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Physical and Chemical Methods: A Review on the Analysis of Deposition Parameters of Thin Film Preparation Methods

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Abstract: The purpose of this review article is to explain an analysis of the various thin film deposition parameters. A thin film is a very thin and useful layer with a thickness of a few nanometers to several micrometers. The process of forming thin films is known as deposition. There are many physical and chemical deposition methods available. This review paper elaborates on the various deposition methods and conditions such as thermal evaporation, electron beam evaporation, molecular-beam epitaxy, sputtering processes, chemical vapor deposition, sol-gel and spray pyrolysis technique etc., and the advantages and disadvantages of each method. Thin film materials are used in a wide variety of applications such as integrated circuits, semiconductor devices, protective glasses, photo conductors, switches, solar cells, superconducting switches, sensors, memories, hard coatings etc., From our review work, the various deposition parameters are analyzed it is clear that chemical methods are the most important methods for depositing thin films and producing high quality films at low cost.

Keywords: Thin films, Deposition conditions, Physical methods, Chemical methods, Spray pyrolysis, Electron beam evaporation, Chemical vapor deposition

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 [1]. A thin film is a very thin and useful layer with a thickness of a few nanometers to several micrometers. The simplest example of thin film is a mirror having film of metal on back that creates a reflective interface. Egyptian developed the first inorganic gold thin film during Bronze Age of thickness 3000 A^0 for decorating tomb and pyramids. For development in solid-state physics and chemistry field thin film characterization is the best way to success [2]. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of the film [3].

1.1 Parameters:

The important physical and chemical parameters of the thin film can be listed in the following table 1:

Table 1: Physical and chemical parameters of the thin films

Thin films	
Category	**Parameters**
Electrical	Conductivity; Resistivity; Permittivity; Stability under bias; Dielectric constant; Dielectric strength; Dielectric loss; Radiation hardness; Polarization; Electro migration.
Thermal	Thermal conductivity; Thermal fusion temperature; Coefficient of expansion; Stability; Volatility; vapor pressure.
Mechanical	Intrinsic, residual, and composite stress; Anisotropy; Adhesion; Density; Ductility; Elasticity; Fracture; Hardness.
Optical	Absorption; Birefringence; Dispersion; Refractive index; Spectral characteristics.
Magnetic	Coercive force; Permeability; Saturation flux density.
Chemical	Composition; Corrosion and erosion resistance; Carcinogenicity; Etch rate; Impurity barrier effectiveness; Reactivity with substrate and ambient; Thermodynamic stability; Toxicity.

1.2 Applications:

Thin films have been used in a wide variety of applications in a wide variety of fields. It can be summarized as shown in Figure 1:

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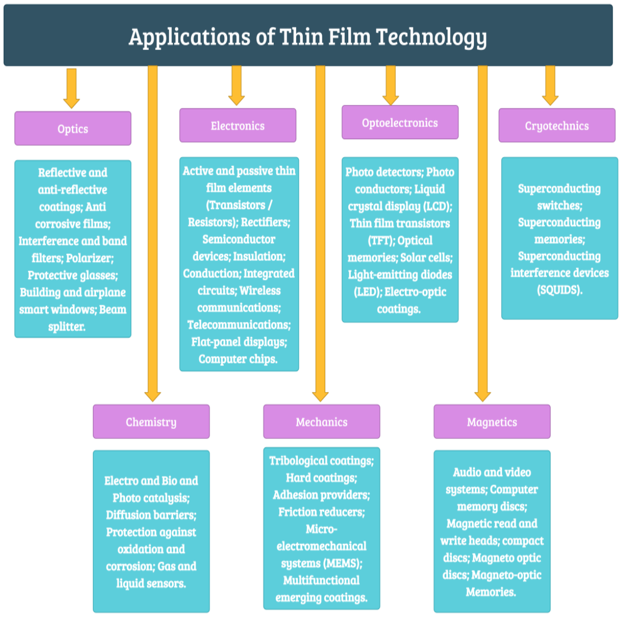

Fig 1: Applications of Thin Film Technology

2. Classification of Thin-Film Deposition Techniques:

Nowadays, thin films can be made in a variety of ways. The deposition techniques can be divided into physical and chemical methods as described in Figure 2.

