Chapter

Nanocomposites Thin Films: Manufacturing and Applications

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Abstract

Thin films of nanocomposite materials arouse a lot of interest due to their excellent mechanical, electrical, optical, tribological properties and also by the vast field of application. This chapter covers some techniques of thin films growth, such as the processes of physical vapor deposition, such as magnetron sputtering; the processes of chemical vapor deposition; layer-by-layer; among other techniques. Additionally, relevant features and applications of some nanocomposites thin films are presented. The wide variety of thin films growth techniques have allowed the development of several devices including those that act as: transistors, actuators, sensors, solar cells, devices with shape memory effect, organic light-emitting diodes (OLEDs), thermoelectric devices.

Keywords: thin films, coatings, nanocomposites, PVD films, CVD films

1. Introduction

The possibility of improving the surface properties of a material preserving the original properties of the bulk is a major interest in the application of thin films. In general, the purpose of coatings is to obtain films of high hardness and resistant to wear and corrosion deposited on the surface of metallic materials. A class of thin films that has been gaining prominence is that of nanocomposites thin films (NTFs) that in addition to the advantage allow the union of different materials whose combination of properties allows obtaining specific characteristics for use in each application [1–4].

The NTFs are widely applied in the automotive, chemical, aerospace, electronics, and biomedical industries due to their attractive properties such as high hardness, good tribological properties, excellent resistance to corrosion and oxidation at high temperatures [5–7].

An important fact to be observed is the synergism of the properties of nanocomposite materials. Often a monolithic thin film is not able to gather specific properties in isolation, and the complement of these properties can be obtained by inserting another type of material that presents the characteristics that were missing.

As an example, we can mention the Cr-C nanocomposite thin film that coats devices exposed to the action of seawater. C improves adhesion, toughness and decreases surface roughness while Cr exhibits excellent anticorrosion properties [8]. Thus, we can note that the combination of elements Cr and C provides the obtaining of a thin film that brings together the best characteristics of the two elements.

There are several techniques for NTF growth. In general, these techniques are inserted in the following groups: (a) processes of physical vapor deposition (PVD) and (b) chemical vapor deposition (CVD) processes. In PVD processes, the material is converted to its vapor phase in a vacuum chamber and condensed on the substrate surface in the form of a thin film. In CVD processes, there is the spraying of the substance to be deposited, where the vapor is thermally decomposed into atoms and molecules, which can react with other gases, vapors, or liquids in order to produce a solid film on the substrate surface [9–12].

Some control parameters differentiate well the techniques belonging to these groups, which makes in many cases a technique more interesting or more appropriate than another. For example, in conventional CVD processes, the treatment temperature is high, while PVD processes occur at lower temperatures [13–15].

This chapter presents some techniques for NTF growth based on the processes of physical vapor deposition, chemical vapor deposition, and layer-by-layer technique. For each case the advantages, disadvantages and applications are mentioned. We hope that this brief chapter will encourage researchers to study the NTF in terms of improving their properties and in the knowledge or development of other thin films growth techniques.

2. Nanocomposites (thin films)

The nanocomposites are multiphase solid materials obtained by insertion of nanoscale crystals dispersive in a second phase. The most common nanocrystals are based on hard phases such as transition metal nitrides and carbides. The second-phase materials usually present in two types: (a) the hard phase, where the nanocomposite exhibits ultrahardness, but demonstrates brittle failure at high loads; and (b) the soft phase, where the resulting nanocomposite has high hardness and a super-tough structure [8].

The ratio control of these phases allows the obtaining of nanocomposites whose properties of one of the phases complement those of the other phase resulting in materials that can be applied in several areas. In the field of coatings, NTFs arouse a lot of interest due to the various combinations of properties. In the next paragraphs, we will highlight some studies in NTF in terms of the properties obtained in each case.

Lakra et al. [16] carried out the fabrication and electrochemical characterization of cobalt oxide (Co_3O_4)/graphene nanosheets nanocomposite deposited on stainless steel substrates as efficient electrode for supercapacitor application. The supercapacitor can achieve a power density in the range of 0.3–0.8 kW/kg with energy density of 2.4–9.8 Wh/kg, and it shows good electrochemical stability with a loss of 5% in capacitance after 1000 cycles. For the authors, the performance of the device can be improved by optimizing appropriate concentration of CO_3O_4 and graphene in the nanocomposite. The better performance was attributed to the synergistic effect of graphene and CO_3O_4 in the composite.

