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Chapter 8

Advance Deposition Techniques for Thin Film and Coating

Asim Jilani , Mohamed Shaaban Abdel-wahab and Ahmed Hosny Hammad

Additional information is available at the end of the chapter

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Abstract

Thin films have a great impact on the modern era of technology. Thin films are considered as backbone for advanced applications in the various fields such as optical devices, environmental applications, telecommunications devices, energy storage devices, and so on . The crucial issue for all applications of thin films depends on their morphology and the stability. The morphology of the thin films strongly hinges on deposition techniques. Thin films can be deposited by the physical and chemical routes. In this chapter, we discuss some advance techniques and principles of thin-film depositions. The vacuum thermal evaporation technique, electron beam evaporation, pulsed-layer deposition, direct current/radio frequency magnetron sputtering, and chemical route deposition systems will be discussed in detail.

Keywords: thin films, coatings, physical deposition, sol-gel, chemical bath deposition, chemical route

1. Introduction

Nowadays, most of the technologies are used for minimizing the materials into nano-size as well as nano-thickness leading to the emergence of new and unique behaviors of such materials in optical, electrical, optoelectronic, dielectric applications, and so on. Hence, a new branch of science/materials science is called thin films or coatings. Thin film can be defined as a thin layer of material, where the thickness is varied from several nanometers to few micrometers. Like all materials, the structure of thin films is divided into amorphous and polycrystalline structure depending on the preparation conditions as well as the material nature. Thin films comprise

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two parts: the layer and the substrate where the films are deposited on it. Also, thin films can be composed of different layers such as thin-film solar cells, electrochromic cells, and so on.

In order to obtain thin films with good quality, there are two common deposition techniques: physical and chemical depositions. It can be summarized as shown in **Table 1**.

Physical deposition	**Chemical deposition**
1. Evaporation techniques	**1. Sol-gel technique**
a. Vacuum thermal evaporation.	**2. Chemical bath deposition**
b. Electron beam evaporation.	**3. Spray pyrolysis technique**
c. Laser beam evaporation.	**4. Plating**
d. Arc evaporation.	**a.** Electroplating technique.
e. Molecular beam epitaxy.	**b.** Electroless deposition.
f. Ion plating evaporation.	**5. Chemical vapor deposition (CVD)**
2. Sputtering techniques	**a.** Low pressure (LPCVD)
a. Direct current sputtering (DC sputtering).	**b.** Plasma enhanced (PECVD)
b. Radio frequency sputtering (RF sputtering).	**c.** Atomic layer deposition (ALD)

Table 1. Methods of thin films deposition.

This chapter describes some common deposition techniques for thin films in detail to give some confidential and important points of view for readers on how thin films can be formed.

2. Physical deposition techniques

2.1. Evaporation techniques

Evaporation methods are considered as the common deposition of materials in the form of thin-layer films. The general mechanism of these methods is obtained by changing the phase of the material from solid phase to vapor phase and converting again to solid phase on the specific substrate. It takes place under vacuum or controlled atmospheric condition.

2.1.1. Vacuum thermal evaporation technique

Vacuum evaporation technique is the simplest technique used to prepare amorphous thin films especially chalcogenide films such as CdSSe [1], MnS [2], Ge-Te-Ga [3], and so on. In general, chalcogenide materials can be used for memory-switching applications [4, 5], phase-change materials [6, 7], and solar applications [8].

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The technique of thermal evaporation is strongly dependent on two parameters: thermally vaporized material and applying a potential difference to the substrate under medium- or higher-vacuum level ranging from 10^{-5} to 10^{-9} mbar. The schematic diagram for thermal evaporation is shown in **Figure 1** taken from elsewhere [9].