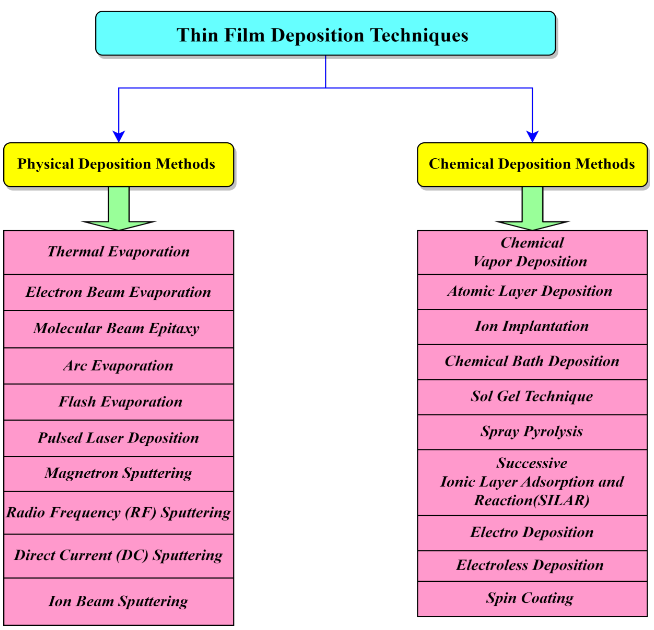

Fig. 2: Classifications of Thin-Film Deposition Techniques

2.1 Physical Deposition Methods (PDM):

There are many types of physical deposition methods, but in this review article, we focus on the some important PDM techniques.

2.1.1 Thermal evaporation:

Thermal evaporation is a well-known method for coating a thin layer in which the source material evaporates in a vacuum due to high temperature heating, which facilitates the vapor particles moving and directly reaching a substrate where these vapors again change to a solid state [4].

2.1.2 Electron beam (E-beam) evaporation:

The deposition chamber is evacuated to a pressure of 10^{-5} Torr or lower. The material to be evaporated is in the form of ingots or a compressed solid. The E-beam can be generated from electron guns by thermionic emission, field electron emission or the anodic arc method. The electron beam is accelerated to a high kinetic energy and focused on the starting material. The kinetic energy of the electrons is converted into thermal energy that will increase the surface temperature of the materials, leading to evaporation and deposition onto the substrate [5].

2.1.3 Molecular Beam Epitaxy:

Molecular Beam Epitaxy (MBE) is a thin film deposition process in which thermal beams of atoms or molecules react on the clean surface of a single- crystalline substrate, held at high temperatures under ultrahigh vacuum conditions, to form an epitaxial film. The vacuum requirements for the MBE process are typically better than 10^{-10} torr. This makes it possible to grow epitaxial films with high purity and excellent crystal quality at relatively low substrate temperatures [6].

2.1.4 Arc Vapor Deposition:

Arc vapor deposition uses a high current, low voltage arc to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions ("film ions") to the substrate surface. Arc vapor deposition is used to deposit hard and decorative coatings [7].

2.1.5 Flash Evaporation:

Liquid will be overheated and thereby evaporated when it enters into the environment with lower saturation pressure than that corresponding to its initial temperature. This phenomenon is called flash evaporation. Due to strong evaporation behavior, flash evaporation is accompanied with phase changes during absorption of heat. It has been used in more and more fields, including seawater desalination, national defense, health care, aerospace, and electronic industry [8].