Scharf et al. [17] analyzed the synthesis, structure, and friction behavior of titanium doped tungsten disulfide (Ti-WS2) nanocomposite solid lubricant thin films deposited on Si (100) substrates. The pure WS2 thin films show columnar-plate morphologies with porosity between the plates, which leads to early fracture at room and high temperatures. With the addition of Ti, the room temperature friction coefficient measurements show some improvement when low amounts of Ti are added to WS2. This behavior was also identified for high-temperature (500°C) friction tests.

Dang et al. [18] studied the influence of Ag contents on structure and tribological properties of TiSiN-Ag nanocomposite coatings deposited on Ti-6Al-4V substrates. In this study, the authors observed that the variation of the Ag content directly influences the hardness, friction coefficient, and wear resistance. For low Ag content (1.4 at.%), the coating exhibited high hardness (36 GPa), but poor wear resistance. As the silver content increased from 5.3 to 8.7 at.%, the films exhibited small variation in hardness and greater layer homogeneity. A better performance in terms of wear resistance in artificial sea water was observed for a silver content of 5.3 at.%, while in ambient air, the wear resistance was higher for the coating with 7.9 at.% Ag. Further increasing the Ag content (21.0 at.%), there is a very large loss in hardness although possessing low friction coefficient both in ambient air and in artificial seawater.

3. Thin film growth techniques

The thin films growth can be carried out through several techniques where they can be deposited as vapor, liquid, solid phases, or a combination of these phases through plasma enhancement, ion bombardment, self-assembly, chemical treatment, among others [19, 20]. In this chapter, four thin film deposition techniques will be presented: magnetron sputtering, cathodic cage plasma deposition (CCPD), PECVD, and layer-by-layer.

3.1 Magnetron sputtering

Within the PVD processes, the magnetron sputtering technique is one of the most used in research with nanocomposites [21, 22]. The conventional sputtering technique has very low deposition rates, and an alternative found to increase this rate is the magnetron sputtering technique [23, 24].

The mentioned fact occurs because magnets are positioned in the vicinity of the target to act as electron traps. Due to electron trapping in the region close to the target, the plasma will also be restricted to this region resulting in a higher sputtering rate [24].

Figure 1 shows the principle of sputtering with a planar magnetron where it is possible to observe the confinement of electrons in the region close to the magnet. During the process, the target is intentionally positioned close to this region to increase the deposition rate.

The advantages of this technique include low plasma impedance and thus high discharge currents from 1 A to 100 A (depending on cathode length) at typical voltages around 500 V; deposition rates in the range from 1 to 10 nm/s; low thermal load to the substrate; dense and well-adherent coatings; large variety of film materials available (nearly all metals and compounds). Some disadvantages of this technique include improvement requirement of target utilization; stabilization of the reactive process in the transition regime [25]. The magnetron sputtering technique can be applied for wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings, and coatings with specific optical or electrical properties [21–25]. The **Figure 2** shows schematic diagram of magnetron sputtering process.

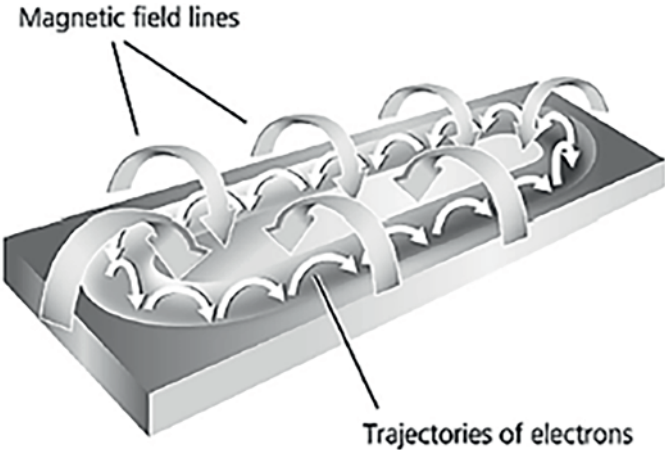

Figure 1.
The principle of magnetron sputtering [25].

