pH = 10$, (c) $[Zn]:[EN] = 1:2.25$, $pH = 12$ [7].

Zinc oxide commonly exists in the hexagonal (wurtzite) form. In this section, the crystal form has been identified by X-ray diffraction ($\text{Cu K}\alpha$ 1.5418 Å), d-spacings were calculated for films deposited onto glass and compared with the standard values (Table 4). The data indicate that the ZnO is in the hexagonal form, ($a = 3.253 \text{ Å}$; $b = 3.253 \text{ Å}$; $c = 5.213 \text{ Å}$; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 120^\circ$). A comparison with standard ASTM data for ZnO shows that almost all the reflections are present for a good quality film (Fig. 10a), whereas a number of reflections are absent in the poor morphology films (Fig. 10b and Fig. 10c). The XRD pattern of a specular and adherent film is shown in Fig. 11, which indicates the absence of a preferred orientation of ZnO in the deposited film.

3.1.4.1.2 ONE-STAGE CHEMICAL DEPOSITION OF ZNO WITH ACTIVATION OF SUBSTRATE

In this method, CBD was carried out in a beaker with a soak aqueous solution containing 0.1 M zinc nitrate and 0.03 M dimethylamineborane placed upon a heater-stirrer during the growth process at temperatures 60°C . Prior to deposition, the glass substrate was activated by an industrially employed two-step Pd/Sn process using sensitizer (SnCl_2 , 1 g/L; 32% HCl, 1 ml/L) and activator (PdCl_2 , 0.1 g/L; 32% HCl, 0.1 M), then the substrate was immersed in the soak solution for 30 min. Finally, the substrate was rinsed with DI water and dried with nitrogen gas then baked on hot-plate at 100°C for 5 min [8].

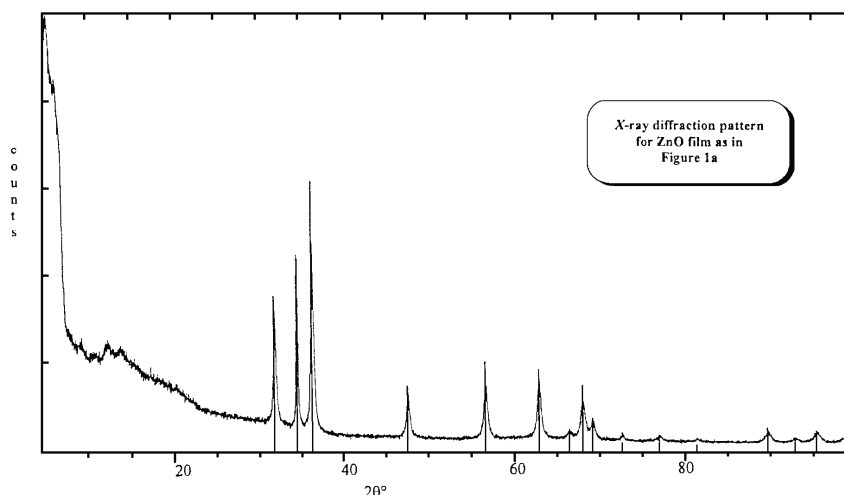


Fig. 11. XRD pattern for a ZnO film grown on glass. $[Zn] = 0.0188 \text{ mol/cm}^3$, $[Zn]:[EN] = 1:2.25$, $pH = 11$, $T = 50^\circ\text{C}$, $\text{time} = 1\text{h}$ [5].

As it is mentioned previously, the preferential direction of growth of chemically deposited zinc oxide is (002). The regular direction growth can be explained as follows: for the electroless deposition, the crystalline morphology was led by nucleation and growth conditions. The primary crystal growth of ZnO could be enhanced by means of $\text{SnCl}_2/\text{PdCl}_2$ two step surface pretreatment. Sn^{+2} ions adsorb on oxygenated groups of substrate through the formation of Sn- O covalent bonds using SnCl_2 solutions, i.e. through the sharing of their valence electrons. Pd^{+2} ions then attach onto the tin species via chemical adsorption. The primary ZnO crystallite would grow on the Pd catalyst sites by means of heterogeneous nucleation [9].

3.1.4.1.3 ONE- STAGE CHEMICAL DEPOSITION OF ZNO WITH HEAT TREATMENT

In this method, a 0.75 M precursor solution was prepared by stirring the components zinc acetate dehydrate and monoethanolamine (MEA) in a molar ratio of 1:1 in 2- methoxyethanol for 3h at 80°C under argon gas in a closed flask. Prior to film deposition, substrates were cleaned with organic solvents followed by annealing in air at 800°C for 1h.

The precursor solution was deposited onto the substrates by spin coating at 5000 rpm for 30 sec. The as deposited films were preheated on a hotplate at 300°C for 10 min. In a further step the films were heated in a furnace at 500°C for 5h and finally heated to 850°C with a rate of 15°C/min . The sample was kept at 850°C for 12 h, and all the heating was performed in air [10].

3.1.4.2 TWO- STAGE CHEMICAL DEPOSITION

One another method of chemical deposition of zinc oxide is two- stage chemical deposition, TSCD. To prepare the ZnO nano film via TSCD method, we used a technique of successive immersion of the substrate into two separate solutions. First solution is solution of zinc ion complexes and the other is hot water. The TSCD method can be performed with direct immersion of substrate and without direct immersion of substrate.

In the TSCD method without direct immersion of substrate, the substrates were put into the bottom of conical flask and then the conical flask were put into the water tank with constant temperature 60°C for 24 h, and then taken out, cooled to the room temperature. The time required to prepare the oxide layer is large. Also, the control of thickness of nano films is very difficult.

In the TSCD method with direct immersion of substrate, a clean substrate was immersed first in a cold solution of the complex and then in boiling water for 1- 2 sec. In this way, the substrate was covered with a thin layer of the complex solution which decomposed to ZnO when placed in boiling water. Kinetics, mechanism, the effect of surfactants and different dopants on the characteristics of nano films obtained via TSCD method are discussed in the next sections.

3.1.4.2.1 TWO- STAGE CHEMICAL DEPOSITION WITHOUT DIRECT IMMERSION OF SUBSTRATE

A 0.6586g zinc acetate dehydrate was dissolved in 30 ml methanol solution under vigorous stirring at room temperature, then ultrasonicated for 10min, and a transparent solution was obtained. The little plates were put into the bottom of a conical flask for ZnO particle deposition. The distilled water with different volume ratio (Table 4) was added into the mixed solution. The conical flasks were put into the water tank with constant temperature 60°C for 24h, and then taken out, cooled to the room temperature [11].

The XRD patterns of as-prepared particles are shown in Fig. 12. Regardless of the volume of added H₂O, the four XRD patterns show the same incompletely ordered lamellar compound formed in the solution which can be recognized as the layered basic zinc acetate indicated in Fig. 12. All the other peaks except for the Al₂O₃ ones that belong to ceramic plates can be indexed as the hexagonal ZnO with lattice constants in agreement with the values in the standard card. Under the condition without adding H₂O, the diffraction peaks of the wurtzite ZnO is broader than that of three others, suggesting that the size of ZnO particle is smaller than the others. However, on increasing the volume ratio of adding H₂O/methanol, the diffraction peaks become sharp, implying the full crystallization. Moreover, compared to the standard card, the (002) peak's relative intensity becomes stronger which indicates the orientation of ZnO and the large-scale appearance of (0001) crystal plane.

Table 4. Different process parameters of the experiment [11]

Zinc Acetate, M	Methanol, ml	Distilled water, ml	Volume ratio of water : Methanol	pH
0.1	30	0	0	6.7
0.1	30	4	2:15	6.72
0.1	30	5	1:6	6.85
0.1	30	6	1:5	6.8
0.1	30	7	7:30	6.77
0.1	30	8	4:15	6.61
0.1	30	9	3:10	6.6
0.1	30	10	1:3	6.57
0.1	30	15	1:2	6.54

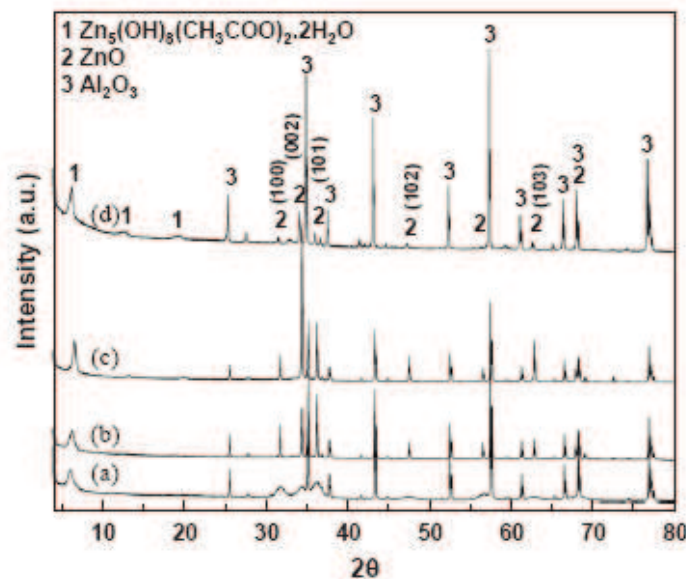


Fig. 12. XRD patterns of samples at different volume ratio: (a) no added water, (b) 1: 6, (c) 1: 3, (d) 1:2 [11].

The FE-SEM images are shown in Fig. 13. Without adding H₂O (Fig. 13a), the prepared ZnO particle film is compact and equable with irregular morphology and the average particle size 50 nm. Also, nanosized ZnO particle film can be prepared with few distilled water (volume ratio < 1/20). On increasing volume ratio of adding H₂O /methanol, the compact ZnO particle film becomes incompact and the morphology varies from irregular particle, plate (Fig. 13b) to regular cone (Figs.13c–e) with the average size changing from nano-into micro-scale. Fig. 14 is the schematic diagram of the prepared ZnO particle in the condition of volume ratio ≥ 1/6 .

From the results of figures 12 and 13, it can be concluded that the morphology and size of ZnO markedly depend on adding H_2O , revealing that H_2O can control the ZnO crystal growth well in our experiment.

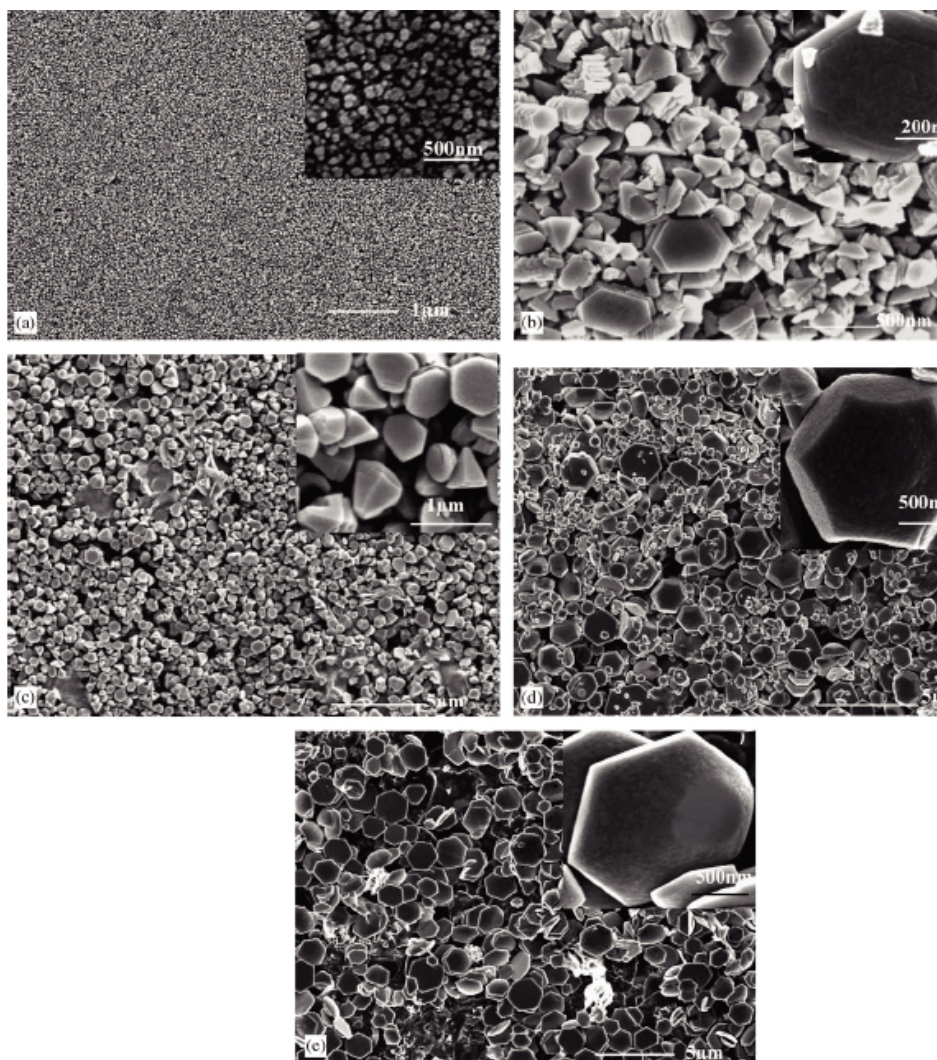


Fig. 13. FE- SEM images of the different samples: (a) no adding water; (b) 2:15; (c) 1:6; (d) 1:3; and (e) 1:2 [11].

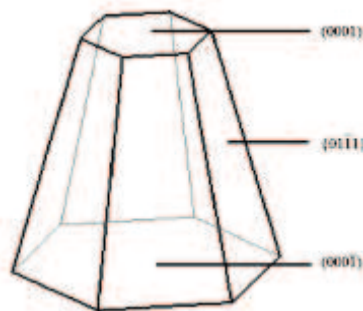


Fig. 14. The schematic diagram of ZnO particle [11].

3.1.4.2.2 TWO- STAGE CHEMICAL DEPOSITION WITH DIRECT IMMERSION OF SUBSTRATE

Compared with the technologically demanding vapor deposition techniques, the deposition of ZnO film from aqueous solution represents a simple and effective route. In addition, the solution growth technology is suitable to obtain stoichiometrical ZnO film because of its oxygen- rich deposition environment, which may be beneficial to the suppression of deep level related luminescence and the enhancement of UV emission. Among several solution growth technologies, SILAR and CBD are two methods widely used to prepare ZnO layer from aqueous solution. In SILAR method, the film is formed via the precipitation of adsorbed precursors, and is distinguished for such merits as the layer- by- layer growing feature and the separate precursor of anionic and cationic solutions. The disadvantages of SILAR include the very slow film growth rate and the difficulties objective material, i.e., the heterogeneous precipitation on substrate. However, the bulk precipitation in precursor solution (i. e., the homogeneous precipitation) is inevitable, which will be inevitable to impair the quality of obtained film. Also, the presence of both anions and cations in one reaction vessel makes it difficult to control the film deposition process precisely. Therefore, the development of novel solution growth techniques with higher deposition rate and higher film quality is of great importance.

TSCD method described here enables the deposition of ZnO nano films with a thickness and conductivity which can be controlled during the preparation procedure. The deposition can be performed onto any kind of substrate that is inactive with respect to the chemicals used.

To prepare the ZnO thin films we used a technique of successive immersion of the substrate into two separate solutions. Four different solutions of zinc ion complexes were used for this. The first was an aqueous solution of $(\text{NH}_4)_2\text{ZnO}_2$ prepared in the following way. Concentrated NH_4OH was poured into 100 cm^3 of 0.5 M ZnCl_2 or ZnSO_4 until a white precipitate of $\text{Zn}(\text{OH})_2$ was formed. On the further addition of NH_4OH the precipitate dissolved. The solution was diluted to 500 cm^3 to obtain a 0.1 M solution of the zinc ion complex which was found to be the most convenient concentration to produce a good quality film [12].

The second solution was an aqueous solution of Na_2ZnO_2 , prepared in a similar way to the first, in which NH_4OH was substituted by NaOH . The third solution was a complex solution of $\text{Zn}(\text{OH})_2$ in NaCN obtained by adding granular NaCN to the white precipitate of $\text{Zn}(\text{OH})_2$ and diluting to 500 cm^3 to obtain a 0.1 M complex solution. The fourth solution was 0.1 M aqueous ZnCl_2 .

A thin film of zinc oxide formed on the substrate on decomposition of the zinc ion complex in hot water ($95\text{-}100\text{ }^\circ\text{C}$). ZnO thin films were deposited onto glass, quartz and mica substrates and the physical properties such as crystal structure, optical transmittance, conductivity and photoconductivity were examined.