2.1.6 Pulsed laser deposition:

If a solid or liquid is irradiated with an intense laser beam, a small amount of material on the surface is vaporized and ejected away from the sample. This vapor is a collection of atoms, molecules, ions and electrons, the exact ratio and kinetic energy of which is dependent on the laser parameters (intensity, wavelength, pulse width) and to some degree the target sample. If this vapor comes in contact with another surface, it may recon dense on the surface. Repeated pulses of laser light and subsequently repeated vapor plumes might build up material on the surface to form what is termed a thin film. This process is referred to as pulsed laser deposition [9].

2.1.7 Magnetron sputtering:

Sputtering is the process whereby atoms or molecules of a material are ejected from a target by the bombardment of high-energy particles. However, the main disadvantages of diode sputtering were related to the very low deposition rates and large cost. Then, in the mid-1970s, a magnetically enhanced variant of the diode sputtering known as magnetron sputtering emerged [10]. Magnetron sputtering is a high-rate vacuum coating technique that allows the deposition of many types of materials, including metals and ceramics, onto as many types of substrate materials by the use of a specially formed magnetic field applied to a diode sputtering target [11].

2.1.8 Radio frequency (RF) Sputtering:

Radio frequency (RF) sputtering is a variant of sputtering. The process involves alternating the electrical potential of the current in a vacuum environment at radio frequencies. The cathode (the target) becomes the thin film coating, while the anode is connected in a series on the other side of a blocking capacitor. The capacitor is part of an impedance-matching network that provides the power transfer from the RF source to the plasma discharge. The cathode is bombarded by high voltage at a fixed frequency of 13.56 MHz in a vacuum chamber, which leads to high-energy ions that sputter atoms to become a thin film that coats the substrate [12].

2.1.9 Direct Current (DC) Sputtering:

DC sputtering is made up of a pair of planar electrodes (referred to as the cold cathode and anode). The target material to be deposited is placed on the cathode, and the substrate is positioned at the anode. The working gas inside the deposition chamber is usually argon gas due to the larger mass compared to neon and helium because higher mass correlates to more energetic collision with the target material and lower cost when compared to xenon and krypton. DC voltage is supplied between the cathode (target material) and anode (substrate) to sustain the glow discharge. The gaseous ions resulting from the sustained glow discharges are accelerated towards the target material, and sputtering takes place resulting in deposition of a thin film on the surface of the substrate material [13].

2.1.10 Ion beam sputtering:

In this technique, the energetic ion beam from source gets bombard on the target material to deposit uniform thin films. The prepared film is highly pure, and deposition of target atom does not depend on vapor pressure of the material. It is a high vacuum and costly method as it requires high quality target [14].

This article presents some advanced and popular thin film physical deposition methods and the advantages and disadvantages of each method as shown in table 2.

Table 2: Advantages and disadvantages of PDM

Physical Deposition Methods (PDM) – Advantages and Disadvantages		
Deposition Methods	**Advantages**	**Disadvantages**
Thermal evaporation	High deposition rate; Simple and inexpensive equipment; Good quality films.	Very poor coverage; Difficult deposition process; Needs substrate heating.
Electron beam evaporation	Multiple thin films; High quality deposition; Clean growth process.	Non uniform evaporating rate; More expensive; Damage thin film surface.
Molecular beam epitaxy	High purity films; Produce epitaxial materials; Clean surface films.	Complicated and high-cost equipment; Low deposition rate; Needs high vacuum.
Flash evaporation	Simple and better coatings; Good environment adaptability; High deposition rate.	Low efficient technique; Complicated process; High operating temperature.
Arc evaporation	All electrical conductive materials can be vaporized; Composition control; Removal of inclusions.	Growth defects; Lower melt rate; High cost.
Pulsed laser deposition	Dense and porous coatings; Simple and precise process; Needed lower substrate temperature.	Very expensive; Defected substrate surface and growing film; Slow rate of deposition.
magnetron sputtering	High adhesion; Uniform coating thickness; Low temperature process.	Very expensive method; Low deposition rate; Unstable plasma.