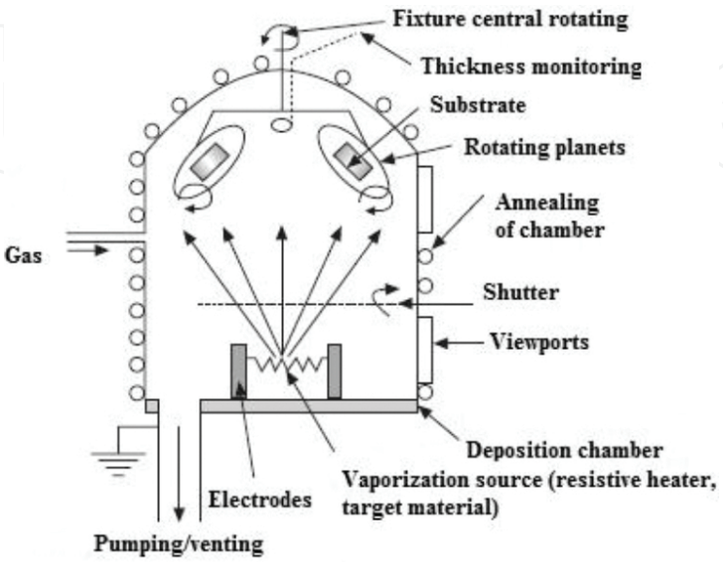


Figure 1. Schematic of thermal evaporation system with substrate holder on a planetary rotation system and directly above the evaporating source.

2.1.2. Electron beam evaporation

This type of evaporation is another method of physical deposition where the intensive beam of electrons is generated from a filament and steered through both electric and magnetic fields to hit the target and vaporize it under vacuum environment as shown in **Figure 2**. Thin films prepared by electron beam evaporation are of good quality and purity [10].

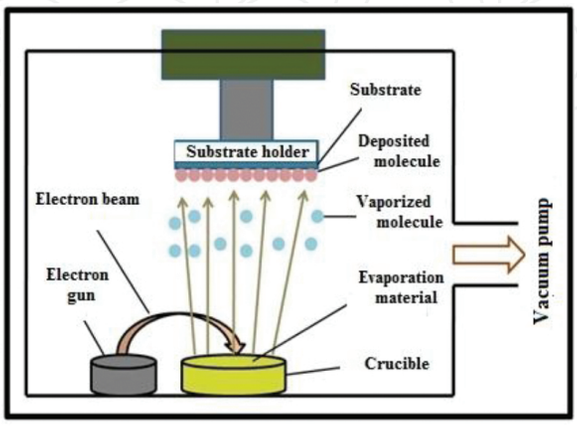


Figure 2. Schematic diagram of electron beam evaporation.

Large categories of materials can be prepared by electron beam evaporation technique [11] such as amorphous and crystalline semiconductors [12], metals [13], oxides [14], and molecular materials [15].

2.1.3. Laser beam evaporation (pulsed-laser deposition)

Pulsed-laser deposition (PLD) is another physical deposition technique to deposit the thin-film-coating system [16]. During the thin-film deposition process, the laser beam is used to ablate the material for depositing the thin films inside a vacuum chamber as shown in **Figure 3**.

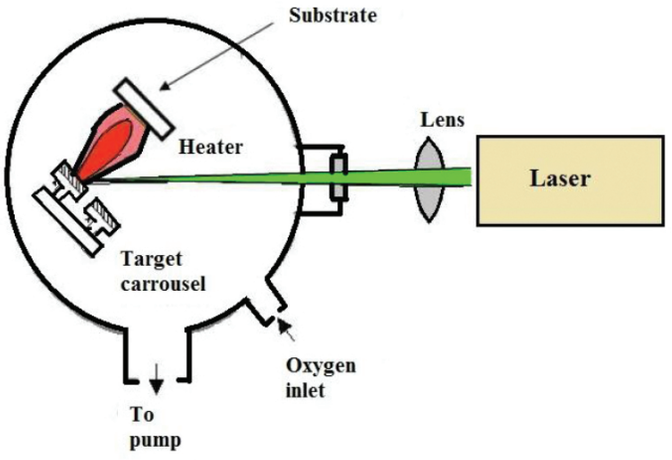


Figure 3. Schematic of pulsed-laser deposition taken from Ref. [17].

Different kinds of laser sources are being used to ablate the target. The most common sources are Nd-YAG laser, KrF (248 nm), and XeCl (308 nm). When the laser beam strikes the target material, it produces the plume which could deposit on the various substrates. The created plume may contain neural- and ground-state atoms and ionized species. In the case of metal oxide thin films, oxygen is used to deposit the oxides of metals [18]. The thin-film quality from the PLD depends on the various parameters such as wavelength of the laser, energy, ambient gas pressure, pulsed duration, and the distance of the target to the substrate [19]. The ablation process during the deposition may control and monitor by using laser-induced fluorescence [20], laser ablation molecular isotopic spectroscopy [21], and optical emission spectroscopy [22]. The morphology of the deposited thin films is also affected by the substrate temperature. The coating of thin films through PLD follows three modes: Frank–-van der Merwe, Stranski–-Krastanov, and Volmer–-Weber [23, 24]. PLD has some advantages over other physical deposition systems because of its fast deposition time and its compatibility to oxygen and other inert gases.

