# Chapter

# Thin Films/Properties and Applications

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#### **Abstract**

Since its discovery in early times, thin films rapidly found industrial applications such as in decorative and optics purposes. With the evolution of thin film technology, supported by the development of vacuum technology and electric power facilities, the range of applications has increased at a level that nowadays almost every industrial sector make use of them to provide specific physical and chemical properties to the surface of bulk materials. The possibility to tailor the film properties through the variation of the microstructure via the deposition parameters adopted in a specific deposition technique has permitted their entrance from the simplest like protective coatings against wear and corrosion to the most technological advanced applications such as microelectronics and biomedicine, recently. In spite of such impressive progress, the connection among all steps of the thin film production, namely deposition parameters-morphology and properties, is not fully accurate. Among other reasons, the lack of characterization techniques suitable for probing films with thickness less than a single atomic layer, along with a lack of understanding of the physics have impeded the elaboration of sophisticated models for a precise prediction of film properties. Furthermore, there remain some difficulties related to the large scale production and a relative high cost for the deposition of advanced structures, i.e. quantum wells and wires. Once these barriers are overcome, thin film technology will become more competitive for advanced technological applications.

**Keywords:** thin films, deposition techniques, characterization, properties, inorganic and organic, applications, structure and morphology, challenges

#### 1. Introduction

This chapter covers the fundamentals of the thin film technology, including deposition techniques, structure and morphology, film properties, characterization techniques and applications. Due to the exceptional diversity of thin films and the large range of applications it is complicated to cover in detail all the areas, however, as many thin films share a number of features in all steps of the production process, characterization, and even applications, it is possible to treat them with a general perspective.

The most widely employed deposition techniques, namely physical vapor deposition (PVD), and chemical vapor deposition (CVD), for thin film production are described with emphasis in the principle, advantages, disadvantages and examples of the common thin film structures produced. Furthermore, the various

types of microstructures and the morphological features as a result of the deposition technique and parameters are reported. The growth mechanism is described considering the conditions for the formation of amorphous, polycrystalline or epitaxial structure, and the resulting morphology is explained based on the temperature-dependence zone models. Subsequently, the mechanical, electrical and optical properties are reviewed, stressing the connection with morphological features such as film thickness, material phase, defects, roughness, grain boundaries etc. The principal characterization techniques used for the characterization of chemical composition, morphology, stress, and electrical conductivity are described along with their principle. In addition, the specific information that can be accessed through the data collection is stated. The most technological relevant areas of application are then outlined along with the type of films mostly employed and. Finally, the main challenges for the thin film technology to progress in various areas are discussed.

# 2. Deposition methods

Thin-films are in general developed to provide special properties, i.e. electrical, optical, mechanical, chemical, that satisfy the needs for specific applications. The desired properties are determined by the resulting film structure, which strongly dependents on the selected deposition method, film material, and substrate. In line with the wide range of applications of thin films, a number of deposition methods have been developed/improved to optimize the film properties, of which, the most commonly employed are described in this section. Broadly speaking, thin-film production can be realized based on two technological groups, namely physical and chemical deposition methods.

### 2.1 Physical deposition methods (PVD)

Physical deposition methods are usually referred as to physical vapor deposition methods (PVD) because the process entails the generation of vapor. PVD essentially consists in removing growth species from a source or target material via evaporation, then this vapor is transported to the substrate surface, and eventually it solidifies in the surface, forming the film. The evaporation is generally carried out under a reduced pressure chamber to avoid impurities in the film formation which are produced due to collisions between vapor particles and residual gas particles in their displacement from the source to the substrate surface. PVD techniques are known to offer a number of advantages, including the deposition of almost any material, high reproducibility of film properties, the use of a large range of substrate materials, the possibility of tailoring the film properties through modification of deposition parameters in single element deposition, and obtaining films with high purity. On the other side, among the main disadvantages are the use of sophisticated and costly monitoring systems for the control of the deposition rate and film thickness, and the mismatch between the composition of the deposited film and the composition of the evaporant in the case of alloys and compounds.

PVD techniques can be classified according to the method employed in the generation of vapor. The most common PVD techniques are vacuum-based evaporation and its heating versions, sputtering, laser ablation, cluster beam and ion pattering, of which, only the most important will be described in detail in the present section. For further detail on the versions of PVD techniques, the reader is referred to [1–3].

## 2.1.1 Vacuum evaporation

It is among the most popular PVD techniques due to its simplicity in operation and high deposition rate. This technique uses heating sources to evaporate the deposition material onto the substrate surface where it condenses forming a thin film, all within a vacuum chamber. This technique is suitable for deposition of elements or compounds at temperatures below 2000 K [4]. According to the method used to evaporate the target material, this technique can be subdivided into resistance-heated evaporation, and electron-beam evaporation.

In resistance-heated evaporation the target material is deposited in one of the multiple configurations of the evaporation source including coil, boats, and baskets. Due to the high temperature required, they are commonly fabricated from refractory metals with high melting points, such as tungsten, molybdenum, and tantalum although stainless steel can also be used in cases where the target material has a low evaporation temperature. The essential condition for the proper selection of an evaporation source is that its evaporation point does not have to be reached at the operation temperature. Once selected an appropriate evaporation source the vacuum chamber needs to reach pressures lower than 10<sup>-5</sup> mbar to optimize the sample coverage during deposition, and provide a high purity of the film. The evaporation of the target material is carried out by the heating of the source through which a high electric current is forced to pass. The deposition rate is controlled with the source temperature due to its direct relationship with the vapor pressure of the target material. Among the main disadvantages of this technique are the limited upper temperature (2000 K) which constrains the use of materials suitable for evaporation, a limited film thickness, and the possibility of contamination related to the heater filament.

In *electron-beam evaporation* the target material is deposited in a crucible which is design to match the heating and power density of the electron-beam. To avoid contamination of the target material in the evaporation stage, the crucible should not be prone to evaporation or erosion at high temperatures. Accordingly, the most widely used crucibles are the water-cooled copper, and ceramic hearth. With these crucibles, which have high melting points (3000–4000) K, it is possible to reach higher temperatures than those achieved for resistance-heated evaporation, and thus, it allows the evaporation of refractory material, reactive materials like titanium and aluminum, dielectrics (SiO<sub>2</sub>), boron, carbon, silicon among others. The evaporation process takes place under vacuum through the incidence of an intensive beam of electrons, emitted by a thermionic filament, which is accelerated towards the target material by an electric field. These energetic electrons collide in the surface of the target material generating a local melting after having being deflected by a magnetic field usually with an angle of 180° or 270°. The deposition rate achieved is high, in the order of 1000 nm/min, relying on the target material, and the distance between the source and substrate. One of the main disadvantages of this technique is the generation of ionized radiation (X-rays) which can penetrate the film producing damage.