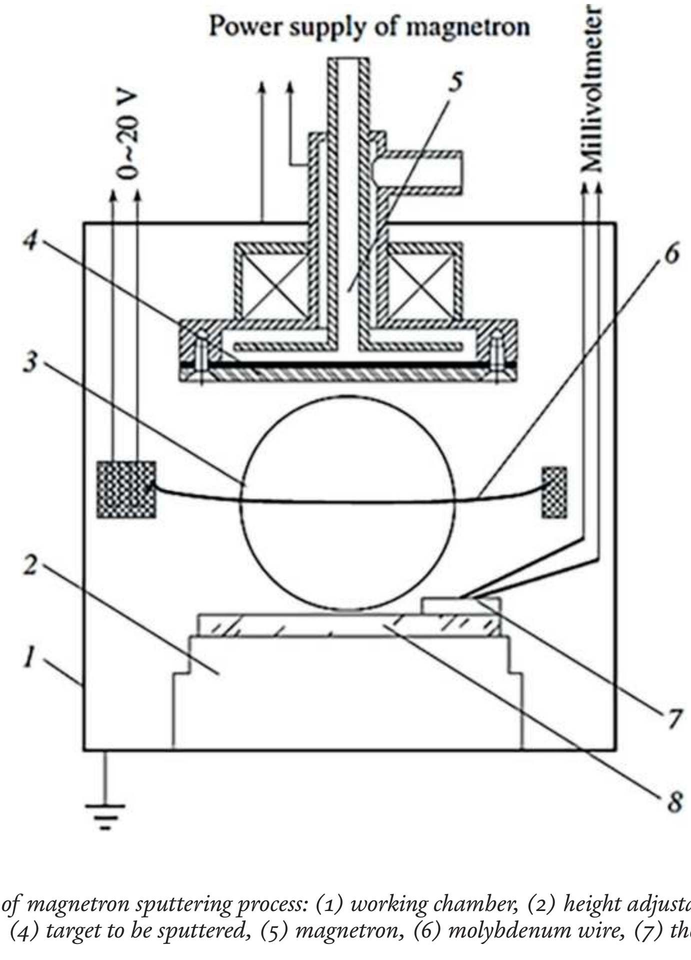

Figure 2.
Schematic diagram of magnetron sputtering process: (1) working chamber, (2) height adjustable substrate holder, (3) quartz window, (4) target to be sputtered, (5) magnetron, (6) molybdenum wire, (7) thermocouple, and (8) substrate [24].

3.2 Cathodic cage plasma deposition (CCPD)

This technique is a variation of the reactive sputtering process; it consists of the use of a cage with well-defined geometry where the effect of cylindrical multicathodes is used to obtain coatings and three-dimensional surface treatments. In this technique, the cage functions as a cathode in which a potential difference that acts only in the cage is applied (for the case of deposition), because the sample remains isolated on an alumina disc [26–28]. **Figure 3** shows a schematic representation of the spatial arrangement of the sample and cage in the sample holder.

During treatment, it is possible to observe the formation of plasma on the surface of the cage as well as the luminous intensification of the cage in each hole of the cage. **Figure 4a** shows the visual aspect of the plasma formed on the cathodic cage.

The process is carried out in a reactor and conducted to very low working pressures (~ 2.5 mbar) with controlled treatment atmosphere (Ar, H_2, N_2, O, for example). During the sputtering process, the atoms ejected from the surface of the cage can combine with the reactive gas of the plasma atmosphere, forming compounds that deposit on the surface of the sample. In this sense, the cage must be made of the material to be deposited. The technique of CCPD allows both nitriding and deposition of a thin film on a substrate and thus a better adhesion between the film and the substrate [30].

For the case of NTF, an example of arrangement for deposition of thin films would be the use of a graphite cylinder with titanium cover. **Figure 4b** shows the example of the cited arrangement. In this example, the film will present the synergism between the properties of the C from the graphite cylinder representing the soft phase and the Ti due to the cover, representing the hard phase.

The advantages of this technique include treatment of parts with complex geometries; minimizing the edge effect and opening of arcs in relation to the conventional sputtering technique; obtaining uniform layers; allowing to carry out both the nitriding process and the deposition of thin films. Some disadvantages of this technique include requiring a vacuum procedure; the production process of the cages can be complex depending on the type of material. The CCPD technique can be used for oxide and nitride deposition, deposition, desorption, and diffusion. It allows the deposition of thin films of high hardness, high wear, and corrosion resistance [26–30].

