“Study of amorphous InGaZnO thin film deposited by pulsed laser deposition for flexible electronic applications”

Thesis Presented to in Fulfillment of the Requirements for the Degree Master of Science in Materials by:

RODOLFO ANTONIO RODRÍGUEZ DÁVILA

Advisor: Dr. Eduardo Martínez Guerra
Co-Advisor: Dr. Manuel Quevedo López

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“Study of amorphous InGaZnO thin film deposited by pulsed laser deposition for flexible electronic applications”
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“To my beloved family, who have always been, by my side”
I would like to thank Dr. Eduardo Martinez, for his advice in the development of this thesis. I am especially grateful with The University of Texas at Dallas (UTD) through the Flexible Electronics Research group headed by Dr. Manuel Quevedo for fruitful discussions and technical facilities.

I also want to thanks to the members of the evaluation committee: Dra. Margarita Sanchez, Dr. Jaime Alvarez and Dr. Shaji Sadasivan for they feedback and observations.

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<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>Thermal diffusion length</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Urbach width</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>Effective mobility</td>
</tr>
<tr>
<td>$\mu_{\text{FE}}$</td>
<td>Field effect mobility</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Optical absorption coefficient</td>
</tr>
<tr>
<td>$\mu_{\text{sat}}$</td>
<td>Saturation mobility</td>
</tr>
<tr>
<td>$1/\alpha$</td>
<td>Optical absorption length</td>
</tr>
<tr>
<td>2nd NN</td>
<td>Second nearest neighbor</td>
</tr>
<tr>
<td>Adatom</td>
<td>Adsorbed atom</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
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<tr>
<td>AOS</td>
<td>Amorphous oxide semiconductors</td>
</tr>
<tr>
<td>a-Si</td>
<td>Amorphous silicon</td>
</tr>
<tr>
<td>at.%</td>
<td>Atomic ratio</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energies</td>
</tr>
<tr>
<td>BM</td>
<td>Burstein moss</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>C</td>
<td>Dielectric capacitance per unit area</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline silicon</td>
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<tr>
<td>CTLM</td>
<td>Circular transmission line method</td>
</tr>
<tr>
<td>DIW</td>
<td>Deionized water</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
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<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
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<tr>
<td>Ga</td>
<td>Gallium</td>
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<tr>
<td>$g_{\text{d}}$</td>
<td>Conductance</td>
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<tr>
<td>$g_{\text{m}}$</td>
<td>Transconductance</td>
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<tr>
<td>HOAO</td>
<td>Highest occupied atomic orbitals</td>
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<tr>
<td>$I_{\text{DSS}}$</td>
<td>Drain current</td>
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<tr>
<td>$I_{\text{GS}}$</td>
<td>Gate Current</td>
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<tr>
<td>In</td>
<td>Indium</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>L</td>
<td>Channel length</td>
</tr>
<tr>
<td>LTPS</td>
<td>Low temperature polysilicon</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
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<tr>
<td>MOS-FET</td>
<td>Metal-Oxide-Semiconductor field effect transistor</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>NN</td>
<td>Nearest neighbor</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>POS</td>
<td>Polycrystalline oxide semiconductors</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>S</td>
<td>Subthreshold swing</td>
</tr>
<tr>
<td>SE</td>
<td>Spectroscopic ellipsometry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning probe microscopy</td>
</tr>
<tr>
<td>TAOS</td>
<td>Transparent amorphous oxide semiconductors</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin film transistors</td>
</tr>
<tr>
<td>TFFT</td>
<td>Transparent thin film transistors</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
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<tr>
<td>VBM</td>
<td>Valence band maximum</td>
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<tr>
<td>VDP</td>
<td>Van Der Pauw</td>
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<tr>
<td>VGS</td>
<td>Gate voltage</td>
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<tr>
<td>VON</td>
<td>Turn on voltage</td>
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<tr>
<td>VTH</td>
<td>Threshold voltage</td>
</tr>
<tr>
<td>W</td>
<td>Channel width</td>
</tr>
<tr>
<td>WAT</td>
<td>Weak absorption tail</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>Zn</td>
<td>Zinc</td>
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Abstract

