**Thin Film Deposition Techniques**

Since all microelectronic solid-state devices are built on material structures produced by thin-film deposition, deposition technology can be considered to be a key component in the development of devices like computers. Deposition technology has had to quickly advance in response to the constant demands of electronic engineers for films with higher levels of sophistication and quality for solid-state devices. The requirements for better and more affordable deposition systems, as well as for in-situ process monitors and controls for measuring film parameters, have been successfully met by equipment manufacturers. The improved knowledge of the physics and chemistry of films, surfaces, interfaces, and microstructures made possible by the remarkable developments in analytical instrumentation over the past 20 years is a significant factor in the quick development of deposition technology. Improved fundamental knowledge of materials results in broader applications and new device designs that use these materials. Coatings with a thickness of between 5 Angstroms and a few micrometers are referred to as thin films [55].

On passive substrates like glass or ceramic as well as active substrates like silicon, various materials may be deposited as thin films. Thin-film deposition is the process of depositing a thin film on a surface. The process of depositing a thin layer of material onto a substrate or onto previously applied layers is known as thin film deposition. Although the term "thin" is ambiguous, most deposition techniques allow layer thickness to be controlled to within a few tens of nanometers, and one (molecular beam epitaxy) even permits the deposition of single layers of atoms at a time. It can be used to create packaging (like aluminum-coated PET film), electronics (layers of insulators, semiconductors, and conductors form integrated circuits), optics (for reflective or anti-reflective coatings, for example), and modern art. Where thickness is not crucial, similar processes are occasionally applied. For instance, copper can be purified by electroplating, and silicon and enriched uranium can be deposited using a method akin to CVD after gas-phase processing.

**Classification:**

Deposition techniques fall into two broad categories:

1. **Chemical Techniques**
2. **Physical Techniques**
3. **Chemical Techniques**

These procedures take advantage of the fact that solid materials can be produced directly from chemical reactions that take place in liquid or gaseous compositions or with the substrate. In most cases, the reaction produces additional products in addition to the solid material. Gases, liquids, and even additional solids are examples of byproducts. Chemical deposition techniques produce thin films that are typically conformal rather than directional.

Depositions that happen because of a chemical reaction are as follows:

* **Chemical Vapor Deposition (CVD**)
* **Electrodeposition**
* **Epitaxy**
* **Thermal oxidation**

1. **Physical Techniques**

A thin solid film is created by physical deposition using mechanical or thermodynamic methods. The material being deposited on the substrate is physically moved in all of these processes. In other words, the substance that forms on the substrate does not result from a chemical reaction. Although it is more convenient to think of casting processes in this way, it is not entirely accurate. As a result of the ongoing development of technology, this list is by no means complete.

Deposits that result from a physical reaction:

* **Physical Vapor Deposition (CVD**)
* **Casting**
* **Molecular beam epitaxy**
* **Thermal evaporation**

The classification of the different deposition processes is illustrated in the Figure 2.8:

**Deposition Techniques**

**Physical Deposition Techniques**

**Chemical Deposition Techniques**

**Electroless Deposition**

**Electroplating**

**Molecular Beam Epitaxy**

**Laser Ablation**

**Electron Beam**

**Thermal**

**Loan Plating**

**Evaporation**

**Radio Frequency**

**DC**

**Magnetron**

**Spin coating**

**Chemical spray Pyrolysis**

**Sputtering**

**Metal Organic**

**Plasma Enhanced**

**Electron Cyclotron**

**Low Pressure**

**Atmospheric Pressure**

**CVD**

**Atomic Layer Deposition**

**Sol-gel**

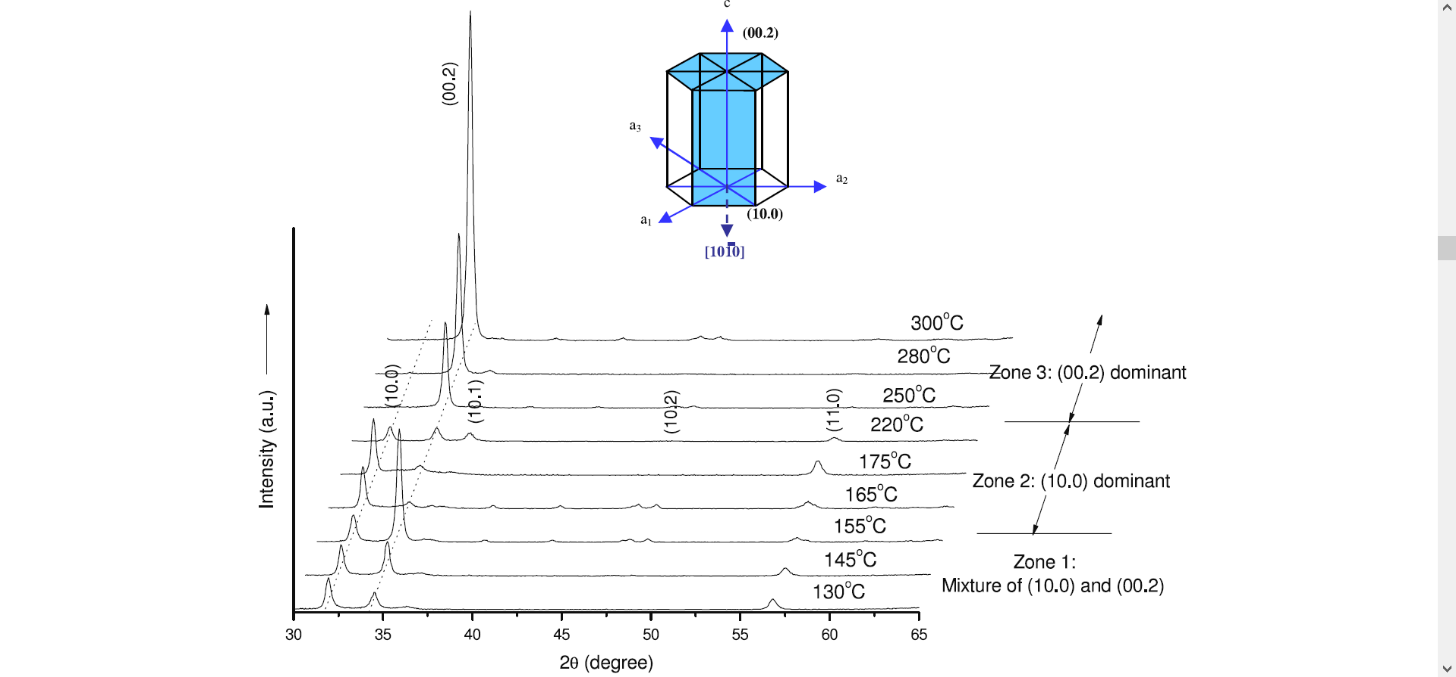
**Planting**

**Solution Based**

**Figure 2.8:** Classification of different film deposition techniques. Reproduced from ref. [56]

**Atomic Layer Deposition:**

The atomic layer deposition technique can be controlled by deposition temperature. The (10.0) orientation have high growth in the temperature ranged between 155°c-220°c and (00.2) orientation have it at high temperature, such as 280°c. And in the range of 130°c, both of (10.0) and (00.2) have preferential growth. Therefore, it is proved that degree of crystallinity in film growth is the function of deposition temperature. For any type of deposition technique, determining the preferential orientation and controlling it have a great importance in the sector of materials science [57]. There are some conditions under which the preferential growth of film can be achievable. Generally, the growth happens due to minimize the surface free energy, and in the equilibrium condition the film grows along the plane which have lowest surface free energy and its direction is parallel to the surface. But it should maintain its temperature below roughening temperature and should not have any influence of epitaxy [58]. As the (00.2) orientation have high atomic packing density and minimum surface free energy, it is the highest probable growing orientation for ZnO by the atomic layer deposition. So, the direction [0001] is the thermodynamically preferable direction for the ZnO of wurtzite structure. Here, the atomic layer deposition was done using Diethyl zinc (DEZn) as the source of zinc and water as the source of oxygen. In this deposition method, the zinc and oxygen deposits alternatively to grow the film.

 **Fig :** The relationship between growth intensity and orientation at different deposition temperature in XRD analysis [59].

**Pulsed Laser Deposition:**

The pulsed laser deposition technique has good scope in the development of epitaxial films. It allows the fabrication of multi-layers and hetero-structures. It can also use in the super lattices. [62] The films which grows through PLD process, has wide range of deposition conditions, which was observed as high optical transparency, electrical conductivity and c-axis oriented having FWHM (Full Width at Half Maximum). In the XRD analysis, the (002) orientations have reflection line less than 0.25°. At room temperature, all the deposited layers were found as amorphous form, no sharp XRD reflection line was found, and exhibited matt surface. At 200°c- 500°c temperature on the substrate, the films which were grown all in c-axis oriented. Then (002) and (004) lines were exhibited, no other lines were found. For wide range of fluences and oxygen partial pressures, the full width at half-maximum of the (002) line was found in less than 0.25° which indicates that it has high quality crystalline structure. The beneficial effects were found from 150°c to 350°c temperature range. But the opposite effects were found above the 400°c. Most of the films which are observed in this study were grown in 350°c. By the observations of various effects which are shown on different partial oxygen pressures, it was shown that best quality films could be obtained in the high-pressure range [60].