Molecular-beam epitaxy (MBE) is the most advance solution for the deposition of compounds and alloys due to its simultaneous control over the evaporation rates of the different constituents, with high precision. This technique enables the epitaxial grow of thin films under ultra-high vacuum (UHV) conditions onto a hot single-crystalline substrate. While the UHV prevents contamination of the film from impurities present in the growth environment producing a high-purity film with an improved morphology, the substrate temperature promotes the diffusion of adsorbed species on its surface to achieve an epitaxial growth. The growing species are provided by the atomic or molecular beams generated by the heating

of a convenient source material which can be either elements or compounds, and that are normally contained in crucibles of high purity. The proper selection of crucibles is fundamental to assure the purity of the molecular beam; the most widely employed crucibles are fabricated based on graphite, pyrotilic boron nitride for high temperatures, and also quartz and stainless steel are for low melting point materials.

One of the most important features of this technique is its ability to accurately control the composition and doping profile in the growth direction. This can be realized thanks to the UHV that enables the film growth to occur in the molecular regime. In this regime the atoms and molecules do not collide in their way to the substrate because the mean free path is larger than the distance from the crucible to the substrate. This feature allows to modify as desired the composition of the feeding phase, blocking abruptly one or more streams of atoms being either a constituent atom or a dopant element with the help of mechanical shutters. Regarding that this blocking process can be carried out in very short times, and the low deposition rate from MBE, it is possible to achieve extremely thin thicknesses between the layers of different composition and/or doping. Advanced nanostructures, such as quantum-wells, superlattices and quantum-dots have been successfully fabricated with this deposition technique [5–7].

#### 2.1.2 Sputtering

Sputtering essentially consists in the bombardment of the target material with energetic particles to dislodge atoms from its surface which travel through the plasma to eventually condensate onto the substrate. Three sputtering techniques are the most employed for thin film growth, including DC diode, RF-diode, and magnetron diode.

*In the DC diode sputtering*, the bottom electrode, called cathode, contains the target material to be deposited while the top electrode holds the substrate. An inert gas, i.e. Ar, Ne, Kr, or Xe [8] is fed into the sputtering reactor at a reduced pressure. A plasma is then formed by the application of a voltage between the cathode and anode with the inert gas inside. The electrons emitted from the cathode are accelerated towards the anode and in their way ionize the gas molecules producing positively charged ions which accelerate towards the cathode, establishing a discharge. The glow discharge can be made self-sustained if appropriate conditions of gas pressure, voltage and distance between electrodes are adopted. If that occurs, a continuous bombardment of positive energetic ions against the cathode is established promoting its surface sputtering, and the subsequent condensation of a thin film onto the substrate. It should be noted that the target material in this system is necessarily a metal as the glow discharge can be maintained only between metals. Thus, deposition of insulators might not be possible using this technique. The main disadvantages of this technique are the low deposition rates, and the absence of self-sustained glow discharge at very low pressures.

Radio-frequency (RF) sputtering offers a solution for the deposition of insulating materials by preventing the accumulation of positive ions in the front side of the insulator to maintain the discharge. A continuous sputtering process of the insulator target is set by the application of an alternating signal to the cathode with a frequency corresponding to radio-frequency (13.56 MHz) [9]. In this way, a larger number of electrons arrive at the surface target during the positive half-cycle which overcompensate the number of ions that accumulate during the negative half-cycle, giving the target a net negative charge. This self-biased charge process is possible due to the higher mobility of electrons with respect to the positive ions in the plasma. Apart from insulators, this technique has successfully been adopted for

the deposition of metals and semiconductors, however, the sputtering rate remains lower than that of the vacuum deposition described above.

The *magnetron sputtering* technique permits to improve the sputtering rate with respect to the previous versions through the optimisation of the ionization of the sputtering gas molecules [4]. In this system, a magnetic field is applied between the cathode (target material) and anode (substrate) in addition to the electrical field where they both make the electrons to change their paths within the discharge from linear to spiral. This longer path followed by electrons in their travel from the target to the anode increases the time they are in contact with the gas molecules, raising the probability of ionization. Also, the fact that electrons remain a longer time in the plasma produces an increase of the current density at the cathode side, which in turn, raises the sputtering rate of the target material. This higher effective gas ionization allows to reduce the sputtering gas pressure to maintain the discharge, which significantly reduces the collisions of sputtered atoms within the plasma in their travel towards the substrate, increasing the deposition rate. A columnar microstructure is usually obtained with this technique with defects concentrated in between the columns. Silicon nitride films are often produced with this technique [10], but in combination with RF sputtering, it is possible to produce films based on Ti, Cr, Fe, Mo, Ag, Cu, among others [11].

#### 2.1.3 Laser ablation

Laser ablation is based on a similar configuration as the previous techniques, i.e. usually an evacuated chamber with a target material to be evaporated, a substrate placed parallel to the target where the film condensates, and in this case, an additional high-power pulsed laser placed outside the deposition chamber which emits the energy for inducing the ablation of the target material [12]. This technique is broadly employed in the deposition of alloys, compounds, polymers, semiconductors, and multilayers due to its excellent stoichiometry transfer from the target to the film. Oxide thin films can also be deposited if oxygen is introduced in the chamber as a background gas. The irradiation from the laser power, i.e. KrF (248 nm), is focused on the target producing a rapid local heating until reaching the melting point, and eventually producing evaporation that will be deposited in the substrate. The laser ablation process and the quality of the sample are affected by a number of parameters, including the characteristics of the target material, deposition conditions, laser parameters, substrate temperature. Although this technique is widely recognized for its diverse and fast applicability, the actual ablation process is yet to be fully understood because the material ejection is not produced solely by a thermal process but also a photochemical is likely present.

#### 2.2 Chemical deposition methods (CVD)

CVD is a deposition method where a volatile compound of a pre-established substance is introduced into a reactor, usually along with an inert gas, to induce a chemical reaction which produces a solid thin film onto a substrate at an elevated temperature. In this technique, unlike PVD, the reaction does not have to be produced under vacuum conditions. Due to its versatility to work with a broad range of reactants and precursors, this technique enables the deposition of a variety of structures, including metal alloys and compound semiconductors with an excellent control of purity and doping (stoichiometric film) [13]. Compared to PVD, this technique offers higher deposition rates, better conformance in rough substrates, easy deposition onto complex surfaces, and high throughput. However, some disadvantages, such as the use of high substrate temperatures, and the toxicity

and flammability of the reactive gases have prevented it from being used in low-scaled developments, but is well justified in applications where high-throughput is required, i.e. semiconductor industry. The CVD processes can be classified based on the type of source employed to initiate the chemical reaction, the range of pressure under which the deposition is carried out, and the type of reactant used. The most established CVD method are described below.

