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"Development and Characterization of Aluminum Doped Zinc Oxide Thin Films by the Sol-Gel Technique"

by

Marcela Cristina Mireles Ramírez Advisor: **Dr. Servando Aguirre Tostado** Co-Advisor: **Dr. Manuel Quevedo López**

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"To my beloved Mother,

who is my strength and my guidance."

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Abstract

Aluminum doped Zinc Oxide (AZO) was elaborated by the sol-gel method and deposited onto glass slides by spin coating. Aluminum chloride or nitrate was used as doping precursor. The process was carried out in the presence and absence of oxygen. Films were thermal treated in a furnace at 500 °C in air or forming gas. Main physical, optical, chemical and electrical properties were characterized. Surface undesired characteristics, such as cracks and wrinkles were found to decrease with the increase in synthesis temperature. Amorphous, polycrystalline and polycrystalline preferentially oriented along the c-axis thin films were obtained through a process carried out in the absence, partial presence and presence of air, respectively. The obtained films are highly transparent in the visible spectrum. XPS results showed an Al $2p_{3/2}$ peak with binding energy of 73.4 eV, which is good indicative of the substitutional nature of the introduced aluminum; desirable behavior on doped materials. Sheet resistance was found to decrease with the increase in synthesis temperature. Overall, films elaborated with aluminum nitrate had better characteristics.

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Resumen

Se elaboró Óxido de Zinc dopado con Aluminio por el método sol-gel, depositado sobre sustratos de vidrio por spin-coating. Se utilizó cloruro de aluminio o nitrato de aluminio como precursor dopante. El proceso se llevó a cabo en presencia y ausencia de aire. Las películas fueron tratadas a 500 °C en un horno tubular, en presencia de aire o forming gas. Las propiedades físicas, ópticas, químicas y eléctricas fueron analizadas. Se encontró que morfologías no deseables, como grietas y arrugas, disminuyen conforme aumenta la temperatura de elaboración. Se obtuvieron películas amorfas, policristalinas y policristalinas preferencialmente orientadas en el eje c mediante un proceso realizado en ausencia, presencia parcial y presencia de aire, respectivamente; además el orden cristalino se ve favorecido en las películas elaboradas con cloruro de aluminio. Las películas obtenidas son altamente transparentes en el espectro visible. La señal de Al 2p_{3/2} analizada por XPS se centró en 73.4 eV, lo cual es buen indicio de la naturaleza substitucional del aluminio; comportamiento deseable en materiales dopados. La resistencia de hoja disminuyó con el incremento de la temperatura de elaboración. En general, las películas elaboradas con nitrato de aluminio presentaron las mejores características.

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Chapter 1

Introduction

1.1. Semiconductor history: silicon revolution

The term "semiconductor" refers to a class of material possessing properties between conductors and insulators. It is a key component in the electronic industry, since their electronic properties can be manipulated through the control of their charge carriers. They have a big impact in the global economy. Silicon has been the main semiconductor material used over the past 60 years.¹

In the end of the 20th century, silicon became one of the most important elements, providing great progress for industry and technology. We still live in the silicon era, in the world of the second most abundant element. Oxygen compounds of silicon constitute three fourth parts of the lithosphere. We are surrounded by products made with inorganic silicon compounds.²

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The basic piece of the electronics puzzle, the transistor; was invented by Bell Laboratories in 1948. This transistor combined small size, lightweight, low power requirements and long lifetime. A decade later in Texas Instruments, Jack Kilby made possible the integration of transistors with resistors and capacitors in a single semiconductor chip, also known as Integrated Circuit (IC). Twenty years later, Intel Corporation invented the microprocessor which allowed the beginning of the personal computer industry and a total revolution of electronics industry.¹

An important trend called, Moore's Law, started as a simple observation that the number of integrated components built in a circuit would double each year. This law has come to represent the exponential growth of electronics an industry \$300 billion dollars worth. Nowadays innovations will continue, however, Moore's Law as initially stated is reaching a technical limit.³

1.2. Transparent electronics

Transparent electronics is a relatively new science and technology, focused on producing "invisible" circuitry. Transparent conductive oxides (TCO's) seem to be a contradiction. Most conducting materials are not transparent, and most transparent materials are not conductive. TCO's are a kind of materials possessing these two properties, generally mutually exclusive. To achieve this combination, a wide band gap and a high concentration of carriers with enough mobility are needed.

| Material | Band gap (eV) | Conductivity (Scm ⁻¹) | Electron concentration (cm ⁻³) | Mobility (cm ² V ⁻¹ s ⁻¹) |
|--------------------------------|------------------|--------------------------------------|--|--|
| In ₂ O ₃ | 3.75 | 10,000 | >10 ²¹ | 35 |
| ZnO | 3.35 | 8,000 | >10 ²¹ | 20 |
| SnO ₂ | 3.60 | 5,000 | >10 ²⁰ | 15 |

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 Table 1 Some electronic properties of common TCO's. Conductivities reported are for best-case

 polycrystalline films

The electronic properties of the most commonly used TCO's are shown in Table 1 above. Tin oxide (SnO_2) and Zinc oxide (ZnO), have been used in IR-efficient architectural window applications.⁴ Indium oxide (In_2O_3) has been doped with Tin (commonly called, ITO) and used for transparent electrode applications. ITO stands as the most used TCO. However, Indium is a toxic material. Moreover, because of the high cost and scarce resources of Indium; a stable ITO supply may be hard to maintain in the near future. For these reasons, there is high interest on finding novel enhance materials such as doped Zinc oxide; which has been proposed as a feasible alternative to ITO.⁵

Transparent or conductive materials are well understood. On the other side, transparent and conductive materials are quite more complex. Since these novel materials are unique, the tune of their intrinsic properties involves unique technology as well. The overall optical and electrical behavior is directly influenced by its concentration and mobility of charge carriers. In fact, TCO's properties are a system, a trade-off in which a balance must be achieved.⁶

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TCO's are key components for new generation optoelectronic devices. The demand for these novel materials has increasingly risen. Materials available today does not quit achieve the requirements of low resistivity, high transmittance, large area of deposition, low processing cost and ability for fine pattering and compatibility with other device materials.⁷

Practically all semiconductors are extrinsic; this means that the electrical properties of such materials are determined by intentionally added impurities. In the n-type semiconductors, an extra electron is loosely bound to the region around the impurity, thus, it is easily removed to become free or conducting. For each of these extra electrons, there is an impurity state lying just below the conduction band, within the band gap. Through excitation, these electrons are promoted to the conduction band and no holes are created within the valence band.⁸

The introduction of impurities, in order to increase the number of carriers, is achieved in two main ways; substitutional doping and oxygen vacancies.

1.2.1. Oxygen vacancies

Oxygen vacancies are the main defects in oxides. They may exist in several charge states. For TCO's, oxygen vacancy system plays a very important role and in some cases determines the electrical properties.

When an oxygen atom is removed from its site in an oxide lattice, it leaves two extra electrons in the crystal. Depending upon the oxide free energy of formation; these two electrons may remain localized at the vacancy site or become free carriers. A low free energy of formation gives rise to free carrier densities of 10^{19} cm⁻³ for ZnO.⁹

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1.2.2. Substitutional doping

Compared with native point defects such as oxygen vacancies, substitutional doping allows better control over the properties and stability of the TCO. The process of doping involves the addition of a small impurity amount, as a substitutional defect. This introduces an excess of electrons or holes to tune the intrinsic electrical properties. For example, an impurity concentration of one atom in 10^{12} atoms is sufficient to produce extrinsic silicon at room temperature.⁸

Traditionally, same period – next row elements are used as doping agents since they represent less disturbance to the crystal and electrical structure.¹⁰ In semiconducting oxides, is generally possible to achieve electron or hole conductivity, but not both. The dopants are also called impurities levels, since they introduce energy levels close to one of the allowed energy bands and are easily ionized as a result. There are also, deep level defects which are structural defects such as vacancies or interstitials. In this case, deep levels are introduced within the forbidden band gap, acting as carrier traps.¹¹

1.2.3. The ideal TCO

It is well known that the electrical properties of a material influences its optical properties and vice versa. High carrier concentration and mobility leads to a low resistivity. However, the increased carrier concentration moves the absorption edge toward the short wavelength portion of the visible spectrum, therefore, affecting the transparency of the material. Increasing the mobility might be the most useful approach to increase the conductivity of an oxide in order to obtain a TCO.¹²

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Despite of the unavoidable trade-off between transparency and conductivity for these materials; nanomaterials offer the possibility of excellent transparency and high electrical conductivity.