**Sputtering Techniques:**

In the previous section we discussed about the chemical and physical methods where the chemical methods have better performance rather than the physical methods. The sputtering techniques have better performance over the chemical process due to its good control of compositions and homogeneity.

The process initialized by the energetic bombardment of substrate, which is assisted by neutral atoms, electrons and ions. This is characterized by total energy flux density which affects the film. And the total energy flux density can be calculated by radio-frequency (RF) power, bias voltage of substrate and concentration of reactive gases. Here the major parameters are total energy flux density and substrate temperature which provide significant role on the crystalline structure of the film. These two parameters have significant influence on the initial phases of film growth like nucleation, clustering or film growth [61].

**Mechanism:**

During sputtering, electrons, ions or atoms are ejected from a material (solid phase) with particles having high energy, typically more than 1 eV. Maintaining conditions like low pressure and high voltage are important so that the plasma consisting of energized electrons can be generated properly. This is called as glow discharge process. Here the cathode performed as target, and the anode as substrate. So, it can also say that, the electrons ejected from the source which is cathodic and anode as substrate. Therefore, the electrons diffuse away and deposited on the anodic substrate. For conducting samples, DC voltage is applied between anode and cathode which is referred as DC sputtering. Amount of DC voltage depended upon the nature of the substrate. On the other hand, for non-conducting samples or insulating materials radio frequency generator of high of high frequency is used [62].

**Magnetron Sputtering:**

In magnetron sputtering, magnets are used which increases the amounts of electrons. That’s why, it has good impact on Ar atoms. Therefore, the path length of electrons increases as well as the ionization efficiency. Magnetron sputtering are used where there are high deposition rates and low substrate temperature are required. In this process both DC and RF mechanism are used. In this mechanism, ejected species with high energy can increase the temperature of the surface which can influence on the crystallinity of the thin film, or may cause damages to the surfaces or films or both. In this process if the bombarding particle have sufficient energy, then it can implant itself into the film, or may be damage the film, or can transfer its momentum to a surface atom [63].

**DC Sputtering:** In this sputtering technique, several semiconductor components and printed circuit board can be constructed. This is a plasma technique in which plasma near the deposition source can increase by using magnetic field. This sputtering can be initiated by igniting a glow discharge or plasma through a large DC bias which is situated between a cathode and an anode. This process is done in a vacuum environment.

**RF Sputtering:** In this technique, deposition of oxide layers like semiconducting ZnO is done. In comparison with the DC method, this has advantages as it involve RF power. Therefore, by this process, operation can be formed in low working gas pressure conditions. The insulating or non-conducting target which need to deposit is attached with one of the electrodes.

**Sol gel process:**

This is basically a chemical method which is done in wetted condition. This process is used in the formation of nano-structured particles. For the synthesis of ZnO based nanoparticles or ZnO thin films, The sol-gel method is a very common one. A molecular precursor like metal alkoxide can dissolve in the water or alcohol. Then it is converted into the gel by hydrolysis.

**Overview:**

The sol-gel process, depicted in figure 2.9, is a technique used in materials science to create solid materials from small molecules. The technique is employed to create metal oxides. During the procedure, monomers are transformed into a colloidal solution (sol), which serves as the precursor for an integrated network (or gel) of discrete particles or network polymers. Metal alkoxides are typical precursors.

The irregular particle sizes and shapes in a typical powder frequently result in non-uniform packing morphologies that cause packing density variations in the powder compact when processing fine ceramics. Microstructural inhomogeneities can also result from uncontrolled flocculation of powders brought on by attractive van der Waals forces. The rate at which the solvent can be removed directly affects the differential stresses that result from non-uniform drying shrinkage, making porosity distribution an important factor. If not relieved, these stresses can lead to crack propagation in the unfired body and have been linked to a plastic-to-brittle transition in consolidated bodies. Furthermore, any variations in the compact's packing density as it is being readied for the kiln are frequently amplified during the sintering process, leading to inhomogeneous densification. It has been demonstrated that some pores and other structural flaws connected to density variations can hinder the sintering process by expanding and thereby restricting end-point densities. It has also been demonstrated that differential stresses brought on by inhomogeneous densification cause internal cracks to spread, becoming the flaws that regulate strength.



**Figure 2.9** Basics of synthesis by sol gel methodology

Instead of using particle size distributions that will maximize the green density, it would therefore seem preferable to process a material in a way that it is physically uniform with regard to the distribution of components and porosity. Total control over particle-particle interactions is necessary for the containment of a strongly interacting assembly of uniformly dispersed particles in suspension. It is possible in monodisperse colloids.

