

Optoelectronic Properties of Tin Doped Indium Oxide Films Fabricated by DC Magnetron Sputtering with Post Annealing in Oxygen Atmosphere

By

Cristian Javier Herrera Rodriguez

Thesis submited as a partial requirment for obtaining the Master of Science Degree with specialty in Electronics at the Instituto Nacional de Astrofisica, Optica y Electronica.

Supervised by:

Dr. Oleksandr Malik

Dr. Francisco Javier De La Hidalga Wade

Tonantzintla, Puebla.

February, 2014.

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DEDICATION

I dedícate this thesis, to the memory of my mother, Maria de Lourdes Rodriguez Z., who helped me with my lessons throughout her life. To my father Pedro J. Herrera Franco, who has been my role model for hard work, persistence and personal sacrifices, and who instilled in me the inspiration to set high goals and the confidence to achieve them. My brothers and niece, Maria Herrera, David Herrera, Pedro Herrera and Estefania Herrera who have been my emotional anchors through not only the vagaries of graduate school, but my entire life. My sister in law Melissa Escalante and my beautiful nephew that's on his way.

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RESUMEN

Las películas de Óxido de Indio dopado con Estaño (ITO) son altamente transparentes en la región visible, exhiben una alta reflectancia en la región de infrarrojo y presentan una conductividad eléctrica cercana a la de un metal. Debido a esta inusual combinación de propiedades ópticas y eléctricas, este material encuentra una gran variedad de aplicaciones en dispositivos optoelectrónicos.

En este trabajo se presentan los resultados obtenidos de depositar películas de ITO en sustratos de Vidrio Corning mediante la técnica de DC Magnetrón Sputtering con una potencia de 100 watts, usando un blanco cerámico de ITO (In₂O₃:SnO₂, 90:10 wt%), en ambiente de Argón, a temperatura ambiente, y un tratamiento térmico posterior a diferentes temperaturas en un ambiente rico en oxígeno.

Mediante mediciones XRD, espectrales, Efecto Hall, y AFM se analizaron las propiedades eléctricas, ópticas y microestructurales de las películas de ITO en función de la temperatura de tratamiento térmico posterior. Se encontró que la película amorfa de ITO se transforma en una estructura policristalina para temperaturas superiores a los 200°C, además de que la resistividad decrece y la transmitancia se incrementa. Los mejores parámetros electro-ópticos de las películas de ITO se obtuvieron cuando se sometieron a un tratamiento térmico posterior a 300°C y en ambiente de oxígeno puro. Esta temperatura permite la fabricación de películas de ITO de alta calidad sobre sustratos de polímeros flexibles Kapton de DuPont. Evidentemente, para el uso de otros sustratos flexibles, por ejemplo Teflón, que son importantes en aplicaciones de películas delgadas fotoeléctricas, se requeriría reducir la temperatura de ese tratamiento abajo de 200°C; este problema y su posible solución son planteados y discutidos como trabajo futuro.

ABSTRACT

Indium Tin Oxide (ITO) films are highly transparent in the visible region, exhibiting high reflectance in the infrared region, and presenting nearly metallic conductivity. Owing to this unusual combination of electrical and optical properties, this material is widely applied in optoelectronic devices.

In this study, ITO films were deposited on Corning Glass substrates by DC magnetron sputtering technique at 100 watts using an ITO ceramic target (In₂O₃:SnO₂, 90:10 wt%) in argon atmosphere at room temperature, and a posterior annealing at different temperatures in oxygen-rich atmosphere. The electrical, optical and microstructural properties of ITO films, as a function of the post-annealing temperature were analyzed by XRD, spectral, Hall Effect and AFM measurements. It has been found that as-deposited the amorphous ITO films transform to a polycrystalline structure at temperatures above 200°C. At the same time, the resistivity decreases and the visible optical transmittance increases. The best electro-optical parameters of the ITO films have been obtained by annealing at 300°C in pure oxygen environment. This temperature allows for the fabrication of high guality ITO films on flexible polymer substrates Kapton from DuPont. The use of other flexible substrates, such as Teflon, which are important for thin film photoelectric applications, is connected with the desire of decreasing the annealing temperature below 200°C; a possible solution to achieve this goal is discussed as a future work.

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ACRONYMS

AFM	Atomic Force Microscope
AMLCD	Active Matrix Liquid Crystal Displays
CVD	Chemical Vapor Deposition
DC	Direct Current
EM	Electromagnetic
FWHM	Full Width at Half Maximum
ITO	Indium Tin Oxide
NIR	Near Infrared
PLD	Pulsed Laser Deposition
RF	Radio Frequency
RMS	Root Mean Square
RF	Radio Frequency
RT	Room Temperature
RMS	Root Mean Square
TCO	Transparent Conductive Oxides
TFT	Thin Film Transistor
UHV	Ultra High Vacuum
UPS	Ultraviolet Photoemission Spectroscopy
UTMF	Ultra Thin Metal Films
UV	Ultraviolet
XRD	X-Ray Diffraction

CHAPTER 1

1.1 INTRODUCTION

One of the most important fields of current interest in material science is the fundamental aspects and applications of transparent conducting oxide (TCO) thin films. The characteristic properties of such coatings are very low electrical resistivity and high transparency in the visible region.

A large number of materials such as indium oxide, tin oxide, zinc oxide and cadmium stannate can be used for TCO coating. Since the electrical and optical properties depend strongly on microstructure, stoichiometry and the nature of impurities present, the growth technique plays an important role. With the increasing sophistication of devices used the TCO films, there has been a need for improved quality and understanding of the basic properties of these films. The mechanisms of doping and conduction are still under investigation. Compositions are still quoted without adequate detailed analysis, especially the oxygen role. Many reviews in this field that have been published up to now have concentrated themselves with deposition techniques and properties.

Tin doped indium oxide films (ITO) present a big interest due to its highlevel optoelectronics parameters. Sputtering is one of the most versatile techniques used for the deposition of TCO films when device-quality films are required. Compared with other deposition techniques, the sputtering process produces films with higher purity and better-controlled composition, provides films with greater adhesive strength and homogeneity, and permits better control of film thickness.

In past years Microelectronics Laboratory of INAOE developed in the frame of the CONACyT project fabrication technology of high quality TCO films by low cost spray pyrolysis technique. One of disadvantage of this method is a significant high fabrication temperature (450-500⁰C) that does not allow using of this technique in area of thin film solar cells based on hydrogenated silicon and germanium. At this moment, the Laboratory has projects for realization of which the TCO films with high-

level optoelectronic parameters need to be fabricated by low temperature deposition method. The sputtering is one more perspective method to achieve this aim.

The Laboratory has projects for realization of which the TCO films with high-level optoelectronic parameters need to be fabricated by low

The sputtering equipment of the Laboratory at this moment in it basic configuration allows deposition of TCO films only at room temperature and in argon (Ar) plasma without the oxygen adding.

The main aim of this work is developing the fabrication process of high quality TCO films using this equipment with post-annealing treatment of the films in oxygen-rich atmosphere. Results of this work are compared with published ones using more traditional sputtering deposition in mixed argon-oxygen atmosphere.

1.2 OBJECTIVES

1.2.1 GENERAL OBJECTIVES

Central task of this research is developing the fabrication technology of high-quality ITO films on Corning glass substrates by direct current (DC) magnetron sputtering at room temperature in pure Ar atmosphere with post-annealing treatment in oxygen-rich environment and a detailed comparison obtained results with existent traditional deposition techniques.

1.2.2 PARTICULAR OBJECTIVES

1. Optimizing deposition process of the ITO films using the sputtering equipment ATC ORION 3 UHV of the AJA International, Inc.

2. Optimizing post-annealing of the ITO films in oxygen-rich environment.

- 3. Optimizing procedure to make using results obtained from:
- XRD data

2

- AFM data
- Hall effect data
- Spectroscopic data

with the aim to obtain better value of the figure-of-merit.

4. Analyzing obtained results with published from other researchers.

5. To make conclusions for the future work directed to decreasing deposition temperature for the possibility to use a flexible substrates.

CHAPTER 2

2. BACKGROUND

The emergence of new optical sensors has drawn attention to the scientific community and industry mainly due to the wide variety of applications that exist for these devices. Optical sensors have a wide range of applications in several areas such as medicine, communications, automotive industry, etc.

A crucial challenge in the optoelectronics industry is the realization of cheap and reliable *transparent electrodes*, i.e., films presenting simultaneously low resistivity with a high optical transparency.

2.1 SEMITRANSPARENT METALS

Thin metal films (<10 nm), become transparent to light still maintaining good electrical properties [1]. In fact, metal-based transparent electrodes have been demonstrated using metal alloys, thin noble metals, alkaline earth metals protected from oxidation by noble metal layers, multicomponent metals, and single-component ultrathin metal films (UTMFs). Single-component UTMFs based on transition metals, such as titanium (Ti) and nickel (Ni), can overcome the high cost of raw materials such as Au or Pt, and can be deposited using a typical industrial processes (e-beam or sputtering). As an example, the transmittance of different metal films with different thicknesses, in the wavelength range of visible light, is shown in Figs. 2.1 and 2.2.



Figure 2.1. Optical transmittance spectra of Au and Al films with different thicknesses.



Figure 2.2. Optical transmittance spectra of Ti and Ni films with different thicknesses.

2.2 TRANSPARENT CONDUCTIVE OXIDES (TCO)

Thin films of certain metal oxides present low electrical resistivity and high optical transmission in the visible region, hence they are suitable as transparent conductive electrodes for a wide range of applications [3-10]. The continued development of technology of TFT's, for example, and the interest in significantly improving the efficiency of photovoltaic cells has increased the need to understand and control the TCO layers which are deposited on thin films of other materials.

The CdO film was the first TCO used in solar cells in the early 1900. In the 40's,a SnO₂film was deposited on glass by spray pyrolysis and chemical vapor deposition (CVD) for electroluminescent panels, since then there have been more deposit methods for different applications. Currently, TCO films are important components used in optoelectronic technology. They are used as mirrors to reflect heat as transparent electrical contacts in flat panel displays, optical sensors, solar cells, among others. Specifically, thin films of indium oxide doped with tin (In₂O₃: Sn or ITO) have experienced a high degree of development, both in their optical and electrical characteristics, and also in preparation methods. This has enabled optical transmission values in the visible above 80% and higher conductivity values to 10^3 S/cm.

2.2.1 INDIUM TIN OXIDE (ITO)

The ITO is the most important and widely used TCO, due to the variety of applications and processes by which it can be obtained. Its presentation in the form of film has a great application in the optoelectronic technology [11-18]. Among its properties, it is a good conductor and presents excellent transparency in the visible region. High quality ITO films can be deposited on glass substrates, polymers and semiconductors, with resistivity values of about $2x10^{-4}$ Ω -cm. Transmission in the visible and the electron mobility depends on the content of Sn and O vacancies in the structure; for example for a Sn content of about 10 wt%, the transmission in the visible, resistivity, and electron mobility are optimal.

Its optical and electrical properties have been studied by different research groups, however there are few studies of ITO films deposited on polymeric substrates, which would have many advantages over glass substrates as a lower weight, bulk, fragility and easy to bend, whereby they will reduce the size of the devices.