1.3. ZnO as an Alternative Material

1.3.1. General Characteristics

Lately, ZnO has received much attention because it has unique properties depending on doping, including conductivity from metallic to insulating, high transparency, piezoelectricity, wide band gap semiconductivity, room-temperature ferromagnetism and huge magneto-optic and chemical-sensing effects. It also has the ability of growing in a variety of different morphologies.¹³

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| Properties | Value |
|--|--|
| Lattice parameter at 300K: | |
| а | 0.32495 nm |
| с | 0.52069 nm |
| c/a | 1.602 |
| u | 0.345 |
| Density | 5.606 g/cm^3 |
| Stable phase at 300K | Wurtzite |
| Melting point | 1975 °C |
| Thermal conductivity | 0.6, 1-1.2 |
| Linear expansion coefficient (/°C) | a: 6.5x10 ⁻⁶ , c: 3.0x10 ⁻⁶ |
| Static dielectric constant | 8.656 |
| Refractive index | 2.008, 2.029 |
| Energy gap | 3.4 eV (direct) |
| Intrinsic carrier concentration | $<10^{6}/cm^{3}$ |
| Exciton binding energy | 60 meV |
| Electron effective mass | 0.24 |
| Electron Hall mobility at 300K for low n-type conductivity | 200 cm ² /Vs |
| Hole effective mass | 0.59 |
| Hole Hall mobility at 300K for low p-type conductivity | 5-50 cm ² /Vs |

Table 2 Properties of Wurtzite ZnO

The basic materials parameters of ZnO are shown above in Table 2. ZnO is an abundant non-toxic material. It is chemically stable to hydrogen plasma processes that are commonly used in the fabrication of devices such as solar cells. It is also a low cost material, compared to ITO and therefore a potential replacement.¹⁴ The considerable current interest is based on the hope to obtain:

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- a material for blue/UV optoelectronics,
- a radiation hard material for electronic devices in corresponding environments,
- a material for electronic circuits, which is transparent in the visible,
- a diluted ferromagnetic material for semiconductor spintronics, when doped with Co, Mn, Fe, V or similar elements,
- a TCO when doped with Al, Ga, In or similar elements, as cheaper suitable alternative to ITO.

1.3.1.1. Crystal Structure of ZnO



Figure 1 Representation of ZnO crystal structure

ZnO crystallizes in the hexagonal wurtzite-type structure as shown in Figure 1 where the schematic blue atoms correspond to zinc and the red ones to oxygen. It has a polar hexagonal axis, the *c* axis; chosen to be parallel to z. It belongs to the point group 6mm and the space group P6₃mc. One zinc atom is surrounded tetrahedrally by four oxygen ions and vice versa. The unit cell contains two formula units of ZnO. The ratio c/a of the translation

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vectors is around 1.60, which deviates slightly from the ideal 1.633. While other zinc materials are able to grow in the zinc blende and cubic structure; ZnO grows preferentially in the wurtzite type.

1.3.1.2. Electronic Structure of ZnO and its Potential as a TCO

ZnO is a direct band gap semiconductor. This means that the lowest point in the conduction band (CB) meets the highest point in the valence band (VB) at the same wave number in the Brillouin Zone.



Figure 2 Schematic representation of ZnO band structure

The bottom of the conduction band, or the lowest unoccupied molecular orbital (LUMO), is formed by the antibonding sp³ hybrid states. The valence band, or highest occupied molecular orbital (HOMO), forms from the bonding sp³ orbitals (Figure 2). The energy of the band gap between the conduction and valence bands is about 3.437 eV at low temperatures.¹⁵

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Figure 3 Energy levels of native defects in ZnO

The control of defects and charge carriers is essential for the applications of a given material. It is important to realize that ZnO has already a number of native defects, shown in the Figure 3. According to the Kröger Vink notation, the donor defects are: $Zn_i^{\bullet\bullet}$, $Zn_i^{\bullet\bullet}$, $Zn_i^{\bullet\bullet}$, $V_0^{\bullet\bullet}$, and the acceptor defects are: $V_{Zn}^{\bullet\bullet}$, $V_{Zn}^{\bullet\bullet}$. Zinc interstitials and oxygen vacancies are known to be the predominant ionic defects. Under reducing conditions and at high temperatures, oxygen vacancies may predominate.

In regard to defects at different oxygen atmospheres, Brouwer diagrams are a useful tool since they plot concentration of carriers versus partial oxygen pressure, pO_2 . A Brouwer diagram showing defects under different oxygen conditions is shown in Figure 4. It can be seen that oxygen vacancies remain as the dominant defect at low pO_2 regime. The switch to Zn vacancies at high pO_2 occurs at 13000 °C with a pO_2 of 1 atm.

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Figure 4 Schematic Brouwer diagram showing defect concentration through different oxygen partial pressure

With impurities and intentional doping, carriers are introduced depending on whether the ions have a lower valence (introducing holes) or a higher valence (introducing electrons); which in the case of ZnO can be lithium (Li^{1+}) and aluminum (Al^{3+}) respectively. There is no dependence on the pO_2 on the carrier concentration from those substitutions.¹³

As previously stated, impurity doped ZnO is an alternative to replace ITO. ZnO doping has typically being achieved by introducing elements of the periodic table group III (B, Al, Ga and In). Among them, aluminum has attracted much interest and therefore remains as the more studied. Furthermore, aluminum salts are non-toxic and cheaper than indium and gallium salts.

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Doped ZnO with c-axis oriented crystalline structure along (002) plane has been extensively studied for many practical applications. The doping agent introduces free carriers which increase the carrier concentration; moreover the oriented crystalline structure improves the mobility by means of reduced scattering of carriers at the grain boundaries.

1.3.1.3. ZnO Existing and Forthcoming Applications

ZnO is produced at levels of 10⁵ tons per year. A large fraction of it is used in the rubber for tyres, preventing deformation caused by heat. In concrete, improves its resistance against water. In the cosmetic industry, ZnO is used as a UV-blocker in lotions; it is also used as a food additive. Highly n-doped ZnO:Al has been used as transparent front contact for solar cells and liquid crystal displays and energy saving or heat protection smart windows; with a transmittance over 87 % in the visible spectrum and high reflectance (50 %) in the near-IR.¹⁶

Transparent thin film transistors (TFT) can be produced with ZnO. As field effect transistors, they even may not need a p-n junction. A transparent OLED deposited on a transparent flexible plastic sheet and driven by a TFT based on ZnO has been reported. If several barriers are overcome then numerous applications will materialized, as an example, ZnO nanorods may be used as nanosized read/write heads for magnetic data storage. The future must show whether there are or not too many barriers to overcome.¹⁵

1.4. Solution Processed Electronics

Aluminum doped ZnO (AZO) films have been elaborated by several deposition techniques such as magnetron sputtering, spray pyrolysis, chemical vapor deposition,

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pulsed laser deposition, reactive electron beam evaporation and sol-gel processes. Most of the deposition techniques require high vacuum and accurate gas-flow control systems, which makes them expensive and increase the manufacturing cost of these devices. Solution processes allow low cost deposition in air atmosphere, offering an excellent compositional control and film homogeneity at the molecular level. Solution based processes are ideal for the implementation of roll to roll manufacturing processes, which reduces cost greatly.¹⁷

Given the focus on large area electronics it has been natural to explore solution-based processing techniques for the development of these materials. Over the last years there has been attention put into these kinds of processes, which can be divided into three broad categories; nanoparticles, nanowires and solution-deposited thin films.

Nanoparticles have received much attention because of two major reasons. First, its reduced melting point enables the fabrication of thin films through low temperature processes. Second, the possibility of encapsulate them with an organic ligand.

Through appropriate synthesis conditions, it is possible to cause nanoparticles to grow faster in one direction resulting in the formation of elongated nanowires. The main potential advantage of these structures is the larger average crystallite size. Assuming tight packing of nanowires, conduction should improve because of increased mobility,

Thin film deposited by solution, must be of higher quality with low carbon contamination. The major disadvantage is that the chemical conversion to the final materials structure is performed directly on the substrate, which may limit the nature of

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them. Various chemical deposition techniques have been developed, such as chemical bath deposition, sol-gel routes and direct oxidation of solution deposited precursors.¹⁰

1.4.1. Chemical Solution Deposition (CSD)

The CSD methods include a range of deposition techniques and chemical routes which are summarized in the Figure 5.