A clean substrate was immersed first in a cold solution of the complex and then in boiling water for 1-2 sec. In this way the substrate was covered with a thin layer of the complex solution which decomposed to ZnO when placed in boiling water. Part of the ZnO formed was deposited onto the substrate as a strongly adherent film and the rest formed a precipitate [12].

The technique of immersion of the substrate into separated chemicals (a cold solution of the zinc ion complex first and hot water second) affected a constant increase in the thickness for each immersion, so that the final thickness of the film was determined by the number of immersions. Using the concentrations mentioned a yellow interference appeared after 24- 25 immersions. Continuing with successive immersions, the interference color changed to red, violet, green and yellow again. In this way, it was possible to monitor the film growth visually. The thickness of the film was calculated from the mass of equally colored parts of the film and it was found that the change in the interference color from red to red corresponded to an increase of 80 nm in the film thickness. The rate of increase in the thickness was constant because the concentration of the solutions was constant during the growing procedure. This is because immersion of the substrate does not change the concentration, and because the chemical reaction, namely the decomposition of the ammonia complex occurs at the interface between the substrate and the hot water.

The higher zinc ion complex concentration gave a higher growth rate but the quality of the film was poor since it contained a powder like deposit. In order to obtain a highly transparent film it was necessary to rub down the film with a piece of cotton after the first immersion. In this way the weakly adherent microcrystals were removed while the strongly adherent microcrystals remained on the surface. These crystals then serve as nuclei for further growth and therefore if the first layer is of good quality further growth will continue with the same quality.

The highest growth rate was obtained in the case of preparation using the ammonia complex solution and the lowest growth rate was obtained from pure ZnCl_2 solution, which was about five times slower. The best film quality (high transparency) was obtained from the ammonia complex solution. For this reason, all the films used for examination of the physical properties were prepared from the ammonia complex solution [12].

3.1.4.2.2.1 KINETIC OF TSCD ZINC OXIDE NANO- LAYER GROWTH

Decomposition reaction could produce new phases comprising of solid, liquid and gas. The ease with which the produced molecules were attached to the growing interface was related to the structure of the interface. Two types of structures could be considered:

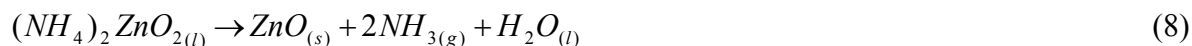
- Ordering of the atoms gradually increasing within the interface towards the fully crystalline side until essentially all the atoms were in their appropriate lattice sites.

- Transition from fluid medium to the solid taking place over a number of atomic layers that comprised a diffuse-interface.

The first type of the growth could produce a flat interface associated with close-packed structure of the molecules. This type of interface could not be attributed to the layers produced in this research. It appears to be most appropriate for vapor deposition processes usually occurring on solid surfaces. The second type of the interface can, however, be most appropriately attributed to the deposition processes occurring in this research.

The rate of thickening of the oxide film on the substrate was related to the difference between hot water temperature and substrate surface covering complex (ΔT). Measurements showed that the growth rate of the layer depends on both time and temperature. The activation energies and the frequency factors of the process were obtained from the empirical information. The first Newton law for convection transfer was combined with the diffuse-interface kinetic model to quantify the information obtained from the experiments.

The thickness of the layer increases with the number of dipping stages. Variation of thickness of the deposited film is plotted against the number of dipping stages in Fig. 15. Fig. 16 depicts the SEM cross sectional image of an oxide film after 100 times of dipping. The formation of the oxide layer via TSCD method involves the following pseudo-decomposition reaction:



The rate of this reaction is experimentally proved to be independent of the concentration of the $(NH_4)_2 ZnO_2$ complex. Growth rate of the ZnO layer depends on the hot water temperature. It is proportional to the difference between the temperature of the hot water and the $(NH_4)_2 ZnO_2$ complex. Its slope gradually decreases with the immersion time inside the water.

ZnO growth can in general be composed of the following kinetic steps:

- (a). Water reaction with complex species to form solid oxide and liquid molecules illustrated in Eq. (8).
- (b). Outwards transfer of the products from the reaction front.
- (c). Joining of ZnO molecules to the thin film or glass substrate to thicken the oxide layer [13].

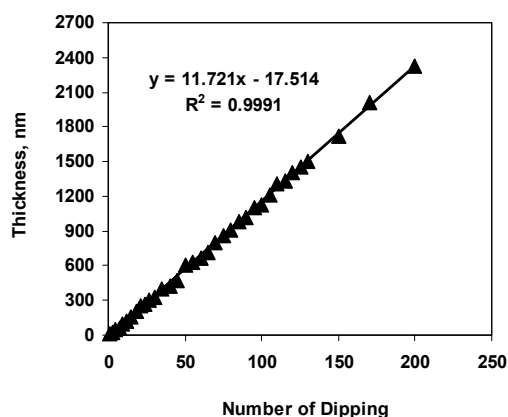


Fig. 15. Measured film thickness versus the number of dipping stages [13].

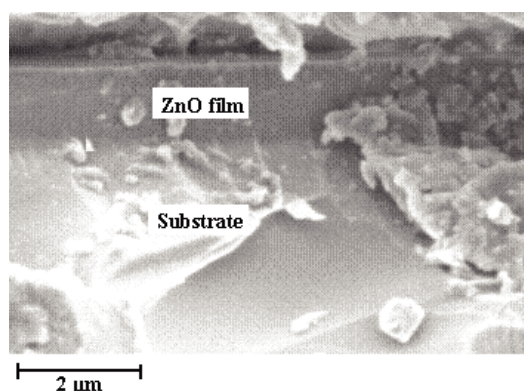


Fig. 16. SEM cross sectional image of the oxide film formed after 100 times dipping of the specimen into the aqueous solution [13].

Changing complex concentration and measuring the thickness of the thin layer against time at various temperatures clearly indicates a zeroth order growth rate with respect to concentration (Fig. 17). Experimentally determined rates prove the approximate independence of the ZnO growth rate from reactant concentration. Effect of concentration on the film growth rate can therefore be ignored:

$$-\frac{dC}{dt} = k C^n \quad n = 0 \quad (9)$$

C is the molar concentration of the complex, t is the time after immersion and n is the order of the reaction, being zero in this case.

Experimental investigations show that the rate of growth of the ZnO is proportional to the difference between the temperature of the hot water and the $(\text{NH}_4)_2 \text{ZnO}_2$ complex, ΔT_1 (Fig.

18). Its slope gradually decreases with submersion time. This seems to be due to the gradual increasing of the complex temperature as a result of rising of the substrate temperature. An external heat transfer model can thus be used to explain the film growth rate:

$$\frac{d\delta}{dt} = \frac{\dot{q}}{\Delta H_G \cdot \rho} M_{\text{ZnO}} = \frac{h \Delta T_1}{\Delta H_G \cdot \rho} M_{\text{ZnO}} \quad (10)$$

Where δ is the film thickness, $\dot{q}$ is the heat flux, ΔH_G is the enthalpy of the reaction, ρ is the density of the solid layer, M_{ZnO} is the molar weight of ZnO and h is the heat transfer coefficient from hot water to the complex layer attached to the substrate. The heat transfer coefficient h depends on the mean temperature of the reactants as defined by Eq. (11):

$$T = \frac{T_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} + T_{\text{Complex}} M_{\text{Complex}}}{M_{\text{H}_2\text{O}} + M_{\text{Complex}}} \quad (11)$$

Effect of liquid stirring on the thickness of the ZnO layer is illustrated in Fig. 19. Due to the stirred nature of the dipping process, the second step (b) is fast enough to be ignored in our evaluation rate. Experimental results provide proof of this effect. Stirring of the liquid with different speeds and at different directions shows a negligible effect on the thickness-time curves. Fig. 19 indicates, for example, that variation of the rate of growth of the ZnO thin layer due to the N_2 bubbling at different positions inside the reaction vessel is lower than 5%, which can be considered insignificant. The first and the third kinetic steps may thus be considered as the rate-controlling steps.

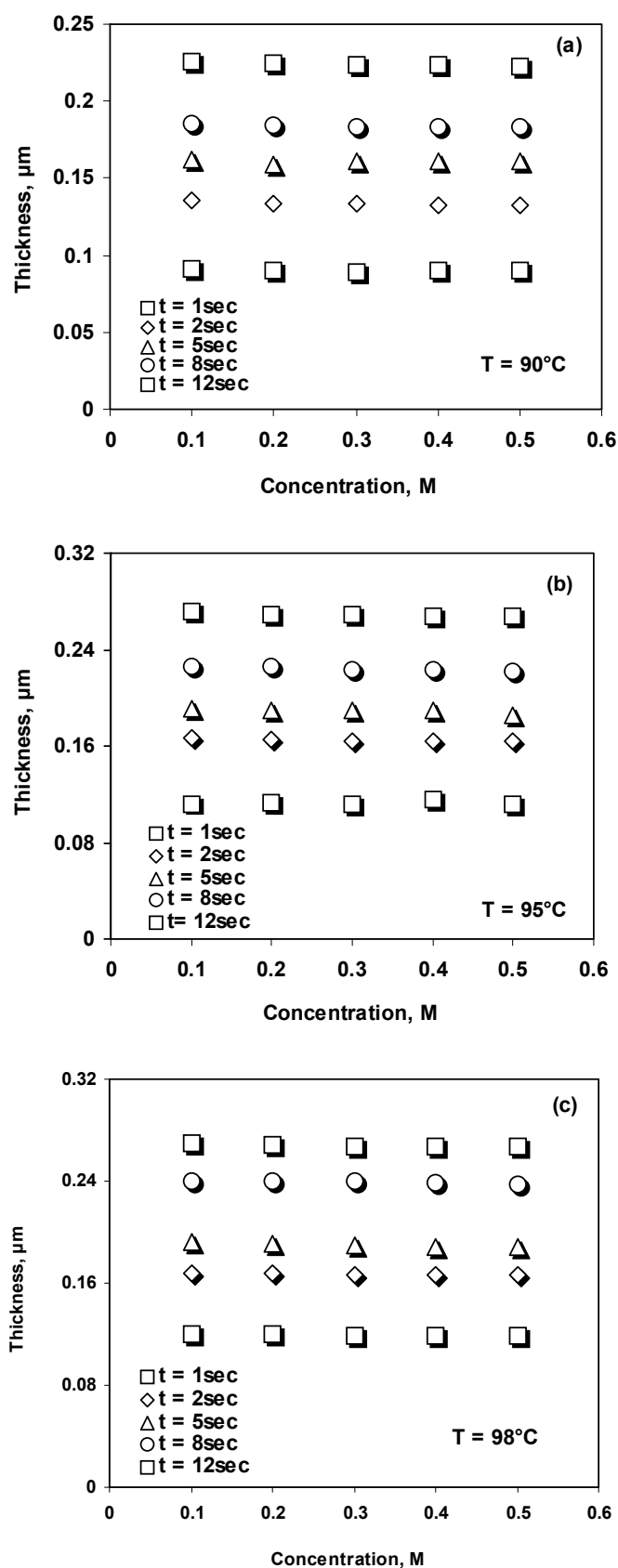


Fig. 17. Effect of concentration on thickness of ZnO layer measured at different times and temperatures [13].

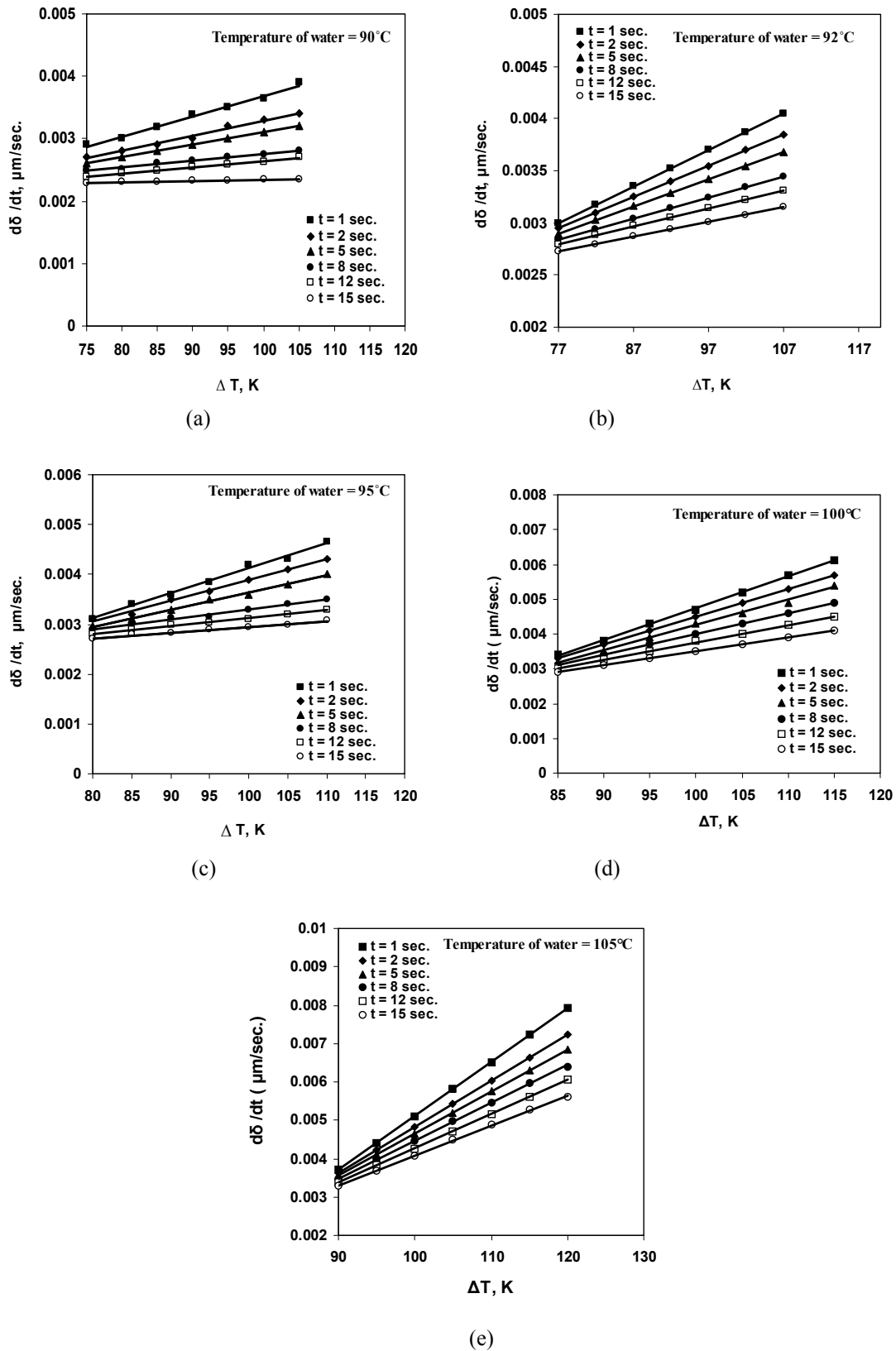


Fig. 18. Effect of the difference between the temperature of the hot water and the complex, ΔT_1 , on the rate of growth of the thickness of the ZnO layer at hot water temperatures of (a) 90, (b) 92, (c) 95, (d) 100 and (e) 105°C [13].

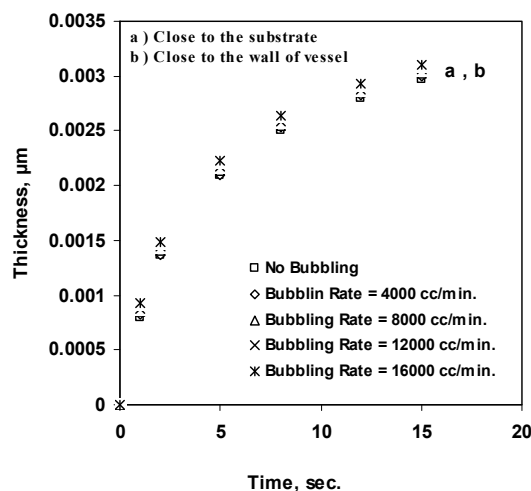


Fig. 19. Effect of liquid stirring on the thickness of the ZnO layer [13].

The coefficient of the rate equation is composed of two independent terms. The first term is related to the Newton law of convection, as illustrated by Eq. (10). The second term is related to the diffuse-interface kinetic model for attachment of the ZnO molecules to the solid substrate. From morphological investigation of the oxide layer, it was found that the interface was at least several layers thick. From the liquid-solid nature of the interface and the decomposition characteristics of the reaction that originated the formation of the solid phase, it was concluded that the interface could not be microscopically flat. The classical laws related to the microscopically flat interfaces could, however, be extended with little difficulty to the slightly diffuse-interfaces expected in liquid-solid transitions that could result in this thin layer deposition process. Diffuse-interfaces could generally grow much easier than the flat ones.