Radio frequency sputtering	Works well with insulating targets; Higher efficiency; Better film quality and step coverage.	Deposition rate is very low; Non uniform deposition; Expensive technique.
Direct current sputtering	Good step coverage; Simple and good coating method; Low temperature technique.	Low sputtering rate; Slower deposition; Inefficient secondary electron process.
Ion beam sputter deposition	Uniform coating thickness; High quality and precision films; Thickness control and stability.	Low deposition rate; expensive method; complicated device.

2.2 Chemical Deposition Methods (CDM):

There are many types of chemical deposition methods, but in this review article, we focus on the some important CDM techniques.

2.2.1 Chemical vapor deposition:

CVD is a method to form thin films by chemical reaction on the surface of substrates by using one or more gaseous compounds or elemental substances containing thin film elements. CVD is widely used in industry for the production of organic and inorganic films on metals, semiconductors, and other materials [15]. CVD has been classified by various processes like atmospheric-pressure chemical vapor deposition (APCVD), low-pressure chemical vapor deposition (LPCVD), ultrahigh vacuum chemical vapor deposition (UHVCVD), plasma-enhanced chemical vapor deposition (PECVD), or plasma-assisted chemical vapor deposition (PACVD), and laser-enhanced chemical vapor deposition (LECVD), metal-organic chemical vapor deposition (MOCVD) etc.

2.2.2 Atomic layer deposition:

ALD is based on surface controlled thin film deposition. During coating, two or more chemical vapors or gaseous precursors react sequentially on the substrate surface, producing a solid thin film. Most ALD coating systems utilize a flow–through traveling wave setup, where an inert carrier gas flows through the system and precursors are injected as very short pulses into this carrier flow. The carrier gas flow takes the precursor pulses as sequential "waves" through the reaction chamber, followed by a pumping line, filtering systems and, eventually, a vacuum pump [16].

2.2.3 Chemical Bath Deposition:

Chemical bath deposition (CBD) which is also known as solution growth, controlled precipitation, or simply chemical deposition, recently has emerged as a method for the deposition of metal chalcogenide thin films. It is an analogue, in the liquid phase, of the well-known chemical vapour deposition in the gaseous phase. The CBD method is presently attracting considerable attention as it does not require sophisticated instrumentation like a vacuum system and other expensive equipments. Simple equipments like hot plates with magnetic stirrer is needed [17].

2.2.4 Sol – gel process:

Sol–gel science is a multidisciplinary technique with physics and chemistry as natural companions. The term sol–gel is an amalgamation of two terms solution and gelation. One of the most important applications of sol–gel processing is in the preparation of thin films. The process includes the formation of liquid suspension called *sol*, which is a stable colloid solution obtained by the hydrolysis and partial condensation of precursors to form metal-oxygen-metal bonds (M-O-M). Further, sol particles upon condensation form an inorganic 3D network called *gel*. The encapsulated liquid is then removed from the gel, thus forming a range of porous or solid materials including xerogel and aerogel [18].

2.2.5 Spray pyrolysis:

Spray pyrolysis (SP) is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition [19]. In this process, the solution is atomized in small drops and these droplets are transferred to the heated substrate due to gas that generates thin films. The thin films produced have a large surface area of substrate coverage and potential and homogeneity of mass synthesis [20].

2.2.6 Successive Ionic Layer Adsorption and Reaction:

SILAR, the acronym for Successive Ionic Layer Adsorption and Reaction, is an evolution and combination of two other deposition methods, the Atomic Layer Deposition and Chemical Bath Deposition. As the acronym implies, the SILAR method is based on the adsorption of a layer of ionic species onto a surface, followed by a reaction triggered by a successive adsorption of a different ionic species. This reaction leads to the formation of an insoluble product, which constitutes the thin-film coating. The process is then repeated to increase the thickness of the deposited layer [21].