Figure 5 CSD techniques and chemical routes

The process starts with the elaboration of a solution with precursors of the desired material and may also include stabilizers, partial hydrolysis or refluxing. Then the solution is deposited onto a variety of substrates by spin, dip or spray coating. Next, the wet film undergoes drying, hydrolysis or condensation reactions depending on the chemical route followed. The resultant film consists of amorphous or nanocrystalline oxides and/or carbonates. Further heat treatment will cause the film to crystallize and the organic material to decompose. Desired thickness is achieved through multiple coatings.¹⁸

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1.4.2. The Sol-Gel Route

The Sol-gel process, also called soft chemistry, allows elaborating a solid material from a solution, using a sol or a gel as an intermediate step and at considerably lower temperature than traditional methods. It enables the powderless processing of thin films. In the Figure 6 the main steps of materials elaboration through sol-gel technique are shown.

For thin film, we can summarize the process in three steps: 1) preparation of the precursor solution, 2) deposition of the sol onto a determined substrate and 3) heat treatment of the xerogel film. This xerogel is the dried gel at ambient pressure (the dried gel in supercritical conditions, is called, aerogel).



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Figure 6 Overview showing two synthesis examples by sol-gel method; (a) films and (b) powder ZnO thin films elaboration involves a set of parameters affecting its final properties:

- nature of the precursor and its concentration,
- type of solvent,
- type of additive species and their concentrations,
- aging time of the early mixture,

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- method of coating substrates and its speed,
- nature of the substrate,
- pre- and post- heat treatment of the material.

It should be noted that several works have resulted in significantly different outcomes; even if the experimental conditions were very close to each other. Making difficult to clearly correlate or predict the principles underlying this whole phenomena.¹⁹

1.5. Literature review

There is a considerable amount of reports regarding AZO synthesized by Sol-gel process, varying the chemical system used and conditions of elaboration. An overview of relevant works on this matter is summarized in Table 3, conditions of elaboration are presented.

All works used Zinc acetate dihydrate (ZAD) as Zinc precursor dissolved in an alcohol. This combination has proved to produce the best reproducible results. However, ZAD is not very soluble on alcohols, especially ethanol and IPA; therefore the use of a stabilizer is needed. The stabilizers prevent the precipitation of zinc hydroxide, promoting a stable solution. The drying and final thermal treatments are the most important conditions determining the crystalline orientation of the films. Drying temperature must be higher than the solvents boiling points, since this step is crucial to the evaporation of the organic compounds. The final thermal treatment is a wide field to explore, temperature, duration, atmosphere and steps have been varied. The important objective of this treatment is to

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increase the mobility and the number of carriers. Better crystalline orientation and electrical performance has been found when increasing the temperature, up to a maximum to then decrease with further temperature increase.¹⁹

The morphology is of the same nature among the different films. Composed of spherical particles densely packed, which grow with the increase in temperature up to a point where voids start to coalesce obtaining a porous film. Cracks begin to appear when the substrate softens. The majority of the works lead to films with a wurtzite type crystalline structure, preferentially orientation along the (002) plane. Also, it seems that the use of amorphous substrates promotes this orientation.¹⁹

The good transmittance of the films has been the less diverse parameter, regardless of the deposition conditions. It has constantly been above the 90 % and in some cases above 80%. Optical band gap is expected to increase by a doping process, although a decrease has also been obtained. However optical band gap is not commonly reported.

The chemical properties of the films have not been extensively studied. Far-infrared and X-ray photoelectron spectroscopy (XPS) have been performed in very few works. Kim *et al*²⁰, studied the binding energy of the Aluminum (Al) $2p_{3/2}$ on doped ZnO thin films. Reported the contribution of, Al in ZnO lattice and Al₂O₃, to the peak detected. However, does not differentiate Al, from a substitutional or interstitial site.

In 2009, Mehmet²¹, studied AZO thin films through temperature cycling and accelerated delamination tests determining the high physical reliability of them since none of the specimens showed delamination.

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Oxygen adsorbed at the grain boundaries creates a depletion layer, acting as a barrier for the charge carriers. Heat treatments play two important roles in lowering the resistivity, increasing mobility and number of carriers. The enhance mobility results from the refinement of the microstructure and also from the movement of Al atoms into substitutional Zn sites. The number of carriers increases through oxygen vacancies which also eliminates the depletion layer.²² Reduced resistivity by means of heat treatments in nitrogen atmospheres have also been observed by Tseng.²³

Since diverse treatments have been used, different behaviors have been obtained as a result. Sheet resistance as high as $1.2E6^{21}$ and as low as $32.2 \Omega/sq^{24}$ have been reported. The considerable decrease is attributed, mainly, to the thermal treatments involved. A scheme drawn with the information provided in the publications above is presented in Figure 7 below.

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Figure 7 Comparison of thermal treatments used for Mehmet et al (top) and Rydzek et al (bottom)

Thermal treatments description is reported in more detail by Rydzek, nevertheless, huge differences can be noted. Mehmet, implemented the use of two atmospheres, air and forming gas (Fg); in addition to these, Rydzek also used and oxidizing and an inert atmosphere. The difference in time spent in the treatments is dramatically increased by the number of layers. The resultant sheet resistance difference is of six orders in magnitude. Rydzek's process remains as the best suited to produce films with the lowest sheet resistance reported.

Finally, the electrical performance remains as the less optimized factor. Although, in the last few years, great knowledge on the subject have been achieved.

Aluminum **Final Thermal** Author, Year Solvent / Stabilizer Drying (°C) precursor Treatment (°C) IPA** Kim, 2007²⁰ 500 to 700-air AlCl₃ 275 MEA*** IPA $Al(NO_3)_3$ Mehmet, 2009²¹ 275 550-air+550-Fg (Ethanolic MEA solution) Ethanol 420 to 550-air+500-*JianLin, 2009²² 420 $Al(NO_3)_3$ vacuum Diethanolamine Glycolmonoethilether Tseng, 2010²³ 110 - 160 Al(NO₃)₃ 550-nitrogen+500-Fg MEA IPA 500-oxygen+noble *Rydzek, 2011²⁴ gas flux+500-Al(NO₃)₃ 500 Diethanolamine oxygen+450-Fg

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*Dip coating; **Isopropyl alcohol; ***Monoethanolamine

Table 3 Relevant publications

1.6. Justification

Since the 1950's when the integrated circuits enabled miniaturization of devices, the electronics industry went through an accelerated development with an impact never seen before. The importance of this industry has many approaches; however, it relies in the fact that it is so present in everyone's life. From technologies applied to cars, displays, solar cell panels to cell phones, portable audio/video players, memory cards, watches, calculators among others we all have common daily contact with the electronics industry.

Silicon was the key material enabling that progress. A great amount of research has been made on those affairs. Industry has been able to build affordable integrated circuits with increasing number of transistors. This number of transistors has doubled

Mireles Ramirez, Marcela approximately every two years, as predicted by Moore's law.²⁵ Even though this law is described by an exponential function, it has a technical limit.

Research is in the path of technology scaling and is nowadays greatly interested in emerging nanoelectronics and new materials that allow the fabrication of smaller, more efficient and non-silicon devices.²⁶ These materials will make possible another accelerated development of the electronics industry and ultimately will enable technologies such as flexible electronics.

In the search of new materials the transparent semiconducting oxides have attracted much attention. From saving energy technologies in solar cells and automobile improvement, to the display possibilities of flexible electronics; there is a wide scope of applications for these materials in an industry valued in billions of dollars.²⁷

Indium tin oxide, also known as ITO, is one of the TCO's that came into play. There is a lot of research on ITO, where devices with great performance have been achieved. Nevertheless, indium resources are rare, which makes devices expensive and with no good future, also indium is toxic. This has turned interest in new directions. ZnO is a wide direct band gap semiconductor with an energy gap of approximately 3.37 eV, it is an abundant element and has no toxicity. Commonly doped with group III elements, AZO, as known when doped with aluminum, is a suitable alternative for ITO.^{13,14,15}

1.7. Objectives

1.7.1. General Objective

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Study of the effects of the elaboration conditions on the overall properties of Aluminum doped Zinc Oxide (AZO) thin films.