We tried, therefore, to investigate this phenomenon with a simple quasi-chemical model in line with the ideas generally developed for a vapor deposition process. To perform this treatment, let us imagine an ideally close-packed flat interface, except that there is an indentation in a step present at the interface. If an ion deposits on the solid at a point on the close-packed flat face, it would join to the three nearest neighbors. If it deposits at a jog, it has three nearest neighbors below the closed-packed plane and three other nearest neighbors on its own plane. The driving force for deposition of the ion at the jog is hence twice that at the position on the close-packed face. This indicates that any ion depositing at a point on the close-packed face can lower its energy further by migrating towards and depositing at a jogged position. Jogs help the deposition and the solid layer grows further. This phenomenon seems especially interesting because of high concentration of jogs present on an ideally diffuse-interface layer.

Kinetics of growth of the solid phase can simply be determined in terms of the classical theoretical rate. The frequency ω_1 with which molecules (composed of positive and negative

ions) would pass from the complex containing solution to the oxide layer is exponentially related to the temperature:

$$\omega_1 = \omega_0 \cdot \exp\left(\frac{-Q_1}{RT}\right) \quad (12)$$

ω_0 is the frequency of vibration of the molecules and Q_1 is the activation energy for transport of the molecules from the solution to the oxide layer. Solid molecules will similarly jump in the reverse direction, from oxide layer to the solution. The reverse frequency of molecules, ω_2 , can similarly be given by:

$$\omega_2 = \omega_0 \exp\left(\frac{-Q_2}{RT}\right) \quad (13)$$

where Q_2 is the activation energy of molecules transferring from the oxide layer to the solution. The net jumping frequency of the molecules across the interface, ω_G , can thus be determined from the difference between the forward and backward transport frequencies of the molecules as follows:

$$\omega_G = \omega_1 - \omega_2 = \omega_0 \left[\exp\left(\frac{-Q_1}{RT}\right) - \exp\left(\frac{-Q_2}{RT}\right) \right] \quad (14)$$

Substituting $\Delta G_G = Q_1 - Q_2$ in Equation (14), we find:

$$\omega_G = \omega_0 \cdot \exp\left(\frac{-Q_1}{RT}\right) \left[1 - \exp\left(\frac{\Delta G_G}{RT}\right) \right] \quad (15)$$

From general thermodynamics relationships, we also have:

$$\Delta G_G = \Delta H_G - T \Delta S_G \cong \Delta H_G - T \frac{\Delta H_G}{T_{DP}} = \Delta H_G \cdot \frac{\Delta T_2}{T_{DP}} \quad (16)$$

in which ΔG_G , ΔH_G and ΔS_G are changes of free energy, enthalpy and entropy of the deposition process, respectively and ΔT_2 is the difference between the zinc containing complex and solid substrate. T_{DP} is referred to the equilibrium deposition temperature which

is a constant value and can be experimentally measured. Substituting Equation (15) into Equation (16) and assuming that the exponent is small, the following relationship is obtained:

$$\omega_G = \omega_1 [1 - \exp(-\frac{\Delta H_G \cdot \Delta T_2}{R \cdot T_{DP}^2})] \quad (17)$$

Assuming all sites on the interface are favorable for growth, the rate of continuous growth V_G is equal to $d_m \cdot \omega_G$, where d_m is the distance that the interface advances when a molecule is added into it. Hence:

$$V_G = d_m \cdot \omega_1 [1 - \exp(-\frac{\Delta H_G \cdot \Delta T_2}{R \cdot T_{DP}^2})] \quad (18)$$

The dependence of the jumping frequency to the diffusion coefficient of the molecule is given by:

$$\omega = \frac{6D}{d_m^2} \quad (19)$$

The frequency with which each atom strikes the solution – film interface is usually taken to be one-sixth of its jumping frequency in the bulk solution. Therefore, we have:

$$\omega_1 = \frac{D_1}{d_m^2} \quad (20)$$

where D_1 is the mean diffusion coefficient of the depositing species into the oxide layer. Substitution of Equation (20) into (18) yields:

$$V_G = \frac{D_1}{d_m} [1 - \exp(-\frac{\Delta H_G \cdot \Delta T_2}{R \cdot T_{DP}^2})] \quad (21)$$

Equation (21), termed the *Sadrnezhaad- Vaezi* equation [13] gives the growth rate of the thin film produced by TSCD method on the soda-lime substrate. According to this equation, a greater difference between the complex and the substrate temperatures results in a greater growth rate. This phenomenon is, however, limited to the decomposition conditions at the reactants position.

In order to determine the equilibrium deposition temperature, variations with temperature of both pH and weight of the deposited complex were determined and plotted against temperature, as shown in Fig. 20. Concomitant blank tests were also performed in order to determine the general decomposition effects. Both samples were submerged horizontally into the corresponding solutions so that the partial pressures of the gases could remain invariable. At temperatures about 10°C, the general complex decomposition resulted in very slow changes in the pH reduction as well as the weight gain (Fig. 20). Careful examinations indicated that the equilibrium decomposition temperature is equal to 10±2°C. Complex decomposition process continued above this temperature. Changes of the temperature could, therefore, affect on both ΔG_G and pH values of the system.

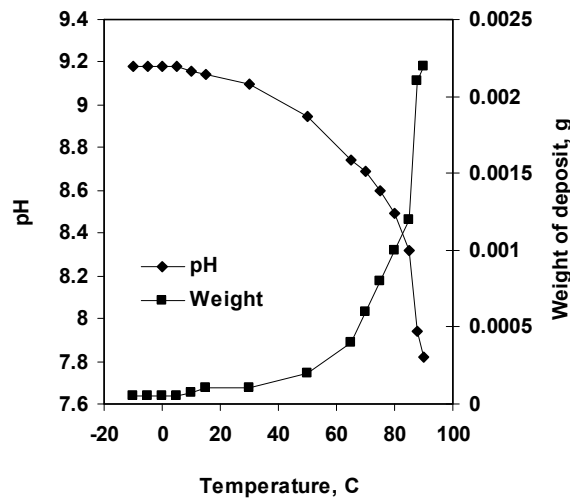


Fig. 20. Effect of temperature on weight of deposit and pH of the solution [13].

Total conversion time of the process can be determined by addition of the conversion times obtained from heat transfer and molecular deposition process. The result can lead us to the following rate equation:

$$\frac{d\delta}{dt} = \frac{\Delta T}{\frac{\Delta H_G \cdot \rho}{h} + \frac{d_m R T_{DP}^2}{D_1 \cdot \Delta H_G}} = U \cdot \Delta T \quad (22)$$

Where U is an overall growth rate constant for the film deposition process and ΔT is the difference between the temperature of the hot water and the substrate. Table 5 gives the values of U obtained at different times and temperatures. Arrhenius law calculations made based on Eq. (23) yields overall activation energy and frequency factor of the growth process:

$$U = U_0 \exp \left(-\frac{Q}{RT} \right) \quad (23)$$

The results obtained are as follows:

$$Q = 17.20 \pm 0.42 \text{ kJ.mol}^{-1} \quad (24)$$

$$U_0 = 2.81 \pm 0.07 \text{ } \mu\text{m.s}^{-1} \quad (25)$$

These values are within the ranges of external transport phenomenon occurring in the ordinary rate system [13].

Table 5. Overall growth rate constant, U, for the film deposition process calculated from the experimental data for different temperatures and times [13].

Temperature of hot water (°C)	U (μm/K.sec)					
	t = 1 (sec.)	t = 2 (sec.)	t = 5 (sec.)	t = 8 (sec.)	t = 12 (sec.)	t = 15 (sec.)
90	0.000030	0.000025	0.000020	0.000015	0.000010	0.000002
92	0.000040	0.000035	0.000030	0.000026	0.000020	0.000010
95	0.000050	0.000040	0.000030	0.000027	0.000020	0.000010
100	0.000090	0.000080	0.000070	0.000060	0.000050	0.000040
105	0.00019	0.00017	0.00015	0.00012	0.000090	0.000080

Scanning electron microscope images of the surface of the oxide layers produced after 100 times immersion into hot water are illustrated in Fig. 21. Morphologies shown in the figure indicate that the ZnO coverage increases with the water temperature.

3.1.4.2.2.2 THERMODYNAMIC OF TSCD ZINC OXIDE NANO- LAYER GROWTH

Atoms laying on a surface of liquid or solid exert attractive forces to the adjacent phases. Since the disorder decreases with the surface adsorption of an atom, the entropy change is usually negative for an adsorption reaction to occur. It is therefore necessary for an adsorption reaction to be exothermic to satisfy its spontaneity. Two types of surface adsorption can be recognized on the basis of the values of the energies exchanged. Physical adsorption proceeds with small physical force and small energy of the activation. In chemical adsorption, the formation of more than one atomic layer on the solid surface is not possible. Physical adsorption can be performed at low temperatures and many atomic layers can be adsorbed on the solid surface of the substrate. Because of weak interactions, physical adsorption has no effect on chemical reactions. Measurement of area of the surface porosity can help in the determination of the type of adsorption. Like distillation process, physical

adsorption can be applied to different surfaces. Degree of physical adsorption is considerable under the boiling temperature.

The amount and rate of the surface adsorption are evaluated here. Langmuir adsorption criterion is used to decide on ideality or non-ideality of the process. Oxide species adsorbed on the surface of the substrate has been characterized for the first time in this investigation.

Based on the following assumptions, the rate of surface adsorption can be determined from the aid of the Langmuir isotherm:

- (a) adsorption process is only carried out on the specific sites on the surface
- (b) each surface site adsorbs one particle
- (c) surface coverage is monolayer
- (d) because of adsorption at special sites, adsorbed molecules possess localized concentration
- (e) The distribution of energy on the surface is uniform
- (f) There is no interaction among the adsorbed species

In order to evaluate the nature and the type of complex, FTIR measurements was performed. Infrared spectrum is an important record, which provides information about the structure of a compound. In this technique, almost all functional groups in a molecule characteristically absorb a definite range of frequency. Transmission of IR radiation causes various bonds in the molecule to stretch and bend with respect to one another. In this research work, the complex powder was prepared by evaporating the complex solution, spontaneously and the remaining powder-like material analyzed by Fourier transform infrared (FTIR) spectroscopy. Infrared transmission spectrum of the complex powder obtained in this way is recorded to be in the range of $400\text{--}4000\text{ cm}^{-1}$. The resulting spectrum is shown in Fig. 22.

The aim of the present IR spectral analysis on the complex powder includes, confirming the complex formation, in addition to proving the absence of any unwished materials in the complex powder. The systematic interpretation of the IR spectrum can be of great help to determine whether a reaction has occurred to give the predicted product or not, since there may be a possibility of other reaction having occurred. The absorption region from 650 to 1500 cm^{-1} generally represents the finger print region of those materials which are unique in characteristics. As reported in the literature, Zn-H vibrations (both symmetric and asymmetric) are indexed around 1500 cm^{-1} and N-H is observed around 3200 cm^{-1} . The presence of Zn-H vibration may be attributed to the adsorption of hydrogen during the evaporation of the complex solution. Therefore it is concluded that the adsorbed material on the substrate can be assumed to be $(\text{NH}_4)_2\text{ZnO}_2$.

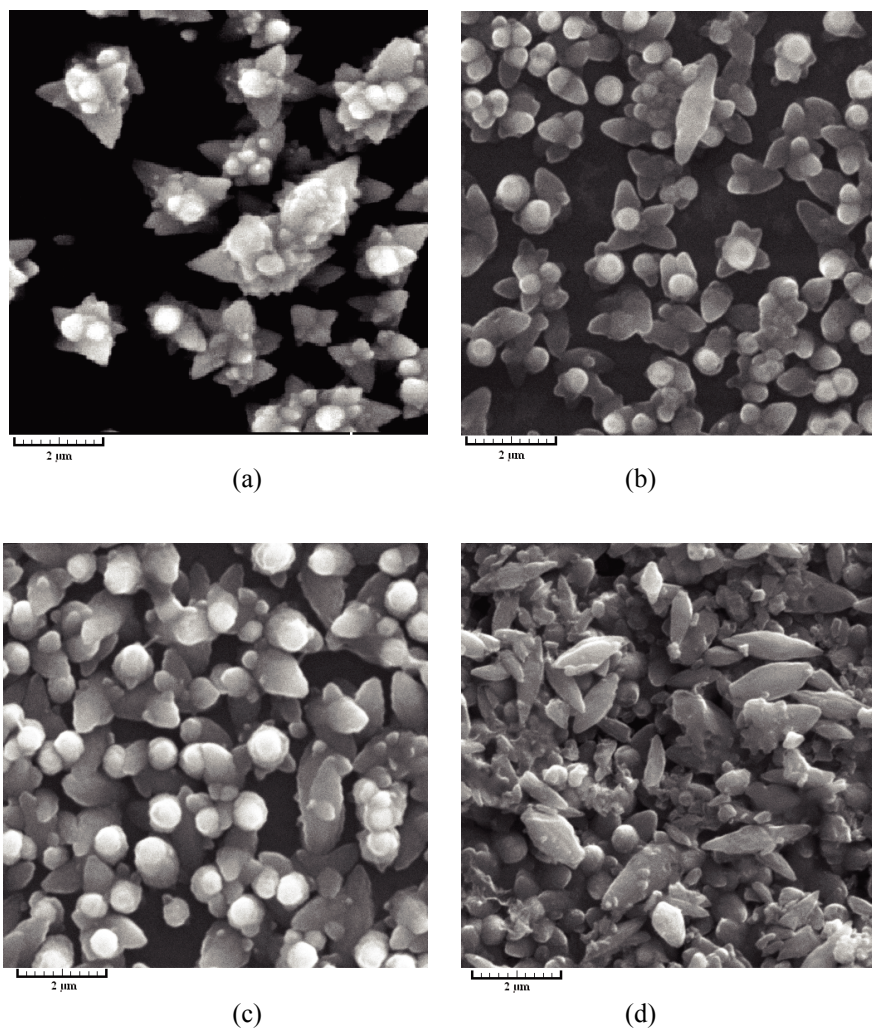


Fig. 21. SEM micrograph of the surfaces of oxide films produced after 100 times of dipping in water at (a) 75°C, (b) 90°C, (c) 95°C, (d) 100°C [13].

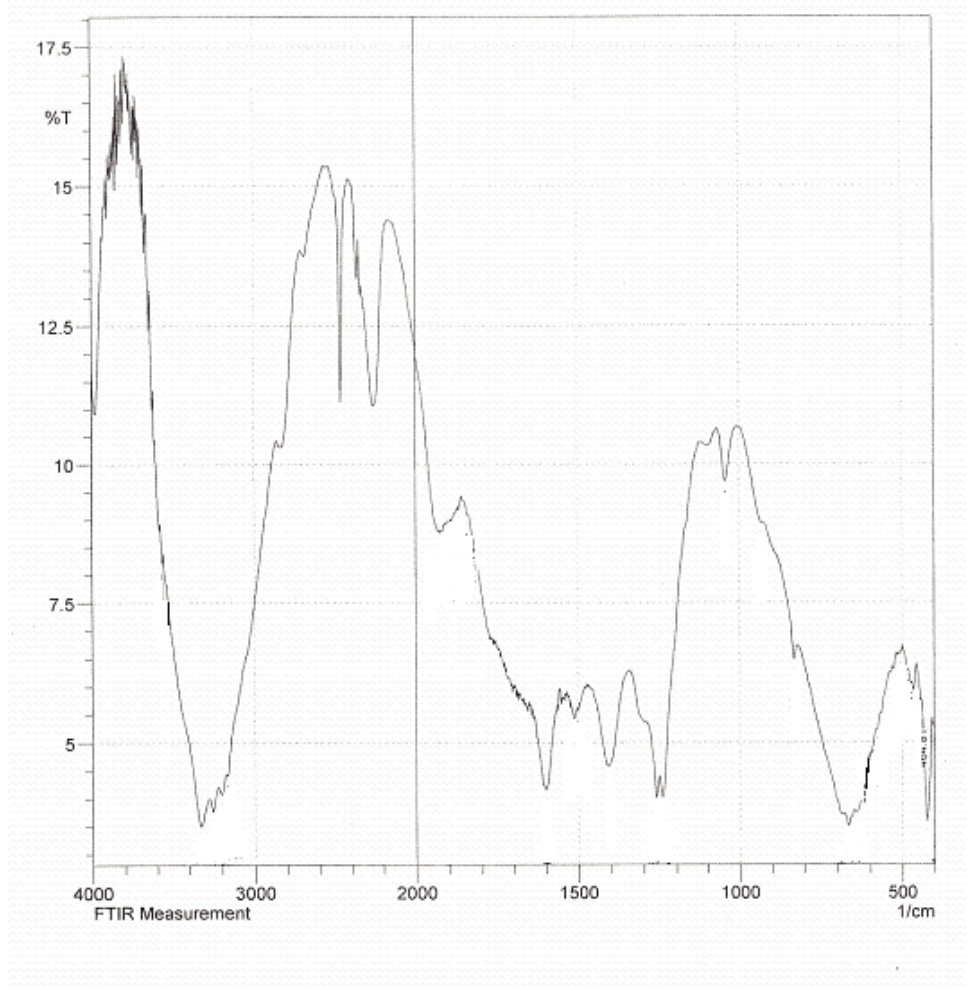


Fig. 22. FTIR spectrum of complex powder [14].