2.2. Sputtering technique

Sputtering technique is mostly used for depositing metal and oxide films by controlling the crystalline structure and surface roughness [11, 25]. The simple form of the sputtering system

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consists of an evacuated chamber containing metallic anode and cathode [25] in order to obtain a glow discharge in the residual gas in the chamber. Also, an applied voltage in the order of several KeV with pressure more than 0.01 mbar is sufficient for film deposition. The sputtering process depends on the bombardment of the ions released from the discharge to the molecules in the cathode leading to the liberation of the molecules from the cathode with higher kinetic energy. The atomic weight of the bombarding ions should be nearly to that of the target material in order to maximize the momentum transfer. These molecules move in straight lines and strike on the anode or on the substrate to form a dense thin film [25]. The diagram of the sputtering system is shown in **Figure 4**.

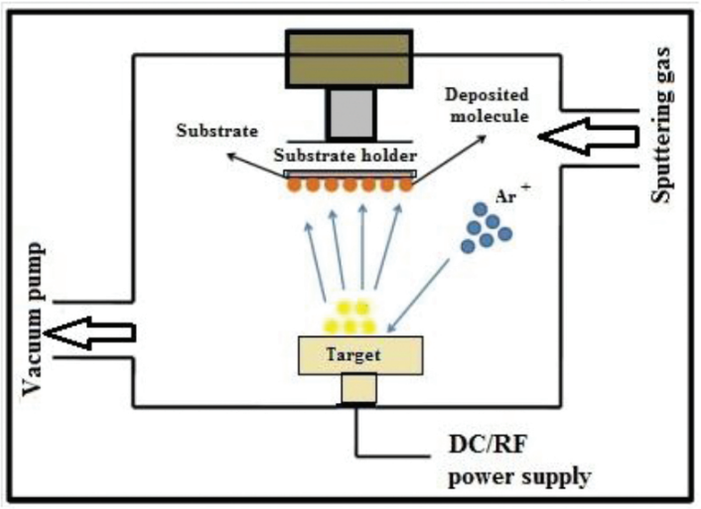


Figure 4. Sputtering system diagram.

The process of sputtering has several advantages. High-melting point materials can be easily formed by sputtering. The deposited films have composition similar to the composition of the starting materials. Sputtering technique is available to use for ultrahigh vacuum applications. The sputtering sources are compatible with reactive gases such as oxygen. Contrarily,' thick coatings cannot be obtained and there is a difficulty to deposit uniformly on complex shapes.

There are two common types of sputtering process: direct current (DC) and radio frequency (RF) sputtering. The first one depends on DC power, which is generally used with electrically conductive target materials. It is easy to control with low-cost option. The RF sputtering uses RF power for most dielectric materials. A common example for sputtered films is aluminum nitride films. These films were prepared by both DC- and RF-sputtering technique, and their structure and optical properties were compared [26, 27].

3. Chemical deposition techniques

Although the production of thin films via physical methods as previously described gives good quality and functionalizes properties, it is highly expensive and perhaps requires a large

amount of material target. Since the need to produce good-quality thin films with low economical cost is necessary, chemical deposition techniques are widely used globally. These techniques are cheap producing good-quality films. Most of them do not require expensive equipment. The chemical deposition is strongly dependent on the chemistry of solutions, pH value, viscosity, and so on. The most common chemical deposition has been obtained via sol-gel route, chemical bath deposition, electrodeposition, chemical vapor deposition (CVD), and spray pyrolysis technique. This section is concerned only on sol-gel and chemical bath deposition techniques because they can form good film quality with low equipment requirement.