2.2.2 GENERAL PROPERTIES OF ITO FILMS

The unique properties of ITO films are determined by its structure and composition. Indium oxide presents a cubic bixebyte structure, which is shown in Fig. 2.3. One unit cell contains 16 units of In₂O₃. Therefore, for defect free In₂O₃ crystal, there are 80 atoms in one unit cell. The reported lattice constant is 10.118Å [19], whereas the theoretical density is 7.12g/cm³. As shown in Fig. 2.3 [20], two kinds of non-equivalent indium sites are present in the In_2O_3 crystal structure. In Fig. 2.3 (a), the separation between indium and oxygen atoms is 2.18Å, and the oxygen atoms are positioned at the corners of the cube with two body-diagonally opposite corners unoccupied. In Fig. 2.3 (b), the In-O separations are 2.13, 2.19 and 2.23Å, where the oxygen atoms occupy positions at the corner of the cube with two face-diagonally opposite corners unoccupied. Based on the above description, both indium sites can be viewed as an incomplete body centered cubic structure, with an indium atom located at the center and oxygen atoms at the corners. One fourth of the anions are missing. To vary the material properties, In₂O₃ can be extrinsically doped with tin. When tin atoms substitute indium atoms, it forms either SnO or SnO₂. The material retains its bixebyte structure. However, if the doping level is extremely high, the tin atoms may enter interstitially and distort the lattice structure. As a polycrystalline structure, the ITO crystal grain size depends on various processing parameters such as the substrate temperature and deposition rate.



Figure 2.3.Cubic bixebyte structure showing the anion vacancy [20].

2.2.3 ELECTRICAL PROPERTIES OF ITO FILMS

Indium oxide is a wide band gap semiconductor. The band gap of In_2O_3 was reported as 3.75eV [21]. Generally, the In₂O₃ crystal structure is not ideal since oxygen vacancies are present. The accurate formula of indium oxide is $In_2O_{3-X}(V_0)x$, where V_0 is a donor-like doubly charged oxygen vacancy, and x is the oxygen vacancy portion and depends on the oxidation state. The typical value of x is less than 0.01. At room temperature, the excitation of electrons from valence band to conduction band is negligible. Oxygen vacancies dominate the conduction mechanism in In₂O₃ and the free charge carrier concentration has been reported to be in the 10¹⁹-10²⁰ cm⁻³ range. Extrinsic doping can vary the electrical properties of indium oxide significantly. If In₂O₃ is doped with tin atoms, tin atoms will replace indium atoms and form tin oxide SnO₂. When SnO₂ is formed, it acts as donor since it gives off an electron. Both vacancies, tin and oxygen, contribute to the conductivity of ITO. The free carrier concentration can be expressed as $n=[Sn \cdot]_A+2[V_o \cdot \cdot]$, where $[Sn \cdot]_A$ is the active tin atom concentration.

The doping level is critical for electrical properties. As the tin concentration increases, the carrier concentration increases until a saturation level is reached. An increase in the tin concentration above

this saturation level causes a decrease in the free carrier concentration. This is due to an increased probability of the occupation of adjacent cation positions by two or more tin atoms, which can deplete the active tin concentration. The carrier concentration as a function of the tin doping level is shown in Fig. 2.4. The highest carrier concentration, which corresponds to the lowest resistivity, occurs when the tin doping level is about 10%. The solid solubility of tin in indium oxide is approximately 8%. Beyond this range, the tin oxide phase will be formed, distorting the lattice structure. This will eventually cause a decrease of the free carrier concentration.

In order to obtain conductivity above $10^{3}\Omega^{-1}$ cm⁻¹without the formation of the tin oxide phase, the doping level is typically chosen in the 8-10% range. This doping level will produce a degenerate ITO [21]. Fig. 2.5 shows the energy diagram of In_2O_3 and ITO. ITO presents metal-like electrical properties because the carrier concentration is typically in the 10^{20} - 10^{21} cm⁻³ range. For heavily doped indium oxide, the contribution of oxygen vacancies to the conductivity is negligible.



Figure 2.4.Experimental and calculated carrier concentrations as a function of the tin doping level at different deposition temperatures [19].



Figure 2.5. Band structure for a) undoped In2O3 and b) tin-doped In2O3 [22].

2.2.4 OPTICAL PROPERTIES OF ITO FILMS

The theoretical treatment of the dielectric function of ITO films was derived by Bender et al. [23]. From the imaginary part of the dielectric constant, the absorption coefficients of the films were derived as shown in Fig. 2.6. Two absorption edges can be seen, one at photon energies below 1eV, which is due to the free electrons, and one at photon energies above 4eV which is caused by the excitation of valence electrons into the conductance band. In the region between 1 to 4eV, the imaginary part of the dielectric constant is negligible which corresponds to a high transmission region in the visible and NIR region.



Figure 2.6. Absorption coefficients of the ITO films [23].

2.2.5 ITO FILMS APPLICATIONS

Deposits of ITO have been very important in the development of technology in recent years. The main application of this material is to obtain a conductive and simultaneously transparent layer.

One application is to use this film as an insulator of electromagnetic radiation. The electromagnetic isolation is used for various functions, from medicine where it is needed to isolate atmospheres where a large amount of electromagnetic radiation that could be dangerous to humans, to the protection of electronic devices in order to prevent electromagnetic interference. In most applications, is also very important transparency to visible light having radiation isolating devices.

A typical installation of a system with these features could be as shown in Fig. 2.7, where two conductors deposited on the outside can be connected electrically to obtain different effects of the electromagnetic isolation layers.



Figure 2.7.Basic schematic of an EM isolator.

Another important application is the possibility of heated glass, as shown in Fig. 2.8. This is achieved by depositing a conductive layer on the inner surface of a glass panel.



Figure 2.8.Basic schematic of a heated glass.

The heated glass can be used in construction, in order to avoid the condensation of water in glasses. Other applications are in touch screens, most of them are based on resistive and capacitive effects and the transparent electrodes usually are made of ITO. A schematic of an existing type of touch screens is shown in Fig. 2.9.



Figure 2.9. Basic schematic of a touch screen.

In all the applications mentioned above the layers work statically. However, there are some other applications where the layers operate in a dynamic way, i.e., their properties of the film change with time through an electrical control. In these regards we can mention displays based on optoelectronics. Generally, these devices are liquid crystal displays, plasma screens and glass panels with a spectral reflectance or transmittance electrically controlled (electrochromic windows). For this application, generally a conductive layer is deposited on glass.

TFT screens are based on arrays of many liquid crystal cells. Each pixel and each cell is driven by a transistor [25], thus each pixel is independent and its state depends on that transistor, which prevents the possible interference between pixels. Since a large number of transistors must be integrated in a small area, the manufacturing cost is very high. A schematic of the TFT display operation is shown in Fig. 2.10. ITO layers are conductive layers of material existing in the two glass plates whose function is to permit the biasing of the liquid crystal.



Figure 2.10.Schematic of the TFT display operation.

CHAPTER 3

3. DEPOSITION METHODS

ITO films present different properties depending on the method used for the deposit. This is because the optical and electrical properties depend on the structure, morphology, and the impurities of the film. In this section, we will mention the various techniques of deposition.

3.1 CHEMICAL VAPOR DEPOSITION (CVD)

The CVD process can be defined as the reaction of one or more compounds in the form of gas or vapor to give a solid film. Precursor sources of these films are usually in the form of gas or liquid. In both cases, the reactants (gas or vapor) must be introduced into the reaction chamber in the proper proportion to produce the material through the corresponding reaction. A schematic of the process is shown in Fig. 3.1. The precursor gases are fed through the entry door of the reactor, whereas the gaseous sub-products of the reaction are removed through a suitable evacuation system.



Figure 3.1.CVD process scheme.

An important aspect of the reaction of CVD is the need to activate the precursor gas to produce the reaction, because in normal operating conditions (pressure and temperature) the reaction rate is generally very

low. It is precisely the method used in the activation what distinguishes the different CVD techniques: activation by temperature, the use of a plasma, or electrical discharge between two electrodes, electromagnetic radiation, etc., although, in most cases, it is necessary to have some thermal contribution to achieve a full activation of the reagents.

One of the distinguishing features of the CVD technique is that the deposited materials are produced by reaction of one or more compounds. CVD reactions are usually classified as homogeneous and non-homogeneous (or heterogeneous), according to which the reaction occurs in the gas phase or in contact with the surface of the substrate to be coated, respectively. Homogeneous reactions lead to the formation of very small diameter particles (tens or hundreds of nanometers), which are deposited by gravity onto the substrate and other parts of the reactor.

3.1.1 CHEMICAL VAPOR DEPOSITION OF ITO FILMS

Even though this process does not require a high vacuum, and is easier for the production of large scale applications, this technique has not been fully exploited for the deposition of ITO films [26-28]. However, there are some reports of the deposition of ITO films with this technique, using indium acetylacetonate and tin (II) acetylacetonate, obtaining a polycrystalline film [29], with a reaction temperature in the 350-500°C range.

Maruyama and Fukui [26] prepared indium-tin oxide films with an atmospheric-pressure chemical vapor deposition method. The source materials were the mentioned previously, which are nontoxic and easy to handle. For a 215-nm-thick polycrystalline film deposited at 450°C, the

resistivity was $1.8 \times 10^{-4} \Omega$ -cm and a transmittance of 90% at a wave number above 400 nm. The atomic ratio Sn/In of the film was 0.031. Jeffrey Gaskell and David Sheel [30] used an unreported precursor combination; dimethylindiumacetylacetonate, [Me₂In(acac)] and monobutyltintrichloride, MBTC. The ITO film was deposited at a

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substrate temperature of 550 °C with growth rates exceeding 15 nm/s and growth efficiencies between 20 and 30%. The resistivity was $3.5 \times 10^{-4} \Omega$ cm and a transmittance > 85% was obtained for a 200 nm film.

3.2 SPRAY PYROLYSIS DEPOSITION

This technique has been used for the deposition of thin films or ultra-fine powders of different materials ranging from semiconductors to superconductors, and materials for optical and magnetic applications. The spray pyrolysis technique basically consists of the generation of an aerosol, containing a suitable solvent to deposit the precursor material. The solvent should have low viscosity so that it can easily produce the aerosol. With respect to the solute or compound, it must be chosen according to what we want to deposit, with the condition that it must be soluble in the solvent selection. The aerosol is then transported to the substrate where it makes the process of pyrolysis (decomposition by heat), thus allowing the deposition of a film whose characteristics depend on the components dissolved in the precursor solution.

Upon coming in contact the aerosol droplets with the hot substrate, most of the solvent contained in these drops is evaporated and the resulting products of the pyrolytic reaction are deposited on the substrate surface. The kinetics of this reaction depends on the nature of the components of the solution and the substrate surface temperature, since in this type of reaction we can have successive decompositions of the compounds dissolved in the precursor solution, surface diffusion of the atoms, and structural arrangement. In general, the spray pyrolysis technique can consider four deposit mechanisms that depend on the temperature of the substrate. These mechanisms are shown schematically in Fig 3.2.



Figure 3.2.Deposition mechanisms of the spray pyrolysis technique at different substrate temperatures.

Case A, in this type of deposit the substrate temperature is low, then the aerosol droplets reach the surface in a liquid form. Slowly evaporating the solvent on the substrate leaving a dry deposit.