The thermal activated CVD is the most conventional method where the thermal energy produced inside the reactor triggers the chemical reactions. Two variants are noticeable within this process in relation to the pressure range under which the deposition materializes, namely atmospheric pressure CVD (APCVD), and low pressure CVD (LPCVD) [14]. Both variants essentially comprise the same chemical reactions which overall consist in the creation of vapor from reactants; then these vapor species are directed into the reactor, where depending on the deposition parameters, homogeneous chemical reactions take place in the gas phase while heterogeneous reactions occur near the substrate surface. Finally, the crystallization of a solid film occurs in the substrate surface. An alteration of the rate-limiting process occurs when the pressure is reduced in LPCVD about 1000-fold with respect to the atmospheric pressure CVD [13]. This reduced pressure substantially increases the rate of mass transport of reactants overpassing the rate of reactions in the substrate surface. This makes the kinetics in the substrate surface to be the rate-limiting step in the deposition process. In the APCVD instead, the mass transport of reactants is lower than the rate of reactions in the substrate surface, thus making the process limited by the diffusion of reactants. The introduction of unwanted impurities is reduced in LPCVD with respect to the APCVD. Moreover, high uniform films with a higher throughput can be produced for commercial applications using LPCVD, however, a disadvantage in this variant is the still high temperature needed for deposition. Polysilicon and silicon nitride films are among the films produced with this technique [15].

Plasma-enhanced CVD (PECVD) is one of the most widely used variations of CVD because it provides an alternative for deposition at lower temperatures using organic, inorganic and inert precursors [4]. In this method a plasma energy, in addition to the thermal energy, is incorporated to improve the dissociation of the reactive gases. The plasma is created when an energy, usually in the form of an electric field, is introduced into the reactor which contains the reacting gases in the space between two electrodes. Then, complex chemical reactions occur in the plasma under reduced pressures which produce energetic ions and radicals that travel towards the substrate bombarding its surface and promoting reactions that give rise to a solid film. Unlike APCDV or LPCDV, this variant allows deposition of conformal films at lower temperatures (200-400 K) [13]. This deposition method has been enhanced through the excitation of plasma by radio frequency field (RF = 13.56 MHz), and microwave frequency field (2.45 GHz) which draws on the effect of electron cyclotron resonance (ECR) to reduce the pressure. The higher frequency of the latter allows for a higher-energy and a higher concentration of electrons in the plasma leading to a boost in the degree of ionization up to ~1000 times than that realized with RF field [16]. PECVD is an established deposition method for research and industrial production, including antireflective coatings, microelectronics, photovoltaics, and transistors.

Metalorganic CVD (MOCVD) basically follows the same process as the CVD where volatile metalorganic compounds are used as precursors instead of inorganic ones. This technique allows the deposition of a broad range of materials with an amorphous, polycrystalline and epitaxial microstructure. The metalorganic compounds are decomposed through pyrolysis reactions at low temperatures which permits to carry out the film deposition at lower temperatures than in thermal CVD.

Both deposition temperature and pressure play an essential role in determining the rate-limiting process. Deposition is usually performed in the range 550–1150 K, noticing a kinetic reaction limited behavior for temperatures below 500 K, and a diffusion-rate limited for temperatures above 800 K [13]. At low pressures (<1 kPa) the reactions are kinetic limited while above that threshold the reactions become diffusion-rate limited. This technique is attractive because the gas flow rate and the partial pressure of the precursors can be controlled allowing the fabrication of films with the right stoichiometry at high deposition rates. Among the disadvantages are the relative high cost of metalorganic compounds along with the difficulty to obtain highly purity version with minimum oxygen content to fabricate high quality semiconductors. Both semiconductor and superconductor thin films have been deposited through this technique [16]. A list of the most used metalorganic precursors for the deposition of semiconductor, metallic, and dielectric films is presented in Ref. [13].

#### 3. Thin films structure

Different and complex chemical reaction occur during the deposition process depending on the technique employed and deposition parameters, such as substrate temperature, deposition rate, pressure, and alignment of vapor stream with substrate, which give rise to a variety of microstructures. The resulting microstructure in turn defines the physical and chemical properties of the film, which means that an appropriate management of these variables is essential to obtain tailored film properties. The resulting microstructure can be either amorphous, polycrystalline or epitaxial, which are briefly described below.

Amorphous thin films are essentially short-range order structures derived from deviations in the bond length and bond angle from a perfect crystalline lattice [17]. Overall, in most materials the growth of amorphous films take place at low substrate temperatures where the mobility of adatoms (adsorbed atoms) at the substrate surface is very limited. With a low temperature the adatoms approach to a thermal equilibrium with the substrate limiting the energy available for diffusion through its surface. Instead, these nearly immobile adatoms are incorporated almost at the point of strike with the substrate surface. High deposition rate is another parameter to induce amorphous growth because it prevents adatoms from migrating to more energetic sites to reach equilibrium due to the limited time for diffusion, and they are incorporated into the film structure almost at the point of strike with the substrate surface. Some developments have also reported the formation of this disordered microstructure by the incorporation of certain gases, i.e. oxygen, nitrogen, that inhibit the growth of crystallites during the deposition process [13]. Both PVD and CVD techniques are suitable for deposition of amorphous structures. Deposition of amorphous thin films are required in a number of applications, such as solar cells, transistors, optoelectronics, dielectric films, etc.

Polycrystalline thin films consist in a large number of nano/micro crystallites with different orientations separated by grain boundaries. The crystallite size is mainly determined by the deposition parameters, i.e. deposition temperature, and deposition rate. A higher deposition temperature than that applied to obtain amorphous structures may lead to the formation of polycrystalline thin films. When adatoms are not in thermal equilibrium with the substrate due to a high substrate temperature, they have enough energy to continue diffusing in the substrate surface until adhering to an existing island or giving rise to new islands. These islands do not become thermodynamically stable until their size reach a nucleation threshold. The stable islands continue growing until saturation, and then, a coalescence process

initiates between islands giving rise to the formation of a polycrystalline layer [4]. As adatom-diffusion is a temperature-dependent process, the crystallite size is expected to increase in line with the increase of substrate temperature. Another driver for the crystallite size is the film thickness. While the crystallite growth in the lateral direction is limited by the coalescence process, in the cross plane direction, the growth is limited by the film thickness. The typical microstructure of this material is of great importance for some applications where the scattering of carriers and phonons need to be controlled, i.e. thermoelectrics [18, 19].