3.1. Sol-gel technique

The sol-gel technique is broadly used for the synthesis of oxide materials [28]. Sol-gel process is one of the famous wet-chemical methods. It works under lower-temperature processing and gives better homogeneity for multicomponent materials. The word "'sol"' means the formation of a colloidal suspension and 'gel' means the conversion of 'sol' to viscous gels or solid materials. Two routes are used to prepare transition metal oxides (TMOs) as follows:

a. Preparing of inorganic precursors via inorganic salts in aqueous solution.

b. Preparing of metal alkoxide precursors via metal alkoxides in nonaqueous solvents.

In this section, we are concerned on the famous route "the metal alkoxide precursor solution by an alcoholic solution."

3.1.1. Alkoxide precursors in organic solvents

The sol-gel technique is based on the polycondensation of metal alkoxides **M (OR)**$_z$ in which **R** represents an alkyl group (R = CH_3, C_2H_5, …) and **z** is the oxidation state of the metal atom $\mathbf{M}^{z+}$ [29]. It can be synthesized via the reaction of metal salt (chloride, acetate, nitrate, etc.) with alcohol as follows:

$$\left(CH_3COO\right)_z M + zROH \rightarrow M\left(OR\right)_z + zCH_3COOH \quad (1)$$

After this process, two important steps should be involved:

1. *Hydrolysis:* this step is aimed to form reactive **M-OH** groups [30]:

$$M — OR + H_2O \rightarrow M — OH + ROH \quad (2)$$

2. *Condensation*: condensation is the second step after hydrolysis leading to the departure of a water molecule. The process of condensation can be either olation process or oxolation process.

- *Olation:* a hydroxyl bridge ("ol" bridge) is formed between two metal centers as shown in **Figure 5**.

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- *Oxolation:* oxolation is a reaction in which an oxo bridge (—O—) is created between two metal centers. When the metal is coordinately unsaturated, oxolation with rapid kinetics leads to edge- or face-shared polyhedral as shown in **Figure 6**.

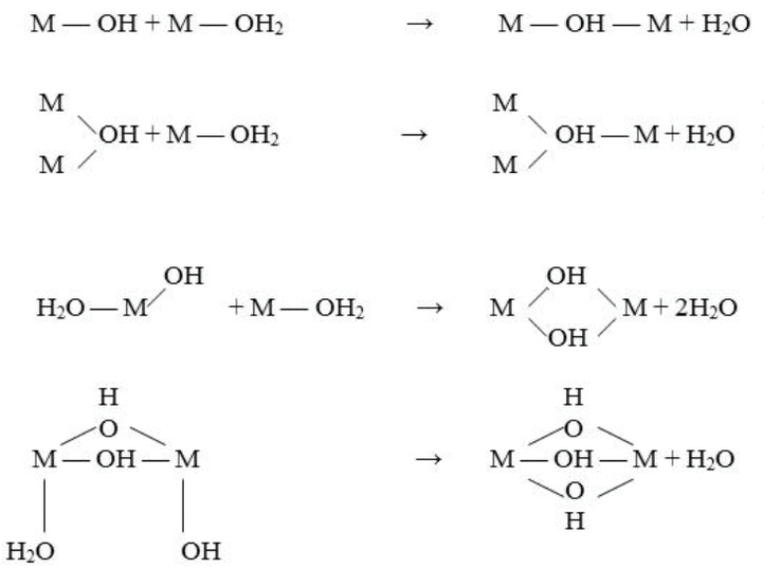


Figure 5. Several types of OH bridges can be formed by olation condensation process.

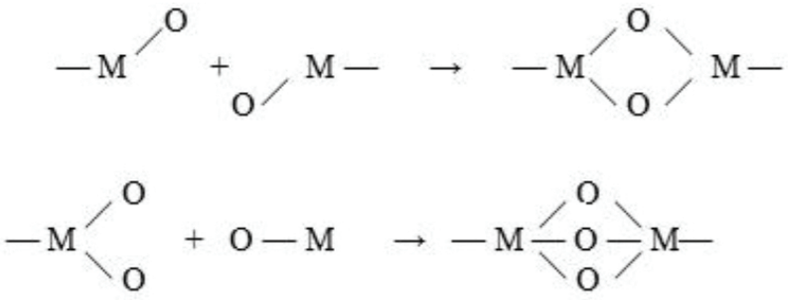


Figure 6. Formation of oxo-bridging links between two metal centers.

Hence, olation process occurs mainly for lower oxidation states of cations **($z < 4$),** whereas oxolation is mainly observed with cations of high oxidation state **($z > 4$)** [29, 31].