The effect of oxygen pressure on the structural, morphological, chemical, optical and electrical properties of amorphous InGaZnO (a-IGZO) deposited by pulsed laser deposition, at room temperature, is investigated. Films were prepared on highly doped p-type silicon <100> and glass as substrates. X-ray diffraction spectroscopy (XRD) measurements showed that all films exhibit an amorphous structure. Also, the morphological analysis shows that the roughness of the films increase as pressure increase, but, despite this, all films showed smooth and uniform surfaces with RMS roughness less than 2 nm. Furthermore, The X-ray photoelectron spectroscopy (XPS) analysis indicates that there are no metallic states of In, Ga or Zn. However, the oxygen vacancies concentration decreases as pressure increases, suggesting that the oxygen vacancies could be the main defects that affect the physical properties of the film. The energy gap changes from 3.08 to 3.41 eV with increasing oxygen pressure. Also, small band tails (less than 0.07 eV) where found for all the films. The electrical resistivity change from 2x10^2 Ω•cm to 1.6x10^7 Ω•cm as pressure increase from 10 to 30 mTorr, exhibiting highly dependence with the oxygen pressure. This trend is in accordance with the XPS results. Furthermore, films show degenerated conduction for N_e>2x10^{19} cm^{-3} and percolation hopping conduction over potential barriers, formed around the conduction band bottom, for N_e < 2x10^{19} cm^{-3}.

Films deposited at 30 mTorr were used as active channel in TFTs with bottom common gate staggered structure. A field effect mobility of 2.09 cm^2V^{-1}s^{-1}, subthreshold swing of 0.1 V/dec, an I_{on}/I_{off}>10^6 and I_{off} < 10^{-10} A were found. The results suggest that a-IGZO could replace a-Si:H in the new generation of LCDs, but more study is required to increase the TFT performance.
Chapter 1

Introduction

Displaying video imagery when required on windows, while simultaneously converting solar energy into electricity; or using an automobile windshield to lay out visual information such as speed, navigation directions and alerts directly on the driver’s viewing field; are tasks on the verge of becoming a reality. With the fabrication of transparent electronic circuits, it would be possible to incorporate a new type of electronics, with a range of functions, into large area like windows. The demand for transparent conducting materials for their use as transparent electrodes and semiconductors, is rapidly growing for diverse technical applications.

The field of transparent electronics is reviewed through this chapter, specially, focusing on In-Ga-Zn-O: an amorphous oxide semiconductor material with impressive electrical properties; which open the door to completely disruptive creations such as electronic paper.

1.1. Transparent amorphous oxide semiconductors (TAOS)

Materials exhibiting both: high optical transparency in the visible range of the electromagnetic spectrum and high electrical conductivity ($\sigma$) are not common among conventional materials (metals, polymers and ceramics). The trick to making an electrical conductor transparent is to concoct a material with two special features: a wide enough energy
gap between the valence and conduction band ($E_g>3eV$) (Figure 1a); and some, but not too many, electrical carriers ($>10^{19} cm^{-3}$) with a mobility larger than $1 cm^2 V^{-1}s^{-1}$.

Transparency and conduction can be achieved in thin metal films, sulfides, selenides, nitrides, nanotube composites, graphene, polymers, and oxides.\textsuperscript{1-8} Oxide materials in the undoped stoichiometric state are insulators (completely filled valence and empty conduction band) with a band gap of about 3 eV or more. To become a transparent conductive oxide (TCO), the oxide host must be doped to displace the Fermi level within a band with a large density of states to provide high carrier concentration.\textsuperscript{9} The high energy dispersion of the conduction band also ensures a pronounced Fermi energy displacement up above the conduction band minimum (CBM), which is called the Burstein moss (BM) shift (Figure 1b).\textsuperscript{10, 11} This shift helps to broaden the optical transparency window and to keep the intense optical transition from the valence band out of the visible range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Electronic band gap designed for transparency,\textsuperscript{12} (b) Schematic electronic band structure of an oxide material host with a band gap $E_g$ and a dispersed parabolic conduction band. (c) and (d) Schematic band structure and density of states of a TCO.}
\end{figure}