Epitaxial thin films consist in a solid crystalline film deposited onto a substrate surface with a nearly perfect lattice structure, whose crystal orientation is aligned with the crystallographic orientation of the substrate surface. Depending on the nature of substrate employed, the epitaxial growth can be divided into homo and hetero-epitaxial, with the former referring to the growth of a film onto a substrate of the same material, and the latter, onto a substrate of different material. Various deposition techniques have been developed to enable the deposition of epitaxial films, including MBE and vapor-phase epitaxy; they are mostly used in the semiconductor industry where high quality and complex films, i.e. quantum wells, quantum wires, are required [20]. Achieving epitaxial film growth depends on a number of factors, such as equilibrium thermodynamics of nucleation, creation of vapor from reactants, substrate surface reactions, and mobility of species through the substrate surface. The complex interaction of these atomic processes may lead to the formation of epitaxial films only if they occur over a certain temperature called "epitaxial temperature", which depends on the specific system and deposition parameters. Epitaxial grow usually takes place at high substrate temperature to promote the mobility of adatoms in the substrate surface forming islands that become stable after they reach a certain size, and their continuous growth increases the nucleation density giving rise to a solid film with a preferential orientation. The quality of epitaxial growth is strongly influenced by the strain created in the film during deposition due to lattice misfit, and thermal strain produced as a result of the different coefficients of thermal expansion between the films and substrate. Substrate surface contamination also influences the growth by interrupting the formation of epitaxial layers. To prevent this, deposition is normally carried out under reduced pressures or vacuum to promote the effusion of impurities from the substrate.

# 4. Thin film morphology

Establishing the correlation between deposition parameters with the resulting morphology of deposited thin films is very complex because of the interaction of a number of factors, which influence the nucleation and growth phases. However, despite the wide spectrum for variability, it is possible to find some typical morphological features that are common in a broad range of thin films.

Probably one of the most common morphological features found in many thin films grown by vapor-based techniques is a columnar structure whose growing direction is not necessarily perpendicular to the substrate. The way how the adsorbed atoms are integrated into the growing process determine the final morphology of thin films. When the atoms strike the substrate surface they may contribute to the creation of islands. These islands increase in size due to the feeding of atoms coming from the diffusion in the substrate surface and also from the vapor flux, forming complex arrangements of islands or compact islands. The flux of atoms diffusing in the substrate is suppressed once the islands start an interfering process between each other due to the progressive growth, and only the

contribution from the vapor flux remains active shifting the growth to the thickness direction. The accumulating growth in the thickness direction gives rise to a columnar structure with an appearance of cauliflower-like in the top view [4, 17, 21].

It was reported that, for the formation of a columnar structure with a rough surface, both a limited surface mobility of adatoms and a vapor flux arriving non-normal to the substrate are necessary conditions [4]. The former tends to control de size of the crystallites growing at the interface and defines the area at the base of the columns. The latter gives rise to a geometrical shadowing growth process. The atoms from the source of various deposition methods, i.e. CVD, sputtering, not always strike the substrate surface perpendicularly. This deviation from a normal incidence forces the development of a columnar growth in a direction towards the vapor flux. Overall, it has been observed that the angle between the substrate normal and the column direction falls in between the angle formed by the substrate normal and the vapor flux.

The evolution of the morphology in thin films as a function of substrate temperature (adatom mobility) can be classified according to a model introduced by Movchan and Demchishin in 1969 [22], named structure zone model (SZM). This model provides three structural zones depending on a homologous temperature (*T*<sub>h</sub>) which results from the ratio between the substrate temperature  $(T_s)$  and the melting point temperature of the deposited material. In the zone I for a  $T_h \le 0.3$ , the relative low substrate temperature allows for a low diffusion of adatoms which are not enough to compensate the density of defects. As a result, amorphous or nano-crystalline columns with high density of defects between them are formed with a cauliflower-like appearance in the top surface, which is enhanced by the shadowing process. In the zone II for a  $0.3 < T_h < 0.5$ , with a higher substrate temperature, the diffusion of adatoms is higher and enough to compensate the defects, producing a columnar structure with a lower concentration of defects and larger crystallites. In the zone III where  $T_h > 0.5$ , the higher substrate temperature produces a dominant bulk diffusion in the layer giving rise to a structure formed by coarse crystallites [23].

# 5. Properties of thin films

In this section a brief description of the mechanical, electrical, and optical properties in connection with the morphological features will be provided.

#### 5.1 Mechanical properties

Thin films, due to their versatility to provide tailored properties, have found application in a number of sectors going from simple coatings for wear and corrosion protection, to more advanced applications such as antireflective coatings, microelectronics, photovoltaics, etc. Although these material structures have been selected due to exclusively their functional properties, they must be able to provide a reliable service operation with a proper mechanical and chemical resistance during the lifetime. These films, during deposition and operation, are prone to develop large stresses that might cause deformation and eventually mechanical failure, and therefore, it is essential to understand the microstructural processes involved in such effects to attempt to mitigate through the control of microstructure during the fabrication. Unlike bulk structures where the mechanical properties do not show a clear dependence on the sample size, in reduced structures like these, these properties are strongly affected by the resulting microstructure giving rise to a different behavior as compared to their bulk counterparts.

Let us assume a thin film deposited on relative tick substrate as illustrated in **Figure 1**. If strain by any means were produced on the film, it would change its dimensions relative to the substrate where it is deposited to maintain the equilibrium. If, hypothetically, the film were not adhered to the substrate, it would be visible the change in dimensions, for example, when the strain has expanded the original dimensions of the film, as shown in part b of **Figure 1**. The action of matching again the expanded film into the substrate entails the application of a deformation to force the film to adopt the substrate dimensions as shown in part c, giving rise to the generation of stress within the film. The stored stress naturally tends to be released to reach equilibrium, but depending on the degree of the substrate stiffness, part of this strain can be absorbed if the substrate is compliant which is reflected in a bending produced in the film/substrate system, or can remain entirely in the film if the substrate has a high stiffness.