The previous description provides the preparation of the precursor solution. In order to make thin film from the precursor solution, there are two processes for the production of the films, that is, dip-coating and spin-coating techniques.

3.1.2. Dip-coating technique

Dip-coating technique is almost used to fabricate transparent layers of oxides on a transparent substrate with a high degree of planarity and surface quality [32]. Other substrates are also

possible to use. Well-defined film thicknesses up to 1 μm can be deposited. Several additive layers can be superimposed.

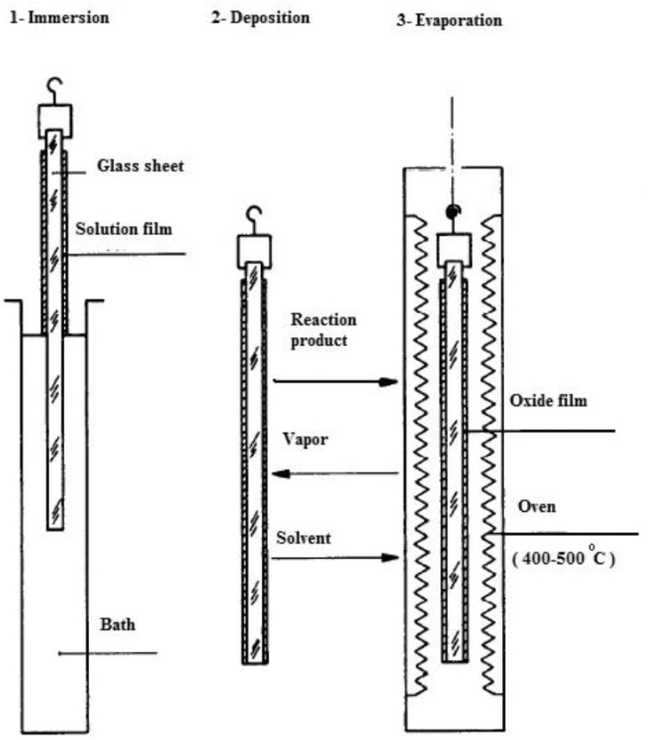


Figure 7. Dip-coating process levels.

Scriven [33] described the dip-coating process in five stages: immersion, start-up, deposition, drainage, and evaporation. Hence, the evaporation normally accompanies the start-up, deposition, and drainage steps as shown in **Figure 7**.

3.1.3. Spin-coating technique

Another technique is also available for usage after the precursor solution is prepared known as spin coating or spinning. The solution is dripped onto a spinning substrate and spreads evenly. The spinning process is most suitable for the coating of small disks or lenses but is not very economical. The process of spinning film can be described as shown in **Figure 8**.

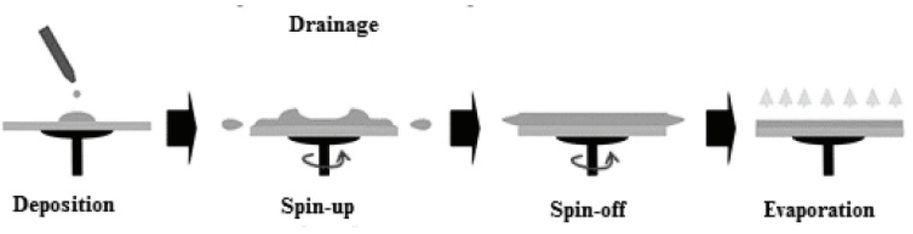


Figure 8. Spin-coating process.

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3.2. Chemical bath deposition technique

Chemical bath deposition method is also known as solution growth technique or controlled precipitations [34]. It is the oldest method to deposit films on a substrate. Solution growth technique is mostly used to prepare chalcogenide films as well as metal oxide films. Also, the deposition can be performed at lower temperatures. In the solution growth method, the precursor solution of metal ions must be complexed by ligands. The complex solution is almost obtained with ammonia solution, triethanol amine, ethylene-diamine-tetraacetic acid (EDTA), citric acid, and so on. When the complexation is completed, the addition of the anions should take place. These anions come from the thiourea, thioacetamide, thiosulfate, and sodium Sulfide solutions [34] as sources of sulfur anions or selenourea and sodium selenosalfate for selenium anions to deposit the chalcogenides. Substrates are put in vertical, horizontal, or specific position inside the solution and left until the desired film thickness is obtained. The deposition of oxide films is quite different than chalcogenides. After making the complexation by controlling the pH value, the substrate is immersed in the solution under the desired temperature varied in the range 60°–100 °C to deposit in most cases the metal hydroxide films. The hydroxide film can then be transferred to oxide by the annealing process. **Figure 9** represents the simple chemical bath deposition method taken from Ref. [34]. Indeed, much