The adsorption of zinc complex layer and oxide species produced from the decomposition of the complex on the surface of the substrate can be demonstrated by Eqs. (26) and (27):



The signs $()$, $[\]$ and $\square$ represent adsorbed molecule, occupied site and unoccupied sites (un-s), respectively. Assuming that the rate of adsorption is proportional to both the number of incident molecules (concentration of complex containing zinc ions) and the number of vacant sites available on the surface, the rate of surface adsorption can be determined from:

$$\left(\frac{d\theta}{dt} \right)_1 = k_f \cdot C_A (1 - \theta) \quad (28)$$

in which θ is the fraction of the occupied sites, subscript f stands for the forward direction, k_f is the rate constant of the forward process and C_A is the concentration of the adsorbed material.

Because the decomposition reaction of complex containing Zn^{2+} to zinc oxide is unidirectional and the desorption rate of oxide particles, $\left(\frac{d\theta}{dt}\right)_2$ is very low, it is concluded that the above-mentioned reaction is unidirectional and $\left(\frac{d\theta}{dt}\right)_2$ is negligible. Therefore the net rate of adsorption is:

$$\frac{d\theta}{dt} = k_f C_A (1 - \theta) \quad (29)$$

To determine whether the adsorbed oxide particles act as Ideal adsorbed material, it can be used from the measurements of layer porosity, $1 - \theta$, at different concentrations of complex solution. The equilibrium constant of the reaction can be related to the fractional coverage and the fractional unoccupied sites. According to Eqs. (26) and (27), the equilibrium constants can be calculated as:

$$K_1 = \frac{a_{[(NH_4)_2 ZnO_2]}}{a_{((NH_4)_2 ZnO_2)} \cdot a_{un-s}} = \frac{\gamma_1 \cdot \theta}{\gamma_2 \cdot C_{complex} \cdot (1 - \theta)} = \frac{\gamma \theta}{C_{complex} \cdot (1 - \theta)} \quad (30)$$

$$K_2 = \frac{a_{[ZnO]}}{a_{(ZnO)} \cdot a_{un-s}} = \frac{\gamma'_1 \cdot \theta}{\gamma'_2 \cdot d C_{Zn^{2+}} \cdot (1 - \theta)} = \frac{\gamma' \theta}{d C_{Zn^{2+}} (1 - \theta)} \quad (31)$$

Where d is the decomposition percent of complex to zinc oxide and its value is less than unit. In order to determine d, consider the reaction of decomposition of complex to ZnO as follows:



the theoretical weight of zinc oxide, $m_{th.}$ can be determined by knowing the weight of complex deposited on the surface of substrate, m.

$$m_{th.} = \frac{m \cdot M}{M'} \quad (33)$$

in which M and M' are the molecular weight of zinc oxide and complex, $(\text{NH}_4)_2 \text{ZnO}_2$, respectively.

The average of d can be obtained from the comparison of the weigh of zinc oxide determined experimentally, m_{ex} , at various times. The values of m_{th} and m_{ex} are given in Table 6.

Table 6. The values of m_{th} , m_{ex} and average of d [14].

Dipping Time (sec)	m_{th}	m_{ex}	$\frac{m_{\text{ex}} - m_{\text{th}}}{m_{\text{th}}} \times 100$	$\bar{d}$
1	9.27×10^{-3}	5×10^{-4}	94.6062	90.84% = 0.9084
2	6.95×10^{-3}	7×10^{-4}	89.928	
5	5.9×10^{-3}	9×10^{-4}	84.77	
8	0.0119	1.2×10^{-3}	89.916	
12	0.0259	1.3×10^{-3}	94.9806	

Therefore it is concluded that: $C_{\text{ZnO}} = 0.9084 C_{\text{Zn}^{2+}}$. Eqs. (30) and (31) can be rewritten as:

$$\frac{\theta}{1-\theta} = \frac{k_1}{\gamma} C_{\text{complex}} \quad (34)$$

$$\frac{\theta}{1-\theta} = \frac{k_2}{\gamma'} d C_{\text{zn}^{2+}} \quad (35)$$

If the adsorbed material act as an ideal species, its activity coefficient is unit and therefore, k_1/γ and k_2/γ' are constant.

The percent of porosity of oxide layers and complex at various concentrations of aqueous solution are given in Tables 7 and 8. Also, the values of $\theta/1-\theta$, k_1/γ and k_2/γ' are given in Tables 7 and 8. As it is shown, k_1/γ and k_2/γ' is not constant and it is concluded that the adsorbed material is non-ideal. It is necessary to note that even if k_1/γ and k_2/γ' are constant, it is possible the adsorbed materials have a non-ideal behavior.

Table 7. The percentage of porosity, $\theta/(1-\theta)$ and k_2/γ' related in the process of adsorption of oxide layer on the surface [14].

Concentration (M)	% porosity, $(1-\theta)$	θ	$\theta/(1-\theta)$	k_2/γ'
0.05	0.6	0.4	0.666	14.66
0.1	0.63	0.37	0.5873	6.465
0.2	0.65	0.35	0.5385	2.964
0.3	0.68	0.32	0.4706	1.727

Table 8. The percentage of porosity, $\theta/(1-\theta)$ and k_1/γ related in the process of adsorption of the complex on the surface [14].

Concentration (M)	% porosity, $(1-\theta)$	θ	$\theta/(1-\theta)$	k_1/γ
0.05	0.82	0.18	0.2195	4.39
0.1	0.75	0.15	0.2	2
0.2	0.67	0.33	0.4925	2.4625
0.3	0.60	0.40	0.666	2.22

The dependence of $\theta/(1-\theta)$ versus the concentration in the adsorption of the complex and oxide layer respectively is given by:

$$\begin{aligned} \theta/(1-\theta) &= 0.48 C_{\text{complex}} - 0.027 \\ \theta/(1-\theta) &= -0.78 d C_{\text{Zn}^{2+}} + 0.68 \end{aligned} \quad (36)$$

According to Eq. (36) the percent of porosity and the occupied surface sites can be theoretically calculated at the various concentrations of aqueous solution [14].

3.1.4.2.2.3 EFFECT OF SUBSTRATE MATERIALS AND ANNEALING TEMPERATURE OF CHEMICALLY DEPOSITED ZINC OXIDE

The study of the role of the substrate type in influencing the chemical deposition and characteristics of ZnO coatings is both of fundamental scientific interest and potential technological significance. In general, the characteristics of chemically deposited coatings may be dependent on the substrate type. For example, the substrate type influences some of the deposit and deposit/substrate interface properties such as stress and adhesion [15].

In this work [15], the chemical-deposition of ZnO was studied using quartz glass (Q-G), soda-lime glass (SL-G) and high purity alumina (HPA) substrates. The experimental deposition conditions used to study the deposition of ZnO on the above-mentioned substrates were the same. All deposits were of the same thickness.

Figure 23 shows the effect of number of dipping on the rate of growth of the deposits formed on the substrate. As can be seen, the rate of increasing of the thickness of the layers for Q-G and SL-G substrates is about the same. This rate is, however, much greater for HPA substrate. All thicknesses increase linearly with the number of dipping of the samples. The curve for the HPA substrate is obviously shifted up towards higher thicknesses. The thickness value for the deposits formed on Q-G, SL-G and HPA substrates at 100-times dipping are, for example, 1.21, 1.10 and 2.16 microns, respectively. This finding may be attributed to differences in the adsorption of a layer of complex solution when immersed in it for three substrates. However, this fact should only affect the early stages of TSCD process. In addition, the difference in the growth behavior when the adequate nuclei are formed, may also contribute to the obvious variations in the thickness. Another possible explanation for the higher affinity of oxide layer to deposit on HPA may be lower surface energy barrier between those two ceramic materials (ZnO and HPA), which facilitates the formation of nuclei of a ZnO layer with an increased thickness. These nuclei form the basis for further growth and show the progressive growth. It should be noted that the progressive growth has been proved from the surface morphologies of the oxide layers produced on SL-G and Q-G substrates (Figs. 24-26):

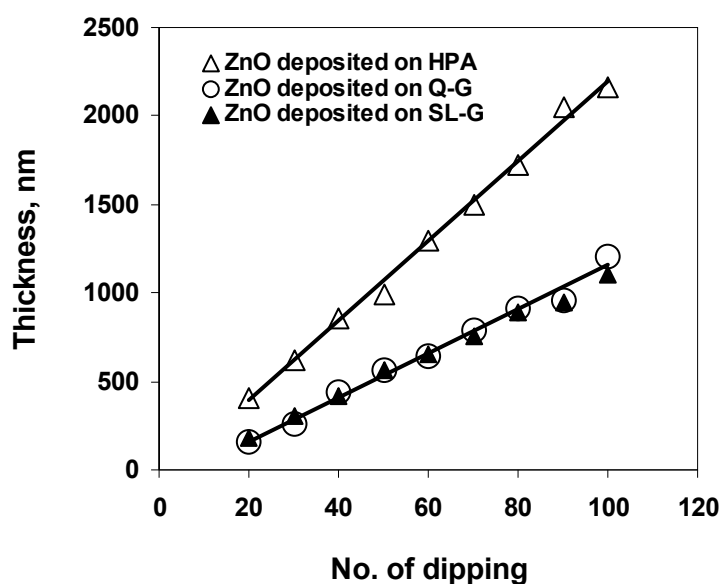


Fig. 23. The variation of film thickness vs. the number of dipping [15].

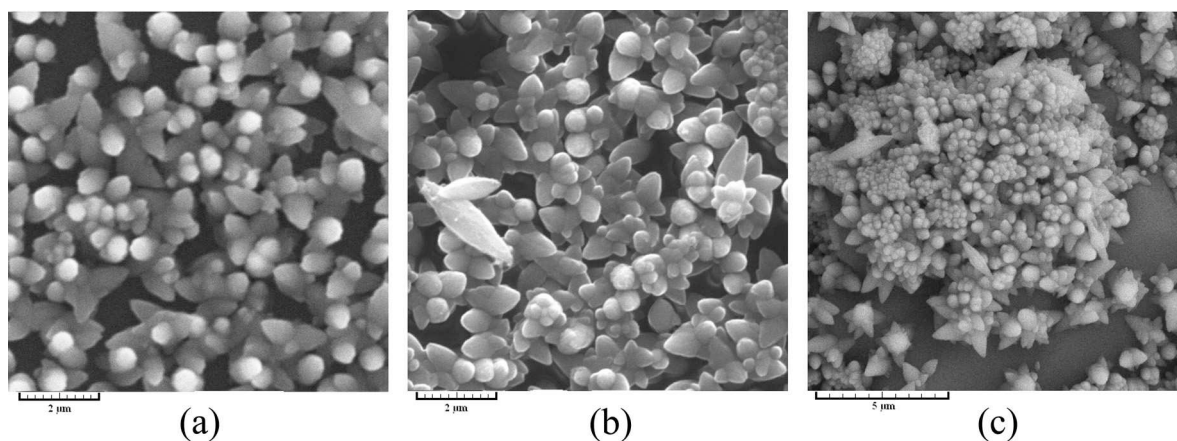


Fig. 24. SEM micrographs showing the morphology of zinc oxide deposits without annealing treatment on (a) Q-G, (b) SL-G, and (c) HPA substrates [15].

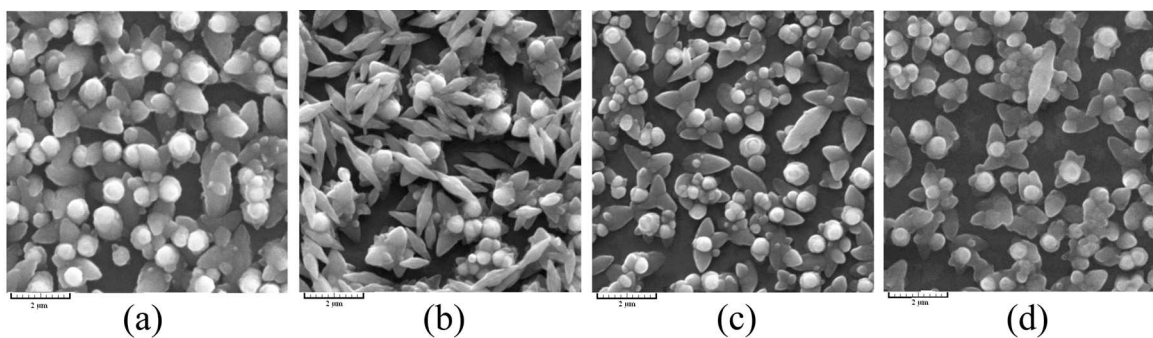


Fig. 25. SEM micrographs showing the morphology of zinc oxide deposits on Q-G substrate annealed at (a) 180 °C, (b) 300 °C, (c) 500 °C, and (d) 800 °C [15].

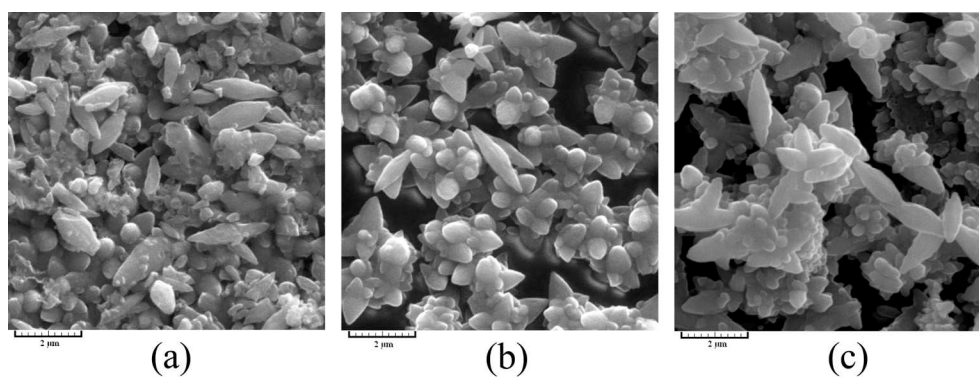


Fig. 26. SEM micrographs showing the morphology of zinc oxide deposits on SL-G substrate annealed at (a) 180 °C, (b) 300 °C and (c) 500 °C [15].

The surface morphologies of the non-annealed deposits after 100 times dipping are shown in Fig. 24. A slight morphology change is observed when the substrate changes from Q-G to SL-G, while a much more distinguishable change occurs when HPA is used for this purpose. HPA substrate causes clustering of the ZnO crystallites, while Q-G and SL-G substrates do not distinguishably show this effect. The SEM micrographs clearly indicate that the zinc oxide layers deposited on all three substrates are composed of oval shaped crystallites preferably oriented perpendicular to the surface of the substrate. Crystallites deposited on the HPA substrate are more compact than those deposited on the other two.

Observations show that clustering is intensified by annealing at temperatures higher than 180°C (see Figs. 25-27). As can be seen, the average size of the oval-shaped crystallites reduces from left to right in the following order:

$$\text{Q-G} > \text{SL-G} > \text{HPA}.$$

Semi-oval shaped crystallites have apparently formed in some of the samples. Figure 25 clearly indicates the presence of such grains.