The means by which strain can be produced in the films during deposition basically derive from the deposition method employed and from thermally-induced effects. Various vapor-based techniques such as sputtering and PECVD are wellknown for producing stress due to the incorporation of gas into the microstructure or due to ion bombardment, whose degree can be controlled through a strategic balance of deposition parameters [24]. Impurity incorporation into the microstructure of a host material has also been ascribed as responsible for stress creation. Depending on their size, the introduction of dopant atoms cause a local deformation of the lattice producing stress. A notable example of this case is the fabrication of SiGe thin films [25], where the introduction of Ge atoms into the Si matrix increases the stress, which collaterally contributes to enhance the thermoelectric properties [26]. Thin film deposition is commonly realized at relative high temperatures and cooled down latter on. This change of temperature along with a difference in the coefficients of thermal expansion between the film and substrate material generate stress in the film microstructure as well [27]. For some thin films like hydrogenated microcrystalline silicon, widely used in the photovoltaic sector, large stress creation has been reported in the phase transition from amorphous to microcrystalline silicon [28].

The stress contained in the films affect the mechanical properties such as yield strength and hardness. The yield strength of thin films is reported to be higher than the bulk version due to the influence of the microstructure. The value of this property is reported to increase with a smaller grain size, and with a higher density of dislocations present in the microstructure [29]. The deformation mechanism model that may explain the strengthening of thin films is based on the dislocation motion.

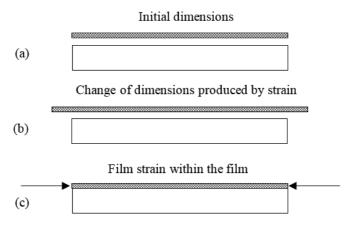


Figure 1. Schematic of stress/strain creation within thin films.

A number of dislocations present in the microstructure move as a function of the stress applied to the film, and for a dislocation to move, the stress applied must be comparable or higher than the energy necessary to deposit a misfit dislocation. However, it is important to consider that dislocation motion can be constrained by the interaction with other microstructural defects such as extended defect, point defects, and other dislocations which contribute to film strengthening. When the film/substrate system is considered instead of free-standing films, the constraints to the mobility of dislocations provided by the substrate and any oxide present in the substrate surface have to be considered to determine the strength. These additional constraints have demonstrated to strengthen the film in comparison to free-standing ones [30]. These microstructural features also explain the larger hardness exhibited in thin films in comparison to bulk materials.

### 5.2 Electrical properties

Electrical properties within thin films comprise a broad field if one considers the different resulting microstructure, whether they are metallic films, semiconductors or insulators films, and the type of substrate on which they are deposited. However, much of these films possess some common morphological features that derive in similar transport mechanisms that allow to treat the conductivity in a global perspective.

One of the main factors for the deviation of conductivity in thin films with respect to bulk material is the size effect. The electron mean free path of the bulk material reduces as the material thickness reduces due to the activation of additional scattering mechanisms. In a simplified approximation, dictated by the direct proportionality of conductivity with the electron mean free path in bulk materials, the conductivity undergoes a reduction. This correlation works for either epitaxial, polycrystalline or amorphous structures as the maximum crystallite size is limited by the film thickness, preserving the size effects, considering that all the other constituent components of the conductivity remain unchanged [4, 31]. However, as described in previous sections, the microstructure might contain a large number of structural defects and grain boundaries which can act as scatters for charge carriers, further reducing the conductivity.

In one of the most complex microstructures where the film is a semiconductor formed by small crystallites embedded in amorphous tissue and surrounded by a large number of grain boundaries, and containing either electrons or holes as majority carries, the transport mechanism becomes very complicated owing to the simultaneous interaction of various scattering mechanisms. In this type of microstructure, a larger crystalline volume fraction favors the conductivity by allowing a higher carrier mobility unlike the amorphous phase. The grain boundaries are considered as a disordered region were mobile carriers are scattered in their travel between crystallites. As an example, the electrical conductivity of polycrystalline and nano-crystalline materials is substantially lower than the bulk single crystalline counterpart attributed to a reduced carrier mobility in spite of having a similar carrier concentration [32]. Microstructural defects such as voids, dangling bonds, and localized defects, which are found mostly in the grain boundaries, also contribute to further reduction of conductivity. These defects are known to trap mobile carriers of doped semiconductors, forming a potential energy barrier which limits the motion of charge carriers between crystallites [33]. Accordingly, electrical conductivity is reduced by the decrease in the number of free carriers available for conduction and a reduction of the carrier mobility. Additional scattering mechanisms appear in doped semiconductors such as ionized impurity scattering, carrier-carrier scattering at room temperature, and carrier-phonon scattering at high temperatures which further contribute to the reduction of electrical conductivity.

## 5.3 Optical properties

The optical behavior of thin films is determined by the resulting microstructure that depends on the deposition parameters. Before explaining the relationship of the optical properties with microstructural features, it is necessary to define the optical coefficients. The optical response of thin films can be characterized based on the reflection and transmission coefficients. In a general arrangement a thin film with a thickness  $d_1$  and refractive index  $n_1$  is deposited onto a substrate of similar/different material with a refractive index  $n_2$ . When a beam of light strikes the interfaces formed by the incident medium and the film, and the film-substrate interface, multiple reflections and transmissions occur at both interfaces at specific angles whose total amplitudes are computed from the sum of individual reflections directed back into the incident medium, and the individual refractions traversing into the substrate, respectively. The main difference between nonabsorbing and absorbing layers is that the refractive index from the nonabsorbing layer becomes more complex by integrating a quantity *k* named *extinction coefficient* in the absorbing layer, which defines the absorption of energy within the film. Thus, it can be inferred that the optical coefficients strongly depend on the refractive indexes of each medium, the extinction coefficient, and the film thickness.

Due to the consistent results reported in literature, it is possible to generalize the behavior of optical properties with film thickness even though specific details related to film deposition are not provided. Both refractive index and extinction coefficients show a strong dependence on the film thickness. For most metallic films, i.e. Au, Ag, while the former decreases from a value higher than that corresponding to a bulk material as the film thickness increases, the extinction coefficient tends to increase, from a very low value, approaching that of the bulk [4]. These optical coefficients also behave differently depending on the wavelength of the incident beam because they become dominated either for intra-band transitions in the visible, or free electrons in the infrared region. The electronic contribution to the optical behavior explains the effect of film thickness on the optical response. As the thickness is reduced the surface scattering mechanism increases, reducing in turn the electronic mean free path and the scattering time, which limits the contribution to the optical conductivity. The reduction of these both parameters produces an increase of electrical resistivity, and thus, a connection between optical properties and resistivity can be established. This correlation implies that structural defects such as voids, unsaturated bonds, point defects, extended defects, band tail states, and structural features like grain boundaries and oxide, all of which contribute to increase the carrier scattering, influence the optical properties.

The behavior of reflection and transmission is also a function of the degree of roughness in the film created during deposition [34, 35]. Essentially the roughness degrades the film uniformity producing a thickness variation across the film which affect the transmission and optical coefficients.