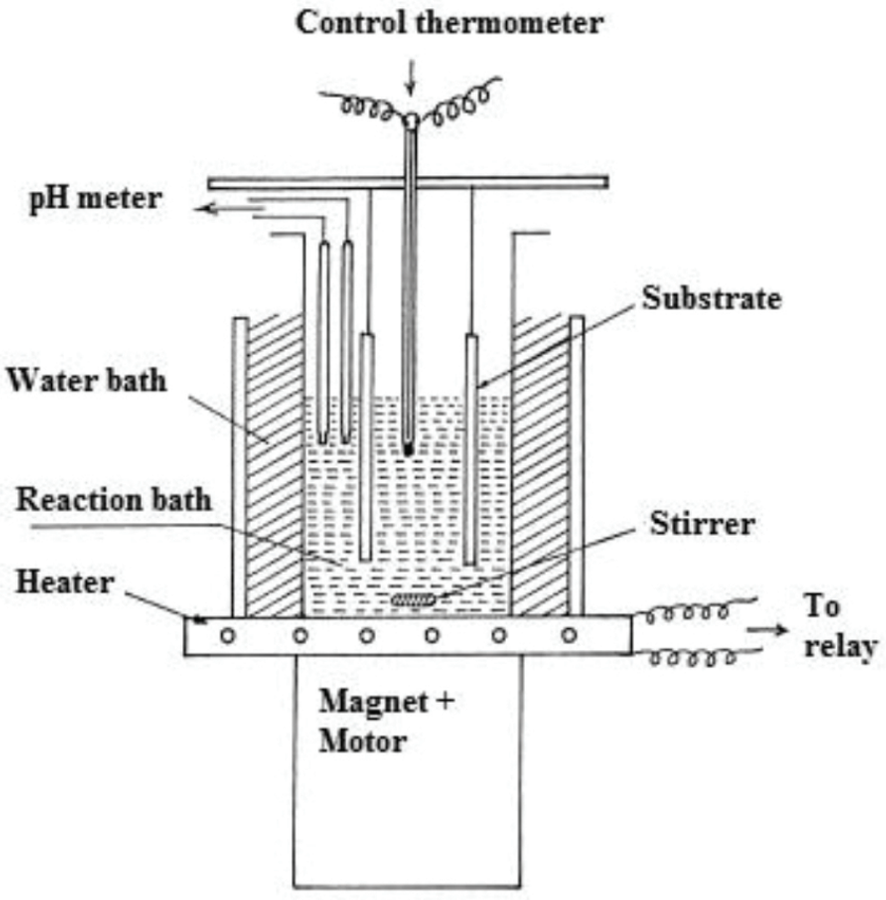


Figure 9. Home-made chemical bath deposition technique.

reviews and literature, which describes the chemical bath deposition for both chalcogenide and oxide films, are found elsewhere [34–36].

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References

[1] Hassanien AS, Akl AA. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. Superlattices Microstruct. 2016;89:153–169. DOI: 10.1016/j.spmi.2015.10.044

[2] Hannachi A, Segura A, Meherzi HM. Growth of manganese sulfide (α-MnS) thin films by thermal vacuum evaporation: Structural, morphological, optical properties. Mater. Chem. Phys. 2016;181:326–332. DOI: 10.1016/j.matchemphys.2016.06.066

[3] Wang G, Nie Q, Shen X, Chen F, Li J, Zhang W, Xu T, Dai S. Phase change and optical band gap behaviour of Ge-Te-Ga thin films prepared by thermal evaporation. Vacuum. 2012;86(10):1572–1575. DOI: 10.1016/j.vacuum.2012.03.036

[4] Malligavathy M, Kumar RTA, Das C, Asokan S, Padiyan DP. Growth and characteristics of amorphous Sb_2Se_3 thin films of various thicknesses for memory switching applications. J. Non-Cryst. Solids. 2015;429:93–97. DOI: 10.1016/j.jnoncrysol.2015.08.038