Case B, increasing the substrate temperature, the solvent evaporates before the droplet reaches the surface. The precipitate falls onto the surface and the decomposition occurs thereof.

Case C, the temperature is high enough, an a sequence of steps occur: first there is the evaporation of the solvent followed by sublimation or gasification of the solute, the gas diffuses into the surface of the substrate where it reacts chemically in a gas-solid phase to give the final product. This case is known as Chemical Vapor Deposition CVD.

Case D, the temperature is now very high, the chemical reactions take place before the steam reaches the substrate. Therefore, the product of this chemical reaction is a fine powder falling on the substrate.

Is possible to obtain films on each of the above cases but the adhesion to the substrate is poor in cases A, B and D. The adhesion of the films could be significantly improved by an appropriate thermal treatment; this, however, does not guarantee that the resulting material presents good optical properties. Furthermore, the material obtained in the C case, exhibits good adhesion and optical quality without the need for further thermal treatment. Experimentally, it is desirable to obtain films under the conditions of case C. Therefore, according to the discussion above, the spray pyrolysis technique can be classified among the CVD techniques.

3.2.1 SPRAY PYROLYSIS DEPOSITION OF ITO FILMS

For this deposition technique of ITO film [31-34], tin doping is performed by adding stannic chloride hydrated in an $InCl_3$ solution. The gas flow rate is of the order of 31 liters/min. The temperature of the substrates for this technique is usually in the 400-700°Crange. It has been observed that the incorporation of tin in the films has a strong dependency on the nature of the substrate, as seen in Fig 3.3.



Figure 3.3. Sn/In atomic ratio in the In₂O₃:Sn films on different substrates [31].

M. Ait Aouaj et al. [34] deposited several ITO films at a substrate temperature of 400°C. The x-ray diffraction spectrum showed that the ITO films a (400) orientation preference. The best electrical resistivity values, deduced from optical measurements, were 8×10^{-4} and $6 \times 10^{-4} \Omega$ cm for ITO (6% of Sn).

3.3 VACCUM EVAPORATION

Although it is one of the more used techniques for the deposition of semiconductor films, this deposition method has not been extensively used for the growth of transparent conductors [35-38]. A resistively heated tungsten or tantalum source, or an electron beam heated source, can be used to evaporate the material. The important control parameters are the substrate temperature, evaporation rate, source to substrate distance and the oxygen partial pressure. The conducting films can be evaporated in three ways:

- 1) Directly evaporating metal oxides, i.e. SnO₂, In₂O₃, Cd₂SnO₄;
- 2) By reactive evaporation of the metal in the presence of oxygen;
- 3) Post-oxidation of metal films.

When oxide materials are evaporated, there is always some deficiency of oxygen in the films. Either the films must be evaporated in an oxygen partial pressure or there must be a post-deposition heat treatment in air. In reactive evaporation, the corresponding metal or alloy is evaporated at rates of 100-300 Å/min in oxygen atmosphere onto substrates heated to about 400°C. The partial pressure of oxygen is achieved by first creating a vacuum of approximately 10⁻⁶Torr and then introducing the oxygen such that the pressure increases to 10⁻⁴Torr. Recently, activated reactive evaporation has been employed to grow better quality transparent conducting films at a higher growth rate (500 Å/min). In this method, the reaction between the evaporated species and the gas is activated by employing a thermoionic-assisted plasma in the reaction zone. A dense plasma is generated by using a thoriated tungsten emitter and low voltage anode assembly. In the case of post-oxidation of metal films, the conductivity and transparency of the films are controlled mainly by the oxidation temperature, which is usually in the 350-500°C range.

3.3.1 ITO FILMS DEPOSITED BY VACUUM EVAPORATION METHOD

The vacuum evaporation of ITO films from In_2O_3 and SnO_2 powders [36] using two independently controlled beryllia crucibles gave the best results at a substrate temperature of 400°C, an oxygen partial pressure of $3x10^{-4}$ Torr, and 5wt% of SnO₂. Reports on growth of ITO thin films, from a single crucible with a pellet of ITO by vacuum evaporation, suggest no trace of any oxide phase of tin even for heavily doped films [37]. Annealing of reactively evaporated ITO thin films in the 100°C-320°C temperature range indicated an increase in bandgap of the thin films [38]. This study used a 90:10 In-Sn alloy source for the evaporation, and the annealing was carried out under nitrogen atmosphere. A minimum resistivity of $4.5x10^{-3}\Omega$ -cm and a maximum carrier concentration of $1.94x10^{20}$ cm⁻³ were observed for an annealing temperature of 150°C.

3.4 PULSED LASER DEPOSITION

PLD is conceptually very simple, as illustrated schematically in Fig. 3.4. The simplest experimental setup consists of a substrate holder and a target holder. A beam of high intensity pulsed laser is impinged on the target, vaporizing and depositing a thin film on the substrate.



Figure 3.4.Pulsed Laser Deposition scheme.

The complexity of the physical processes involved in PLD contrasts with its conceptual simplicity. On the surface of the material (target) the laser radiation is absorbed, causing electronic excited states that decay to the ground state by emitting phonons. In this rapid conversion electron-phonon, heating of the material occurs, depositing a large amount of energy in a very small volume and in a very short time (6-12 ns). Thus the surface temperature of the target increases and a solid-liquid interface appears moving inward. The interface between the melted and the solid material continues to advance while the material is vaporized in the form of a plume.

Photon absorption by the vapor of the material gives rise to the formation of a plasma consisting of a variety of elements, as ions, molecules and other species and even droplets, particles of the target material of the target, which are plucked entirely from it. Once the plume is formed it will spread in the direction of the target.

Finally, when the laser pulse ceases, the target surface solidifies, changing its physical characteristics and morphology, and in some cases, even in composition.

3.4.1 PULSED LASER DEPOSITION OF ITO FILMS

The electro-optical properties of the films deposited by PLD from a 90:10 wt% ITO target showed a strong dependence on the oxygen pressure during deposition [39]. High quality films were obtained in the vicinity of 1×10^{-2} Torr oxygen pressure. The films deposited at room temperature were amorphous and had the lowest resistivity of $5.35\times10^{-4}\Omega$ -cm. Heungsoo Kim and James S. Horwitz [42] grew ITO films by the pulsed laser deposition method on PET, glass and YSZ substrates. The resistivity of these films were of $4.1\times10^{-4}\Omega$ -cm, $2.2\times10^{-4}\Omega$ -cm and $1.8\times10^{-4}\Omega$ -cm respectively. These films present a transmission in the visible range of approximately 90% and the film surface roughness was about

0.5nm. The carrier mobility and concentration were in the $28-34 \text{ cm}^2/\text{V-s}$ and $1.0-1.2\text{X}10^{21}\text{cm}^{-3}$ ranges, respectively. Thian-Khok Yong et al. [43] used a 2-inch diameter disk of ITO target with a composition of 90 wt.% In_2O_3 and 10 wt.% SnO_2 . The deposition rate was estimated to be about 0.5 nm/s and the ITO film thicknesses were always maintained at 200 nm. The crystal structure of the ITO films were determined by X-ray diffraction, showing four major diffraction peaks corresponding to (222), (400), (440) and (622) orientations.

3.5 SPUTTERING

If a surface is bombarded with energetic particles such as accelerated ions, this may cause the ejection of atoms from the surface of a material, this process is known as sputtering. These ejected atoms can be condensed on a substrate to form a thin film. In most cases, the positive ions of noble gases such as argon are used to bombard the surface of materials. Materials of high melting point can be used as easily as a low melting point, using sources of RF or DC, sputtering of both materials can be achieved, hence both, metals and insulators, can be deposited

3.5.1 SPUTTERING SYSTEM

This system is based on a vacuum chamber, which has inside two electrodes (anode and cathode); an electric discharge is established between the anode and the cathode in a low pressure environment controlled by a supplied residual gas. Due to the potential difference, the residual gas atoms are ionized. Residual gas ions collide against the cathode, on which the target of a specific material is located, and this is disintegrated by ionized molecules. The ejected atoms of the material form a cloud that is deposited on the surrounding surfaces. This phenomenon is called cathodic sputtering.
The atoms of the eroded material leave the electrode surface either as free atoms or in chemical combination with the residual gas molecules. A number of atoms released are condensates on surfaces surrounding the cathode, whereas the remainder atoms are returned to the cathode by collision with gas molecules.

Once expelled, the target atoms travel until they reach a surface, or substrate. The deposited layer is formed or grows on the substrate structure and is influenced by some parameters such as deposition rate, substrate temperature, pressure and gas composition, and composition of the target.

Argon is an inert gas, and is chosen in the most common sputtering systems because it is a heavy and especially abundant gas. It also has a low ionization potential. The inert nature of argon inhibits the formation of compounds to on the target surface.

If the target is conductive, a source of direct current can be used (DC sputtering), while RF sputtering (RF source) is preferred when nonconducting targets are used. Then if the target is an insulator the neutralization process results in a positive charge on the target surface. This load can increase the point that the bombing ions are repelled and the process will stop sputtering. To continue the process, the polarity of the target must be turned upside down to attract enough electrons of the discharge to remove the charged surface.

3.5.2 MAGNETRON SPUTTERING

The operation of a magnetron sputtering, as shown in Fig. 3.5, is based on the electrons undergo a superimposed electric and magnetic field at the cathode will have circular orbits. In this system a device with a magnet, which combined with the inner electric field present in the two electrodes, cause the electrons to perform helical paths, producing longer paths that those existing without the magnetic field. This new distance of the electrons causes an increase in collisions with atoms of residual gas, allowing the possibility of reducing the working pressure range as 10^{-5} Torr or more commonly than 10^{-2} Torr. Another serious consequence of using the magnetron is the increased plasma density, which leads to an increased current density and increasing the deposition ratio.



Figure 3.5. Magnetron Sputtering Operation.

A disadvantage of magnetic field assisted sputtering is that the erosion of the material is not uniform, and there is a waste of materials, as shown in Fig. 3.6. This is because the sputtering is more intense where the magnetic field lines are parallel to the surface of the cathode. The visible result is that the target is eroded in the form of V.



Figure 3.6. Wastage of the target on a magnetron sputtering system.

3.5.3 SPUTTERING DEPOSITION OF ITO FILMS

Sputtering technique can be employed to deposit highly transparent and conducting ITO films [44-46]. Usually, In-Sn alloys and In_2O_3 :SnO₂ targets are used with a 10% tin concentration for the latter. The

deposition rate of sputtered metal targets depends strongly on the oxygen partial pressure and the sputtering power[47], independently of the total sputtering pressure. For high power sputtering, the number of oxygen atoms decreases preventing the oxidation of the target surface making it more metallic. The effect of using a higher power is that the number of sputtered species increases, but there is a higher consumption of oxygen atoms needed to oxidize the target surface and the sputtered atoms. For lower power, the surface of the target is non-stoichometrically oxidized and the sputtered atoms can oxidize further during their transport or during the film growth. The annealing of the films is found to enhance the quality of the films. The use of oxide targets is found to help the stoichiometry of the films more precisely.