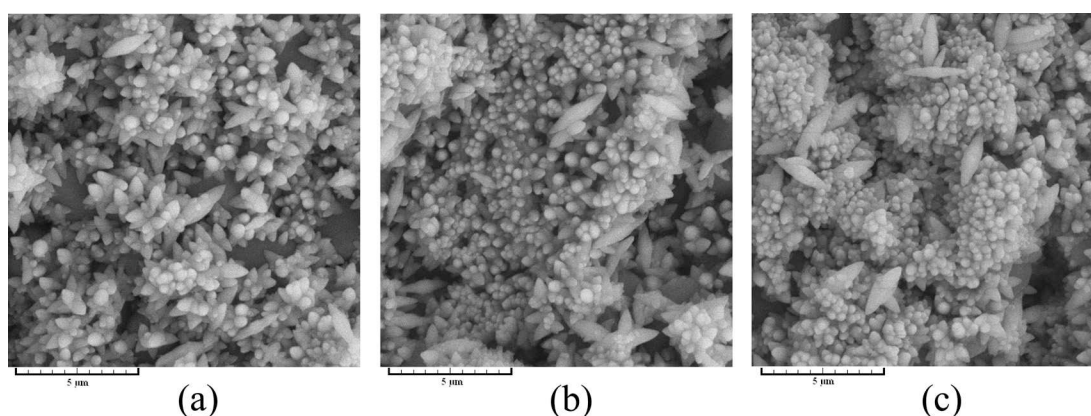


Fig. 27. SEM micrographs showing the morphology of zinc oxide deposits on HPA substrate annealed at (a) 180°C, (b) 300°C and (c) 800°C [15].

XRD patterns for deposits produced on Q-G, SL-G and HPA substrates are shown in Figs. 28-30. Effect of annealing temperature on XRD patterns of the deposited layers are demonstrated in these figures. It is concluded that changing the substrate type influences the intensity of the preferred crystallite orientation, but does not affect on the growth direction. In these X-ray diffraction spectra, the peaks at $2\theta = 31.3, 34.6, 36.2,$ and 47.6 corresponds to the planes (100), (002), (101), and (102) of the hexagonal ZnO, respectively. The preferred orientation peak occurred at $2\theta = 34.6$. These spectra indicate a good crystalline character for the deposited layer showing a preferential orientation with the c axis perpendicular to the substrate. The same preferred orientation of the films was found in the

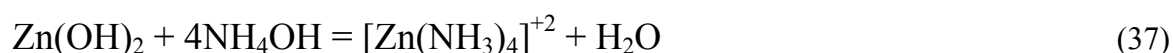
case of ZnO films prepared using other methods. The substrate material does not influence on the preferred growth directions. Samples without annealing or annealed at lower temperatures show the characteristic peaks of Zn(OH)_2 at the 2θ angles of 56.1 and 63.1. As it is shown in Figs. 28-30, increasing of the annealing temperature up to 300°C causes the increasing of the intensity of the peak corresponding to the (002) plane. If the annealing temperature exceeds 300°C, the intensity of the peak corresponding to the (002) plane decreases and the peaks belonging to Zn(OH)_2 are eliminated. It was concluded that the most appropriate temperature for annealing was approximately 300°C [15-20].

3.1.4.2.2.4 GROWTH MECHANISM FOR ZNO NANO FILM

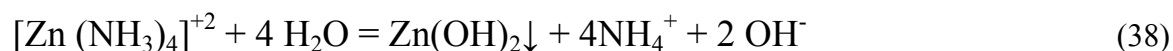
Precipitation of ZnO from the aqueous solution containing Zn^{+2} requires higher ion product than the solubility product of Zn(OH)_2 . Super-saturation degree (S) is an important factor for examination of the precipitation process in aqueous solutions. Its value is defined as the ratio of the ion product to the solubility product. When S is lower than 1, no precipitation occurs in the solution. When S is between unity and S_c (a critical super-saturation value), heterogeneous precipitation occurs on walls of the vessel and on the substrate. This is due to the insufficient value of S for nuclei formation in the bulk solution. For S greater than S_c , a large quantity of nuclei will be formed in the bulk solution. This is called homogeneous precipitation.

Principle task for deposition of high quality film from aqueous solutions is to control the value of S. In order to induce a heterogeneous precipitation on the substrate, one needs to suppress the homogeneous precipitation in the bulk solution by lowering of the value of S.

This paper [insert reference] deals with the thermal decomposition of $[\text{Zn(NH}_3)_4]^{+2}$ to release Zn^{+2} and OH^- ions into the solution. $[\text{Zn(NH}_3)_4]^{+2}$ is produced according to Eq. (37):



In presence of excessive ammonia, reaction (37) results in the formation of the precursor. Dipping into the hot water results in decomposition of $[\text{Zn(NH}_3)_4]^{+2}$ to form zinc hydroxide precipitate:



When temperature exceeds 50°C, solid ZnO particulates may be formed in the aqueous solution [4]:



Starting from immersion of a substrate into the hot water, reactions (37) to (39) occur with the same sequence. Heterogeneous and homogeneous precipitations can therefore result in formation and growth of thin solid layers on the substrate. By adjusting the reaction time or temperature, each chemical reaction progressing within the liquid film can be terminated. In the second stage, the precipitation of zinc hydroxide can be stopped, for example, by controlling of the temperature or time for the reaction. After a series of successive deposition

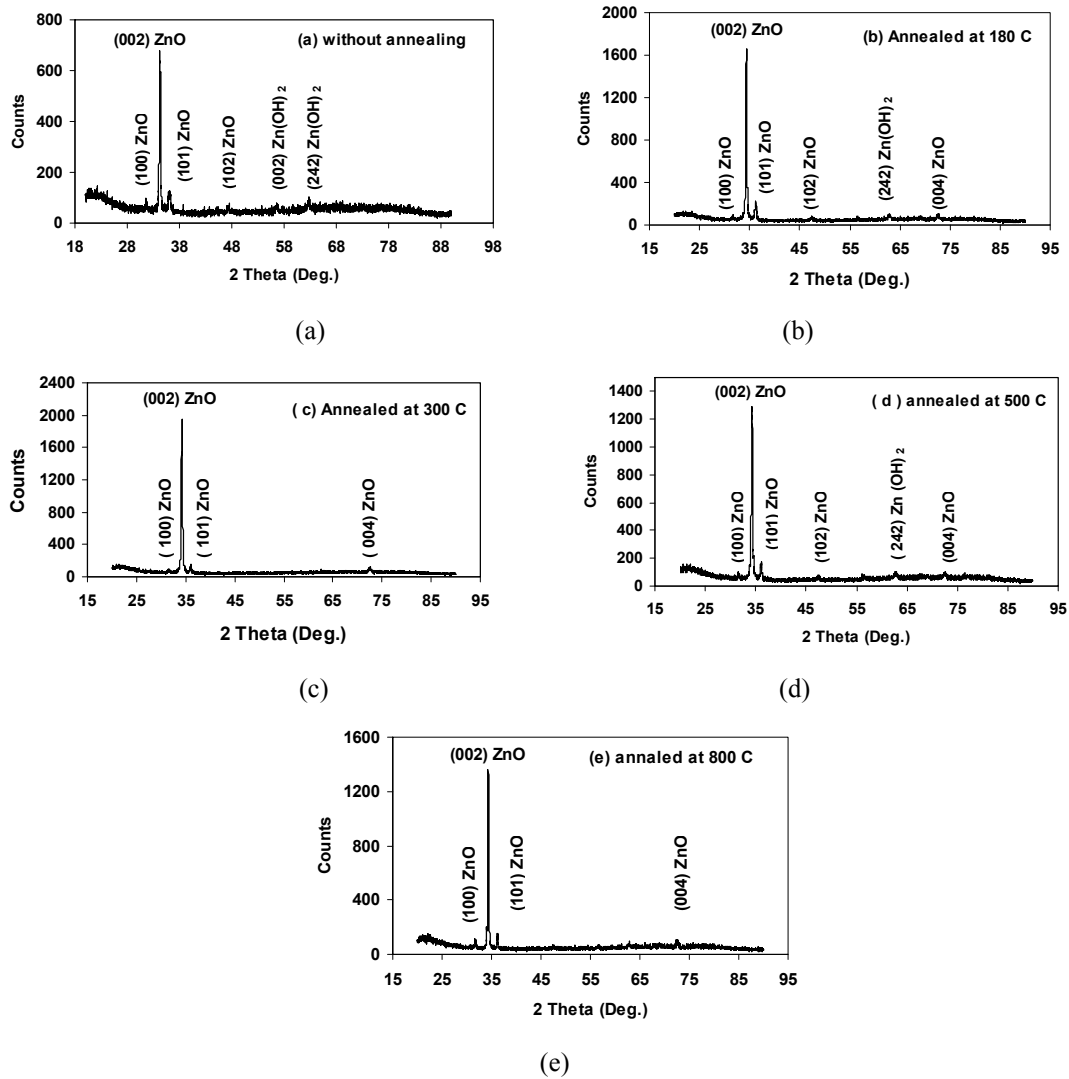


Fig. 28. XRD patterns for ZnO deposits on Q-G substrate (a) without annealing, (b) annealed at 180°C, (c) annealed at 300°C, (d) annealed at 500°C and (e) annealed at 800°C [15].

cycles, a ZnO film with a certain thickness can be made. The quality of the layer can thus be controlled by a similar way [21, 22].

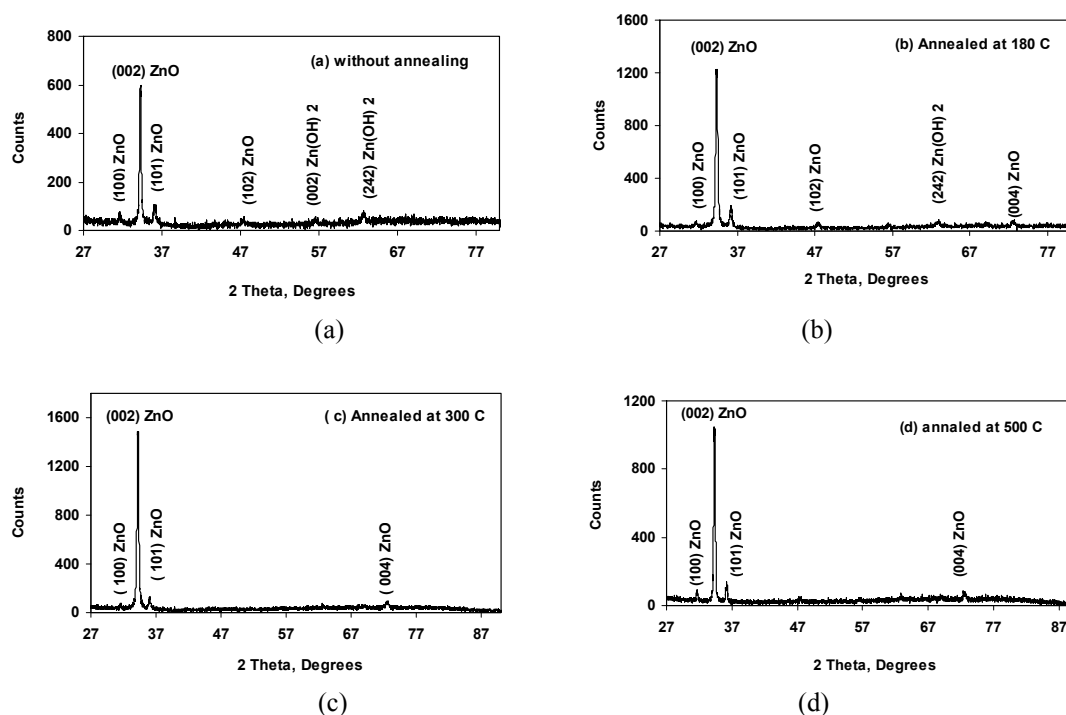


Fig. 29. XRD patterns for ZnO deposits on SL-G substrate (a) without annealing, (b) annealed at 180°C, (c) annealed at 300°C and (d) annealed at 500°C [15].

3.1.4.2.2.5 EFFECT OF SUBSTRATE ETCHING

Figure 31 shows SEM micrographs of zinc oxide film deposited on the HPA substrates after 100 times of dipping and etched for various periods of times indicated in the figure. As it is seen, at intermediate times of dipping, i.e. 10 and 15 sec., the microstructure of the deposited film changes and the acicular grains are produced on the initially formed grains. It is evident from figures 31-a and 31-d that etching for both insufficient (i.e. 5 sec) and long periods of time (i.e. 20 sec) do not considerably change the microstructure. This is due to the fact that at insufficient times of etching the surface of substrate has not been properly etched and at long times, the substrate has been highly etched and there are many micro pores that due to their low size involve no sharp edge. Etching has therefore no significant effect on microstructure of the film produced on the substrate. Figures 32 and 33 demonstrate the effect of substrate etching at two different times for low thickness film (less than 70 times of dipping). As it is shown in figures 32 and 33, the acicular grains have not been produced. This can be explained as follows: At low number of dipping, zinc oxide nuclei are dispersedly distributed on the surface of substrate and the role of etching is not considerably distinguishable. Further etching results in formation of the microscopic sites for nucleation of zinc oxide nuclei and

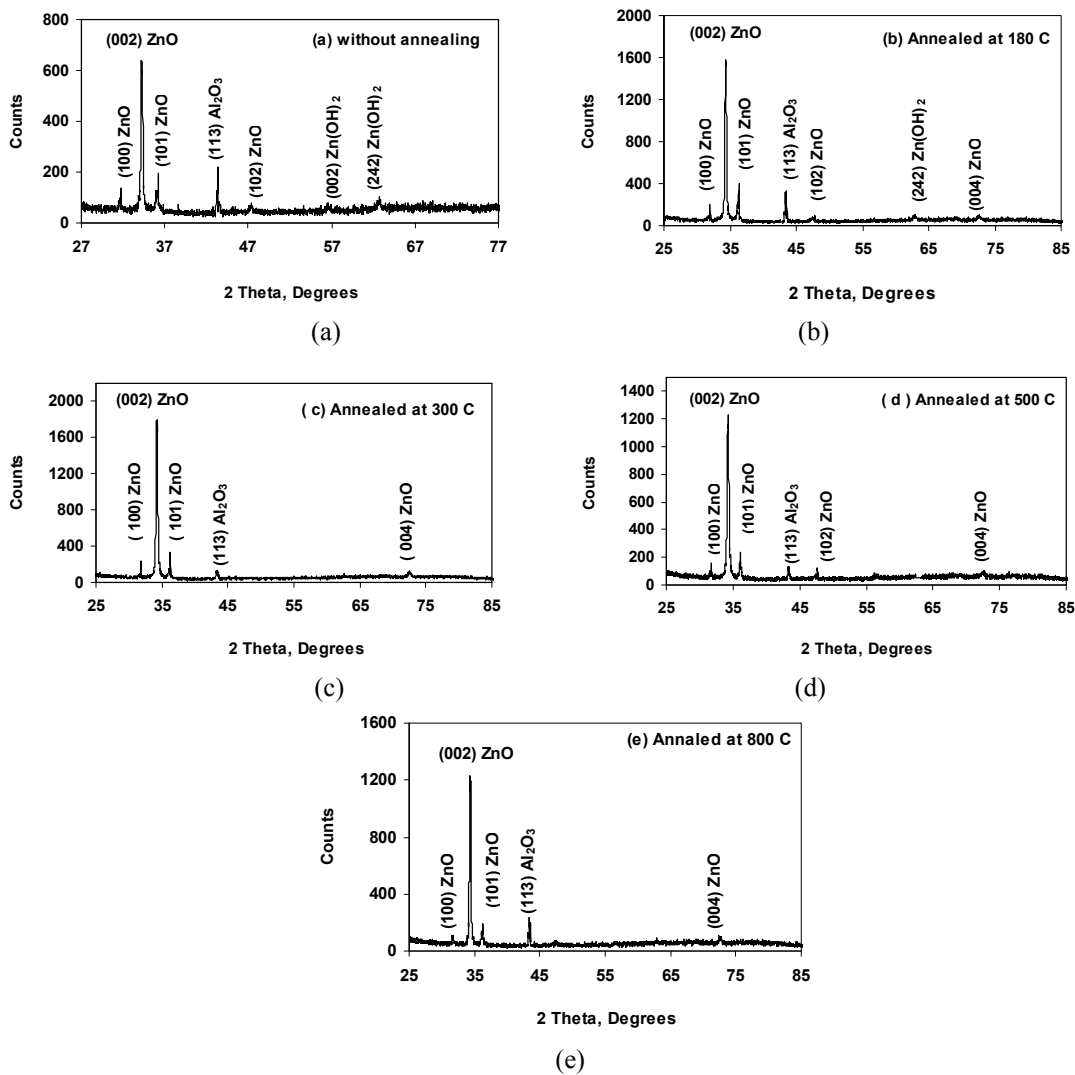


Fig. 30. XRD patterns for ZnO deposits on HPA substrate (a) without annealing, (b) annealed at 180°C, (c) annealed at 300°C, (d) annealed at 500°C and (e) annealed at 800°C [15].

creation of many micro pores. At higher dipping numbers, zinc oxide covers the depth of the pores having sharp edges as appropriate sites for preferred growth. Acicular grains are therefore formed. It can be concluded that the effect of substrate etching is not considerable for films of lower thicknesses. Increasing the etching time decreases the grain size. This is due to production of more nucleation sites by zinc oxide etching process (see Figures 31-33).