TCOs could be broadly divided into two categories:

a) Polycrystalline oxide semiconductors (POS) such as ZnO,\textsuperscript{13-17} SnO$_2$,\textsuperscript{18} In$_2$O$_3$\textsuperscript{19}. Table 1 shows the basic electrical properties of these materials.

b) Amorphous oxide semiconductors (AOS) including In-Zn-O,\textsuperscript{20-24} In-Sn-O,\textsuperscript{25} Zn-Sn-O,\textsuperscript{26-28} Zn-In-Sn-O,\textsuperscript{29, 30} and In-Ga-Zn-O (a-IGZO).\textsuperscript{31-34}
Thin film transistors (TFTs) made of POS show high field effect mobilities comparable to amorphous silicon (a-Si:H) TFTs. POS exhibit a polycrystalline structure which possesses grain boundaries that can deteriorate the reproducibility and uniformity of the device characteristics.\textsuperscript{37} Another problem is that it contains high carrier density, which makes difficult to control the conductivity of the active layer on the TFT. As a highlight: the most essential expected feature of a semiconductor is that the carrier concentration should be controllable over several orders of magnitude.

On the other hand, AOS have good uniformity and reasonably high mobilities (field effect and Hall),\textsuperscript{38, 39} even when deposited at room temperature on plastic substrates.\textsuperscript{31} AOS are preferred over POS TFTs due to a unique and key advantage: \textit{capability of large-area deposition of uniform thin films (smooth surfaces) at low temperatures}. Figure 2 summarizes the advantages and possible applications of Transparent AOS (TAOS) materials.

![Figure 2. Characteristics other than transparency for TCOs.\textsuperscript{40}](image-url)
1.2. Brief history of TAOS

Research on amorphous semiconductors started in the 1950s to seek materials which could be deposited over a large area at room temperature. In 1954 a research group from Sheffield University in UK reported electronic conductive glasses containing a large amount of V$_2$O$_5$. This report broke a common statement: “a glass is an insulator”. Since then, a series of oxide glasses composed of a variable-valence transition metals and glass-forming oxides has been investigated. The first controllable amorphous material was hydrogenated amorphous silicon (a-Si:H), discovered by Spear and LeComber in 1975. Figure 3 summarizes the brief history of amorphous semiconductors.

![Figure 3. History of amorphous semiconductors and landscape of novel materials for transparent electronics.](image)

In 1996 Hosono et al. proposed a working hypothesis for wide band gap amorphous oxides with high electron mobilities: “All oxide materials composed of heavy metal cations with an electronic configuration \( (n-1)d^{10}ns^0 \) and \( n \geq 5 \) have a large overlap between relevant orbitals, which is required to obtain high mobilities. However, the overlap is insensitive to the structural randomness, intrinsic of an amorphous state”. Figure 4 shows the candidate metallic elements which satisfy these basis criteria. A series of amorphous oxide semiconductors was found, following the Hosono’s hypothesis in the subsequent years, which includes: CdO-PbO$_2$, AgSbO$_5$, SnO$_2$-ZnO, In$_2$O$_3$-ZnO (IZO), In$_2$O$_3$-Ga$_2$O$_3$, In$_2$O$_3$-SnO$_2$, and the most studied, InGaZnO$_4$.

Nomura et al. suggested in 2003 (following the Hosono’s hypothesis) to use a complex InGaO$_3$(ZnO)$_5$ (or IGZO) single-crystalline semiconductor layer in a TFT. This layer was epitaxially grown on an yttria-stabilized zirconia substrate and allowed to obtain an impressive
effective mobility of 80 cm$^2$V$^{-1}$s$^{-1}$, turn-on voltage of -0.5 V and on/off ratio of $10^6$. Even if a very high temperature of 1400 °C was necessary to attain this level of performance, this paper made history, since it proved the reality of the high-performance oxide semiconductor TFTs.