1.7.2. Specific Objectives

- Elaborate AZO thin films under different conditions regarding chemical system, drying, annealing and deposition
- Evaluate the properties (structural, morphological, optical and chemical) of the elaborated thin films
- Correlate the properties of the films to the elaboration conditions

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Chapter 2

Experimental Methods

2.1. Substrates

The substrate cleaning is of key importance, since it affects the adhesion of the film. It has the function of removing all contaminants from the substrates surface. Substrates used were, Corning glass slides 1 x 1", 2 mm thick. Substrates were previously cleaned in an ultrasonic bath with a succession of solvents; acetone, IPA and deionized water, for 10 min each. Slides were dried with nitrogen gas. Cleaned slides were used as substrate for the thin film deposition.

2.2. **Precursor solution**

The chemical system used involves a precursor for Zn, zinc acetate dihydrate $Zn(CH_3COO)_2 \bullet 2H_2O$ and for Al: aluminum chloride hexahydrate, $AlCl_3 \bullet 6H_2O$ (Precursor A) or aluminum nitrite nonhydrate, $Al(NO_3)_3 \bullet 9H_2O$ (Precursor B). Precursors were dissolved in a solution of IPA and MEA, solvent and stabilizer, respectively. Only the

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Aluminum nitrate was first dissolved in 1mL of ethanol and then added to the ZAD in the IPA and MEA.

The molar ratio of MEA to Zn was equal to 1.0. The concentration of ZAD was 0.5 $molL^{-1}$. The concentration of Al as a dopant was 1.0 at.% with the respect to Zn. The solution was stirred at 60 °C for 1 h until a clear and homogeneous solution was obtained. The solution was finally aged at room temperature for 24 h.

2.3. Spin Coating Deposition

A cleaned substrate was placed in the spinner plate and the precursor sol was dropped over the entire surface of it. Then a thin film of the sol was created by operating the spinner at 3000 rpm for 20 s, no temperature applied. Spin coating is a simple deposition system, which has parameters that can be varied such as rotation speed, acceleration and steps, although in this case all the parameters for the spin coating deposition were kept constant.

2.4. Drying

Deposited film was dried at 150 or 250 °C for 10 min. After drying, more coats can be deposited by the same simple process. In this case all samples had a total of 5 coats.

2.5. Final Thermal Treatment

After deposited, the films underwent a thermal treatment in a tubular furnace. Films were treated for 1 h at 500 °C in an atmosphere of air or Fg ($N_2 - 5$ % H₂).

2.6. Elaboration Atmosphere
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In this work the effect of the elaboration atmosphere has been investigated. Precursor solution and film deposition was performed in two different atmospheres, air (laboratory hood) or nitrogen (inside a Glove box).

An overview of the elaboration process is summarized in Figure 8, below.



Figure 8 Elaboration process, overview

2.7. A Few Words Before Results

In Figure 9 below, varied conditions are summarized as a scheme. Results are divided into two chapters; the first corresponding to the precursors and atmosphere analysis and the second one dedicated to a comparison between selected films.

X-ray diffraction (XRD), UV-Vis transmittance and Mid-Fourier transform infrared spectroscopy (FTIR) were performed for all films. Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Far-FTIR and XPS analysis were performed only for selected films. Results are classified into: 1) Crystalline structure (XRD), 2) Physical

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properties (AFM, SEM), 3) Optical properties (UV-Vis transmittance) and 4) Chemical properties (FTIR, XPS).

As a remainder, samples are 5 coats thick; 150 and 250 °C are drying temperatures. No TT, Air and Fg refer to the thermal treatment being; none, in Air or Fg respectively; performed at 500 °C for 1 h. Films elaborated in air are in normal laboratory conditions and those elaborated in nitrogen are inside a glove box filled with nitrogen.



Figure 9 Schematic diagram of varied parameters

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Chapter 3

First part

In this chapter the results for films elaborated with Precursors A and B for aluminum are presented. Beginning with the films elaborated in air, following by the ones elaborated in nitrogen.

3.1. Physical Properties

3.1.1. Precursor A (Aluminum Chloride)

XRD data is plotted over 2 Theta range versus the Intensity in counts per second (cps) with logarithmic scale. Three main peaks are identified for ZnO hexagonal wurtzite type structure, corresponding to plane (001) at 32°, plane (002) at 34° (20) and plane (101) at 37° (20). XRD data presented in Figure 10, corresponding to the films elaborated with Precursor A in air; shows a slightly decrease in crystallinity for films treated in Fg in comparison to those treated in air. It can also be seen, higher drying temperature promotes preferential orientation along the (002) plane. Is worth to be noticed the difference in

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crystallinity for the films with no thermal treatment at different drying temperature. A wide diffraction peak was found when dried at 250 °C in comparison to films dried at 150 °C for which no diffraction peaks were found.



Figure 10 XRD spectra for films elaborated in air using precursor A dried at 150 °C (left) and 250 °C (right), films were thermally treated at 500 °C for 1 h, treatment atmosphere is indicated

In Figure 11 same films, this time elaborated in nitrogen are presented. There is a great decrease in crystallinity for all films with the change in elaboration atmosphere, although the tendency to higher crystallinity for higher drying temperatures and thermal treatment in air was still found.

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Figure 11 XRD spectra for films elaborated in nitrogen using precursor A dried at 150 °C (left) and 250 °C (right), films were thermally treated at 500 °C for 1 h, treatment atmosphere is indicated

3.1.2. Precursor B (Aluminum Nitrate)

Diffraction results for films elaborated in air with Precursor B are shown in Figure 12. Same behavior as in films elaborated with Precursor A was found. In addition, a decrease in the overall intensity was observed as common phenomena for this precursor (B), especially in the films treated in Fg in which the diffraction peaks practically disappeared when dried at 150 °C and greatly decreased when dried at 250 °C. Nevertheless the wide diffraction peak in the film dried at 250 °C with no final thermal treatment was still found.

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Figure 12 XRD spectra for films elaborated in air using precursor B dried at 150 °C (left) and 250 °C (right), films were thermally treated at 500 °C for 1 h, treatment atmosphere is indicated

As seen in the films elaborated with Precursor A, where crystallinity greatly decreased when elaborated in nitrogen; Precursor B films behave the same. In Figure 13 XRD data for the latter films is shown. Crystallinity is almost lost and there is no preferential orientation.



Figure 13 XRD spectra for films elaborated in nitrogen using precursor B dried at 150 °C (left) and 250 °C (right), films were thermally treated at 500 °C for 1 h, treatment atmosphere is indicated

As stated by Lamia Znaidi, the drying temperature seems to be the most important factor affecting the crystal quality of the films since it determines the solvent vaporization,

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zinc acetate decomposition and ZnO crystal growth.¹⁹ Nevertheless, a general tendency for higher crystalline order in films elaborated with Precursor A is evident. This might be due to a special role of the chlorine ions contained in this precursor which seem to be promoting the transition from zinc hydroxide to zinc oxide.

In this work we also found an important correlation between the atmosphere involved in the process and the films crystallinity. Films elaborated and thermal treated in air exhibited higher crystallinity than those films elaborated inside the glove box and thermal treated in nitrogen (Fg). This relation is shown schematically in Figure 14 where the six different atmospheres combinations of air and nitrogen are compared with the crystalline order. Normalized crystalline order was calculated as average intensity (are under the curve) of the two drying temperatures and both precursors, for each atmosphere combination.

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Figure 14 Correlation between atmosphere and crystalline order

It was found that the general tendency for better ordered films, regardless of the precursor, was to bring more temperature and presence of air to the process. The better order was due to the preferential nature of those films, in the *c*-axis. The importance of crystalline orientation relays in the fact that the higher the *c*-axis preferred orientation, the lower the scattering of carriers at the grain boundaries and the lower the resistivity of the film.²⁰ Films elaborated in air without a final thermal treatment seem to be more ordered than those elaborated in nitrogen; however this is due to the broad diffraction peak.