[5] Kumar RTA, Das C, Lekha PC, Asokan S, Sanjeeviraja C, Padiyan DP. Enhancement in threshold voltage with thickness in memory switch fabricated using $GeSe_{1.5}S_{0.5}$ thin films. J. Alloys Compd. 2014;615:629–635. DOI: 10.1016/j.jallcom.2014.07.068

[6] Rafea MA, Farid H. Phase change and optical band gap behaviour of $Se_{0.8}S_{0.2}$ chalcogenide glass films. Mater. Chem. Phys. 2009;113(2–3):868–872. DOI: 10.1016/j.matchemphys.2008.08.045

[7] Sangeetha BG, Joseph CM, Suresh K. Preparation and characterization of $Ge_1Sb_2Te_4$ thin films for phase change memory applications. Microelect. Eng. 2014;127:77–80. DOI: 10.1016/j.mee.2014.04.032

[8] Salomé PMP, Alvarez HR, Sadewasser S. Incorporation of alkali metals in chalcogenide solar cells. Sol. Ener. Mater. Sol. Cells. 2015;143:9–20. DOI: 10.1016/j.solmat.2015.06.011

[9] Orava J, Kohoutek T, Wagner T. Deposition techniques for chalcogenide thin films. In: Adam JL, Zhang X, editors. Chalcogenide Glasses Preparations, Properties and Applications. Oxford: Woodhead Publishing Series; 2014. DOI: 10.1533/9780857093561.1.265

[10] Lokhande AC, Chalapathy RBV, He M, Jo E, Gang M, Pawar SA, Lokhande CD, Kim JH. Development of Cu_2SnS_3 (CTS) thin film solar cells by physical techniques: A status review. Sol. Ener. Mater. Sol. Cells. 2016;153:84–107. DOI: 10.1016/j.solmat.2016.04.003

[11] Barranco A, Borras A, Elipe ARG, Palmero A. Perspectives on oblique angle deposition of thin films: From fundamentals to devices. Progress Mater. Sci. 2016;76:59–153. DOI: 10.1016/j.pmatsci.2015.06.003

[12] Merkel JJ, Sontheimer T, Rech B, Becker C. Directional growth and crystallization of silicon thin films prepared by electron-beam evaporation on oblique and textured surfaces. J. Cryst. Growth. 2013;367:126–130. DOI: 10.1016/j.jcrysgro.2012.12.037

[13] Mukherjee S, Gall D. Structure zone model for extreme shadowing conditions. Thin Solid Films. 2013;527:158–163. DOI: 10.1016/j.tsf.2012.11.007

[14] Schulz U, Terry SG, Levi CG. Microstructure and texture of EB-PVD TBCs grown under different rotation modes. Mater. Sci. Eng. A. 2003;360(1–2):319–329. DOI: 10.1016/S0921-5093(03)00470-2

[15] Yang B, Duan H, Zhou C, Gao Y, Yang J. Ordered nanocolumn- array organic semiconductor thin films with controllable molecular orientation. Appl. Surf. Sci. 2013;286:104–108. DOI: 10.1016/j.apsusc.2013.09.028

[16] Lorenz M, Rao MSR. 25 years of pulsed laser deposition. J. Phys. D. Appl. Phys. 2014;47:030301–030303. DOI: 10.1088/0022-3727/47/3/030301

[17] Rainer W. Electronic Materials Research Laboratory [Internet]. Available fromml: http://www.emrl.de/r_m_1.html

[18] Lowndes DH, Geohegan DB, Puretzky AA, Rouleau CM. Synthesis of novel thin film materials by pulsed laser deposition. Science. 1996; 273(5277):898–903. DOI: 10.1126/science.273.5277.898.