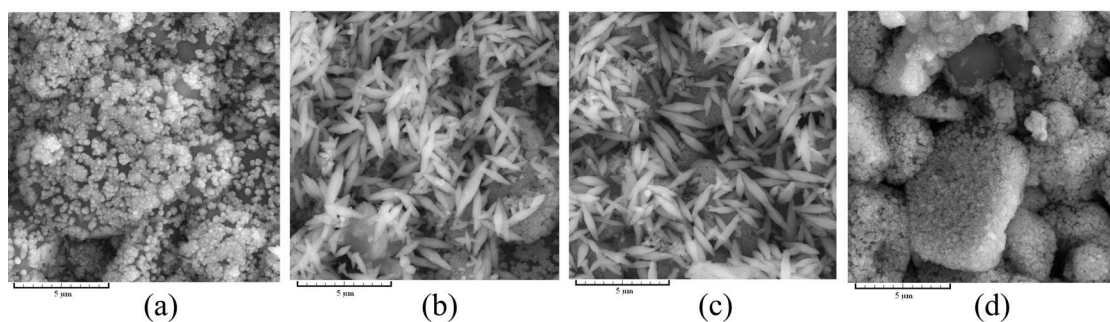


Fig. 31. SEM micrographs of ZnO thin films (100 times of dipping) produced on the HPA substrate etched at (a) 5 sec, (b) 10 sec, (c) 15 sec and (d) 20 sec [21].

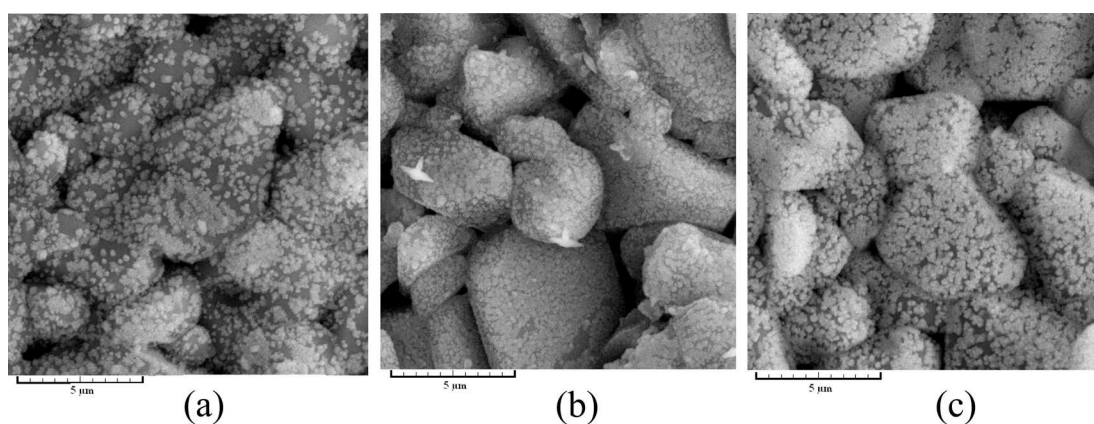


Fig. 32. SEM micrographs of ZnO thin films deposited after (a) 30, (b) 50, and (c) 70 times of dipping on the HPA substrate etched for 10 sec [23].

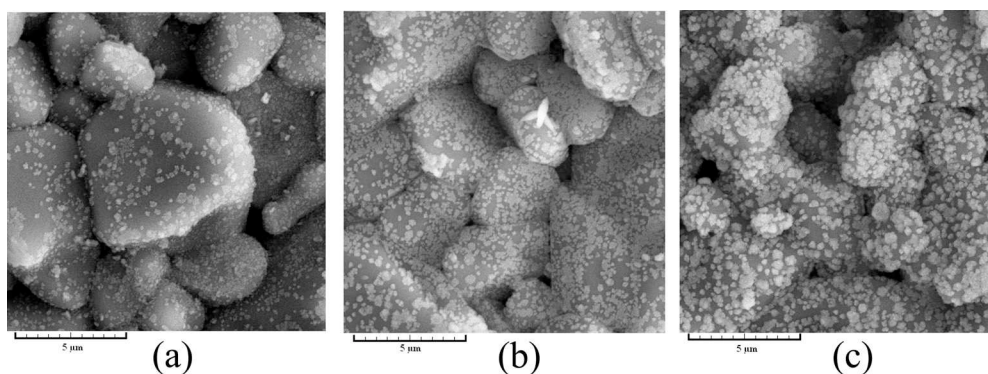


Fig. 33. SEM micrographs of ZnO thin films deposited after (a) 15, (b) 30, and (c) 50 times of dipping stages on the HPA substrate etched for 15 sec [23].

3.1.4.2.2.6 EFFECT OF DOPING

Effect of addition of Sn^{+2} dopant and increasing of the dipping number on the thickness of the deposited ZnO film is presented in Fig. 34. It is seen that the doping process decreases the average deposition rate. The average deposition rate per dipping stage was estimated to be $0.012\ \mu\text{m}$ and $0.008\ \mu\text{m}$ for undoped and Sn-doped films, respectively. Figure 34 shows that the relation between the thickness of the film with the dipping number is linear. The rate of increasing of the thickness is therefore constant. Unchanged solution concentration during the growing process seems to be responsible for this effect. Fig. 35 shows the effect of addition of Sn dopant on microstructure of the chemically deposited zinc oxide having a constant thickness (100 times of dipping). Less than 2% Sn addition (e.g. 1%) prevents the growth of the zinc oxide nuclei. It poisons the deposit and prevents the growth process. Greater than 2% Sn addition induces poisoning of the nucleation stage and hinders the fine grain formation. Same effect is observed in addition of other surfactants. With a dense/nodular-shape appearance, the film produced from the precursor of zinc complex containing 2% Sn is composed of ZnO particles in even sizes of 110-190 nm. It is concluded that the Sn-doped films containing 2% Sn are suitable for gas sensing application. At lower numbers of dipping, the surface of the substrate is not completely covered with ZnO particles. Growth of the nuclei is not therefore observed. At a low number of dipping, Sn dopant does not significant affect on the microstructure of the doped ZnO thin film formed on HPA substrate (Fig. 36).

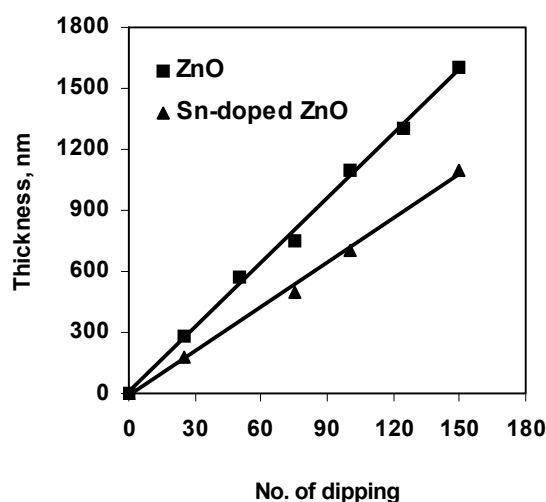


Fig. 34. Effect of number of dipping and Sn doping on ZnO film thickness [17].

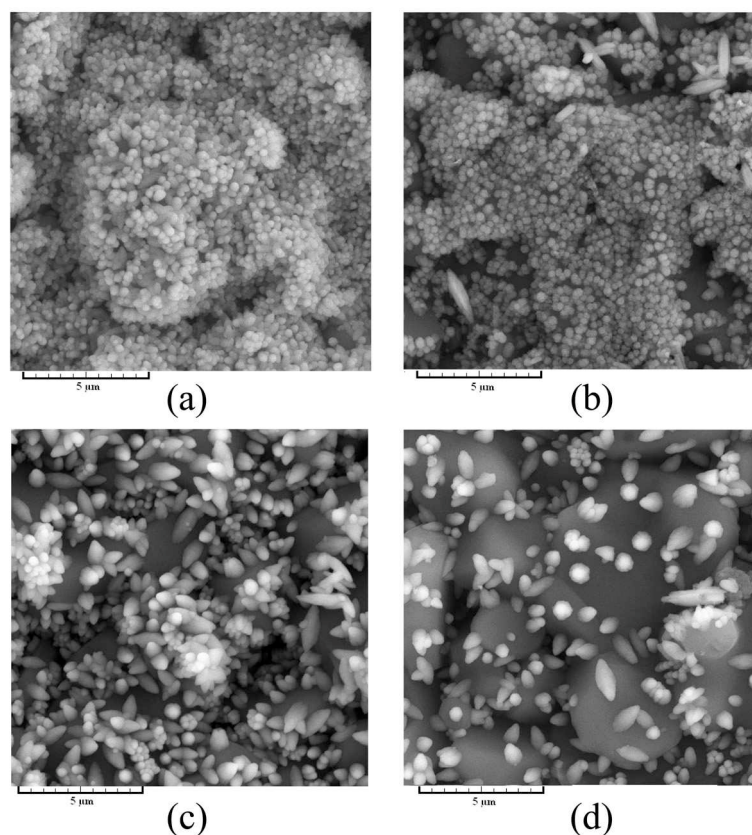


Fig. 35. SEM micrographs of Sn-doped ZnO thin films deposited after 100 times of dipping containing (a) 1% Sn, (b) 2% Sn, (c) 4% Sn and (d) 6% Sn [23].

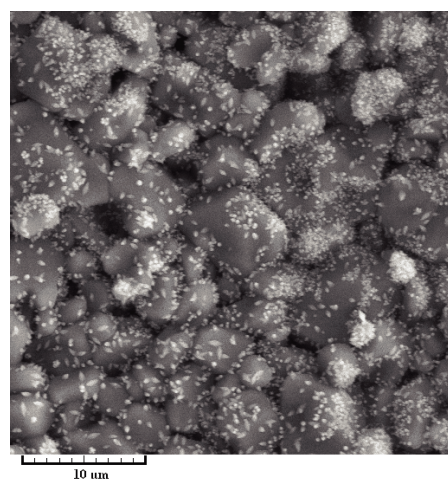


Fig. 36. SEM micrograph of Sn-doped ZnO thin films deposited after 30 times of dipping in a solution containing 1% Sn [23].

3.1.4.2.2.7 EFFECT OF SURFACTANT

Figure 37 shows the effect of addition of Tiron, as a surfactant, on microstructure of the chemically deposited zinc oxide layer with the constant thickness (100 times of dipping). Addition of 2 drops per liter, d/l Tiron prevents the growth of zinc oxide particles nucleated on the substrate and poisons the growth stage of the deposition. The further addition of Tiron causes to poison the nucleation stage and therefore the formation of fine-grained structure is hindered. It is concluded that the optimum concentration of Tiron which can produce the fine-grained structure is 2 d/l.

A combination of both substrate-etching and Tiron-addition effects on zinc oxide microstructure is shown in Fig. 38 for various thicknesses. As it was previously mentioned, the substrate etching has no effect on the microstructure of zinc oxide deposit at low dipping numbers. This is observed in the case of the combined effect of etching and Tiron addition (Fig. 38). As is shown, the microstructures of zinc oxide at low number of dipping do not change (Figures 38-a, 38-b, and 38-c). A comparison between Fig. 38-d and Fig. 38-b shows that Tiron prevents the formation of the acicular grains.

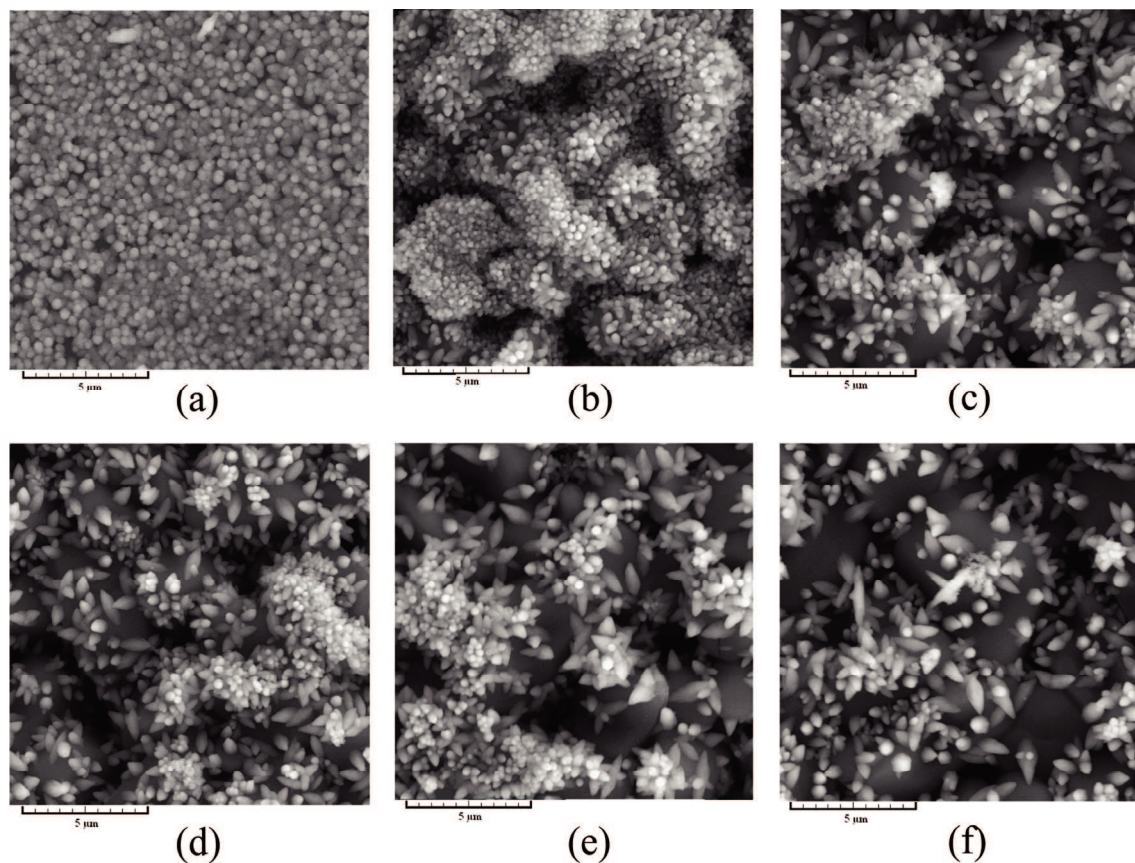


Fig. 37. SEM micrographs of ZnO thin films (after 100 times of dipping) produced from a precursor containing (a) 2 drops, (b) 4 drops, (c) 6 drops, (d) 8 drops, (e) 10 drops and (f) 12 drops of Tiron [16].

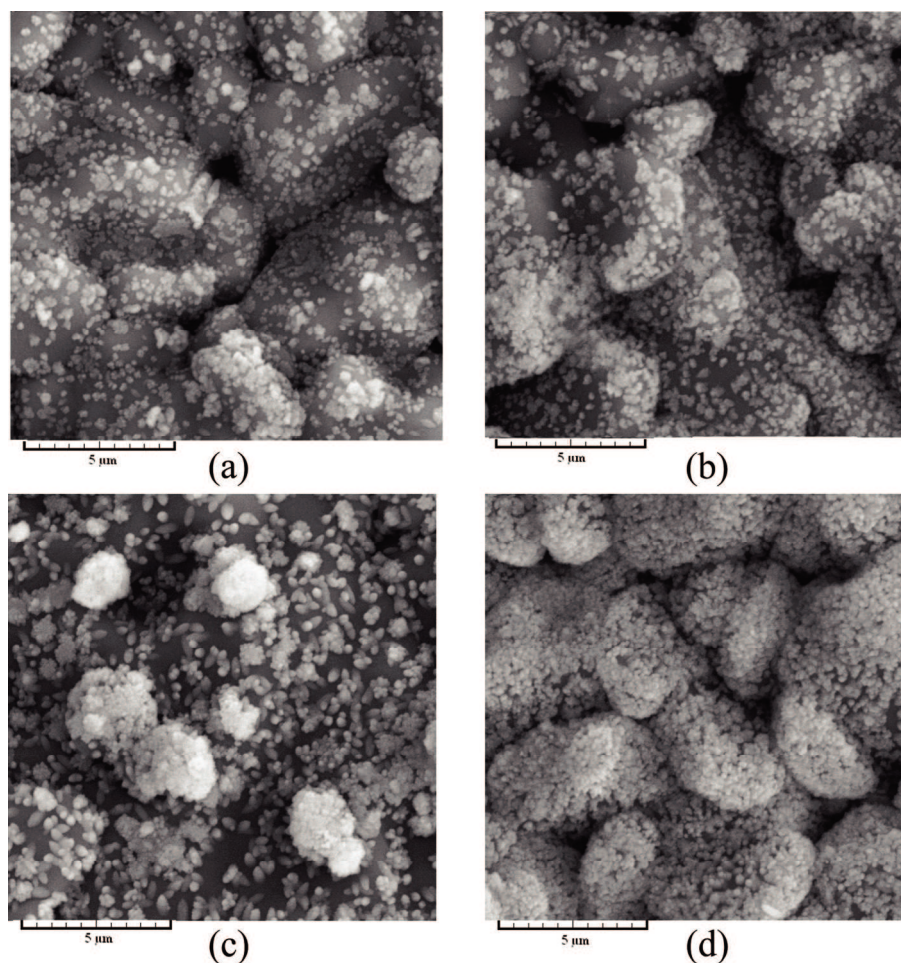


Fig. 38. SEM micrographs of ZnO thin films produced after (a) 30, (b) 50, (c) 70, and (d) 100 times of dipping (precursor contains 2 drops Tiron and substrate was etched for 10 sec) [21].