3.2. Chemical Properties

3.2.1. Both precursors (A and B)

FTIR measurements were performed for all films in the mid part of the spectra, from $4000 - 600 \text{ cm}^{-1}$. Only films not thermally treated are shown in the range of $2000 - 1250 \text{ cm}^{-1}$ (Figure 15), since peaks were only found for these films in this region. Peaks can be correlated to the presence of Zn as precursor^{28,29} and are more intense in the films

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elaborated in nitrogen. It can be noted the influence of the drying temperature in the acetate decomposition, 250 °C seems to be adequate, regardless of precursor. Moreover, in the films elaborated in air, presence of acetate could not be found. This is due to the fact that organic matter decomposes easily in an oxidizing atmosphere rather than inert.



Figure 15 Mid FTIR results for No TT films elaborated in air (left) and nitrogen (left) for both precursors dried at 150 or 250 °C. FTIR bands found are identified on the left

3.3. Partial Conclusion

From the results found at this point we can draw a simple summarized conclusion as follows. In order to elaborate ZnO thin films with good quality regarding preferred crystalline orientation and chemical composition; two conditions must be brought to the process: 1) a high drying temperature (250 °C) and 2) an oxidizing atmosphere (air) for the elaboration and final thermal treatment.

To come to a complete conclusion, 6 films were selected to be further characterized in terms of physical (SEM and AFM) and chemical properties (Far-FTIR and XPS). In Table 4 the conditions of selected films are stated.

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Table 4 Split table of selected films conditions

As a remainder, selected films presented different crystalline characteristics, going from amorphous to polycrystalline and preferentially oriented polycrystalline.

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Chapter 4

Second part

4.1. Physical Properties

4.1.1. Precursor A

4.1.1.1. Scanning Electron Microscopy (SEM)

Micrographs of selected films elaborated with precursor A are shown in Figure 16, two micrographs for each, corresponding to 60,000X (left) and 240,000X (right). SEM images show morphology of the films. No grain formation was found for the film without final thermal treatment (A.Air150NoTT, Figure 16). This indicates that the drying step, where the organic matter decomposes, serves as the earliest orientation of the final film, but it is not enough to contribute to the grain formation. Also, the films present small cracks and wrinkles.

Then for a similar film, this time with a final thermal treatment in air (A.Air150500Air, Figure 16), grains are finally formed, cracks and wrinkles are still present; indicating the importance of the final thermal treatment in the grain formation.

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Finally, micrographs for a similar film, this time dried at a higher temperature (250 °C) are shown (A.Air250500Air, Figure 16). Grain size seems to be slightly smaller but more important, no cracks or wrinkles were found.

Overall, the key influence of a high drying temperature and a final thermal treatment to promote a smooth surface morphology was demonstrated. These conditions are also found to promote preferred orientation along the c axis, as seen in previous section.



Figure 16 SEM micrographs for selected films elaborated with precursor A; 60,000X (left) and 240,000X (right), all films were elaborated in air and the different thermal treatment is indicated

4.1.1.2. Atomic Force Microscopy (AFM)

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For AFM analysis, two types of images were recorded; the first corresponds to the topography and the second to the phase of the films. Images for the films elaborated with precursor A are shown in Figure 17. From SEM micrographs, it was expected to observe a reduction in roughness with the increase in the total temperature process. AFM images were analyzed to calculate the root mean square (RMS) as an indicative of the film roughness. RMS was found to greatly decrease from 40.03 to 4.34 nm, with the increase in the total temperature process, as expected (Figure 17).

From the phase images (Figure 17) it can be noted, first a segregation of multiple phases in the film without final thermal treatment (A.Air150NoTT) and finally the formation of a single phase (A.Air250500Air) due to higher drying temperature and final thermal treatment. These latter results are correlated to XRD data (inset) where an evolution from no diffraction peaks to a single peak was observed.

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Figure 17 AFM images for Precursor A selected films. Elaboration conditions and RMS for each film are listed (top), topography (middle) and phase (lower) images are shown. Also, an XRD spectrum is shown as an inset on phase images (lower)

4.1.2. Precursor B

4.1.2.1. Scanning Electron Microscopy (SEM)

SEM micrographs for selected films elaborated with Precursor B are shown in Figure 18, presented in the same manner. No significant changes in the morphology were found regarding the different Precursor used (A, B). The only notable difference is the loss of the scatter small aggregates in the film with higher drying temperature and final thermal treatment (B.Air250500Air).

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Figure 18 SEM micrographs for selected films elaborated with Precursor A; 60,000X (left) and 240,000X (right), all films were elaborated in air and the different thermal treatment is indicated

4.1.2.2. Atomic Force Microscopy (AFM)

AFM images of selected films elaborated with precursor B are shown in Figure 19. Same behavior as observed for precursor A was obtained. RMS decreased from 44.35 nm in the film without final thermal treatment to 3.71 nm for the film with the higher total temperature involved in the process. Also, it was seen the formation of a single phase film for the latter film (Figure 19). Again, the XRD data is shown as an inset to confirm the evolution of this film to a preferentially oriented film.

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Figure 19 AFM images for Precursor A selected films. Elaboration conditions and RMS for each film are listed (top), topography (middle) and phase (lower) images are shown. Also, an XRD spectrum is shown as an inset on phase images (lower)

To summarize, selected films presented different characteristics, A/B.Air150NoTT are amorphous, with no formed grains and high roughness; A/B.Air150500Air are polycrystalline, with formed grains presenting cracks and wrinkles; finally A/B.Air250500Air are preferentially oriented, with formed grains and no cracks nor wrinkles.

As a general rule; in order to elaborate ZnO thin films with good quality regarding preferred crystalline orientation, morphology and roughness; two conditions must be brought to the process: 1) a high drying temperature (250 °C) and 2) an oxidizing atmosphere (air) for the elaboration and final thermal treatment.

4.2. **Optical Properties**

4.2.1. Both precursors

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4.2.1.1. UV-Vis Transmittance

The optical properties of the selected samples were evaluated in the UV-Vis spectrum. Transmittance spectra are shown in Figure 20. Precursor A average transmittance in the visible region (400 – 800 nm) was found to be 83.93, 91.82 and 96.72 % for A.Air150NoTT, A.Air150500Air and A.Air250500Air respectively. Precursor B average transmittance in the same region was 84.91, 80.45 and 98.61% for B.Air150NoTT, B.Air150500Air and B.Air250500Air respectively. It can be seen that the overall transmittance is high in the visible region. Although it is higher for the films processed at higher total temperature process. As seen before, SEM micrographs showed a smoother surface morphology, denser films and decrease in the average grain size; also calculated roughness from AFM images was found to decrease; both behaviors were observed when total temperature process increased. The latter led to a decrease in the optical scattering and thus the higher transmittance observed.

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Figure 20 Transmittance spectra of selected samples for both precursors. Deposition conditions are indicated

For a direct transition semiconductor, there is a relation between the absorption coefficient (α) and the optical band gap (E_g) which, according to Tauc's relation stands as follows:

$$\alpha h \nu \alpha (h \nu - E_g)^{1/2}$$

where *h* is the Plank's constant and v is the frequency of the incident photon.³⁰ The optical energy gap (E_g) was determined by extrapolating the plot of $(\alpha hv)^2$ vs. *hv*; results for both Precursors (A and B) selected films are shown in Figure 21.

The E_g depends on many factors such as crystalline structure, nature and concentration of impurities, structural defects and impurity states. At high doping concentrations several characteristics of the material might change, such as impurity ionization energy, density of states in the vicinity of the band edges, absorption edge and the energy of the fundamental gap. Effects causing those changes are the Mott transition which takes place at a critical

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impurity concentration, band tailing effects, the Burnstein-Moss (BM) shift and band gap renormalization.³¹

In this case, E_g was found to decrease approximately 0.1 eV, with the increase in total temperature process (Figure 21). This behavior can be explained as follows.

The E_g shift is the result of two competing mechanisms. The first, Burnstein-Moss effect which occur when absorption transitions cannot take place between the top of the valence band to the bottom of the conduction band, due to band filling; this results in a widening of the energy gap. The second, band gap renormalization occurs because of reduced electron energies due to many-body effects which are interactions between electrons, donors and acceptors causing the narrowing of the band gap.³¹



Figure 21 Calculated band gap of selected samples for both precursors. Deposition conditions are indicated in the x axis

At this point we already found that high temperature processes and oxidizing atmosphere promotes the formation of ZnO thin films with good quality (according to

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crystalline structure, morphology and roughness). In addition, we now know that both, good transmittance and the E_g narrowing are achieved regardless of the deposition conditions or precursor.