[19] Ashfold MNR, Claeyssens F, Fuge GM, Henley SJ. Pulsed laser ablation and deposition of thin films. Chem. Soc. Rev. 2004;33(1):23–31. DOI: 10.1039/B207644F

[20] Lynds L, Weinberger BR, Potrepka DM, Peterson GG, Lindsay MP. High temperature superconducting thin films: The physics of pulsed laser ablation. Physica C. 1989;159(1–2):61–69. DOI: 10.1016/0921-4534(89)90104-4

[21] Russo RE, Mao X, Gonzalez JJ, Zorba V, Yoo J . Laser ablation in analytical chemistry. Anal. Chem. 2013;85(13):6162–6177. DOI: 10.1021/ac4005327

[22] Geyer TJ, Weimer WA. Parametric effects on plasma emission produced during excimer laser ablation of $YBa_2Cu_3O_{7-x}$. Appl. Spectros. 1990;44(10):1659–1664. DOI: 10.1366/0003702904417454

[23] Karl H, Stritzker B. Reflection high-energy electron diffraction oscillations modulated by laser pulse deposition $YBa_2Cu_3O_{7-x}$. Phys. Rev. Lett. 1992;69(20):2939–2942. DOI: 10.1103/PhysRevLett.69.2939

[24] Lippmaa M, Nakagawa N, Kawasaki M, Ohashi S, Inaguma, Itoh M, Koinuma H. Step-flow growth of SrTiO3 thin films with a dielectric constant exceeding 104. Appl. Phys. Lett. 1999; 74(23):3543–3545. DOI: 10.1063/1.124155

[25] Angusmacleod H. Recent developments in deposition techniques for optical thin films and coatings. In: Piegari A, Flory F, editors. Optical Thin Films and Coatings from Materials to Applications. Oxford: Woodhead Publishing Series; 2013. p. 3–-25. DOI: 10.1533/9780857097316.1.3

[26] Morosanu C, Dumitru V, Cimpoiasu E, Nenu C. Comparison between DC and RF magnetron sputtered aluminum nitride films. In: Prelas MA, Benedictus A, Lin LTS, Popovici G, Gielisse P, editors. Diamond Based Composites and Related Materials. 1st ed. Petersburg, Russia: Springer Science+Business Media Dardrecht; 1997. p. 127–132. DOI: 10.1007/978-94-011-5592-2_9

[27] Dumitru V, Morosanu C, Sandu V, Stoica A. Optical and structural differences between RF and DC Al_xN_y magnetron sputtered films. Thin Solid Films. 2000;359:17–20. DOI: 10.1016/S0040-6090(99)00726-9

[28] Livage J, Sanchez C, Henry M, Doeuff S. The chemistry of sol-gel process. Solid State Ionics. 1989;32–33(2):633–638. DOI: 10.1016/0167-2738(89)90338-X

[29] Livage J, Ganguli D. Sol-gel electrochromic coatings and devices: A review. Sol. Ener. Mater. Sol. Cells. 2001;68:365–381. DOI: 10.1016/S0927-0248(00)00369-X

[30] Tjong SC, Chen H. Nanocrystalline materials and coatings. Mater. Sci. Eng. R. 2004;45(1–2):1–88. DOI: 10.1016/j.mser.2004.07.001

[31] Brinker CJ, Scherer GW. Sol-Gel Science. San Diego: Academic Press; 1990.

[32] Klein LC. Sol-Gel Technology for Thin Films, Fiber, Preform, Electronics and Specialty Shapes. Park Ridge, NJ, USA: Noyes Publications; 1987. DOI: 10.1002/pi.4980210420

[33] Scriven LE. Physics and applications of dip coating and spin coating. In: Brinker CJ, Clark DE, Ulrich DR, editors. Better Ceramics Through Chemistry. 3rd ed. Pittsburgh, PA: Materials Research Society; 1988. p. 712–729.

[34] Mane RS, Lokhande CD. Chemical deposition method for metal chalcogenide thin films. Mater. Chem. Phys. 2000;(1):1–31. DOI: 10.1016/S0254-0584(00)00217-0

[35] Pawar SM, Pawar BS, Kim JH, Joo OS, Lokhande CD. Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films. Curr. Appl. Phys. 2011;11(2): 117–161. DOI: 10.1016/S0254-0584(00)00217-0

[36] Hammad AH, Elmandouh ZS, Elmeleegi HA. Structure and some physical properties of chemically deposited nickel sulfide thin films. In: Proceedings of the 4th International Congress APMAS 2014; 24–27 April 2014; Fethiye, Turkey. Acta Phys. Polonica A: Polish Academy of Sciences Institute of Physics; 2015. p. 901–903. DOI: 10.12693/APhysPolA.127.901

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