3.2 APPLICATION OF CERAMICS NANOLAYERS

Effect of addition of Mn^{+2} and Sn^{+2} dopant and increasing of the dipping number on the thickness of the deposited ZnO film is presented in Fig. 39. It is seen that the doping process decreases the average deposition rate. The deposition rate per dipping was averaged to $0.012\mu\text{m}$, $0.01\mu\text{m}$ and $0.008\mu\text{m}$ for undoped, Mn-doped and Sn-doped films, respectively. Figure 39 shows that the thickness variation vs. dipping number is linear and that the rate of increasing of the thickness is constant. Unchanged solution concentration during the growing process seems to be responsible for this effect.

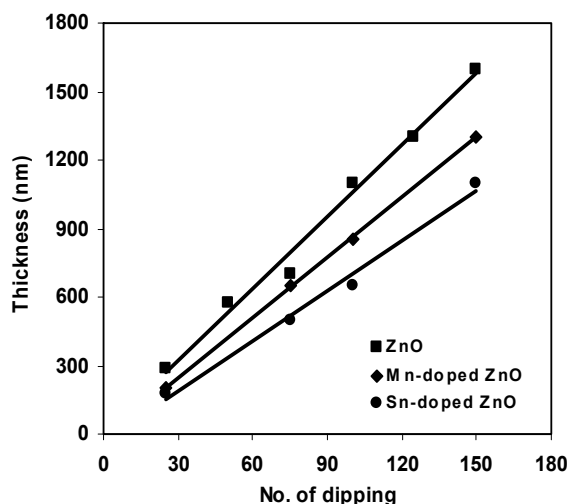


Fig. 39. The variation of film thickness vs. the number of dipping [24].

X-ray diffraction patterns of (a) undoped, (b) Mn-doped and (c) Sn-doped zinc oxide thin films are shown in Figures 40-42. Crystal structure and chemical composition of the phases are determined from these graphs. It is concluded that the deposited thin film is pure ZnO. Other materials such as impurities are below limits of detection. Comparing the peaks pronounced at $2\theta = 34.3$ (in Fig. 40) and $2\theta = 36.2$ (in Figs. 41 and 42) with standard ones show that the preferred orientations of the microcrystals of the film are along the c axis normal to the surface of the substrate, (002) and (101) crystal planes. From the recorded spectrums, one can understand that the degree of crystallinity improves with the number of dipping. This result shows that the preferred orientations of the film microcrystal changes with the doping process.

The crystallite sizes (R_x) of the undoped and doped films were calculated from the XRD peak broadening of the (002) peak for the undoped film and the (101) peak for the doped films at a diffraction angle $2\theta \sim 34.3$ and 36.2 , respectively. Using Scherrer's equation:

$$R_x = (0.9 \lambda) / (\beta \cdot \cos \theta) \quad (40)$$

where λ is the wavelength ($1.5406 \text{ \AA}$ for Cu $K\alpha$ radiation) and β is the full-width-half-maximum (FWHM) of a peak in radians. The calculated grain size by Scherrer's formula exhibits increasing grain size with the number of dipping (Table 9). As it is indicated in Table 9, the crystallite size of the doped films is less than that of the undoped films. The crystallite size of the Sn-doped films is considerably less than that of the Mn-doped films.

The crystallite size of the Sn-doped films is considerably less than that of the Mn-doped films. The Sn-doped films are, therefore, considered as suitable candidates for manufacturing of the thin film gas sensors due to their better sensing power.

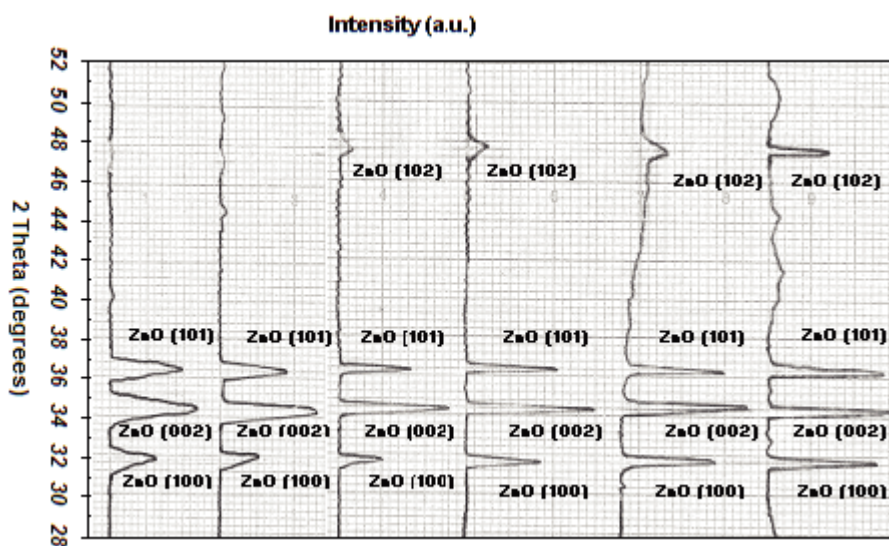


Fig. 40. X-ray diffractograms of undoped ZnO thin films [24].

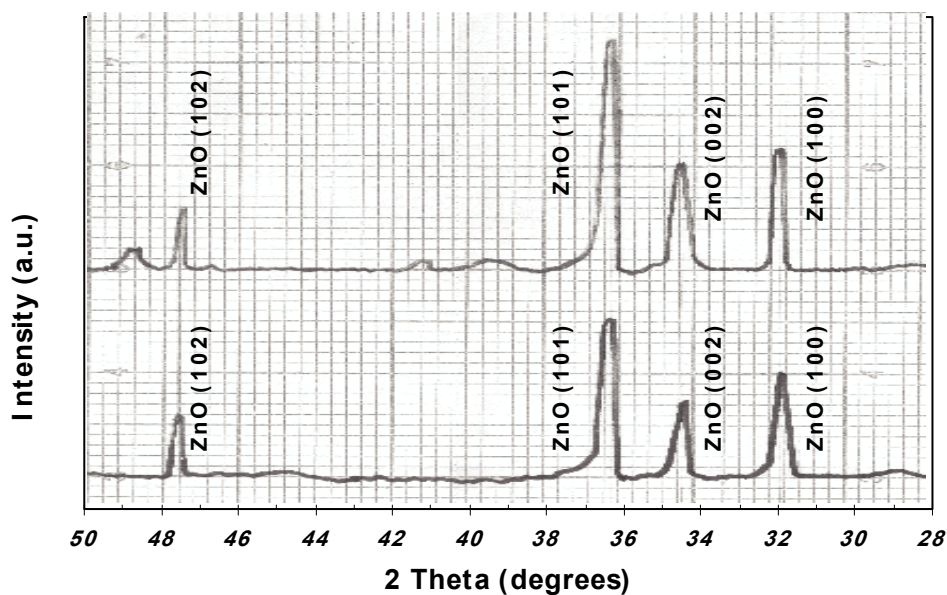


Fig. 41. X-ray diffractograms of Mn-doped ZnO thin film [24]

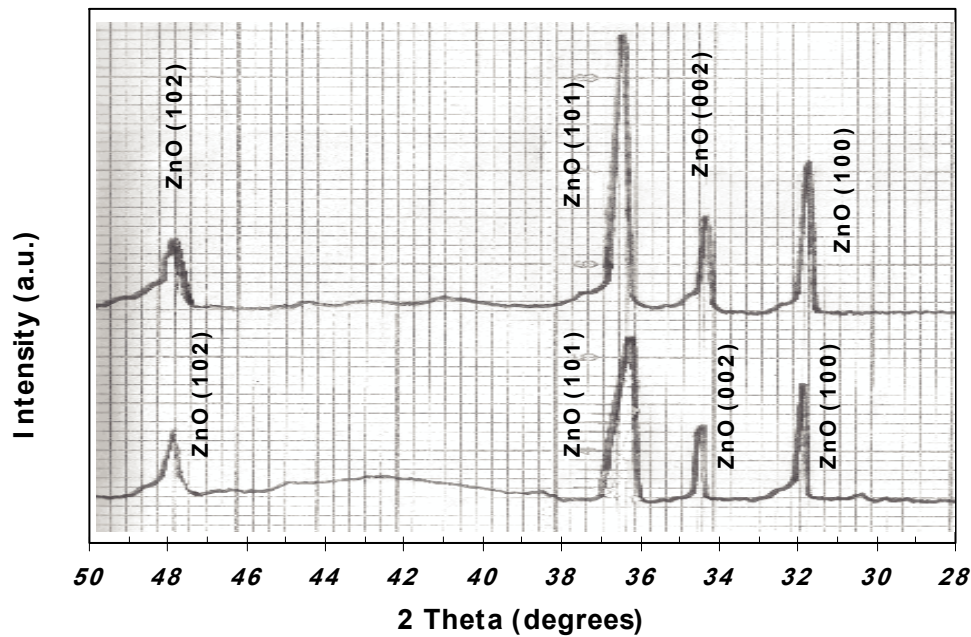


Fig. 42. X-ray diffractograms of Sn-doped ZnO thin film [24].

Table 9. Crystallite size (R_x) calculated from [002] (undoped films) and [101] (doped films) X-ray diffraction peaks [24].

No. of Dipping	R_x (nm) ZnO	R_x (nm) Mn-doped ZnO	R_x (nm) Sn-doped ZnO
25	10	8	5
50	13	-	-
75	15	-	-
100	22	-	-
125	26	-	-
150	32	25	20

3.2.1 OPTICAL TRANSMISSION

Effect of dipping number on transmission spectrum of the undoped ZnO film measured with fluorescence spectrophotometer is presented in Fig.43. Highest transmittance was attained at 550 nm wavelength with a dipping number of 75 or higher. It was observed that annealing at 300°C, no matter periodic or continuous, causes better alignment of the

textured films. This effect was increased with the number of dipping and finally led to reduction in free carrier absorption and low reflection loss, resulting in enhancement of the transmission percentage.

As is seen in Fig. 43, there is a high transmission region exceeding 90% with a sharply defined absorption edge at 320 nm. This region corresponds to an energy band gap of 3.25 eV determined from extrapolation of $(\alpha h\nu)^2$ vs. $h\nu$ to zero energy. This value agrees well with the reported band gap values given for bulk undoped ZnO before [6]. The sharp absorption onset and high transmission values of ZnO film at wavelengths above 400 nm exhibit the optical quality and low concentration of defects such as voids.

The transmission spectra of Mn-doped and Sn-doped ZnO films are presented in Fig. 44. These spectra show the same fundamental absorption edge but not so sharply defined. The undulating shape of the transmission curves is caused by interference of the light in the film itself. They display relatively higher optical transmission values than ZnO thin film doped with MnCl_2 or doped with Sn. It can therefore be concluded that the doping of the film with Sn^{+2} and Mn^{+2} decreases the resistivity of the film. This can therefore be quite helpful to control the doping process.

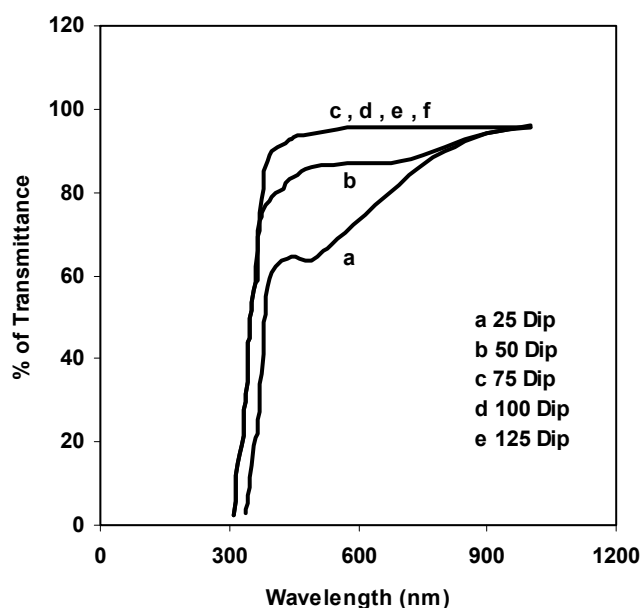


Fig. 43. Optical transmission spectrum of undoped ZnO thin films for different dipping numbers [24].

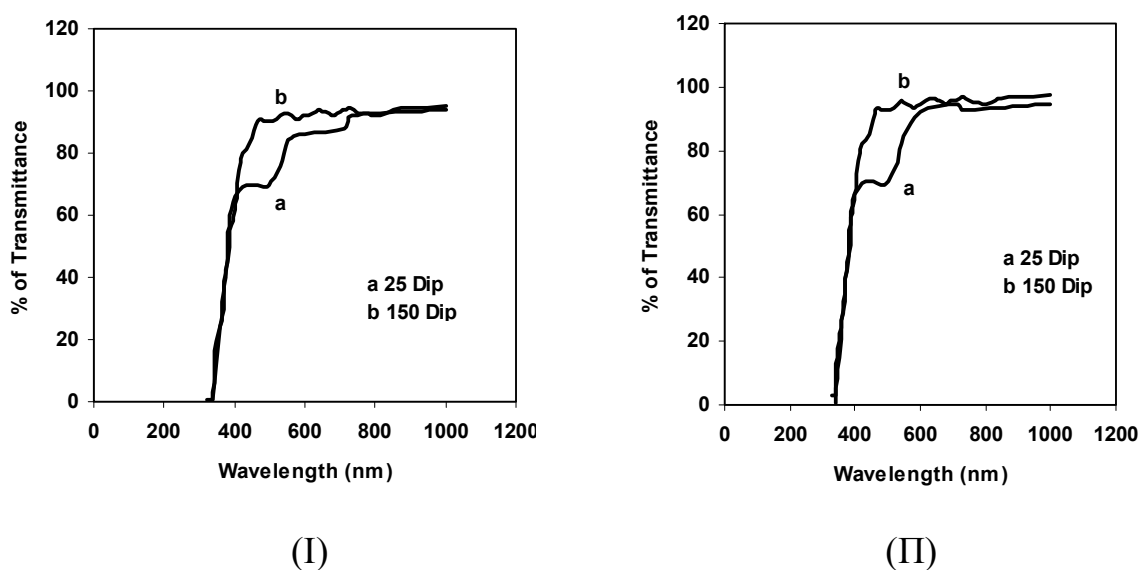


Fig. 44. Optical transmission spectrum of Mn-doped (I) and Sn-doped (II) ZnO thin films [24].

3.2.2 GAS SENSORS

Efforts towards the development of simple, inexpensive and reliable devices have recently been increased with the aim to control air pollution and to detect toxic or smelling gases at low levels in the air and in the field of domestic and industry applications. Semiconductor oxides are widely used as sensing materials due to their surface properties involved in the reaction mechanism with the gas to be detected. Thin film type gas sensors have drawn much interest because of their potential applications for sensors. But truly thin film gas sensors, deposited by conventional thin film methods, have generally shown poor gas selectivity and poor long- term stability. Double layer thin film gas sensors were investigated to improve the gas- sensitive properties of thin film gas sensors. In the present work, the SnO_2 - ZnO double-layer thin film sensor was used. The aim of the work is to show selectivity and stability improvements obtained by double- layer SnO_2 - ZnO thin film production.

The gas sensing materials, tin oxide (SnO_2) and zinc oxide (ZnO) were prepared by using sol- gel and two- stage chemical deposition (TSCD) techniques, respectively.

High purity alumina (HPA) plates were used as the solid substrate for film growth. After degreasing, the plates were washed with deionized water and dried in a steam of hot air.