## 6. Characterization techniques

In order to understand the connection between deposition parameters, the resulting morphology and the physical properties of thin films, it is necessary to characterize each of these features. The reduced volume of thin films, however, does not allow to employ universally all the characterization techniques developed for bulk materials. Accordingly, in this section the most common characterization techniques suitable for thin film measurements are briefly described.

#### 6.1 Mechanical characterization

The mechanical characterization comprises the determination of residual stress commonly created during deposition, and the physical properties such as Young's modulus and hardness.

The well-known Stoney Equation [36] is widely used to characterize the stress generated in a film deposited onto a thicker substrate. The principle behind this equation is the linear correlation between the stress crated within the film, and the amount of bending produced in the substrate as a result of the constraint condition among them. The application of this technique requires the knowledge of the radius of curvature of the substrate before and after the film deposition. The radius of curvature is often measure with an optical profilometer or drawing on any high resolution microscopy method that allows to reproduce the sample profile. The accuracy of this method is subjected to the compliance of certain conditions, i.e. the film thickness is much thinner than the substrate, very small strain and rotations, both film and substrate should be homogeneous and isotropic, equi-biaxial stress in the plane of the film, spherical deformation of the system film/substrate, and spatial invariability of stress and curvature in the whole surface. Even though some of these conditions are not fully in compliance, this technique has still been used for stress determination in a number of investigations including semiconductor-based thin films in the solar sector, thin film transistor industry among others [37, 38].

Physical properties such as hardness and Young's modulus are usually characterized drawing on the nano-indentation technique [29, 39]. This method consists in moving a sharp indenter towards the surface of the film until making an effective contact, then the applied load and the displacement are repeatedly recorded. In this way a correlation of the applied load through the indenter and the depth of indentation is established. As the indenter penetrates into the film, the slope of the loading curve progressively increases due to stronger contact between them; this correlation allows for the calculation of the hardness at any point of the curve by dividing the load to the contact area in that point. The Young's modulus of the film instead can be determined from the unloading curve once the contact area is defined considering that the Young's modulus and Poisson's ratio of the indenter are known. This is possible thanks to the direct correlation that is established between the backward motion of the indenter and the elastic properties of the film during the unloading.

#### 6.2 Chemical composition

A number of techniques are available to obtain the elemental composition of thin films, which can be classified in two groups, ion scattering and spectroscopic-based techniques. In the first group both Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA) are included. They both are based on the elastic scattering of energetic ions produced when they strike the atoms in the film surface; in this process they transfer an amount of energy to the target species atoms via collisions generating backscattered, forward scattered, and recoils particles. While in RBS the backscattered yield and its energy distribution are measured by a detector, in ERDA the corresponding quantities for the coiled particles are recorded allowing the formation of an energy spectrum from which the compositional depth profile can be extracted. These both techniques can be used as complement of each other as the RBS is suitable for detection of heavy elements while ERDA provides a higher accuracy for light elements. The main disadvantage of RBS is a shallow depth into the film that can be probed while in ERDS complications to distinguish elements with similar masses arise.

In the spectroscopic-based techniques, the X-ray photoelectron spectroscopy (XPS) is one of the most widely employed for elemental composition characterization. The XPS is based on photoelectric effect through which electrons localized either in the core or valence band are emitted when a beam of X-rays, with an energy higher than the binding energy of the electrons, is irradiated onto the film surface. Then, these ejected electrons are driven first to an analyzer to measure their kinetic energy, and subsequently they arrive to a detector where the number of electrons is counted considering their kinetic energies. The information of this kinetic energy along with the known photon energy allow to compute the electron binding energy. A spectra is then formed that correlates the electron count vs. the calculated binding energy. The binding energy constitutes a signature for the identification of each constituent element of the film since each element possesses a unique value. On the other side, the intensity of the spectra instead reflects the concentration of the element. This technique is suitable for probing the sample in a depth of a few nanometers as it is limited by the interactions of emitted electrons with the atoms present in the film.

# 6.3 Microstructure and morphology

A number of methods are available for the microstructure characterization in terms of crystalline volume fraction, crystallite size, and crystallographic orientation.

The distinctive microstructure and material phase of thin films as a result of deposition conditions can be extracted from Raman microscopy, and X-ray diffraction (XRD). The Raman technique [40] is a non-destructive method based on the scattering of incident photons, coming generally from a laser beam, caused by the vibrational modes of molecules or atoms present in the film. The scattering of photons can be either elastic, or inelastic; within the latter, photons can be scattered with a frequency lower than incident photons (stokes) or higher than incident photons (anti-stokes). A Raman spectrum is formed considering the intensity and the frequency of the scattered light (inelastic) corresponding to the specific vibrational mode of the molecule in question. The material phase fraction in volumetric terms can be extracted from the Raman line-shape. The different peaks observed in the Raman spectrum designates different material phases, which can be extracted by isolating the integrated intensity of the required peak. This isolation is usually carried out by a deconvolution of the Raman spectra using specialized software that allows to perform a peak fitting analysis. The average crystallite size can also be extracted from the Raman spectrum by means of a correlation length model which is suitable for sizes larger than 5 nm. However, certain considerations are necessary to avoid the superposition of simultaneous effects such as stress and local heating due to a high laser power.

The X-ray diffraction technique [41] is based on the scattering principle where a monochromatic beam of X-rays is directed onto a specimen which contains a set of lattice planes. The incident X-rays are scattered in different angles by the lattice planes according to the Bragg's law, giving rise to constructive interference which build up the peaks of the diffraction pattern. The peak shape defines the material phase for the substance under study providing a broad peak for amorphous regions, and sharp peaks for crystalline ones. In this way, the fraction of crystallinity can be determined once the integrated intensities of each characteristic peak is obtained. The peak width also provides information about the crystallite size, which shows a broadening for small crystallites and shrinking for larger ones. The crystallite size is computed drawing on the well-known Scherrer's formula. In the case of crystalline orientation it can be inferred from the relative change of the peak height.

The morphology of the film can be investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM is one of the most widely used tools to characterize the morphology of thin films. This technique is based on the interplay of a beam of electrons with the sample surface. This interaction produces the emission of electrons from the sample with different energies due to either elastic, inelastic scattering or photons, which are collected by a detector to produce a distribution map based on the intensities of the signal. Each of the three emitted scattered electrons allows the reproduction of images which provide different information about the sample, i.e. images from secondary electrons (inelastic scattering) are suitable for the study of topographical features. From a top view this technique permits the visualization of the crystalline columns emerging at the sample surface, and the different material phases, either crystalline and/or amorphous, due to the contrast created by the secondary electrons, while the film thickness can be evaluated form a cross-sectional SEM analysis.