4.3. Chemical Properties

4.3.1. Both precursors

4.3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

Indication of the quality level chemical composition and crystallization can also be analyzed by FTIR. A low frequency E_1 mode is associated with the vibration of the heavy Zn sub-lattice corresponding to the Zn-O stretching vibration for a tetrahedral surrounding of Zn atoms; while the high frequency E_2 mode involves only the oxygen atoms. E_1 mode splits into transverse (TO) and longitudinal (LO) phonons.³² A broadening of the bands is symptomatic of a reduced chemical and crystalline quality.³³

References concerning the location of ZnO Far-FTIR bands are ambiguous. They go from 400 to 513 cm⁻¹.^{34,35,36,37} The band positions and numbers of absorption peaks are depending not only on chemical composition and crystalline structure but also on film morphology.³⁸

Selected films were measured in the Far-FTIR region. Results for films elaborated with precursor A are shown in Figure 22, plotted from 600 to 350 cm⁻¹. A wide band centered in 450 cm⁻¹ was found for the film without final thermal treatment (A.Air150NoTT). XRD data, where no diffraction peaks were found and SEM micrographs where no formed grains were observed can be taken into account for this behavior.

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Similar film this time with a final thermal treatment in air (A.A150500Air) shows a band spiking in 411 cm⁻¹ with a broad shoulder around 450 cm⁻¹. The differences in FTIR signal can be correlated with differences in crystalline structure and surface morphology. XRD data shows this film to be polycrystalline and SEM micrographs shows formed grains, cracks and wrinkles.

The narrowest band was found in the film with the highest total temperature process (A.Air250500Air), this can also be correlated with XRD data which shows a preferentially oriented film and SEM micrographs were formed grains and neither cracks nor wrinkles are observed. Results indicate the good quality of ZnO chemical composition and crystal growth in this film, which agrees with SEM and XRD data.

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Figure 22 Far-FTIR spectra for selected films elaborated with Precursor A (left) correlated with XRD spectra (middle) and SEM micrographs (right). Process conditions are indicated

Results for the films elaborated with Precursor B are presented in the same way in Figure 23. Same behavior as with precursor A, was found and can also be correlated to XRD and SEM results. The important difference relays in the narrower signals obtained for the three films measured. This, places Precursor B as the most suitable option to obtain a higher quality material.

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Figure 23 Far-FTIR spectra for selected films elaborated with Precursor B (left) correlated with XRD spectra (middle) and SEM micrographs (right). Process conditions are indicated

As stated before; in order to elaborate ZnO thin films with good overall quality two conditions must be brought to the process: 1) a high drying temperature (250 °C) and 2) an oxidizing atmosphere (air) for the elaboration and final thermal treatment and based on FTIR results, Precursor B might take place as the third condition.

4.3.1.2. X-ray Photoelectron Spectroscopy (XPS)

The chemical bonding configurations which directly affect structural, electrical and optical properties are of great importance. XPS is a sophisticated characterization tool through which, detailed information regarding chemical bonding can be found. Although, information find through XPS data is huge, interpretation remains as the key element.

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In Figure 24 XPS spectra for Zn before and after a sputtering process, to penetrate the surface, is shown. Plots show intensity in cps versus binding energy (BE) in electronvolts (eV). Peaks centered on 1021.4 eV are attributed to Zn 2p_{3/2} electronic level and peaks.



Figure 24 XPS spectra for Zn2p_{3/2} before and after sputtering for both Precursors (A, B). Experimental results are shown in void marks while fitted data is shown with solid lines. Line centered at1021.5 eV, is drawn for reference. Samples elaboration conditions are indicated at the top

Shifts found in binding energy are due to change in bonding strength. In the case of non-stoichiometric oxides, are commonly due to differences in oxygen rich/deficient regions within the matrix. In the case of Zinc it can be seen that all samples appeared at around 1021.4 eV which can be attributed to oxidized Zinc (Figure 24). Differences in BE

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and height showed by the films without final thermal treatment are most likely due to high roughness and low homogeneity. Also, these films showed a shift towards lower binding energy, which can be attributed to the less oxidized nature of the material before the final thermal treatment.



Figure 25 XPS spectra for Al2p before and after sputtering for both Precursors (A, B). Experimental results are shown in void marks while fitted data is shown with solid lines. Line centered at 73.5 eV, is drawn for reference. Samples elaboration conditions are indicated at the top

Peaks centered between 74 and 73 eV are due to the Al 2p electronic level (Figure 25). In this case, a general shift of approximately 0.5 eV, in all samples after sputtering was

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observed. This is an indicative of Al being less oxidized at the bulk of the film than at the surface.

Reported shift for Al 2p goes from 72.30 to 75.20 eV, when going from metallic Al (Al°) to oxidized Al $(Al_2O_3)^{39}$. Al atoms must substitute Zn atoms from its site on the lattice to be a successful doping process. In terms of binding energy, the lowest will correspond to an interstitial Al and the highest will correspond to a completely oxidized Al. Therefore, Al with binding energy in between those will most likely correspond to an Al atom successfully substituting a Zn atom in its lattice.

In general terms, all selected films showed a peak with binding energy around 73.4 eV which can be attributed to an Al 2p electronic level of a substitutional Al atom.

Relative compositional analysis can be performed through XPS data, taking into account the relative areas and the sensitivity factors for each peak. Sensitivity factors can be understood as a consideration for the factors affecting the analysis, such as depth of escape and cross-section. Results for Zn and Al concentration are shown in Figure 26, relative to the total quantity of Zn, Al and Oyxgen in the film.

It can be seen that after the sputtering (bulk) there is a higher concentration of Zn than before (surface). The contrary behavior occurs with Al, which is more present in the surface than in the bulk; except for the films without final thermal treatment. In that case, there is higher concentration of Al in the bulk for films made with Precursor A; films made with Precursor B, showed only a slight increase. In the case of the films without final thermal

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treatment, there is no correlation; most likely because these films are inhomogeneous and showed high roughness.

Films dried at 250 °C showed higher concentration of Al than those dried at 150 °C. This difference can be explained taking into account that XPS is a surface analysis technique which collects information of less than 10 nm deep. Therefore, the physical nature of the samples surface under analysis plays such an important role. As seen in earlier sections; films dried at 250 °C had the least roughness which means that the electrons are more able to escape the sample and arrive at the detector. In the other hand, electrons coming from a rough surface sample would more likely scatter at the surface imperfections not arriving at the detector.

Relative compositional analysis also showed more concentration of Al in the samples elaborated with the Precursor B. Aside from the effect explained above; in this case the increased Al concentration is due to the nature of the precursor and its interaction in the solution.

Water molecules strongly bounds to metal ions, forming a cluster around the ion. It is a co-ordinate association through the lone electron pairs from the water molecules. In the case of aluminum there is an sp^3d^2 hybridization of the orbitals in third level which gives six hybridized orbitals. Three hybridized orbitals with one electron. Three hybridized and three atomic orbitals with no electrons. Six lone pairs from the water molecules fill the six empty orbitals leaving a complex with three unpaired electrons. Finally, the 3+ charge distributes around the molecule.⁴⁰

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In Precursor A, chlorine fills these three half-filled hybridized orbitals. In Precursor B, three nitrate ions interact first with the other three water molecules giving a nitrate ion water complex, $H_2NO_4^-$ which then filled the half-filled hybridized orbitals.⁴¹

The size of the molecule and the ionic nature of the bond binding the aluminum complex with the chlorine atoms gives a more stable molecule (Precursor A) than whit the nitrate ion water complex (Precursor B) which will lose the aluminum complex more easily.

In the case of the films without final thermal treatment, no correlation was found. As discussed before, because these films are inhomogeneous and showed high roughness.



Figure 26 Relative atomic percentage composition of Zn (top) and Al (bottom) over the Zn-O-Al matrix, before and after the sputtering for both precursors (A, B). Elaboration conditions are indicated

4.4. A Word on Electrical Properties

ZnO is a wide band gap semiconductor with special electronic properties. With no doubt, the most interesting characteristic of this kind of materials it's the possibility of

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manipulate their electronic behavior. In the semiconductor's band structure, the VB is completely filled and is separated from an empty CB through the E_g . For very pure materials there are no electronic states in the E_g .

Electrical conductivity is strongly dependent on the number of free electrons available for conduction; however is not the only important factor. In addition, electrical conduction is related to the arrangement of electron states or levels.