3.3 Plasma-enhanced chemical vapor deposition (PECVD)

The PECVD technique is a form of CVD, which uses plasma to enhance/enable the reactivity of organic/inorganic chemical monomers for the deposition of thin films. In this technique, it is possible to use precursors in solid, liquid, or gaseous form for

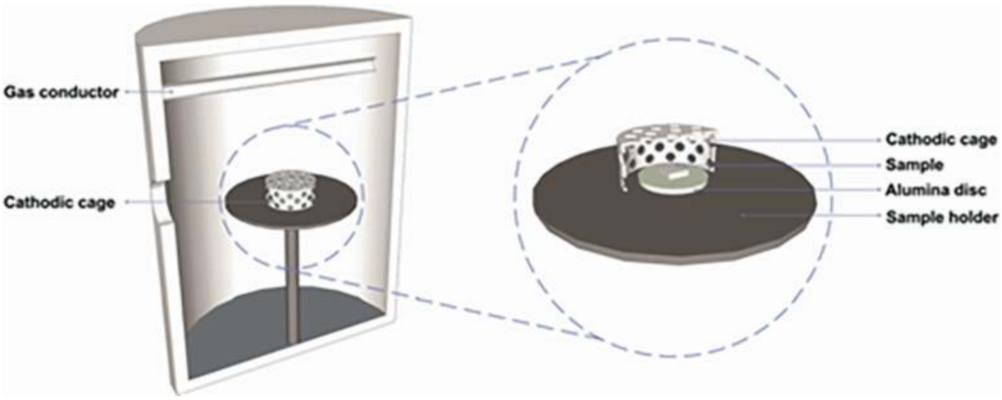

Figure 3.
Sample and cathodic cage arrangement over the sample holder [29].

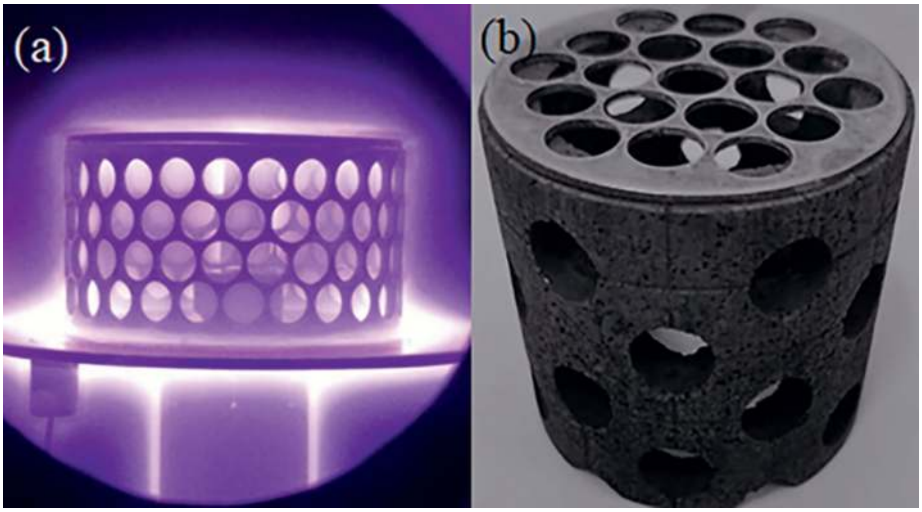

Figure 4.
(a) Visual aspect of plasma formation on the surface of the cage. and (b) Example of arrangement for treatment by CCPD (graphite cylinder and Ti cover).

the deposition of thin films [31]. The precursors are typically decomposed by temperature or a combination of temperature and plasma chemistry [32].

In conventional CVD processes, high treatment temperatures are used and the use of plasma by PECVD technique activates the chemical vapor precursor, and it allows the deposition to progress at a lower temperature than is normally used for CVD [32].

A schematic representation of the standard PECVD thin film deposition process is shown in **Figure 5**.

The advantages of this technique include highly cross-linked, uniform, robust films with good surface adhesion; compatible with solid, liquid, and gas monomers; leading to higher deposition rates and high density of cross-linking; working with low and atmospheric pressures. As a disadvantage, this technique may suffer from high internal stresses, which can cause film delamination. This technique can be used for highly cross-linked, uniform, robust films with good surface adhesion; corrosion and wear resistance; deposition of various types of materials with different microstructures [31–34].