C. Guillen and J. Herrero [48], reported that the ITO films deposited on an argon ambient, and at room temperature, exhibited to be amorphous for films with a thickness of 100-200nm and showed crystalline growth for thicker films or annealed films at temperatures above 200°C. ITO films thermally annealed in N₂ ambient at 400°C showed the minimum resistivity, but having a maximum transparency in the NIR for films at a temperature of 300°C. M. Gulen et al. [49] used this deposition method on a DC Magnetron Sputtering system for the production of ITO films using a ceramic target (In₂O₃:SnO₂, 90:10 wt%). The films were grown at room temperature, in argon ambient, and then annealed on a 100-700°C temperature range.

CHAPTER 4

4. TCO FILMS CHARACTERIZATION METHODS

Characterization is an important step in the development of new materials. The complete characterization of any material consists of analysis, compositional and structural characterization, micro-structural analysis and surface characterization. In this chapter, we describe different analytical instrumental techniques used to characterize our transparent films paying special attention the relevant operating principles.

4.1 OPTICAL PROPERTIES CHARACTERIZATION METHODS OF THE TCO FILMS

4.1.1 FILM THICKNESS AND REFRACTIVE INDEX MEASUREMENT USING ELLIPSOMETRY.

The ellipsometer measures the thickness and refractive index of semitransparent films. This instrument depends on the fact that the reflection at the interface of a dielectric depends on the polarization of the light, while the transmission of this light through the layer of the transparent film changes the phase of the incoming wave depending of the refractive index of the material. This method can be used to measure layers as thin as 1nm.

The basic components of an ellipsometer are indicated in Fig. 4.1. The monochromatic light source is commonly a He-Ne laser (λ =632.8nm). The monochromatic light passes through a polarizing prism, which results in linearly polarized light. This light is now reflected off the film of interest. The film should be very smooth to get a good reflection. The polarization of the light is changed by the reflection so it is now elliptically polarized. The reflected polarized light is then passed through another prism which is rotating about the axis of the light and finally onto

a photodetector. The output signal of the photodetector is shown on a display. The angles of the polarizer and analyzer are then processed with a software that calculates the thickness and refractive index of the measured sample.



Figure 4.1.Ellipsometer system configuration.

4.1.2 FILM TRANSPARENCY USING A SPECTROPHOTOMETER

The spectrophotometry is one of the most used analysis methods, and it is based on the relation between the absorbed light on behalf of a compound and its concentration. A spectrophotometer is a system that measure light intensity at different wavelengths. It produces light with a light source, and after the light passes through a sample, the light is diffracted into a spectrum that is detected by a sensor and interpreted. The output of a spectrophotometer is usually a plot of light intensity versus wavelength. The data collected to generate this plot can typically be saved as a table of wavelengths and intensities. The y values of the graph can be represented as either transmittance or absorbance. The transmittance is the fraction of incident light at а specified wavelength that passes through a sample. The transmittance of the sample is expressed between 0 and 1 (as a fraction) or between 0 and 100 (as a percentage). A diagram of a spectrophotometer is shown in Fig. 4.2.



Figure 4.2. Optical diagram of a spectrophotometer.

4.2 STRUCTURE AND MORPHOLOGY CHARACTERIZATION METHODS OF THE TCO FILMS

4.2.1 X-RAY DIFFRACTION (XRD)

X-ray diffraction (Fig. 4.3) is a technique widely used in the analysis of the crystal structure of solid materials. The diffraction phenomenon depends on the crystal structure of the material and the wavelength of the incident photon. It is used to identify the crystalline phases of the samples and to measure their structural properties, size and orientation of the crystals.



Figure 4.3. X-ray Diffractometer.

In this technique, a beam X-rays with wavelengths between 0.5 and 2A, is incident on the sample. This beam is diffracted by the crystal planes of the sample, according to well known Bragg's law

$$2dSen\theta = n\lambda \tag{1}$$

Where d is the distance between the atomic planes of the crystalline phase, λ is the wavelength of incident photons and θ is the angle of incidence. If the wavelength of the x-ray photons is comparable or smaller than the lattice constant (λ <2d), the results are diffracted beams in different directions to the incident beam. The diffracted x-ray intensity is measured as a function of the diffraction angle 2 θ . Constructive interference (Fig. 4.4) will occur when Bragg's law is satisfied.



Figure 4.4. Interference of photons scattered by ordered structures.

Knowing the experimental parameters θ and λ , one can identify the orientation of the planes involved in the diffraction based on the distance d between them. The resulting spectra are very specific, they are like a fingerprint for each crystalline material. Each diffraction peak has a position itself in the spectrum of each material. The peak width analysis allows us to calculate the crystallite size in that direction that diffracted. This is possible using the well known Scherrer equation:

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta} \tag{2}$$

Where:

- *τ* is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size.
- *K* is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite.
- λ is the X-ray wavelength.
- β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$.
- θ is the Bragg angle.

4.2.2 ATOMIC FORCE MICROSCOPE (AFM)

The atomic force microscope (Fig. 4.5) is a microscope of scanning probe type of very high resolution, which proved to be fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The AFM is one of the main tools to generate images and measure nanoscale superficial properties. The term microscope used for this equipment is erroneous, as this involves observation when in fact the information is collected by scanning the surface with a mechanical probe.



Figure 4.5. AFM Mechanism

The AFM consists of a cantilever probe of microscopic size, with a fine point at the end that is used to scan the sample surface. The probe is typically made of silicon or silicon nitride, with a radius of curvature at the tip of the order of nanometers. When the tip approaches the surface of the sample, the forces between the tip and the sample produce a deflection of the probe according to Hooke's law, which states that the amount of deformation on the materials body is linearly proportional the stress applied to this.

$$F = -K * \chi \tag{3}$$

Where F is the force, x is the distance of the deformation and K is the deformation constant of the material. Depending on the situation the forces that can be measured in the atomic force microscope include mechanical contact force, the Van der Waals forces, capillary forces, the chemical bond, electrostatic forces, magnetic forces, etc. Commonly, the deflection is measured using a laser light beam reflected at the top of the needle to a set of light detectors. Other methods for the deflection measurement are based on optical interferometry or using piezoresistive sensing. These probes are manufactured with piezoresistive materials, which act as a deformation meter, using a Wheatstone bridge, which is an instrument that measures electrical resistance. The deformation of

the probe due to the deflection can be measured, but this method is a little bit less sensitive as laser light deflection.

If the probe tip swept at a constant height, a risk would exist that this collide with the surface causing damage to both, therefore, most of the systems have a feedback mechanism that is used to adjust the distance of the tip to the sample and thereby maintain a constant force between the two. Generally, the sample is mounted on a piezoelectric tube, which can move the sample along the z axis to maintain a constant force and the x and y axes to sweep the sample. Alternatively, a piezoelectric crystals tripod can be used to sweep the three axes x, y and z with a crystal by direction. This eliminates some of the distortion effects that occur with the scanner tube. The resulting map swept area represents the topography of the sample.

4.2.2.1 ROUGHNESS PARAMETERS

To better understand the morphology of a surface a quantitative description of the surface topography must be carried out. The topography matrix data should be treated over all profiles extended the analysis to surface (3D). The most important S parameters are described below.

 S_a (Roughness average). The Roughness average is the arithmetic mean of the absolute values of the surface departures from the mean plane. S_a is normally used to describe the roughness of machined surfaces. It is useful for detecting variations in overall surface height and for monitoring an existing manufacturing process. A change in S_a usually means a change in the process,

$$S_a = \frac{1}{MN} \sum_{j=1}^{N} \sum_{i=1}^{M} |z(x_i, y_j)|$$
(4)

where M and N are the number of data points in X and Y.

 S_q (Root mean square roughness). The root mean square (RMS) roughness, obtained by squaring each height value in the dataset, then

taking the square root of the mean. It is used for finish of optical surfaces. Represents the standard deviation of the profile and is used to calculate the skewness and kurtosis. S_q cannot detect spacing differences or the presence of infrequent high peaks or deep valleys.

$$S_q = \sqrt{\frac{1}{MN} \sum_{j=1}^{N} \sum_{i=1}^{M} z^2(x_i, y_j)}$$
(5)

 S_{sk} (Skewness). Skewness measures the asymmetry of the profile around the mean plane. Negative skew indicates a predominance of valleys, while positive skew is seen on surfaces with peaks. S_{sk} can illustrate load carrying capacity, porosity, and characteristics of nonconventional machining processes. Surfaces that are smooth but are covered with particles have positive skewness, while a surface with deep scratches/pits will exhibit negative skewness. If S_{sk} exceeds ±1.5, you should not use average roughness alone to characterize the surface. Skewness is very sensitive to atypical values in the surface data

$$S_{sk} = \frac{1}{MNSq^3} \sum_{j=1}^{N} \sum_{i=1}^{M} z^3(x_i, y_j)$$
(6)

 S_{ku} (Kurtosis). Kurtosis is a measure of the "spikiness" of the surface, or the distribution of spikes above and below the mean line. For spiky surfaces, S_{ku} > 3; for bumpy surfaces, S_{ku} < 3; perfectly random surfaces have kurtosis of 3. Kurtosis is also a measure of the randomness of surface heights. Kurtosis is useful for evaluating machined surfaces and is sometimes specified for the control of stress fracture. S_{ku} is high when a high proportion of the surface falls within a narrow range of heights. If most of the surface is concentrated close to the mean surface level, S_{ku} will be different than the one when the height distribution contains more bumps and scratches. The farther the value is from 3, the less random (i.e., the more repetitive) is the surface.

$$S_{ku} = \frac{1}{MNS_q^4} \sum_{j=1}^N \sum_{i=1}^M z^4(x_i, y_j)$$
(7)

4.3 ELECTRICAL PROPERTIES CHARACTERIZATION METHODS OF THE TCO FILMS

4.3.1 FOUR POINT PROBE METHOD

The sheet resistance of a deposited film on a substrate can be measured using the four-point probe method as shown in Fig. 4.6. The distance between the electrodes is always constant, and applying a certain current between the extreme electrodes, we measure the potential difference appearing between the inner electrodes.



Figure 4.6. Four point probe diagram.

Under these conditions, the sheet resistance can be obtained as:

$$R_s = 4.532 \frac{U}{I}, \left(\frac{\Omega}{\Box}\right) \tag{8}$$

Where 4.532 is a geometric factor. If the film thickness is known, the bulk resistivity ρ (in ohm cm) can be calculated by multiplying the sheet resistance by the film thickness t in cm.

$$\rho = R_s * t \tag{9}$$

4.3.2 VAN DER PAUW METHOD

This technique consists basically in injecting a current on two contacts and measuring the tension between the other two.



Figure 4.7. Van der Pauw measuring technique.

To obtain the value of the sheet resistance (Rs) of the material we use the following equation:

$$e^{\frac{-\pi R_A}{R_S}} + e^{\frac{-\pi R_B}{R_S}} = 1$$
 (10)

Bulk electrical resistivity is calculated as follows:

$$\rho = R_s * t \tag{11}$$

4.3.3 HALL EFFECT

If on a conducting or semiconducting material which current flows is set in a transverse magnetic field, a transverse electric field appears to the latter and a potential difference (V_H). This phenomenon is known as Hall effect.





Figure 4.8.Hall Effect measurement configuration.

The Hall coefficient is determined by:

$$R_H = \frac{V_H q}{I|B|} \tag{12}$$

Where I is the current that flows in the sample, B is the applied magnetic field. The Hall coefficient can be positive or negative. The sign depends on the majority carriers of the sample, being negative (electrons) or positive (holes).