For semiconductors, electronic states positioned at the top of the filled valence band are not available for conduction. They must be promoted across to the E_g into the nearest empty electronic states at the bottom of the conduction band; which is only possible by supplying enough energy, approximately equal to the energy of the E_g . Electrical resistivity increases with increase in the E_g . The electrical conductivity of most materials can be expressed as follows:

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

Where *n* and *p* are the number of free electrons or holes per unit volume, |e| is the absolute magnitude of the electrical charge on an electron or a hole, finally μ_e and μ_h are the mobility of electrons or holes in a given material. The electron mobility is an indication of the frequency of scattering events which cause an electron to loss kinetic energy and to change its direction of motion. These scattering events are caused by impurity atoms, vacancies, interstitials, dislocations and even thermal vibrations of the atoms themselves. Mobility can be seen as the ease with which free electrons move.⁸

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The conductivity is the reciprocal of the resistivity; the latter is easy to evaluate by measuring the resistance. A common resistance technique is known as the Kelvin measurement, also known as the 4-point probe technique; which is an arrangement of 4 aligned contacts. A current is applied trough the two outer probes and the voltage drop measured on the two inner probes. This arrangement allows to measure a materials resistance with more accuracy since it excludes the contact resistance of the probes.⁴²



Figure 27 Sheet resistance for both precursors selected films, A (solid squares) and B (solid triangles). Elaboration conditions are indicated on the *x* axis

In this work, films were measured using the 4-point probe technique. All films were found to possess high sheet resistance, inhomogeneous through the total area of the sample. This behavior may be due to a low concentration of free carriers, low mobility or both; these can be affected by several factors regarding the elaboration process and the phenomena taking place on a doped material.

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In 2009, Mehmet et al reported AZO thin films obtained through similar conditions with a sheet resistance of $10^{6}\Omega/sq$. In this work films with even lower sheet resistance were synthesized through a 250 °C drying using Precursor B.

It can also be observed that as a general tendency Precursor B showed lower sheet resistance than the Precursor A. Mainly due to the fact that more Al atoms are incorporated to substitutional sites in the material.

Also, the presence of anionic species in the film can affect the electrical properties of the material by scattering of the charge carriers, lowering the drift velovity.¹⁰ This can be attributed to some CI^- and NO_3^- that might be left in the matrix of the film. Results show, that NO_3^- ions are less detrimental than the CI^- .

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Chapter 5

Discussions

Properties stated in Table 5, play an important role on a joint effort to obtain a TCO.

Each one of them influences the others and vice versa, contributing to the overall result.

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| | Desired | If not met, then |
|------------|--|---|
| Physical | Dense film morphology Low grain boundary concentration Preferentially oriented crystalline structure | Higher concentration of voids Scattering events would increase |
| Optical | High transmittance Larger optical band gap than the undoped material | Transparency would be compromised Introduced carriers might not contribute to conduction |
| Chemical | <u>No organic residues</u> Successful Aluminum doping process | Crystalline structure and chemical purity would be poor Not enough free carriers |
| Electrical | Low sheet resistance | Conductivity decreases |

Table 5 Desired properties of a TCO and the consequences when these are not met

Characterization showed that in order to elaborate AZO films with the underlined desired properties three conditions must be brought to the process:

- High drying temperature (250 °C)
- An oxidizing atmosphere (air) for the solution elaboration, deposition and final thermal treatment
- Precursor B

As stated in the literature review, it seemed that the physical properties are constantly good regardless of the chemical system and conditions of elaboration, especially the crystalline orientation. However, to the best of our knowledge; the role of the solution elaboration and deposition atmospheres has never been reported. In this work, we found this parameter hugely influences the crystalline structure of the film. We found that a

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process performed in total presence, partial presence and absence of air produces amorphous, polycrystalline and preferentially oriented polycrystalline films; respectively.

Also, a comparison of Al Precursors has not been reported. We found that $AlCl_3$ promotes a higher c-axis preferred orientation than $Al(NO_3)_3$, however the latter promotes a better morphological, optical, chemical and electrical properties.

In 2007, Young-Sung Kim *et al*[†]**Error! Marcador no definido.**, reported an XPS Al 2p asymmetric peaks deconvoluted in two peaks centered at 74.20 and 74.62 eV named as Al in ZnO and Al₂O₃, respectively. Being attributed to the Al at the grains matrix and the Al oxidized at the grain boundaries, respectively. This was found on AZO thin films made with AlCl₃, as Al precursor, treated at 650 and 700 °C. This research group concluded that the films had two major components, Aluminum not oxidized in the matrix of the ZnO and Aluminum oxidized (Al₂O₃) in the grain boundaries. Similar behavior was found in this work, where Al 2p symmetric peaks were observed, centered at approximately 73.40 eV. As explained in previous section, this is an indicative of a successful doping process taking place.

AZO films with the desired properties have been reported by other authors, summarized in Table 3. In terms of electrical properties, good results have been recently obtained by Rydzek²⁴. Who reported a sheet resistance of 32.2 Ω /sq. Nevertheless, the process reported involves a multistep thermal treatment carried out at high temperatures and under different atmospheres taking a total of 80 hours. A thermal treatment of that

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nature greatly increases the total cost of the material or device. Therefore, desired performance at a reasonable cost remains yet to be achieved.

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Chapter 6

Conclusions

In this work, Aluminum doped Zinc Oxide thin films were elaborated by the Sol-Gel technique. Films were characterized through different methods in order to determine the properties of the elaborated material. Results were analyzed and important conclusions are as follows:

- 1. Aluminum doped Zinc Oxide thin films with good quality were successfully prepared by a solution method.
- 2. A process performed in the presence of Air yielded the highest crystalline order found in this work. To the contrary a process performed in the absence of Air yielded the lowest.
- 3. Precursor B (Aluminum Nitrate) seems to be the most adequate precursor since it liberates Aluminum to the solution more easily and its residues in the film have less negative impact on sheet resistance.
- 4. The key role of the final thermal treatment was evidenced; smoothes and compacts the film which improves the chemical composition, eliminating the organic component.
- 5. Regarding the introduced impurities, good evidence of the substitutional nature of them was found, therefore a successful doping process.

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Chapter 7

Future Work

A key part of the subject relays on the understanding of the Aluminum incorporation mechanism taking place in the films matrix. Since this interaction is essential for the material desired properties. It is also, the study of the films elaborated in Nitrogen in order to get a more complete sense of the atmosphere effect. Finally, process optimization must be achieved to maximize performance and minimize cost.

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Chapter 8

Appendix

8.1. Characterization Techniques

Characterization of samples elaborated in this work, necessarily require techniques that determine the properties of the coating or film and not the substrate. Most characterization techniques involve electrons, photons or ions as a probe striking the sample being analyzed. The beam interacts with the sample in some specific way and the changes in the beam after the interaction are monitored. In other techniques the information comes from the electrons, photons or ions ejected from the sample. In many situations more than one phenomenon is happening at the same time. Differences relay in the experimental array and collection of information.⁴³ Techniques covered in this appendix are those used and are displayed in the order they were performed.

8.1.1. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is a tool for the investigation of the phase and crystalline structure. Diffraction is a non-destructive scattering phenomenon involving a large number

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of atoms periodically arranged in a lattice, scattering X-rays. The rays scattered by those atoms have phase relations between them. These relations are often not in phase (destructive) and so they give no information. However in some specific cases, these relations are in phase (constructive) giving a diffraction pattern. Every material has a diffraction pattern of unique nature, a fingerprint. This phenomenon is governed by Bragg's Law which may be written as follows:

$\lambda = 2dSin\theta$

In this equation, λ is the incident X-Ray wavelength which depends on the source, *d* is the interplanar distance and θ is the Bragg angle in which diffraction occurs.⁴⁴

XRD is the most widely used technique for phase identification, due to its great database of known materials. Phase identification for polycrystalline thin films is also possible down to a thickness of 100Å. For preferred orientations a different experimental array is needed which include Grazing Incidence XRD (GIXRD).⁴³

In GIXRD the X-ray beam is set at a small angle (~ 5°), and the detector scan over a 20 range, which is an asymmetric scan. Under this array diffraction detected comes from the polycrystalline film. This technique is widely used for films grown on single crystal substrates, since Bragg condition for the substrate will not be satisfied under this configuration. Furthermore, since the incidence at low angle gathers information mostly from the film and not the substrate, this technique can also be used for films grown on amorphous substrates.⁴⁵

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In Figure 28, the X-ray spectrometer experimental array is shown with the essential features. X-ray radiation generated by an X-ray tube passes through a set of slits which collimate the X-ray beam. Then, the X-ray beam strikes the specimen and gets diffracted by the specimen forming a convergent beam at the receiving slits before they enter the detector. The diffracted beam passes through a monochromatic filter which suppresses undesired wavelengths, reducing background noise.⁴⁶



Figure 28 The X-Ray spectrometer schematic array

GIXRD was used to evaluate the crystalline structure of the ZnO formed in the films.