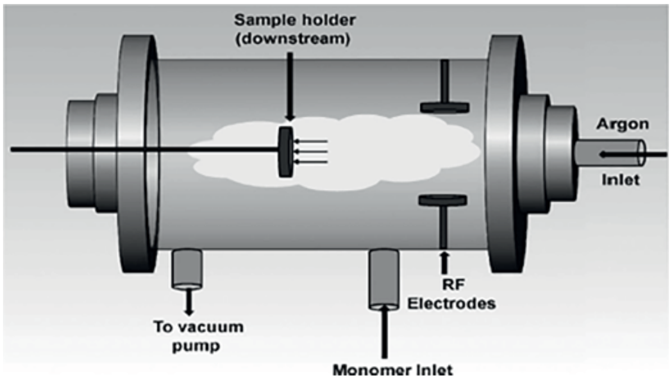

Figure 5.
Schematic representation of a standard chamber used in the PECVD process [31].

3.4 Layer-by-layer (LbL)

Layer-by-layer (LbL) assembly is a prevalent method for coating substrates with functional thin films [35]. It can be applied for coating substrates with polymers, colloids, biomolecules, and even cells, which offers superior control and versatility when compared with other thin film deposition techniques [36]. The versatility is due to the possibility of integrating different materials, creating defined layer sequences, orienting anisotropic materials within layers [37].

The process is based on a sequence of steps that leads to the exposure of the substrate to the material that will be deposited on the thin film. In general, more than one coating layer is formed, that is, multilayer thin films are obtained. Some technologies for films deposition by LbL include immersive; spin; spray; electromagnetic; and fluidic assembly [35, 36]. Immersive LbL assembly is the most widely used method, and it is typically performed by manually immersing a planar substrate into a solution of the desired material followed by three washing steps to remove unbound material [35]. **Figure 6** shows a schematic representation of the immersive LbL assembly method.

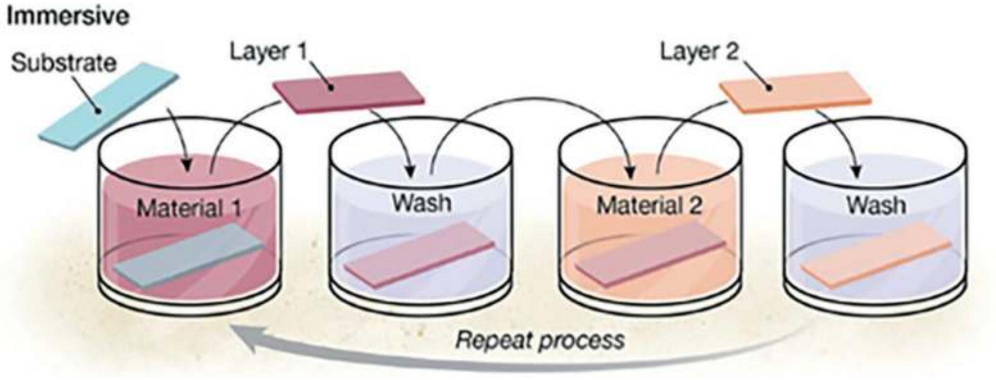

Figure 6.
Schematic representation of immersive LbL assembly. Adapted from Richardson et al. [35].