Its possible to determine the number of charge carriers with the next expression:

$$n = \frac{1}{qR_H} \tag{13}$$

and the mobility is determined with the next expression:

$$\mu = \frac{|V_H|}{R_S IB} \tag{14}$$

So by Hall measurements we can determine the type, concentration and carrier mobility of the material.

CHAPTER 5

5. EXPERIMENTAL

5.1 DEPOSITION SYSTEM

Due to its advantages over other deposition methods and the film properties obtained, DC magnetron sputtering was chosen as the deposition method.



Figure 5.1. AJA ATC Orion 5 UHV DC Magnetron Sputtering System.

The deposition system used is the ATC Orion 5 UHV System (Fig. 5.1) from AJA International Inc. The system is composed basically of two vacuum chambers (main and load), the vacuum systems and the control panel that includes the DC power supply and the gas supply controls.

a) Main chamber: This chamber has the capacity to accept 3 target sources. Fig 5.2 illustrates the scheme of the main chamber, and we can see that the target sources are in the bottom part of the chamber. The substrate holder is placed in the upper part of the chamber and has a rotary mechanism so that the deposition on the substrates is more uniform.



Figure 5.2. ATC Orion 5 UHV main chamber scheme.

b) DC Power Supply: This unit is available at 750 Watt and features integral 3 way switch-boxes. Each generator has 3 coaxial outputs, which are connected to separate magnetron sources. The desired source is selected from either the front panel or via the I/O.



Figure 5.3. DC-XS-1500W-3 DC Power Supply.

5.2 SUBSTRATES USED FOR THE ITO FILMS DEPOSITION

The ITO films were deposited on different type of substrates:

- (100) n-type silicon wafer with a resistivity of 2-5 Ω ·cm
- Corning Glass 2947
- Corning Glass 1737

To obtain the thickness and refractive index using ellipsometry, the film was deposited on the n-type silicon. Both corning glass substrates were used to obtain the transmittance spectra, carrier concentration and mobility using Hall effect, XRD spectra, and AFM film roughness measurements. Below, the cleaning process for all type of substrates as well as the deposition process is described.

5.2.1 CORNING GLASS CLEANING PROCESS

The substrates were immersed in TCE and placed in an ultrasonic vibrator for a period of 10 minutes. Afterwards they were immersed in acetone in the vibrator for 10 minutes. Finally, the substrates were rinsed in DI H_2O and dried in the centrifuge system.

5.2.2 SILICON WAFER CLEANING PROCESS

To start the cleaning process of the samples, they are immersed in trichloroethylene (TCE) and acetone separately for a period of 10 minutes in an ultrasonic vibrator. This step serves to clean the samples of organic waste and oils.

This is followed by the removal of the native oxide that has grown by exposing the silicon wafer to the environment. This step involves immersing the samples in a solution consisting of deionized water (DI H_2O) and hydrofluoric acid (HF) at a concentration of 7:1 (Buffered Solution), respectively. They are immersed in the solution until it is observed that the samples are hydrophobic.

Finally, the RCA I and RCA II procedures are performed. RCA I process is a solution composed of ammonium hydroxide (NH₄OH), hydrogen peroxide (H₂O₂), and DI water (H₂O) in a ratio of 1:1:5, respectively. This process is performed at a temperature of 70°C for 17 minutes. Afterwards, the RCA II process consisting of a solution composed by hydrochloric acid (HCI), peroxide (H₂O₂), and DI water (H₂O) in a ratio of 1:1:6, respectively is performed. The RCA II process is performed at a temperature of 70°C for 17 minutes. These two cleaning processes serve to remove organic and inorganic waste, as well as metal ions from the surface of the samples.

Finally these samples are immersed again in the 7:1 solution for the removal of the chemical oxide grown during the RCA cleaning. They are then immersed in the Super Q system until the water presents a resistivity of 16 M Ω ·cm and then dried by centrifugation.

5.2.3 ITO SPUTTERING DEPOSITION

The deposition of the ITO film was performed in the DC Magnetron Sputtering under the following conditions:

- Chamber Pressure: 3.0mTorr
- Argon gas flow: 12sccm
- DC Power Source: 100W
- Deposition time: 25 minutes.

5.2.4 POST-ANNEALING TREATMENT OF THE ITO FILMS

The post-annealing treatments of the ITO films were conducted in the post-thermal treatment furnace under an O_2 ambient with a constant flow of 44ss during 60 minutes. The temperatures considered for the thermal treatments were 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C.

5.3 FABRICATION OF OPTOELECTRONIC DEVICES

Optoelectronic devices were fabricated on (100) n-type silicon wafer with a resistivity of 2-5 Ω -cm.

5.3.1 WAFER CLEANING PROCESS

The cleaning process for the wafers mentioned was performed identically as described above in5.2.2. They were immersed in TCE and acetone for 10 minutes in an ultrasonic vibrator. Then, the RCA I and RCA II cleaning processes for 17 minutes were proceeded. Finally, the

chemical oxide grown during the RCA cleaning process was removed with the 7:1 solution. Then the wafers were rinsed in DI H_2O and dried in the centrifuge spinner.

5.3.2 DRY THERMAL OXIDATION OF THE SILICON WAFERS

The silicon oxidation was performed in the dry oxidation furnace at INAOE's Microelectronics Laboratory. The temperature chosen for the oxidation was 1000°C. The furnace was previously cleaned from metallic contaminants during 2 hours under a TCE/O₂ ambient. The TCE bubble was maintained at 15°C using a controller from NESLAB. The samples were slowly introduced into the furnace until it finally reached a constant temperature zone. This was done in order to prevent the formation of dislocations and other defects in the silicon due to the temperature stress.

To obtain an oxide thickness of approximately 60 nm, the oxidation growth time was of 90 minutes. During the first 5 minutes, the silicon oxidation was performed in pure oxygen atmosphere to achieve a well-controlled silicon/oxide interface. Afterwards, 85 minutes in O_2/TCE atmosphere was performed. O_2 was introduced at 2 l/min (44 s.s.) constant flow, while TCE was held at 6 l/min (149 s.s.) flow. TCE was introduced in order to neutralize any metallic ions in the furnace. Finally, an annealing step was performed in nitrogen inert atmosphere for another 30 minutes. The samples were withdrawn from the furnace slowly.

5.4 MOS CAPACITORS FABRICATION PROCESS

The MOS Capacitors fabricated in this work have the following structures:

- Al/SiO₂/n-Si
- ITO/SiO₂/n-Si

5.4.1 SAMPLE BACK-SIDE CONTACT DEPOSITION

The back-side oxide was etched using the 7:1 solution applied with a cotton swab, rinsed in DI H_2O , and then dried in the centrifuge system. The aluminum contact at the back-side was deposited in the DC Magnetron Sputtering system with the following conditions:

- Chamber Pressure: 3.0mTorr
- Argon gas flow: 12sccm
- DC Power Source: 200W
- Deposition time: 15 minutes.

For the Al/SiO₂/n-Si structure, the front-side contact was deposited on the SiO₂ surface. Afterwards, the samples were immersed in fuming nitric acid during 10 minutes. Then the samples were subjected into a post metallization annealing step in the alloy furnace at 460°C in a N₂/H₂ ambient, at a constant flow of 60ss and 40ss, respectively, during 30 minutes.

5.4.2 FRONT-SIDE CONTACT SPUTTERING DEPOSITION

For the ITO film deposition, the conditions are the following:

- Chamber Pressure: 3.0mTorr
- Argon gas flow: 12sccm
- DC Power Source: 100W
- Deposition time: 25 minutes.

5.4.3 LITOGRAPHY OF THE FRONT-SIDE CONTACT

Lithography process was then performed on the surface of the front-side contact to obtain the desired structures. A positive photoresist and a bright field mask were used. The photoresist was exposed to UV light, and the samples were immersed in the developer solution to remove the photoresist on the desired regions. The back-side aluminum contact was protected with positive photoresist.

5.4.4 WET ETCHING OFTHE FRONT- SIDE CONTACT

The aluminum front-side contact structures were immersed in an $H_3PO_4/HNO_3/C_2H_4O_2$ solution at 40°C until the aluminum film was etched completely leaving the desired patterns.

Finally, the ITO front-side contact structures were immersed in a DI H_2O/HCI solution in the ratio of 1:1 at 40°C until the ITO film was etched completely leaving the desired patterns.

5.4.5 POST-THERMAL TREATMENT OF THE ITO FILMS

The post-thermal treatments of the ITO films were performed in the postthermal treatment furnace under an O_2 ambient with a constant flow of 44ss during 60 minutes. The temperatures given for the thermal treatments of the films were 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C.

5.5 SCHOTTKY BARRIER DIODE FABRICATION

The cleaning and dry thermal oxidation processes have already been performed for the fabrication of Schottky barrier structures.

5.5.1 LITOGRAPHY AND WET ETCHING OFTHE THERMAL OXIDE

Lithography process was then performed on the surface of the thermal oxide to obtain the desired structures. A negative photoresist and a bright field mask were used. Under a UV light, the chains of organic molecules of the photoresist are broken in the exposed region, allowing for the developer to remove the photoresist in the desired regions. Afterwards, the samples were submerged in a 7:1 solution until the desired patterns of the oxide were removed, and the silicon surface becomes hydrophobic. The backside aluminum contact was previously protected with a positive photoresist so the 7:1 solution does not affect it.

The photoresist was removed with acetone in an ultrasonic vibrator during 10 minutes; later, the samples were rinsed in DI H_2O and dried in the centrifuge system.

5.5.2 ITO SPUTTERING DEPOSITION

The deposition of the ITO film was performed in the DC Magnetron Sputtering under the following conditions:

- Chamber Pressure: 3.0mTorr
- Argon gas flow: 12sccm
- DC Power Source: 100W
- Deposition time: 25 minutes.

5.5.3 LITHOGRAPHY AND WET ETCHING OF THE ITO FILM

Lithography process was performed on the surface of the ITO film in order to obtain the desired structures. A positive photoresist and a bright field mask were used. The photoresist was exposed to UV light and the samples were immersed in the developer to remove the photoresist on the desired regions. The backside aluminum contact was protected with a positive photoresist.

The samples were then immersed in a DI H_2O/HCI solution with a ratio of 1:1 at 40°C until the ITO filmed was etched completely leaving the desired patterns.

5.5.4 THERMAL POST-TREATMENT OF THE ITO FILMS

The thermal post-treatments of the ITO films were performed in the thermal post-treatment furnace under an O_2 ambient with a constant flow of 44ss during 60 minutes. The temperatures for the treatments were 200°C, 250°C, 300°C, 350°C, 400°C, 450°C and 500°C.

CHAPTER 6.

6. EXPERIMENTAL RESULTS: CHARACTERIZATION OF THE ITO FILMS

6.1 PROPERTIES OF THE CORNING GLASS SUBSTRATES

In this chapter, the results obtained from the characterization of the ITO films, grown by the sputtering deposition method and annealed in an O_2 atmosphere, are presented. Also, the discussion and analysis of these results are presented.