TEM consists in the emission of a beam of electrons which are directed onto a very thin sample (a few hundred nm) to allow the transmission of such electrons. The intensity with which these transmitted electrons exit the sample depends on the density and thickness of the sample; thus, these structure-dependent intensities give rise to the formation of a contrast that is projected as an image on a fluorescent screen. In essence, a compact structure produces a higher scattering of electrons projecting a darker image while a porous structure projects a brighter image in a bright field image dominated exclusively by transmitted electrons. TEM constitutes a powerful technique with a spatial resolution higher than SEM for the characterization of microstructure, crystallite size, crystalline orientation, and the film thickness can be obtained via a cross-sectional TEM image.

In some characterization cases two or more techniques are complementarily employed to extract thorough information from thin films. For example, due to the in-depth probing the Raman technique can provide the size of the small crystallites that form a columnar structure in the film while the SEM can be used to determine the diameter of the crystalline columns emerging at the sample surface. Furthermore, the selection of the appropriate characterization technique strongly depends on the characteristics of the film such as the thickness, whether it is a conductor, semiconductor or insulator, whether it is possible to achieve a high vacuum, among others.

#### 6.4 Electrical properties

Perhaps the most widely used technique to measure the electrical resistivity is the four-point probe method. It consists of four metal tips linearly arranged keeping the same separation from each one where an electric current is applied in the outer two probes while the potential difference is measured in the inner two probes. From these measurements the sheet resistance ( $R_{\rm sh}$ ) of the film can be calculated by means of the following equation. The Sheet resistance is defined as the ratio of the resistivity ( $\rho$ ) to the film thickness (t).

$$R_{sh=\frac{\rho}{t}} \tag{1}$$

An extra issue related to the measurement of carrier concentration and carrier mobility appears in semiconductor characterization. The Van der Paw technique [42] provides a solution to obtain these parameters. This method is based on two independent measurement, i.e. resistivity and Hall coefficient. The characteristic resistances are first obtained by the application of a current in two adjacent contacts while the potential difference is measured in the other two remaining contacts, all

of which are located in the periphery of a sample with an arbitrary shape. Then these results are incorporated into an expression developed by Van der pauw where d is the film thickness, f is a correction factor that depends on the ration of the characteristic resistances  $R_{\rm A}$  and  $R_{\rm B}$ .

$$\rho = \frac{\pi d}{\ln 2} \left( \frac{R_A + R_B}{2} \right) f \tag{2}$$

The Hall effect consists in the creation of a voltage when an electric current (I) is applied between opposite contacts of a semiconductor that is under the effect of a magnetic field perpendicular to the plane of the sample (B). This potential difference is created by the migration of charge carriers, either electrons or holes, to the edge of the sample induced by the magnetic force. The sign of this voltage is determined by the type of major carriers dominating the electronic transport. This Hall voltage ( $V_{\rm H}$ ) is used to obtain the Hall coefficient ( $R_{\rm HS}$ ) and the carrier concentration ( $N_{\rm S}$ ) through the following equation.

$$R_{HS} = \frac{V_H}{IB} = \frac{r}{qN_S} \tag{3}$$

where *r* is the scattering factor, and *q* is the elementary charge.

The carrier Hall mobility ( $\mu_H$ ) is obtained by combining the Hall coefficient with the resistivity previously calculated

$$\mu_{H} = \frac{R_{HS}}{\rho} \tag{4}$$

# 7. Applications and challenges of thin films

Thin films technology has historically been used in a wide range applications going from decorative purposes in its early stage, evolving for optical purposes latter on, and an almost endless range of applications with the appearance of advanced deposition techniques, supported by the rapid development of vacuum technology and electrical power. Overall, thin films are used to enhance the properties of bulk materials by depositing a layer with the desired physical and chemical characteristics to improve their functionality. In the following section a brief description of the most technological relevant fields of application of thin films is presented.

Advanced electronics-optoelectronic devices have become an important field for the application of a number of thin film types. In particular, MOSFET and CMOS absorb a great amount of the technological development in semiconductor thin films. The fabrication of MOSFETs requires the use of dielectric thin films, i.e. silicon dioxide (SiO<sub>2</sub>) [43, 44] to insulate the conducting channel from the gate. This thin film has been used due to its ease of fabrication, high impedance due to a large band gap, resistance to high temperatures and chemicals. Also, metallic films are required for the fabrication of multiple microelectronic devices, opto-electronics and optical devices [13, 45]. Al thin films are usually deposited in the channel between the source and drain of MOSFETs to allow the voltage for its operation. Instead, Cu thin films are commonly used in CMOS as gate metallization due to its high electrical conductivity and higher resistance to electromigration. Thin films have also played an important role in data storage devices due to their good magnetic properties in an attempt to replace the traditional flash memory devices for non-volatile memory devices [46]. Thin films such as BiFeO<sub>3</sub>, lead-zirconium titanate films, amorphous Si, organic compounds among others are being explored as candidates as based-material for this application [47–50].

The use of thin films in the photovoltaic sector (PV) is conceived as a potential solution to reduce the cost per watt in the generation of electricity. This sector has been experiencing a rapid market penetration due to the accelerated achievement of higher efficiencies and the development of thin film structures with better stability. In fact, record efficiencies about 23.3% and 22.1% have been reached using copper indium gallium selenide (CIGS) and CdTe thin films as based materials, respectively [51]. Overall, the advantages of thin films in the PV sector is related to the high absorption coefficient of the absorber layer, which permits to reduce considerably the material thickness, contributing to the reduction of material cost; also thin film technology allows the deposition of multiple-juntion devices to capture most of the solar spectrum to increase the conversion efficiency [52]. Additionally, thin films can be deposited into flexible substrate for roll-to-roll manufacturing of PV modules [53]. The state-of-the art of thin films for PV application was initially dominated by amorphous silicon, but evolved into the more efficient CdTe and CIGS, and lately organic and perovskite-based PV cells are under investigation due to its reduced processing cost and feasibility to deposit at low temperatures in flexible substrates [54, 55].