In the Figure 29 a diffraction pattern of the wurtzite ZnO powder is shown.

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Figure 29 ZnO Diffraction pattern created with Mercury 2.3 (Build RC4) software for a wavelength source of 1.54056 Å.

In the diffraction pattern the three main peaks can be observed situated at 2Theta 36.585, 32.156 and 34.501 as the intensity of the peak decrease; corresponding to planes (101), (001) and (002) respectively.^{19,21,47}

8.1.2. UV-Vis Transmission

There are three phenomena taking place when a light probe is incident to a surface; part of the light passes through, part gets absorbed and another part reflected. Optical transmission is used as an indicative of transparency. Transmitted light is measured as a function of wavelength and reported as percentage. The basic experimental array is shown in Figure 30. Light coming from the source (UV and visible) is conducted through an optical fiber and collimated before hitting the specimen. The portion of light passing

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through the specimen is again collimated and delivered by another optical fiber to the detector (Charge coupled device array) and the corresponding spectrum is generated.



Figure 30 UV-Vis transmittance measurement experimental array

Also, the band gap of a material can be determined by measuring the absorption coefficient (α) as a function of the photon energy. Light with energy higher than the band gap is absorbed. For direct band gap semiconductors, α^2 is plotted versus *hv* and the band gap becomes the extrapolated intercept of *hv*. The absorption coefficient is calculated using the following simple formula:

$$\propto = ln\left(\frac{100}{Abs}\right)hv^{48}$$

8.1.3. Profilometer

A mechanical profiler, also called profilometer is used to measure the thickness of a specimen. No sample preparation is required, although it is necessary to create a step as a reference to calculate the thickness of a film. Steps can be created through various techniques according to what is more suitable for both, the sample and the substrate. In this

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case, ZnO can be easily etched with a solution of hydrochloric acid diluted in deionized water (1:1000) after the film has been elaborated. A scheme of the Profilometer is shown in Figure 31. The specimen is fixed through backside vacuum on the stage, the stylus is then lowered, with the desired force, to the surface and a scan passing through the step is performed. Measured height is displayed on the screen and specimen thickness is calculated.



Figure 31 Profilometer schematic overview

Overall, it is a non-destructive technique, since the stylus force can be calibrated to avoid damaging the surface.⁴³

8.1.4. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared energies are not enough to excite electronic levels, but can excite vibrational or rotational states of covalently bonded atoms or groups. Because molecules rotate or vibrate at specific frequencies it is possible to identify molecular groups and bonds.⁴⁵

The infrared portion of the electromagnetic spectrum lies at wavelengths longer than those associated with visible light but shorter than microwaves. Chemists prefer to use

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wavenumber instead of wavelength since they are proportional to energy (higher wavenumber correspond to higher energy). Thus, in terms of wavenumber the infrared extends from 400 to 4000 cm⁻¹.

The FTIR produces a pattern called interferogram, which is essentially a plot of intensity versus time. Through a mathematical operation known as Fourier Transform the individual absorption frequencies can be separated and plotted versus the intensity. The advantage of this equipment is that provides a measurement in only seconds.

A schematic diagram of an FTIR is shown in Figure 32, it uses an interferometer to process the energy incident to the specimen by the beam splitter. As it passes through the specimen, some energy is absorbed and the energy that reaches the detector contains information of the chemical composition. This new information compared to the incident energy produces the final interferogram, which after a Fourier Transform has been applied to it, yields a typical infrared spectrum.⁴⁹



Figure 32 FTIR general schematic array

8.1.5. Scanning Electron Microscopy (SEM)

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SEM is the most widely used type of electron microscope. It images the microscopic structure by scanning the surface with a focused electron beam and collecting secondary or backscattered electrons. The most important feature is the three dimensional appearance of its images caused by its large depth of field. The resulting images can be collected at very high magnification showing features a few nanometers across. Signal from each pixel being scanned are collected by the detector in order to produce point to pint image on a display. Experimental array overview of a SEM is shown in Figure 33. Basically, the electron source generates an electron beam which strikes the specimen producing a signal recollected by the detector which is the amplified and through the software yields an image of the specimen.

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Figure 33 Schematic diagram of a typical Scanning Electron Microscope

When the incident beam strikes the sample elastic and inelastic scattering is taking place. Elastic scattering produces backscattered electrons, which are incident electrons scatter by the atoms in the specimen; typically deflected at large angles from the specimen with little energy loss. This signal is used for elemental composition contrast. Inelastic scattering produces secondary electrons, which are electrons ejected from the specimen at small angles with considerably energy loss. This signal is used for topographic contrast.

Commonly, SEM samples do not need a preparation for its observation. However, nonconductive samples tend to accumulate charge and image is lost, this problem can be solved by coating the sample with a conductive film, generally accomplished by vacuum evaporation or sputtering.

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In addition, SEM enables us to obtain chemical information through an X-ray energy dispersive spectrometer (EDS). X-ray spectroscopy determines presence and quantities of chemical elements by detecting characteristic X-rays emitted from the atoms in the specimen being irradiated with a high energy beam.^{45,46}

8.1.6. Atomic Force Microscopy (AFM)

AFM is a scanning probe technique which involves the force between a sharp tip and the sample. In this case the probe is a cantilever sensor that deflects as a result of the sample induced forces placed on the sharp tip positioned on or above the sample surface. AFM monitors this force and creates an image of the topography. A general diagram of the equipment is presented in Figure 34.



Figure 34 Overview of the Atomic Force Microscope

The cantilever scans the surface of the specimen being analyzed. The deflection of the cantilevers tip is acquired, following the movement of a laser projected onto the tip.

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Information received by the detector is converted to a topographic image of the specimen surface.

8.1.7. X-Ray Photoelectron Spectroscopy (XPS)

XPS is phenomenon of photoemission involving the ejection of an electron. When the vacancy is filled with an electron of higher energy, the difference in energy is emitted in the form of an X-ray photon. The energy of the emitted photoelectrons is analyzed and data is presented as a graph of intensity versus electron energy. The kinetic energy (E_k) of the electron is the experimental quantity measured by the spectrometer, depends upon the photon energy of the X-rays employed and is therefore not an intrinsic material property. The binding energy is then simply given by the relation:⁵⁰

$$BE = hv - E_k$$

It was soon discovered that this energy depends upon the fine chemical surroundings of the atoms being studied. The first observation was made back in 1957, where a shift in the binding energy of metallic copper and copper oxide was observed. The binding energy of the electron (E_B) is the parameter which identifies the electron specifically, both in terms of its parent element and atomic energy level.⁵¹ Information obtained from this experiment corresponds to chemical composition based on peak-shape and core level energy shift.

XPS technique involves an important parameter known as escape depth (λ). The escape depth depends upon elastic and inelastic interactions, directly affecting the surface sensitivity of the measurement.

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Figure 35 X-Ray Photoelectron Spectroscope schematic array

8.1.8. Four-Point Probe

This technique is used to measure sheet resistance of semiconductor thin films without the need of standards. A schematic representation of this technique is shown in Figure 36. A fixed current is passed through the outer probes while a voltage is measured in the inner probes. The probes are evenly spaced. The resistivity of the material is given by:

$$\rho = 2\pi s \frac{V}{I}$$

The above expression divided by the thickness of the layer gives the sheet resistance of the material as:

$$R_{s=\frac{\rho}{t}=\left(\frac{\pi t}{ln2}\right)\frac{V}{I}=4.532\frac{V}{I}}$$

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The two point probe technique seem easer, however, the four point probe method eliminates the effect of the parasitic resistances, thus is a more accurate method.⁵²



Figure 36 4-Point Probe measurement array

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