As mentioned previously, the ITO films were deposited on different Corning Glass for experimental comparisons. The glass substrates have the following properties:

• 2947 Corning Glass is a Soda-lime glass and is prepared by melting the raw materials, such as sodium carbonate (soda), lime, dolomite, silicon dioxide (silica), aluminum oxide (alumina), and small quantities of fining agents (e.g., sodium sulfate, sodium chloride) in a glass furnace at temperatures up to 1675°C and are used as microscope slides.

• 1737 Corning Glass is a boro-aluminosilicate glass slide that is composed of SiO₂, AI_2O_3 , BaO and MgO in a 64:21:7:8 wt%, respectively. One of its main applications is the use as substrates for Active Matrix Liquid Crystal Displays, AMLCD.

6.2 ITO FILM THICKNESS AND REFRACTIVE INDEX MEASUREMENTS

In Fig. 6.1, the thickness and refractive index of the ITO films as a function of the annealing temperature, measured by the ellipsometry technique in different regions of the films, are shown. It should be noticed that the thickness of the films slightly decreases, from a approximately 220nm for a temperature of 200°C, to an average value of 200 nm for temperatures above 300°C and remains constant.

The refractive index also decreases for an increasing temperature, from an average value of 2.082 at 200°C to a minimum value of 1.927 at 350°C. It should be noticed that the refractive index remains almost constant for temperatures above 400°C.



Figure 6.1.Thickness and refractive index of ITO films for different annealing temperatures.

The refractive index was also measured using the F20 Filmetrics spectrometer for a 500-1000 nm wavelength range, as shown in Fig. 6.2.



Figure 6.2. Refractive index comparison between ellipsometry and spectrometry techniques obtained for an annealing temperature of 450°C

The refractive index obtained from the spectrometer at 450°C for a wavelength of 632nm is basically the same as that obtained using ellipsometry.

6.3 STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF THE ITO FILMS.

The AFM images of the surface morphology of the ITO films on Corning Glass 2947 for different annealing temperatures are shown in Fig. 6.3.



Figure 6.3. AFM images of ITO Films on Corning Glass 2947 for different annealing temperatures.

From these images, it can be seen that the annealing temperature is a strong factor in the modification of the surface morphology of the films. For temperatures above 200°C there seems to have some grain

formations on the surface of the films. And this is more notorious for the 300-350°C annealing temperatures where the surface presents a denser granular structure.

Using the commercial software SPIP, the roughness parameters (S_a , S_q , S_{sk} and S_{ku}) were estimated. The average S_a and RMS S_q roughness values are shown in Fig. 6.4. It is noticed that the minimum average roughness value of 0.41nm corresponds to the annealing temperature of 300° C. The same behavior was observed for the RMS roughness value of 1.06nm for 300° C.



Figure 6.4. S_aand S_q roughness parameters of the ITO films on Corning Glass 2947.

In Fig. 6.5, the Skewness S_{sk} and Kurtosis S_{ku} roughness values are shown. It is observed that for annealing temperatures of 400-450°C the values of S_{sk} have an average value close to zero, which means that the ITO films have a symmetrical height distribution at those temperatures.



Figure 6.5. S_{sk} and S_{ku} roughness parameters for ITO films on Corning Glass 2947.

At lower temperatures the S_{sk} values are positive, thus the surface of the films present more peaks than valleys. The values of S_{ku} for annealing temperatures of 250-350°C remain fairly constant, increasing notoriously at 400°C. The S_{ku} values for temperatures of 200-400°C are above 3, indicating that the surface of the films present more peaks than valleys. The surface morphology of the ITO films deposited on the Corning Glass 1737 for different annealing temperatures is shown in Fig. 6.6. For a 250-400°C temperature range the surface of the films presents a more granular structure.



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500 ⁰C Figure 6.6. AFM images of ITO Films on Corning Glass 1737 for different annealing temperatures.

The surface roughness values obtained with SPIP software for the ITO films deposited on the Corning Glass 1737 are shown in Figs. 6.7 and 6.8.



Figure 6.7. S_a and S_q roughness parameters for ITO films on Corning Glass 1737.



Figure 6.8. S_{sk} and S_{ku} roughness parameters for ITO films on Corning Glass 1737.

Differently from the previous substrate, the average roughness value S_a decreases for annealing temperatures above 200°C and presents a minimum of 1.66nm at 250°C. For higher temperatures, the S_a values remain fairly constant, even for temperatures up to 500°C. The RMS roughness value S_q shows a similar behavior with a minimum value of 0.81nmat 250°C. The Skewness roughness value S_{sk} presents a minimum of zero at 300°C and positive values for higher temperatures. It can be noticed that for temperatures above 300°C the S_{sk} values are positive, indicating that the height distribution is asymmetrical and the surface has more peaks than valleys. The Kurtosis roughness value S_{ku} for a 250-400°C temperature range, are above 3, indicating that the surface has a Leptokurtic distribution and also presents more peaks than valleys.

Comparing both substrates, it can be observed that the roughness parameters obtained with the AFM measurements for ITO films on Corning 2947 are higher than that obtained for ITO films on Corning 1737. In Table 1, we can observe the surface roughness parameter values of the uncoated corning substrates. Then, it can be said that the surface roughness of the substrate is an important parameter to be considered when depositing the ITO films on it.

AFM results (nm)	Corning 2947	Corning 1737
Sa	2.66	0.34
Sq	3.9	0.44
S _{sk}	-0.21	0.35
S _{ku}	3.11	4.87

Table 1. Roughness parameters of Cornings Glass 2947 and 1737.

Figure 6.9 shows the X-ray diffraction patterns for ITO films on Corning 2947. As can be observed, there are 6 peaks at the 20 angles 22, 30, 35, 38, 51 and 61° corresponding to the planes (211), (222), (400), (411), (440) and (622) of In_2O_3 bonds, respectively. It can also be observed that the planes (222) and (400) are the preferential orientations with respect to the other crystallographic planes. It is also observed that for an annealing temperature above 200°C the peaks increase corresponding to the (222) and (400) planes. This means that there is a rearrangement of the crystalline structure.

In Fig. 6.10 it is shown that the crystal quality parameter I(222)/(400) has a maximum value at 250°C, decreasing to a minimum at 350°C and increasing for higher temperatures.



Figure 6.9. X-ray diffraction patterns for ITO films on Corning Glass 2947.



Figure 6.10. 222/400intensity ratio for ITO films on Corning Glass 2947 and 1737.

Using the Scherrer-Bragg equation, it was possible to determine the grain size for both planes of the films deposited on Corning 2947 as shown in Fig. 6.11. It can be observed that for annealing temperatures above 250°C the grain size for both planes present similar values, reaching a maximum grain size of approximately 55 nm at 350°C.



Figure 6.11. Grain size of ITO films on Corning Glass 2947 and 1737 for planes (222) and (400).

In Fig. 6.12, the X-ray diffraction patterns for ITO films on Corning Glass 1737are shown. It can also be observed that the planes (222) and (400) are the preferential orientations with respect to the other crystallographic planes. Also, the crystal quality parameter I(222)/(400) varies with the annealing temperature. It reaches a maximum value at 250°C, decreases at 350°C, and remains almost constant up to a temperature of 450°C.



Figure 6.12. X-ray diffraction patterns for ITO films on Corning Glass 1737.

The grain size for the films deposited on Corning 1737 was estimated using the Scherrer-Bragg equation as shown in Fig. 6.11. As it can be seen, the grain size is similar for both crystallographic planes for the 250-500°C temperature range. It can be noticed that the films for both Corning substrates at 200°C, show a weak peaks for planes (222) and (400), indicating that the film has a dominating amorphous structure. The crystal growth orientation of the deposited ITO films has been attributed to the energy of arriving particles to the substrate and this is influenced by sputtering parameters [56-58]. It was found that thermalized particles help crystallize in the (222) direction, where as high energy particles show a growth tendency toward (400) and (440) directions depending on their energy.

The X-Ray diffraction pattern for ITO film on Kapton polyimide substrate annealed at 300°C is shown in Fig. 6.13. As observed the preferential crystalline orientation for the ITO film is the (231) cubic plane or (110) hexagonal plane, but showing signs of a small peak at the orientation (222).



Figure 6.13. X-ray diffraction patterns for ITO films on Kapton Polyimide substrate.

6.4 ELECTRICAL PROPERTIES OF THE ITO FILMS

The sheet resistance of the ITO films obtained with the four-point probe technique is shown in Fig. 6.14. As can be seen, the sheet resistance varies as a function of the annealing temperature. The lowest values for both kind of substrates occur between temperatures of 250-350°C. For higher temperatures, the sheet resistance value for Corning Glass 2947 notoriously increases by approximately 6 times the minimum value. However, for the Corning Glass 1737 the sheet resistance increases only about 2.5 times the minimum value.



Figure 6.14. Sheet resistance of ITO films on Corning Glass 2947 and 1737 measured with four points probe technique.

The resistivity measured using the Van der Pauw technique is shown in Fig. 6.15, which is similar behavior to that observed with the four-point probe technique. Again, the minimum values of resistivity are observed in the 250-350°C temperature range, and the lowest resistivity values for higher temperatures correspond to the corning 1737 substrate.



Figure 6.15. Resistivity of ITO films on corning 2947 and 1737 measured with Van der Pauw technique.

The carrier concentration and mobility for the ITO films were obtained using the Hall Effect. The carrier concentration for the ITO films on Corning 2947 (Fig. 6.16) remains almost constant in the 200-300°C temperature range, presenting a maximum value of 1.6x10²¹cm⁻³ at 250°C, decreasing for annealing temperatures up to 400°C, and then remains constant for higher temperatures. It can be observe that the mobility in the 200-300°C temperature range increases linearly.

It has been noticed that the annealing temperature significantly affects the electrical properties of the films [50]. At temperatures above 200°C, the resistivity initially decreases as the temperature increases. This type of dependence on the temperature may due to the fact that crystalline structure of the films improves when the annealing temperature increases, which leads to an increasing conductivity.

For temperatures of 400-500°C the resistivity of the ITO films seem to increase due to the fact that oxygen vacancies decrease for a higher oxidation temperature. Probably lower temperatures do not produce the complete oxidation of metal substances. Hence, by increasing the oxidation temperature, the oxidation process continues, a decrease in the oxygen vacancies takes place, and consequently, the values of the electrical resistivity increases. It can be noticed that for temperatures

above 350°C, the resistivity of ITO films on Corning 2947 presents a more notorious increase.

Corning Glass 2947 is a soda lime glass substrate and sodium is a major component of it. Sodium ions of the soda lime glass substrate seem to diffuse towards the ITO films during the post-annealing treatment, this affects the conductivity of the films because of the annihilation of the oxygen vacancies [51, 52].



Figure 6.16. Carrier concentration and mobility of the ITO films on Corning Glass 2947.

For ITO films on Corning 1737 (Fig. 6.17), the carrier concentration presents a similar behavior, with a maximum value for a $250-300^{\circ}$ C temperature range, then decreases for annealing temperatures up to 400° C, and then remains constant for higher temperatures. It is also observed that the mobility increases as the annealing temperature increases up to a temperature of 450° C, and then remains constant up to 500° C.


Figure 6.17. Carrier concentration and mobility of ITO films on Corning 1737.