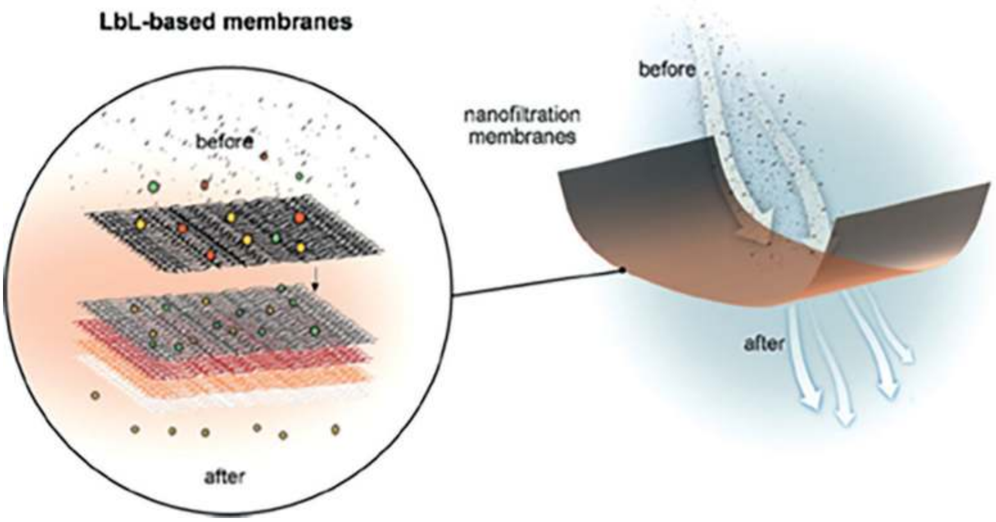

Figure 7.
Layer-by-layer assembly used for membranes for gases and liquids separation [37].

Technique	Advantages	Disadvantages	Applications	References
Magnetron Sputtering	Low plasma impedance/deposition rates in the range from 1 to 10 nm/s/low thermal load to the substrate/dense and well-adherent coatings/large variety of film materials available (nearly all metals and compounds)	Improvement requirement of target utilization/stabilization of the reactive process in the transition regime	Hard, wear-resistant coatings/low friction coatings/corrosion-resistant coatings/decorative coatings/coatings with specific optical or electrical properties	[21–25]
CCPD	Treatment of parts with complex geometries/minimizes the edge effect/uniform layers/both nitriding and deposition process/low deposition temperature	Requires a vacuum procedure/production process of cages can be complex	Oxide and nitride deposition/deposition/desorption and diffusion/thin films of high hardness/high wear and corrosion resistance	[26–30]
PECVD	Highly cross-linked, uniform, robust films with good surface adhesion/compatible with solid, liquid, and gas monomers/leads to higher deposition rates and high density of cross-linking/works with low and atmospheric pressures	May suffer from high internal stresses, which can cause film delamination	Highly cross-linked, uniform, robust films with good surface adhesion/corrosion and wear resistance/deposition of various types of materials with different microstructures	[31–34]
LbL	Simple and versatile process/applied straightforwardly on almost any surface/nanoscale functional films/applied to planar surfaces, spherical particles, inside complex geometries	Requires time for atomistic relaxation at the interfaces	LEDs and OLEDs device manufacturing/water purification/solar cells; optics/batteries/drug delivery/tissue engineering; functional fabrics/antibacterial coatings/biosensors/photonics applications/liquid or gas separation	[35–39]

Table 1.
Summary of some thin film deposition techniques used for NTF growth showing the main advantages, disadvantages, and applications.

The advantages of this technique include simple and versatile process; applied straightforwardly on almost any surface; nanoscale functional films; applied to planar surfaces, spherical particles, inside pores, and onto other more complex geometries; among others. The LbL process requires time for atomistic relaxation at the interfaces. may suffer from high internal stresses, which can cause film delamination. This technique can be used for light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs) device manufacturing; water purification; solar cells; optics; batteries; drug delivery; tissue engineering; functional fabrics; antibacterial coatings; biosensors; photonics applications; liquid or gas separation; among others [35–39].

Schematic representation of an application of coating deposited by the LbL technique with the function of membrane for liquid or gas separation is shown in **Figure 7**.

3.5 Summary table

The thin film deposition techniques presented in this chapter present advantages, disadvantages, and several applications that are commented in **Table 1**.

4. Conclusion

Nanocomposite coatings can be applied in several areas to improve properties such as hardness, wear, and corrosion resistance, tribological properties, among others. The synergistic effect exhibited in nanocomposite thin films shows the importance of mixing materials where specific properties are obtained but which would be difficult or even impossible for individual materials to exhibit. To obtain the synergism of the properties, it is necessary to establish the appropriate treatment parameters and select the most appropriate film deposition technique for a given application. Thin film growth techniques can be performed by several routes, which leads to the development of many variations in thin film deposition methods. Some of these methods/techniques were seen in this chapter and have application field in several areas. We hope that this chapter stimulates research on nanocomposites thin films in terms of studying their properties, developing, or improving thin films and the techniques for growing these films.

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Conflict of interest

The authors declare no conflict of interest.

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