After a required number of dipping (40 times of dipping), the substrate with the deposited ZnO film was annealed at 350°C in a tube furnace for 1h.

SnO_2 thin film was prepared from starting precursor via the sol- gel route in the following way: 12.37 g SnCl_4 (99.99%, Aldrich) was first stirred vigorously with 15 g Isopropanol. A partially alkoxy- substituted tin compound of the type $\text{SnCl}_x(\text{OC}_3\text{H}_7)_y$ is formed in the solution with evolution of heat, as reported in other papers. The solution was cooled down to room temperature and a 3.42 g water- 10 g propanol mixture was added for hydrolysis

reaction, without using a catalyst. The hydrolysis rate and the start of the reactions occurring in sol- gel technique are not exactly known and difficult to study; therefore the preparation route was optimized by evaluating the feature of the film. In order to get reliable results, the preparation procedure was kept constant and reproducible. Figure 45 outlines the steps for preparation of tin oxide.

Tin oxide thin films prepared after 20 times of dipping were deposited on the zinc oxide layer by using dip coating technique. The SnO_2 - ZnO double layer was first dried at 110 °C for 30 min followed by the controlled annealing at a rate of 5 °C/min to 600 °C and held for 30 min. It is necessary to note that the total thickness of the SnO_2 - ZnO double layer thin film is 0.55 μm .

The structure of the SnO_2 - ZnO double layer thin film is shown in Fig. 46. The electrodes and heater had already been affixed to the HPA substrate.

The resistance of the SnO_2 - ZnO film in air (R_a) and in detecting gases (R_g) was measured. Gas sensitivity, S , is defined as $S = R_a / R_g$ [25-28].

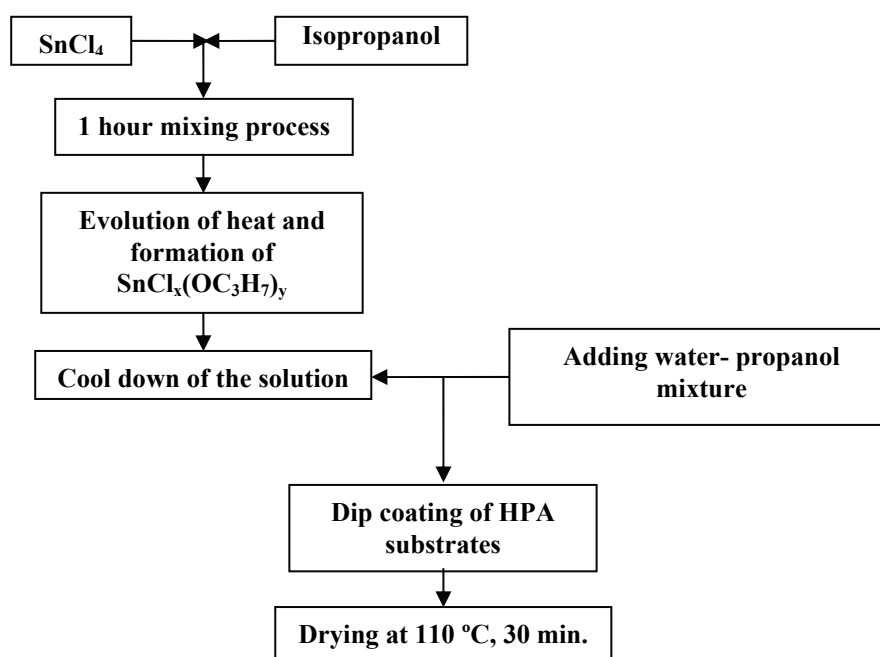


Fig. 45. Flowchart of the process used for production of tin oxide thin film [25].

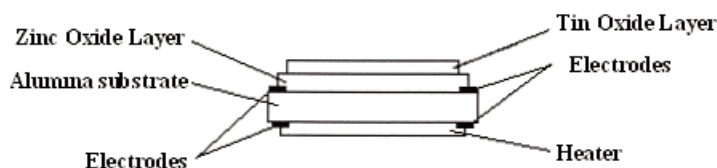


Fig. 46. The structure of SnO_2 -ZnO double layer thin film [25].

Figure 47 shows Auger spectra from the ZnO and SnO_2 /ZnO double layer thin films at different thicknesses of tin oxide after annealing at 600°C . After 1 h. annealing at 600°C , the surface is relatively clean and no peaks of Cl or other impurity exist in the spectra. Obviously, upon deposition of tin oxide, the signal from the Sn increases and those from Zn decreases. For a tin oxide deposit produced after 20 times of dipping, the Zn_{LMM} and O_{KLL} signals are close to the detection limit of AES.

The surface morphology of tin oxide thin film produced after 40 and 20 times of dipping is shown in Fig. 48. Figure 48 shows two detailed views of the surface of a sensitive, SnO_2 thin film deposited on zinc oxide thin film. Fig. 48a shows a general view of tin oxide film, which appears to be without cracks and made up of grains, the size of which is quite homogeneous. Figure 48b shows a more detailed view of the sensitive layer. As it can be seen, grain size is below 40 nm and grains form agglomerates which create a porous layer. XRD pattern for SnO_2 films is shown in Fig. 49. As it is shown in Fig. 49, all the obtained spectra showed in Fig. 49 present the typical tetragonal tin oxide crystalline features.

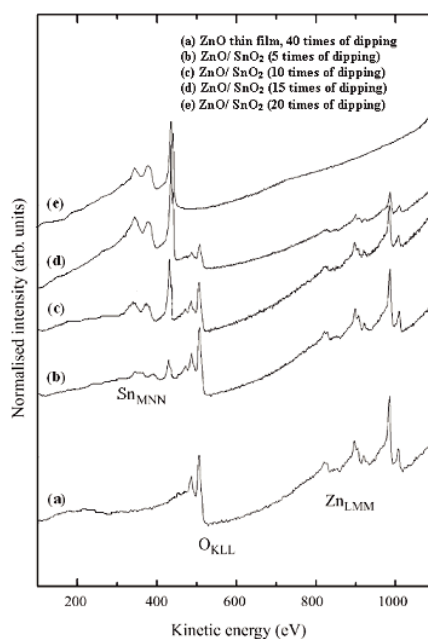


Fig. 47. AES spectra of ZnO (a) and tin oxide thin films produced after 5 (b), 10 (c), 15 (d) and 20 (e) times of dipping [25].

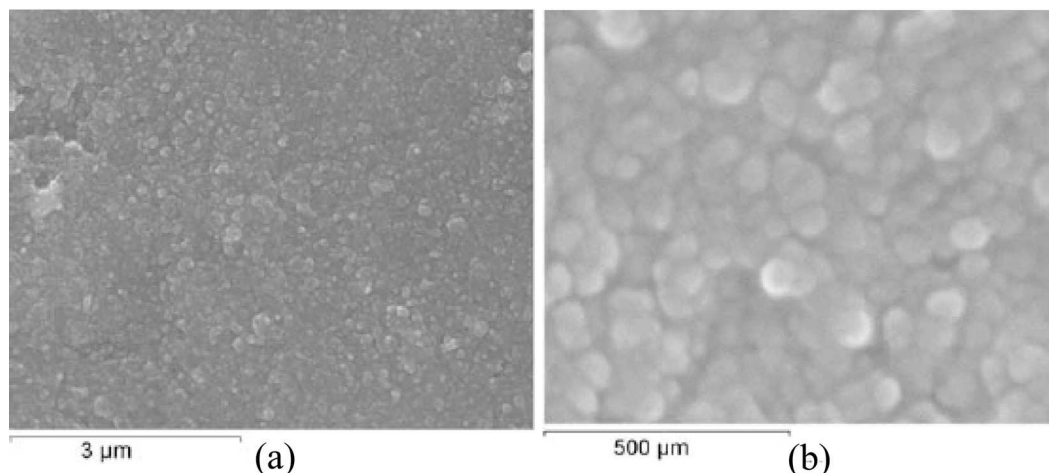


Fig. 48. SEM micrographs showing the morphology of tin oxide layers. (a) General view. Magnification is 1.7×10^4 . (b) more detailed view. Magnification is 1.1×10^5 [25].

The sensitivities of the SnO_2 -ZnO double layer thin film to $\text{C}_2\text{H}_5\text{OH}$, CO and H_2 are shown in Fig. 50. The SnO_2 -ZnO double layer thin film shows a high sensitivity to $\text{C}_2\text{H}_5\text{OH}$ ($S = 24$), but a very low response to CO and H_2 (less than 3). This situation suggests that the SnO_2 -ZnO double layer thin film is a good sensor material to alcoholic gases. It is necessary to note that the selectivity of this sensor is much better than that of SnO_2 or ZnO thin film, although its sensitivity is lower.

In Table 10, the resistance change of SnO_2 -ZnO double layer thin film in air is compared with that of SnO_2 film. The resistance of the SnO_2 -ZnO double layer thin film was stable after about 48 h, while the resistance of the SnO_2 film continued to change even after 84 h. In other words, the stability of the SnO_2 -ZnO double layer thin film was better than that of the SnO_2 film.

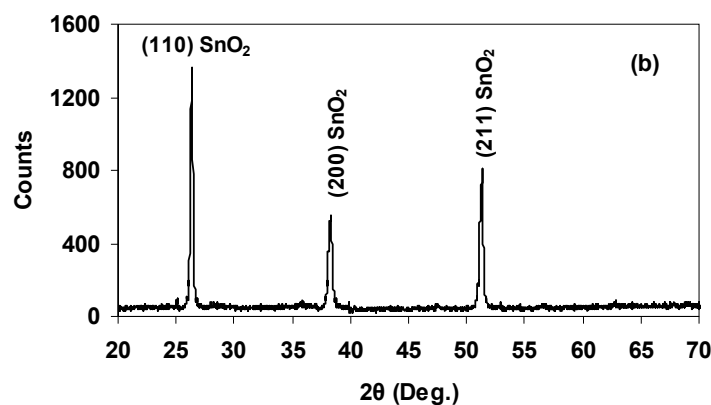


Fig. 49. XRD patterns for ZnO (a) and SnO_2 (b) thin films [25].

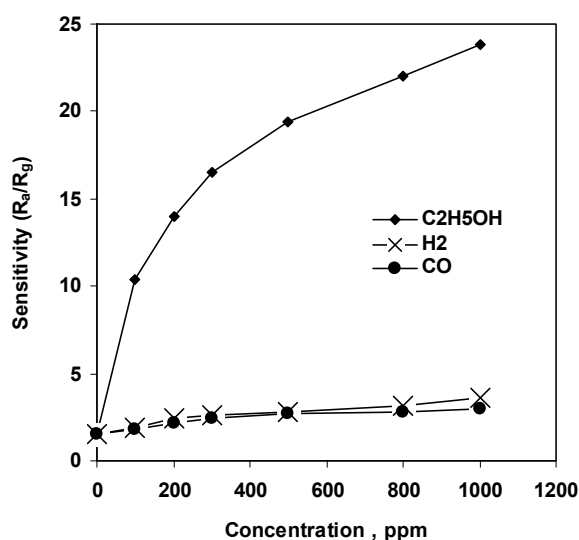


Fig. 50. The sensitivity of SnO_2 - ZnO double layer thin film to various gases as a function of concentration at 300 °C [25].

The surface and interface of the SnO_2 - ZnO double layer thin film were investigated by AES. The distribution of Sn, O and Zn atoms along the vertical section was observed. It was found that Zn diffused into the SnO_2 layer and Zn diffused into the ZnO layer. Thus, an interfacial transition layer was formed between the SnO_2 layer and the ZnO layer (Fig. 51). With the top layer removed, the electronic and gas- sensitive properties of the interfacial transition layer were investigated by AES. It was found that the interfacial transition layer has high resistance and low sensitivity to gases.

Table 10. The resistance change of SnO_2 - ZnO double layer and SnO_2 film in air [25].

Duration (h)	0	12	24	36	48	60	72	84	96	108
Resistance of SnO_2 - ZnO film ($\text{M}\Omega$)	65.4	70.3	72.2	76.3	82.2	82.3	82.4	82.3	82.2	82.3
Resistance of SnO_2 film ($\text{M}\Omega$)	40.8	43.2	45.1	48.4	52.1	53.6	56.9	56.4	55.9	56.3

The SnO_2 - ZnO double layer thin film can be viewed as a parallel collection of two equivalent resistances, R_s and R_z , which refer to the resistances of the SnO_2 layer and the ZnO layer, respectively (Fig. 52).

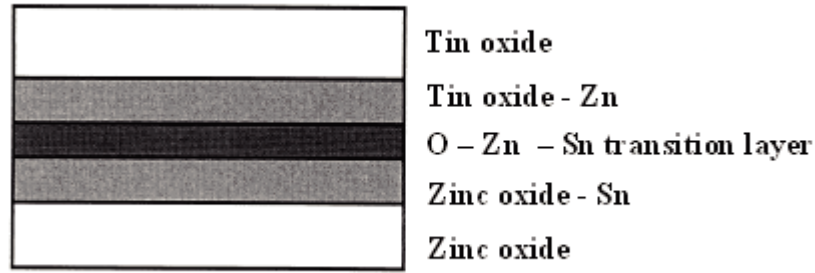


Fig. 51. Schematic of interfacial transition layer in SnO_2 - ZnO double layer thin film [25].

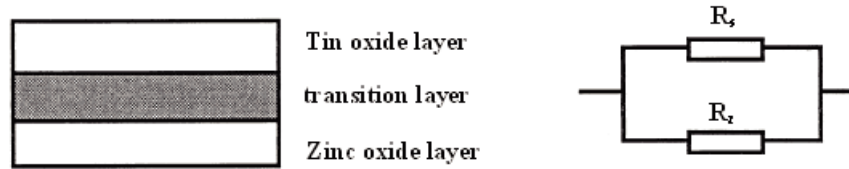


Fig. 52. The equivalent circuit of SnO_2 - ZnO film [25].

A double layer thin film gas sensor is characterized by the separation of the current conduction part and the gas- sensitive part (top layer). The current conduction part needs not only to be controllable in the fabrication process, but also to be stable for a long time. Zinc oxide is suitable for this purpose because of its stable condition.

The sensitivity, S , can be expressed as $S = R_{sa} / R_{sg}$; thus, the sensitivity of SnO_2 - ZnO double layer thin film, S' , can be expressed as:

$$S' = \left(\frac{R_{sa} \cdot R_z}{R_{sa} + R_z} \right) / \left(\frac{R_{sg} \cdot R_z}{R_{sg} + R_z} \right) = \left(\frac{R_{sa}}{R_{sg}} \right) / \left(\frac{R_{sa} + R_z}{R_{sg} + R_z} \right) = S \cdot \frac{R_{sg} + R_z}{R_{sa} + R_z} \quad (41)$$

$R_{sg} < R_{sa}$, thus $S' < S$, i.e., the sensitivity of the double layer film decreases slightly. This coincides with the experimental results. Due to the high sensitivity of SnO_2 film, the slight decrease in sensitivity is not a serious problem.

The expression of stability is resistance change with time. If R_{sa} resistance percentage change is δ , then

$$\frac{(1 + \delta) R_{sa} \cdot R_z}{(1 + \delta) R_{sa} + R_z} / \frac{R_{sa} \cdot R_z}{R_{sa} + R_z} = (1 + \delta) \frac{(R_{sa} + R_z)}{(1 + \delta) R_{sa} + R_z} \quad (42)$$

The result of Eq. (42) is always smaller than $1 + \delta$, thus the double layer film has a decreased resistance change and an increased stability. The smaller the R_z , the smaller the result of Eq. (42), the better the stability.

To show clearly the improvement of the double layer film, let $S=10$ and $R_z = \sqrt{R_{sa} \cdot R_{sg}} = \sqrt{S} \cdot R_{sg}$. Thus in Eq. (41),

$$S' = S \cdot \frac{R_{sg} + \sqrt{S} R_{sg}}{S \cdot R_{sg} + \sqrt{S} R_{sg}} = S \cdot \frac{1 + \sqrt{S}}{S + \sqrt{S}} = \sqrt{S} \cong 3.2 \quad (43)$$

Letting $\delta = 0.1$. Thus, in Eq. (42),

$$1.1 \frac{R_{sa} + R_z}{1.1 R_{sa} + R_z} = \frac{1.1 S R_{sg} + 1.1 \sqrt{S} \cdot R_{sg}}{1.1 S R_{sg} + \sqrt{S} R_{sg}} = 1 + \frac{0.1}{1.1 \sqrt{S} + 1} \quad (44)$$

Letting $S = 10$, the result of Eq. (44) equals 1.02, or a resistance change of about 2%, far less than 10%. This shows that the double layer film greatly improves stability of the sensor [25].

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