The carrier mobility presents a dependency with the quality of films crystalline structure and surface morphology due to a few scattering mechanisms. In the case of ITO, the scattering can be classified as 1) ionized impurity scattering, 2) neutral impurity scattering, 3) grain boundary scattering, and 4) lattice scattering. The mechanism that will certainly operates is the scattering of the electrons by ionized impurities in indium oxide and ITO [53]. This scattering is caused by ionized dopant atoms/clusters, and dominates for free carrier concentrations above 10^{20} cm⁻³ owing to the inherently high oxygen vacancy density when the deposition occurs in a low oxygen environment. The scattering of conduction electrons by ionized impurities has been extensively treated in the Born scattering approximation by Brooks and Dingle [54].

The carrier concentration depends on the number of oxygen vacancies and Sn^{+4} substitution of In^{+3} atoms [55, 56]. When annealing in O₂ ambient, oxygen atoms can be provided to the film and these atoms will combine with non-stoichiometric compounds such as In_2O_3 -x(x is the number of oxygen vacancies) created during the sputtering deposition [59, 60]. After this process, there will be a decrease in the carrier concentration due to the decrease of oxygen vacancies, and the carrier mobility will increase by making the oxygen deficient structures more stoichiometric.

6.5 WORK FUNCTION OF THE ITO FILMS.

Since ITO films exhibit excellent light transmission characteristics in the visible region and a high electrical conductivity, they are widely used in optoelectronics applications such as solar cells, liquid crystal flat panel display devices, and as a hole injecting electrode in organic light emitting diodes (OLEDs). In many of such applications, the work function of ITO has a critical importance in device performance because it affects the energy barrier height at the heterojunction interface. The published values of the ITO work function lie in the 4.1-4.7 eV range [61-65]. The value of 5.53 eV has also been published [66].

Since the work function depends on the fabrication technique, one can see a large difference between reported results. A high value of the work function (above 5 eV) has been obtained after treatment of commercial ITO films in O₂ and ozone plasma [65, 66]. Usually, the work function is determined from ultraviolet photoemission spectroscopy (UPS) measurements in ultrahigh vacuum (UHV) apparatus [64, 65]. Of course, for this work we do not have access to such measurements. However, for the estimation of the work function of the ITO films, we use a well known method for obtaining the work function based on a capacitance-voltage (C-V) measurement of two capacitors, fabricated under the same conditions on a silicon substrate covered by a SiO₂ layer and using Al and ITO gates [67]. The work function of Al is well known, 4.15 eV. Comparing the flat band of the capacitors, the difference of the ITO work function, relative to Al, can be determined.

Here one an important question arises. Do we think that the work function of our ITO films, deposited in the same conditions, on different substrates (Corning glass and thermal grown SiO_2), and annealed in a O_2 atmosphere, is the same? This is a simply speculation.

The chemical content of SiO_2 in the used Corning glass 1737 (amorphous structure) is 60%. The SiO_2 layer thermally grown on the

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silicon substrate also has an amorphous structure. Based on the coincidence of sheet resistance measurements (Fig. 6.18), we are assuming that it is possible to use the capacitance method for the estimation and monitoring of the ITO work function.

Fig. 6.18 shows the resistivity of the ITO films deposited on Corning glass 1737 and the SiO_2 layer thermally grown on the silicon wafer for different annealing temperature in the oxygen atmosphere.



Figure 6.18. Sheet resistance of the ITO films deposited on Corning glass 1737 and thermal grown SiO₂ as function of the annealing temperature.

MOS capacitors were fabricated on n-type 3-5 Ω -cm silicon wafer. The SiO₂ layer, with a thickness of about 70 nm, was grown at a temperature of 1000^oC. Then, the wafer was cut in two parts for the fabrication of the capacitors, one with AI and the other with the ITO gate. An AI layer was deposited at the back for electrical contact. A post annealing in forming gas was applied to the half wafer with AI-SiO₂-Si-AI structures.

ITO layer was deposited by sputtering on the other half wafer with SiO_2 -Si structure with AI back-contact after the heat treatment of this sample together with the AI-SiO₂-Si-AI sample in the forming gas. The sample with ITO-SiO₂-Si-Al was divided on several parts for annealing in oxygen atmosphere at different temperatures. The photolithography process was applied for etching Al and ITO layers to obtain the MOS capacitors. Because the thermal processes used for growing the SiO₂ and annealing in the forming gas are the same for both half wafers, we assume that the positive charge at the SiO₂-Si interface is also the same.

Fig. 6.19 shows a comparison of the quasi-static characteristics of the $AI-SiO_2-Si$ capacitors with those obtained from the ITO-SiO₂-Si capacitors, where the ITO gate was annealed at different temperatures.



Figure 6.19. Quasi-static characteristics of AI-SiO₂-Si capacitor in comparison with characteristics of ITO-SiO₂-Si capacitors. (The ITO gate was annealing at different temperatures)

The difference between the flat band values of the two types of capacitors, allows for the estimation of the work function of the ITO films annealed at different temperatures in the oxygen atmosphere. Films annealed at 300 and 350^oC present a work function very close to that of Al. However, the films annealed at 400 and 450^oC present a very high value of work function, 4.99 and 5.48 eV, respectively.

This experimental fact can be explained as due to the different nature of the oxygen absorbed on the grain boundary inside the ITO films. At low temperatures this absorption is physical.

At high temperatures *a chemical adsorption* takes place [69]. Adsorbed molecules and atoms of oxygen are bounded with the grains by electrons. The presence of negatively charged oxygen ions formed by taking the conducting electrons by adsorbed oxygen atoms at the grain boundary, produces a band-bending eV_s at the grain's surface that increases the work function (Figs. 6.20, 6.21)



Figure 6.20. Oxygen adsorption (index *ad* relates to chemisorbed atom) on the ITO grain boundary. At temperatures more than 350^oC, the oxygen molecule dissociates into oxygen atoms, which take up one conducting electron each from the ITO to form oxygen ions.



Figure 6.21. Schematic representation of the surface potential eV_s at the two grains boundary due to chemisorbed oxygen atoms.

Furthermore, a "consumption" of electrons from the grain reduces the concentration of electrons in the ITO film. Due to a high concentration value of the conducting electrons in the ITO film, the wide of the potential well at the grain boundary is very narrow and the electrons can tunnel through this barrier. Thus the mechanism of the electron scattering does not change for the films annealed at high temperature. The results obtained here allows for making an important conclusion about the possibility of tuning the value of the ITO work function by changing the post-annealing temperature in the oxygen atmosphere. Such tuning is important for the design of optoelectronic devices presenting high level parameters.

6.6 OPTICAL PROPERTIES OF THE ITO FILMS

The ITO films deposited on Corning Glass 1737 for different annealing temperatures are shown in Fig. 6.22.

en, Y., Yuan, J-G. and Yang, Z-Y. (2010). sion on soil chemical and microbiolog mulation in southern China. Geoderma 15 b С d а emaroli, V., Scala, D., Perez-Jimenez, J. 5). T-RFLP analysis of bacterial com eactors developed for biodegradation o obio 201e f g

Figure 6.22. Photos of the ITO films deposited on Corning Glass substrates after annealing at different temperatures in the oxygen atmosphere: a- 200°C, b- 250°C, c- 300°C, d- 350°C, e- 400°C, f-450°C, g- 500°C. Color of the films (b-g) is connected with an interference effect. It can be observed that the color of the films varies due to the interference of the light.

The optical properties of ITO films on Corning Glass 2947 and 1737 were obtained using the F20 Filmetrics spectrometer equipment. Two different analyzes were conducted: measurement of the transparency spectrum from the visible to near-infrared spectral region, and the determination of the optical bandgap shift in the UV spectral region.

In Fig. 6.23 the optical transmission spectrum is shown for ITO films on corning 2947 for different annealing temperatures. It can be observed that all the films have a transparency above 80% in the visible spectral region, presenting a maximum of 92% for temperatures in the 400-450°C range.



Figure 6.23. Optical transmittance spectra of ITO films on Corning Glass 2947 for different annealing temperatures.

The transmittance for longer wavelengths (NIR spectral region), the carrier concentration of the films plays an important role [55]. The infrared optical transmission of ITO films is mostly related to photon

interaction with free electrons, meaning that a higher carrier concentration gives rise to a lower transmittance in the NIR spectral region. It can be noticed that for a temperature of 250°C the transmittance in the NIR spectral region is the lowest of all the films, because it has the highest carrier concentration.

In Fig. 6.24 the optical transmission spectrum is shown for ITO films on Corning glass 1737 for different annealing temperatures. It can also be observed that the ITO films deposited on these substrates present a transparency above 80% in the visible region, and a maximum of 92.4% is shown at 450°C.



Figure 6.24. Optical transmittance spectra of ITO films on Corning glass 1737 for different annealing temperatures.

As mentioned before, the transmittance in the NIR spectral region of the ITO film annealed at 250°C is the lowest of all the films, because of the highest carrier concentration.

The optical transmission spectrum for ITO film on Kapton polyimide substrate annealed at 300°C in air is shown in Fig. 6.25.



Figure 6.25. Optical transmittance spectrum of ITO films on Kapton polyimide.

It can be observed that the transmittance for the annealed film improves for wavelengths in the visible spectral region in comparison with the asdeposited ITO film. For the NIR spectral region the annealed film has higher absorption than the as-deposited film.

In Fig. 6.26 the optical transmittance spectrum of ITO films, for different annealing temperatures, are shown in the UV spectral region. For a comparison purpose, the spectrum of an uncoated Corning 1737 is plotted. To obtain better results in the UV spectral region, the films should have been deposited on quartz or sapphire substrates, due to their higher transparence in this spectral region.



Figure 6.26. Optical transmittance spectra in the UV region of ITO films on Corning Glass 1737 for different annealing temperatures.

It can be observed a blue-shift of the transmission for an increasing carrier concentration of ITO films [70-73], which is the well known Burstein-Moss effect. When the electron density is higher than a certain critical density, a blocking of the lowest states in the conduction band occurs, hence a widening of the optical gap E_g . This leads to a shift of E_g toward lower wavelengths. According to the Burstein-Moss effect, the broadening of the optical band gap is given by:

$$\Delta E_g = \left(\frac{\pi^2 \hbar^2}{2m_r^*}\right) \left(\frac{3n}{\pi}\right)^{2/3} \tag{15}$$

where n is the carrier concentration and m_r^{*} is the reduced effective mass. In Fig. 6.27 the optical band broadening energy values due to the Burstein-Moss effect is shown. It can be observed that the ITO film annealed at 250°C present the largest blue-shift, due to its carrier concentration.



Figure 6.27. Blue-shift energy of the optical bandgap due to the Burstein-Moss effect.

6.7 FIGURE OF MERIT OF ITO FILMS FOR OPTOELECTRONIC APPLICATIONS

The electrical conductivity and optical transparency of ITO films should exceed certain minimum value. Ideally, the two parameters should be as large as possible. However, the simultaneous performance of maximum transmission and conductivity is not possible to achieve in most cases. It is possible to define a figure of merit as:

$$F_{TC} = \frac{T}{R_s} \tag{16}$$

Given that Eq. (16) weighs too much in favor of the sheet resistance, thus resulting in a maximum F_{TC} at a comparatively large film thickness. Haacke [74] redefined the figure of merit for a better balance between transmission and sheet resistance by

$$\phi_{TC} = \frac{T^{10}}{R_s} \tag{17}$$

Following the procedure outlined for F_{TC} , the film thickness, which maximizes Φ_{TC} , is

$$t_{max} = \frac{1}{10\alpha} \tag{18}$$

The difference between F_{TC} and Φ_{TC} arises from the added stipulation that the maximum Φ_{TC} occurs at 90% of optical transmission and not at 38% like F_{TC} . Φ_{TC} provides a useful tool for comparing the performance of transparent conductive films when their electrical sheet resistance and optical transmission are known. Furthermore, the expressions derived for Φ_{TC} can be used to predict the transparent electrode properties of a candidate material from its fundamental properties.