Thins films and coating applications are involved in a large number of fields including optics, and in sectors where the improvement of the mechanical and chemical properties of bulk materials provide a better functionality or larger lifespan. Optical thin films are widely employed in eyeglasses to improve the vision through the use of a polymer-based optical element that is coated to the spectacles. In addition, the undesired transmission of ultraviolet light and undesired reflection are prevented by the use coatings materials able to absorb wavelengths lower than 400 nm, and the use of antireflective coatings usually made of dielectric materials [56]. Architectural glazing has drawn on thin film coatings to enhance the energy efficiency in office buildings [57, 58]. The heat transfer can be managed from outside and inside the buildings by a suitable filtering of the spectral regions of light. Only transmission of visible light from the outside, and reflection of infrared radiation from inside can be set by making the windows to become a multifunctional device-like with thin films with different spectral response, saving energy from air conditioning and heating for the former and latter cases, respectively. Coatings as a means to increase the wear resistance and reduction of friction in cutting tools can be obtained by multilayer deposition of ceramic coatings, i.e. TiN, TiC [13]. Coatings for corrosion resistance are widely spread in numerous sectors including pipes coated with SiC, stainless steel components coated with oxides, i.e. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, engine parts coated with high temperature corrosion protection such as  $MoSi_2$  among others [13].

Organic thin films have attracted a great attention owing to certain unique properties, in particular, flexibility and low cost material processing which are essential to expand the scope of application of many technologies. In photovoltaics for example, although still low, the efficiency has been improved considerably from 0.04% up to about 8.3% [54] in organic-polymer based modules, but its evolution remains fuelled by the low cost of material processing, i.e. printing, spraying, and the possibility to fabricate flexible modules. Likewise, the intrinsic complex fabrication process and rigidity of Si-based field-effect transistors can be somehow overcome by organic thin films field-effect transistors. The use of organic thin film have already been proven in various applications such as memory devices, sensors, electronic papers, and smart cards [59, 60].

The use of thin films has gained a considerable space in *biomedical applications* due to their ability to provide biocompatible and functional properties, for example, invasive devices, tissue engineering substrates, drug delivery, and antimicrobial coatings, to name a few. The surface of implants have to comply special

chemical and mechanical properties, and Ti6Al4V thin films appear to provide appropriate conditions for femur implants [61]. This structure apart from offering a good adhesion and harness, promotes the formation of a calcium layer through a chemical interaction with the biological fluids, improving the osseointegration. Polymer-based thin films have demonstrated to have a good resistance to protein adsorption, which is essential to provide a biocompatible behavior to implants. In this respect, poly (ethylene glycol) PEG, PEGylated thin films are suitable for bone, dental implants and for tissue engineering purposes [62, 63]. Composite thin films have also been used to provide the appropriate mechanical and biological properties to implants in neuronal applications. For example, silicon-based implants have been coated with a nanostructure formed by amorphous silica with fillers of aluminum, silicon dioxide or silver in order to provide microbial protection. Inorganic thin films with piezoelectric properties deposited on flexible substrates are also being investigated for the fabrication of nano-generators and nano-sensors for biomedical applications [64]. These piezoelectric devices have the capacity to convert mechanical energy provided by the movement of internal organs into electrical energy to power for example pacemakers or nano-sensors. Due to the high sensitivity to mechanical movement these devices can also be used to monitor the cell deformation at nanoscale. Higher performance piezoelectric devices have been fabricated using perovskite such as BaTiO<sub>3</sub>, PZNT, and PMN-PT [64, 65].

The broad scope of thin film applications require of tailored physical, mechanical and chemical properties which are linked to the resulting structure and morphology, and they in turn depend on the deposition techniques and deposition parameters adopted. Accordingly, a number of challenges remain to be tackled for a complete understanding of the connection among the different phases involved in the fabrication of thin films. Overall, various versions of CVD and PVD deposition techniques present a still expensive final product, lack of reproducibility, inappropriate attachment of the film to the substrate, high deposition temperatures which prevent the use of cheaper substrates, and limited control over the final properties. Thus, deposition technology needs to evolve with a higher precision to control the microstructure, and with a higher deposition rate suitable for large area deposition to reduce the cost. Moreover, although nanostructured thin films are promising for cutting edge applications such as microelectronics, optics, photovoltaics, and biomedicine, some of them need to be transferred to specific substrates for an appropriate operation. Consequently, the now poor transferring technique has to progress to take fully advantage of thin film technology. Even though a number of characterization techniques are available for tracking almost every feature of thin films, many of them struggle when the film thickness approaches a few nanometers. For example Raman or X-ray diffraction characterization might degrade due to the inevitable contribution from the substrate to the acquired spectra. Sophisticated models to analyze the data are therefore needed to isolate the relevant information. Of primary importance for biomedical applications is the knowledge of protein adsorption in substrates for the appropriate selection of materials; however, the characterization tools for this purpose are still at their infant stage, and they are based on complicated models for data analysis. Therefore, more advanced and specific in vitro models can pave the way for a rapid identification of suitable thin films. In spite of the significant progress in deposition and characterization techniques, the prediction of film properties as a function on the microstructure is still very difficult. This occurs due to the complex transport properties derived from the multiple defects, grain boundaries, material phases, quantum confinement effects in very thin films, interface scattering, among others. Thus, advanced models that incorporate all of these structural variants are necessary to establish the appropriate connection between microstructure and film properties to progress in the thin film technology.

## 8. Conclusions

This chapter attempted to carry out the study of thin films maintaining a tight correlation among the deposition techniques, the resulting microstructure, and their physical properties. It was found that the development of deposition methods are driven to satisfy the needs for films with specific mechanical, physical and chemical properties. Overall, they have evolved to enable the fabrication of thin films with increasingly higher purity, based on a variety of depositing materials and substrates with high reproducibility. However, the cost of material processing of certain structures such as nanostructures, quantum well, quantum wires, and quantum dots is still a challenge for commercial applications. The selected deposition technique and deposition parameters greatly define the final thin film microstructure being either amorphous, polycrystalline or epitaxial. In particular, the deposition temperature and deposition rate strongly influence the adatom-diffusion at the substrate surface giving rise to the formation of islands whose sizes increase with feeding of atoms. The most common morphological feature in many films is a columnar structure formed due to the feeding of atoms from the vapour flux once the adatom-diffusion in the substrate surface has placated due to the interfering process between islands. The mechanical, electrical, and optical properties of thin films are determined by the final morphology. It is important to remark that these properties normally deviate from the values corresponding to their bulk counterparts. For example, the yield strength and hardness are higher in thin films due to the influence of crystallite size, and movement of dislocations usually found in thin films. Likewise, the electrical conductivity is also affected by additional scattering mechanisms appearing due to the reduced film thickness. There are several techniques available for thin film characterization, but their accuracy strongly depends on the depositing material, substrate material, and film thickness. In most cases, two or more techniques are complementary used to access the required information with high precision. Regardless of the progress in thin film technology, important challenges remain to be tackled, including the accurate prediction of film properties based on the final microstructure, more advanced characterization techniques in the biomedicine field, and sophisticated models for data analysis.

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