For instance, colloidal silica monodisperse powders may be sufficiently stabilized to guarantee a high level of order in the resulting colloidal crystal or polycrystalline colloidal solid. The amount of time and space that can be used to establish longer-range correlations appears to be a limiting factor in the degree of order. The first step in developing a more thorough understanding of the mechanisms underlying microstructural evolution in inorganic systems, such as sintered ceramic nanomaterials, is to identify such defective polycrystalline structures as the fundamental building blocks of nanoscale materials science.

Products made from sol gel have a wide range of uses. For instance, it has been used by scientists to create some of the world's toughest ceramics as well as the world's lightest materials. Thin films, which can be created on a piece of substrate by spin coating or dip coating, are one of the most common application areas. These techniques can be used to apply protective and decorative coatings as well as electro-optic components to glass, metal, and other types of substrates. Dense ceramic or glass objects with novel properties that can only be produced this way can be cast into a mold and then further dried and heated. Spraying, electrophoresis, inkjet printing, and roll coating are additional coating techniques.

**Sol gel coating technique:**

The sol-gel method is a low-temperature method for creating metal oxide molecules in solution form from inorganic or metal organic precursors. The process of creating the solution relies on the condensation and hydrolysis of organometallic compounds in alcohol-based solutions. Following that, a number of techniques, including spin coating, can be used to deposit CCZO films using the solutions.

**Spin coating**

In the spin-coating method, the substance to be deposited is dissolved or dispersed in a solvent, which is then applied to the substrate surface and spun off to leave a thin, uniform layer of film. Figure 2.10 depicts the four main stages of the spin-coating process, which are as follows:

**1.** The solution is deposited on the substrate.

**2.** Solution spreading outward (spinning up) from the substrate's center to the sides.

**3.** Spin-off, or gradual solution thinness.

**4.** The evaporation of a solvent cause gelation.



**Figure 2.10** A schematic of spin-coat deposition*.*

Since a balance between the radially outward centrifugal force and the radially inward viscous force occurs, the deposited film tends to be uniform as it is thinned by centrifugal draining. It is possible to achieve extremely homogeneous film thicknesses even with non-planar substrates.

**Dip coating**

In this method, the substrate to be coated is submerged in the solution and then removed under controlled temperature and atmospheric conditions at a predetermined speed. Figure 2.11 displays a schematic. Smooth substrate movement and vibration-free mountings are crucial for maintaining a consistent film thickness. Dip-coating requires more sophisticated equipment than spin-coating does.



**Figure 2.11** A schematic of dip-coat deposition.

**Solgel spin coating techniques**

There are two types of spin coating methods:

**Static process:**

At first solvent is applied and after that rotation started.

****

**Figure:** Static spin coating technique

**Dynamic process:** After starting the rotation, the speed is initially low and then quickly rises. During the period of low speed, solvent is administered.

**Figure:** Dynamic spin coating technique

**Advantages and Disadvantages of Spin Coating**

The benefits of spin coating include the thin and homogeneous coating that can be produced along with how simple and relatively easy it is to set up a process. High airflow and quick drying periods derive from the capacity to spin materials at high speeds, which in turn produces great consistency at both macroscopic and nanoscale length scales.

Spin coating has the drawback of being a batch (single substrate) process by nature, which results in a lower throughput than roll-to-roll techniques. Some specific nanotechnologies that need time to self-assemble and/or crystallize may function worse due to the quick drying times. Last but not least, only about 10% or less of the actual material used in a spin coating process is actually utilized; the remainder is wasted and thrown off to the side. While this is typically not a problem in research settings, it is obviously wasteful in manufacturing.

Spin coating is frequently the starting point and benchmark for most academic and industrial operations that call for a thin and homogeneous coating, despite these limitations.

**Advantages and Disadvantages of the Sol-Gel Technique**

Sol-gel coatings have several advantages over other processes for the creation of thin films since they are a solution processable technology. These includes:

**1)** Excellent control over the coating solutions' stoichiometry and purity.

**2)** The simplicity of compositional changes.

**3)** Eligibility for deposition on substrates with broad surfaces.

**4)** Basic and affordable tools

The resulting films' sheet resistance typically exceeds that of the sputter-coated films by at least one order of magnitude, which is a drawback. One cause could be that there are many more parameters in sol-gel processes that need to be optimized. The properties of the produced thin films may be significantly influenced by the precursors used, the number of layers deposited, the drying and annealing temperatures, and the environment. Additionally, good quality films are less repeatable than sputter-coated ones since sol-gel methods need a lot more manual labor. However, with thorough optimization and process control, this technology has a great deal of potential to replace current low-cost deposition methods [64].