Tables 2 and 3 show the figure of merit for ITO films on Corning Glass 2947 and 1737, respectively.

Temp.,⁰C	T _{max}	T _{min}	T _{mean}	R _s ,	$\Phi_{\rm TC}={\rm T}^{10}/{\rm R}_{\rm s}$.,
				Ω/square	Ω ⁻¹ x10 ⁻³	
200	0.84	0.56	0.73	32	1.34	5.4
250	0.8	0.61	0.74	14.97	3.29	7.1
300	0.91	0.72	0.80	14.64	7.3	26.6
350	0.92	0.82	0.87	37	6.7	11.7
400	0.92	0.80	0.87	113	2.2	3.8
					T _{mean}	T _{max}

Table 2. Figure of merit values for ITO films on Corning 2947.

Table 3. Figure of merit values of ITO films on corning 1737.

Temp.,⁰C	T _{max}	T _{min}	T _{mean}	R _s ,	$\Phi_{\rm TC}={\rm T}^{10}/{\rm R}_{\rm s}$	5,
				Ω/square	Ω ⁻¹ x10 ⁻³	
200	0.828	0.47	0.72	33.2	1.13	4.6
250	0.83	0.55	0.756	15.45	3.95	10
300	0.842	0.646	0.79	14.15	6.7	12.7
350	0.9	0.8	0.83	19.4	8	18
400	0.92	0.76	0.86	46.7	4.7	9.3
450	0.924	0.77	0.864	55.8	4.2	8
500	0.921	0.765	0.862	57.3	3.95	7.7
					T _{mean}	T _{max}

In Fig. 6.28 the Figure of merit obtained for the ITO films on both corning glass for different annealing temperatures is shown.



Figure 6.28. Figure of merit of ITO films for different annealing temperatures.

It can be observed that the ITO film on Corning 2947 presents the highest Figure of merit for a maximum transmittance of ITO film at temperature of 300°C. For ITO films on Corning 1737, the annealing temperature 350°C exhibited the best optical and electrical properties. It can be seen that the Figure of merit obtained for the latter film, is comparable with the one obtained by M. Bender et al [55].

From Table 4, it is possible to observe that the ITO films fabricated with the post-annealing, present comparable values of electro-optical parameters with those fabricated by different techniques reported in the literature.

	Sheet	Transmission	Figure-of-	Reference
Process	resistance	T (%)	merit	
	(Ω/ □)		φ _{τc} (Ω ⁻¹)x10 ⁻³	
PLD	11.17	92	38.8	[75]
PLD	53.55	85	3.67	[76]
PLD	13.83	88	20.13	[77]
Electron Beam Evaporation	10	85	19.68	[78]
CVD	154	90	2.26	[79]
CVD	8.37	90	41.65	[80]
CVD	6.74	80	15.93	[81]
Thermal	75.83	85	2.59	[82]
Evaporation				
Spray Pyrolisis	4.33	85	45.46	[83]
Sol-Gel	200	90	1.74	[84]
Sol-Gel	30	95	19.95	[85]
Sol-Gel	37	90	9.42	[86]
Sputtering, RF, Ar, RT	54	90	6.45	[87]
Sputtering, RF, Ar, RT	5	84	16.8	[88]
Sputtering, RF, Ar+O ₂ , annealing in air 500° C	113.11	80	0.95	[89]
Sputtering, RF, Ar+O ₂ , RT	20	88.1	13.92	[90]
Sputtering, DC, Ar+O ₂ , RT	26	84.6	7.22	[90]
Sputtering, DC, Ar+O ₂ , annealing in air 300°C	8	89	11.2	[91]
Sputtering, RF, Ar+O ₂ , RT	34.54	80	3.1	[92]
Sputtering, DC, Ar, annealing in $O_2300^{\circ}C$,	14.64	91	26.6	This work
Sputtering, DC, Ar, annealing in O ₂ 350°C, Corning 1737	19.4	90	18	This work

Table 4. Comparison of the figure-of-merit ϕ_{TC} for the ITO films prepared by different techniques.

DISCUSSION, CONCLUSIONS, AND FUTURE WORK.

1. The properties of the ITO films depend strongly on the deposit parameters, thus the quality control is a problem for the applications of these films. Some of the disadvantages of DC sputtering in Ar environment, as compared with sputtering in a mixed Ar + O_2 atmosphere, are:

 As the target surface is subjected to intense bombardment by Ar ions, a consumption of oxygen atoms from the ITO target, takes place.
 Therefore the deposited film becomes non-stoichiometric or more metallic with a deficit of oxygen.

• Moreover, the film deposited at room temperature presents an amorphous structure

• To obtain a stoichiometric film with a polycrystalline structure, a postannealing treatment in air or oxygen environment is required. This treatment affects also the grain size of the film, which results in a notorious change in the optical and electrical properties.

2. The advantages of the post-annealing treatment in oxygen allow for the tuning of the work function of the ITO films as a function of the treatment temperature.

3. Moreover, the DC magnetron sputtering in pure Ar environment is cheaper and more controllable than sputtering in a mixed Ar + O_2 atmosphere.

4. Both optical transmission and electrical conductivity of the ITO films should exceed a certain minimum value. Ideally, both parameters should be as high as possible. Nevertheless, a simultaneous achievement of maximum transmission and conduction is not possible in most cases. These parameters depend on the film thickness. To compare the results obtained by different techniques, the figure of merits described previously in section 6.7 needs to be used.

5. Table 4, compares the value of the figure of merit for ITO films prepared using different techniques. In our case it was possible to improve the properties of the ITO films using a post-annealing temperature of 300-350°C.

6. The fabrication method described in this study allows for the deposition of ITO films, with high electro-optical parameters, onto some flexible substrates as DuPont Kapton Polyamide. For other flexible substrates such as Teflon, which are important for thin film solar cells, the deposition temperature or post-annealing needs to be below 200°C. To achieve that, the deposition equipment needs to be updated with an oxygen line and a substrate heater. This is the subject of a future work in the INAOE's Microelectronics Laboratory.

7. Technique developed was successfully applied for fabrication of photo- capacitors and photodiodes with transparent conducting ITO gate.

APPENDIX A. EQUIPMENT USED FOR THE CHARACTERIZATION OF THE ITO FILMS.

ATOMIC FORCE MICROSCOPE (AFM).

The surface morphology of the ITO films was Universal SPM from Ambios Technology (Fig. A1) located at the CIDS department in the Benemérita Universidad Autónoma de Puebla, BUAP.

The USPM AFM unit mainly consists of a microscope unit, which is composed of the probe and scanner, an electronic interface unit (EIU) and a computer.



Figure A1. AMBIOS USPM AFM Unit.

X-RAY DIFFRACTOMETER.

The Bruker D8 Advance (Fig. A2) is a Cu-source, theta-theta diffractometer equipped with a Lynx-eye position sensitive detector. This detector allows for a range of scattering angles to be measured simultaneously, increasing signal detection and decreasing scan times. This XRD is located at the Basic Science and Engineering Division in the Universidad Autonoma Metropolitana (UAM) and in the X-Ray Diffraction Laboratory in the Universidad de Sonora (Unison).



Figure A2.Bruker D8 Advance XRD Diffractometer.

HALL-EFFECT AND VAN DER PAUW MEASUREMENT SYSTEM

The Acopia HMS-5000 Hall Effect Measurement System (Fig. A3) has automated magnet movement, variable temperature capability and powerful analysis software. This measurement system is located at the CIDS department in the Benemerita Universidad Autonoma de Puebla BUAP.



Figure A3. HMS-5000 Hall Effect Measurement System.

FOUR POINT PROBE MEASUREMENT SYSTEM.

Keithley's Series 2400 Source Measure Unit (SMU) Instruments (Fig.A4) are designed specifically for test applications that demand tightly coupled sourcing and measurement. All Sourcemeter models provide precision voltage and current sourcing as well as measurement capabilities. The Sourcemeter has the capability to configure the sensing mode from 2 wire to 4 wire mode to obtain the four point probe measurements of the samples. This measurement system is located at the Microelectronics Laboratory in the National Institute of Astrophysics, Optics and Electronics INAOE.



Figure A4. Keithley Serie 2400 in four point probe mode.

ELLIPSOMETER.

The Rudolph FOCUS Ellipsometer system has fully automatic operation and a scanning stage. Unique optical and detection systems measure ellipsometric parameters over an angle range of 40 to 70 degrees simultaneously, giving more flexibility for measuring multiple film stacks. The scanning stage allows wafer uniformity to be evaluated rapidly. The system automatically calculates film thickness, index of refraction, and the extinction coefficient. Automatic or manual wafer loading; can be used with small pieces or full wafers up to 8" diameter. This ellipsometer is located at the Nanoelectronics Laboratory in the National Institute of Astrophysics, Optics and Electronics INAOE.

F20 UV-VIS FILMETRICS SPECTROMETER

Bench top measurements of transmittance, reflectance, optical constants (n, k) in the spectral range of 250-1100 nm as well as thickness of thin transparent or translucent films are made by the automatic F20 UV-VIS Filmetrics Spectrometer equipped by the special software is shown schematically on Fig. A5 for the transmittance (T) measurements and on Fig.A6 for the reflectance (R) measurements.

Both the measured and calculated T and R spectra are displayed. The measured n and k curves may also be plotted.



Figure A5. Setup configuration of F20 spectrometer for transmittance measurements.



Figure A6. Setup configuration of F20 spectrometer for reflectance measurements.

APPENDIX B. ITO-nSi PHOTODIODES FABRICATED BY SPUTTERING WITH ANNEALING OF ITO FILMS AT DIFFERENT TEMPERATURES IN O_2 ATMOSPHERE.

Figure B1 shows the I-V characteristics at the dark conditions of ITO-nSi Photodiodes fabricated by sputtering with annealing of ITO films at different temperatures in O_2 atmosphere.



Figure B1. I-V characteristics of Schottky ITO-nSi Photodiodes fabricated by sputtering with annealing of ITO films at different temperatures in O_2 atmosphere.

One can see a big difference between I-V characteristics of the photodiodes fabricated at different annealing temperature of the ITO film. At low annealing temperatures (250 and 300° C) the ITO film forms the Schottky barrier at the silicon interface (MS or metal-semiconductor contact). At bigger temperatures, the type of the contact between the ITO film and the silicon is changed due to growing the SiO₂ thin layer on the silicon surface because of diffusion of the oxygen through the ITO film. This type of the structure is related to MIS structure (metal-

insulator-semiconductor) with tunelable insulating layer or an inversion induced p-n due to a high ITO work function. It known that the dark current of such structures are less than one for MS structures.

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