2.2.7 Electrodeposition:

Electrodeposition is the formation of a thin film material on a conductive surface of a substrate using a conductive solution containing the ionic species of that material. Deposition on the conductive surface is enabled by submersing the substrate and a counter electrode into the solution and applying a potential difference between them to cause a reaction of the ionic species on the substrate surface. Although electrodeposition can be carried out in anodic (substrate voltage is positive with respect to the counter electrode) or cathodic (substrate voltage is negative with respect to the counter electrode) mode [22].

2.2.8 Electroless deposition:

Electroless deposition is an elegant and versatile technique for metal plating as well as for developing various metal nanostructures [23]. Noble metal thin film depositions on different substrates are readily obtained via electroless deposition. This technique, often referred to as electroless plating, involves spontaneous reduction of ionic metals in the absence of electric current. Electroless plating is easy to operate, providing a cost effective and scalable alternative to conventional metal plating [24].

2.2.9 Spin-coating technique:

Spin-coating technique is used to prepare uniform thin films in the thickness range of micrometer to nanometer. The substrate is mounted on a chuck that rotates the sample, and the centrifugal force drives the liquid radically outward. Viscous force and surface tension are the main causes for the flat deposition on surface. Finally, the thin film is formed by evaporation. Spin coating consists of several stages, such as fluid dispensation, spin up, stable fluid outflow, spin off, and evaporation, respectively [25].

This article presents some advanced and popular thin film chemical deposition methods and the advantages and disadvantages of each method as shown in table 3.

Table 3: Advantages and disadvantages of CDM

Chemical Deposition Methods (CDM) – Advantages and Disadvantages		
Deposition Methods	**Advantages**	**Disadvantages**
Chemical vapor deposition	High deposition rate; Thick and uniform coating films; High purity and good quality films; Good reproducibility.	Require very high temperature; Expensive and complicated equipment; Organic exhaust gas is hazardous.
Chemical bath deposition	Very simple and low cost deposition; Different thickness films; Works at any temperature; Needs only substrate and solution container; Uniform and hard film deposition.	Wastage of solution after each deposition; Clean substrate is required.
Atomic layer deposition	Excellent adhesion and good quality films; Uniformity and step coverage; Low temperature processing.	Very high energy waste rare; Low deposition rate; Very high material waste rate.
Ion implantation	Low temperature process; Very past and highly controlled method; Improved oxidation performance.	High-cost equipment; Line-of-sight process.
Sol gel	High quality and purity; Low temperature deposition; High adhesion strength; Simple and low cost equipment.	Long processing time; High cost of raw materials; Used limited number of materials; Harmful organic solvents.
Spray pyrolysis	High growth rate; Open atmosphere process; Low cost deposition technique; High quality adherent films of uniform thickness.	Complicated process; Very low yield.
SILAR	Good film growth rate; Low cost and energy saving method; Does not need vacuum chamber; Low deposition temperature.	High working pressure needed; Requirement of sophisticated environment.
Electro deposition	High deposition rate; Cheaper deposition method; Very good adherence; Simple and past process.	Thickness limitation; Not suitable for large scale production; Used only for conductive surface.
Electroless deposition	Low substrate temperature; Low cost method; Good filling capability; Scalability of large areas.	Poor controllability and reproducibility; Low deposition rate; Require pre-treatment.
Spin coating	Simple and easy method; Low cost and past technique; High uniformity.	Less material efficiency; Coating material wastage, difficulty with large area samples.

3. Result and discussion:

In this article we have taken a detailed look at the thin film forming methods i.e. thin films can be made by physical and chemical methods and we have looked at the different types of methods in those physical and chemical methods and their advantages and disadvantages one by one. Hereby, we have summarized the overall information obtained in this study and presented it in table 4. And we have compiled the various types of information given in this table and given it in the next table 5. This will help to understand in detail the deposition parameters required to form thin films.