In 2004, Nomura et al. presented a work that definitely evidenced the enormous potential of oxide semiconductors for TFT applications, by demonstrating the fabrication of a transparent TFT on a flexible substrate using near-room temperature processing. For this end, they used a PLD deposited amorphous IGZO layer (In$_2$O$_3$:Ga$_2$O$_3$:ZnO=1:1:1) as the active layer (semiconductor). Even if the performance was far from the single-crystalline TFTs presented by the same authors, a saturation mobility of 9 cm$^2$V$^{-1}$s$^{-1}$, threshold voltage ($V_{th}$) of 1-2 V and on/off ratio of $10^3$ could still be achieved, mostly because the low sensitivity of these multicomponent oxides to structural disorder.
Nomura’s work opened the door for an impressively growing number of publications, in the following years, regarding to the application of amorphous multicomponent oxides as active layer in TFTs (Figure 5). With the continuous improvements verified on these devices, it is now common to obtain remarkable electrical properties, considerably superior to a-Si:H\textsuperscript{59} or organic TFTs. Such as mobilities above 10 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, turn-on voltages close to 0 V, on/off ratio exceeding 10\textsuperscript{7} and subthreshold swing of 0.2 V dec\textsuperscript{-1}, with the indium based semiconductors having the added advantage for very low or even room temperature processing.

It is important to note that if flexible and fully transparent TFTs are envisaged, the optimization of highly conducting TCOs deposited near room temperature for application as source, drain and gate electrodes is also a crucial requirement.\textsuperscript{36}

1.3. \textit{InGaZnO} properties

The a-IGZO features are summarized as follows:

a) Large electron mobility of 1 to 100 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, which is higher by 1 or 2 orders of magnitude than glassy semiconductors, amorphous chalcogenides or amorphous silicon.

b) Degenerate state can be achieved by doping, because strong ionic bonding form a shallow tail having small density of states. This is totally different from other amorphous semiconductors, for instance, a-Si:H, for which such state has not been attained to date.\textsuperscript{60}

c) Low deposition temperature, even room temperature.

1.3.1. Structural properties

Single crystalline InGaZnO\textsubscript{4} (sc-IGZO) has a complex layered structure with alternating layers of InO\textsubscript{2} and GaO(ZnO)\textsuperscript{+} as seen in Figure 6a. The XRD simulation pattern of this structure is shown in Figure 6; and is highly consistent with those obtained for high quality crystalline films. The In\textsuperscript{3+} ions in the InO\textsubscript{2} layers form an InO\textsubscript{6} octahedra (Figure 6b), which are two dimensionally connected in an edge-sharing network contributing to reducing the In-In distance and increasing the overlap between 5s-orbitals (the spatial overlap of the
“s” orbitals of metal cations is very important to design high mobility oxide semiconductors. The Ga and Zn ions occupy the trigonal-bipiramidal sites in the GaO(ZnO)+ block (Figure 6c). \(^{61}\)

```
Figure 6. (a) Structure of InGaZnO\(_4\) crystal; (b) octahedral; (c) trigonal bipiramidal structure.\(^{61, 62}\)
```

```
Figure 7. Bond length of various a-IGZO obtained by EXAFS analyses along with Hall mobilities.\(^{63}\)
```

The edge-sharing networks of InO\(_n\) are retained even in the disordered structure, with coordination number smaller than 6. Figure 7 shows the distance between the nearest-neighbor (NN) (i.e., In-O, Zn-O, and Ga-O) and the second nearest-neighbor (2nd NN) (In-(In, Ga, Zn)) ions in a-IGZO films with various chemical compositions obtained by EXAFS.
analysis. It shows that the NN distances are not changed by chemical composition change. Meanwhile, the 2nd NN In-(In, Ga, Zn) distances decrease with an increase in the In content, which is accompanied by the increase in the portion of the edge-sharing network of \((\text{InO}_n)\) polyhedral and would be associated with the increase in the mobility to some extent. This trend is consistent with the fact that the CBM in a-IGZO are mainly made of In s-orbitals and the In-In distance affects the CBM dispersion and consequently the electron mobility.

1.3.2. Electronic structure of IGZO

It had been believed that amorphous semiconductors cannot have large mobility, due to the strong scattering by the disordered structure, and are considerably degraded compared with their corresponding crystalline phases. There is the case for silicon, because intrinsic crystalline silicon \((\text{c-Si})\) exhibits an electron mobility higher than 1000 cm\(^2\)V\(^{-1}\)s\(^{-1}\), but the mobility deteriorates to less than 1 cm\(^2\)V\(^{-1}\)s\(^{-1}\) in a-Si:H. Degenerate band conduction and large mobility (>10cm\(^2\)V\(^{-1}\)s\(^{-1}\)) are possible in AOS containing post-transition-metal cations, where the conduction mechanism is very different from that in crystalline, and specifically, covalent semiconductors.

![Figure 8. Schematic orbital drawing for the carrier transport paths (that is, conduction bottoms) in (a) crystalline and (b) amorphous covalent semiconductors.](image)

In silicon, the average carrier transport paths consist of sp\(^3\) orbitals with strong directivity (Figure 8a) and, therefore, the bond angle fluctuation significantly alters the electronic levels, leading to high density deep tail states. The low mobility of amorphous
silicon is associated with the intrinsic nature of the chemical bonding (Figure 8b): average carrier transport paths in covalent semiconductors (such as a-Si:H) consist of sp\(^3\) orbitals with strong directivity and, therefore, the bond angle fluctuation significantly alters the electronic levels, leading to high density deep tail-states. Table 2 summarizes the bonding nature and carrier transport of various classes of amorphous semiconductors.

<table>
<thead>
<tr>
<th>Material system</th>
<th>Chemical bond</th>
<th>Mechanism</th>
<th>Hall voltage sign</th>
<th>Mobility (cm(^2)V(^{-1})s(^{-1}))</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedral</td>
<td>Covalent</td>
<td>Hopping</td>
<td>Abnormal</td>
<td>~1</td>
<td>Si:H</td>
</tr>
<tr>
<td>Chalcogenide</td>
<td>Covalent</td>
<td>Hopping</td>
<td>Abnormal</td>
<td>&gt;10(^{-3})</td>
<td>Ti(_2)Se-As(_2)Se(_3)</td>
</tr>
<tr>
<td>Oxides (glass sem.)</td>
<td>Covalent+ionic</td>
<td>Hopping</td>
<td>Normal</td>
<td>~10(^{-4})</td>
<td>V(_2)O(_5)-P(_2)O(_5)</td>
</tr>
<tr>
<td>Ionic amorphous oxides sem.</td>
<td>Covalent</td>
<td>Band conduction</td>
<td>normal</td>
<td>10~30</td>
<td>In-Ga-Zn-O</td>
</tr>
</tbody>
</table>

The advantages of AOS came from their strong ionic bond, which can be understood from the Madelung potential\(^66, 67\): when a metal atom (M) and an oxygen atom (O) are apart in vacuum, the energy levels of the highest occupied atomic orbitals (HOAO) are not largely different as illustrated in Figure 9b. When they come close, charge transfer occurs due to the different electron affinities. The ionized ions form a negative electrostatic potential at the cation site and a positive at the anion sites, which is called the Madelung potential (Figure 9c). The Madelung potential lowers the energy levels in the oxygen ions and rises those in the cation site (Metal), where, the CBM is mainly made of empty “s” orbitals of the metal and VBM is fully occupied O2p. The wide band gap of ionic semiconductors came from the larger Madelung potential.
The CBM (carrier transport path) in AOS, is primarily composed by spatially spread metal “ns” orbitals with isotropic shape (where “n” is the principal quantum number), and direct overlap among the neighboring metal “ns” orbital is possible (Figure 10). The spatial spread of the s-orbital is primarily determined by the principal quantum number (n) of a cation and is modified by the charge state of the cation as shown in Figure 12. The magnitude of the overlap is insensitive to the distorted metal-oxygen-metal (M-O-M) chemical bond that intrinsically exists in the amorphous materials. Therefore, AOS exhibit Hall-effect mobilities similar to those of the corresponding crystalline phase, even if they are deposited at room temperature. These carrier transport properties are unique in AOS.

![Figure 10. Schematic orbital drawing for the carrier transport paths (CBM) in (a) crystalline- and (b) amorphous- oxide semiconductors. Spheres denote metal “s” orbitals.](image)

The valence band (VB) in IGZO, is formed mainly by O 2p and Zn 3d orbitals while the conduction band is formed by the s and p orbitals of the three metals, with some influence by the O 2p orbitals. The In 5s partial density of states (DOS) shows a shoulder peak on the lower-energy density side (Figure 11). Therefore, the conduction band minimum (CBM) is formed by In 5s band only as shown in Figure 13.