Table 4: Parameter analysis of physical and chemical deposition method

Physical / Chemical deposition methods	Deposition Parameters								
	Cost	Quality of film	Deposition time	Deposition rate	Equipment design	Process	Process Temperature	Safety	Film Thickness
Thermal evaporation	High	Moderate	High	High	Simple	Slow	Low	High	Thin
Electron beam evaporation	High	Moderate	Low	High	Simple	Past	Low	High	Thin
Molecular beam epitaxy	High	Excellent	High	Low	Complicated	Slow	High	High	Thin
Flash evaporation	High	Excellent	Low	High	Simple	Past	High	High	Thin
Arc evaporation	High	Excellent	High	Low	Complicated	Slow	High	High	Thin
Pulsed laser deposition	High	Excellent	High	Low	Simple	Slow	Low	High	Thin
magnetron sputtering	High	Excellent	High	Low	Simple	Slow	Low	High	Thin
Radio frequency sputtering	High	Excellent	High	Low	Simple	Slow	Low	High	Thin
Direct current sputtering	High	Excellent	High	Low	Simple	Slow	Low	High	Thin
Ion beam sputter deposition	High	Excellent	High	Low	Complicated	Past	Low	High	Thin
Chemical vapor deposition	High	Good	Low	High	Complicated	Past	High	Low	Thick
Chemical bath deposition	Low	Good	High	Low	Simple	Slow	Low	Low	Thick
Atomic layer deposition	High	Excellent	High	Low	Simple	Slow	Low	High	Thick
Ion implantation	Low	Excellent	Low	High	Simple	Past	Low	High	Thick
Sol gel	Low	Excellent	High	Low	Simple	Slow	Low	Low	Thick
Spray pyrolysis	Low	Excellent	Low	High	Simple	Slow	High	Low	Thick
SILAR	Low	Excellent	Low	High	Simple	Past	Low	Low	Thick
Electro deposition	Low	Excellent	Low	High	Simple	Past	High	Low	Thick
Electroless deposition	Low	Excellent	High	Low	Simple	Past	High	Low	Thick
Spin coating	Low	Excellent	Low	High	Simple	Past	High	High	Thick

Table 5: Parameter results of physical and chemical deposition methods

Parameters	Physical methods	Chemical methods
Cost	High	Low
Quality of film	Moderate / Excellent	Excellent
Deposition time	High	Low
Deposition rate	Low	High
Equipment design	Simple / Complicated	Simple
Deposition process	Slow	Past
Process Temperature	Low	High
Film Thickness	Thin	Thick
Safety	High	Low

The results obtained in the present review study are as follows:

(1) The various parameters of thin film deposition methods have been studied and summarized.

- ✓ Physical methods are more expensive compared to chemical methods.
- ✓ Chemical methods produce better quality films as compared to physical methods.
- ✓ Long term deposition is observed in physical methods as compared to chemical methods.
- ✓ Higher deposition rates are observed in chemical methods as compared to physical methods.
- ✓ Equipment design is simpler in chemical methods compared to physical methods.
- ✓ The deposition process is slower in physical methods compared to chemical methods.
- ✓ Lower process temperatures are observed in physical methods as compared to chemical methods.
- ✓ Thicker thin films are observed in chemical methods as compared to physical methods.
- ✓ Physical methods provide more protection as compared to chemical methods.

(2) From the results obtained so far, we can conclude that chemical methods provide high quality thin films at low cost compared to physical methods.

4. Conclusion:

Thin film is latest technology and always developing branch of sciences. In this review, thin-film deposition methods have been described and classified into two major groups: physical deposition methods will be investigated and discussed, and the deposition parameters of each method have been analyzed in detail. Important methods from each of the physical and chemical groups have been discussed with respect to the basic principles, key features, typical applications, advantages and disadvantages. Compared to physical deposition methods, chemical deposition methods are used to produce high quality thin films at low economic cost. Most of the chemical deposition techniques do not require high-cost equipment. Hence these are widely used all over the world.

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