Since the work of Anderson, it is known that disorder (i.e. spatial fluctuation of bond length, bond angle and/or dihedral angle) will lead to broadening of the edges of the conduction and valence bands, constructing the band tails. In the band tails, the electronic states have a localized character and their nature changes from localized to delocalized at a critical boundary called the mobility edge, as shown in Figure 14a. The energy separation between the two mobility edges of the conduction and valence band is called the mobility gap or, in a more common sense, the band gap. With increasing disorder, the mobility edges move further into the bands, and eventually, the whole band becomes localized.
Figure 11. Partial density-of-states (DOS) curves for InGaZnO₄ crystal structures. The top of the valence band is located at zero energy.⁷¹

Figure 12. Calculated values of the overlap integral between the ns orbitals functions of metals with (n-1)d⁰ns⁰ electronic configuration vs the distance.⁶⁵

Figure 13. Red surfaces show isosurfaces of the CB wave function Ψ². The blue-to-red planes show cross sections of the Ψ² on the edge planes of the cell.⁶¹

Figure 14b shows a schematic electronic structure of a-IGZO (In:Ga:Zn=1:1:1). The CBM is explained well by the Tauc-Lorentz Model⁷² (TL) but non-localized tail-states exist in the sub-gap region.⁴⁶, ⁷³-⁷⁶ Hard x-ray photoemission spectroscopy (HX-PES) revealed that the high-density electron traps exist just above VBM with the energy range of ~1.5 eV,⁷⁶ which would be the reason why a-IGZO TFTs have never operated in p-channel TFT mode.
1.3.3. Electronic transport and electrical properties of IGZO

Figure 15 summarizes the structure, Hall mobility ($\mu_{\text{Hall}}$) and carrier concentration ($N_e$) for the In$_2$O$_3$ – Ga$_2$O$_3$ – ZnO system in function of the composition. All the films were deposited at the same conditions: SiO$_2$ glass substrates at RT on oxygen partial pressure of 1.0 Pa by pulsed laser deposition. From Figure 15b, a-IZO has higher electron mobilities than a-IGZO, but it is difficult to decrease the carrier density into a required level for TFTs ($>10^{17}$ cm$^{-3}$). Ga-O bonds are much stronger than In-O and Zn-O bonds, meaning that the incorporation of gallium suppresses the formation of oxygen deficiencies (vacancies) and the consequent generation of mobile electrons. On the other hand, the incorporation of gallium content deteriorates the electron mobility (Figure 15b). Therefore, the addition of an appropriate amount of a stabilizer ion, that forms a strong chemical bond with the oxygen ions, is important to obtain stable AOS materials and TFTs.
Both the hall mobility and the carrier concentration rapidly decrease with the increase of the Ga\textsuperscript{3+} ion content. However, introduction of high density carriers became very difficult in the large Ga content films. It is a disadvantage for electrical applications because high carrier concentration means higher conductivity, which is required for contact applications, for example. However, it is not required for electronic applications, because the difficulty in the carrier doping, by oxygen vacancies, suggests better controllability and stability of carrier concentration, especially at low Ga concentration. Even if high density doping is difficult by choosing deposition conditions, it is still possible to induce high density carriers by external electric field if TFT structures are employed.

Figure 16a shows the controllability of the carrier concentration of the a-IGZO, (In:Ga:Zn=1:1:1) and a-IZO (In:Zn=2:3) films; carrier concentration is plotted against oxygen partial pressure. The carrier concentration was well controlled from \(<10^{15}\) to \(10^{20}\) by varying oxygen pressures from 0.1 to 7 Pa for a-IGZO. In contrast, it is hard to reduce carrier concentration down to \(10^{17}\) cm\(^{-3}\) for a-IZO.

Figure 16b summarizes the relationship between carrier concentration and hall mobilities measured at RT. It shows that hall mobility strongly depends on carrier concentration, and steeply increases from \(6.9\times10^{15}\) cm\(^{-3}\) to \(10^{17}\) cm\(^{-3}\) and reaches \(~13\) cm\(^2\) V\(^{-1}\)s\(^{-1}\) at \(>10^{19}\) cm\(^2\) V\(^{-1}\)s\(^{-1}\). These results imply that electronic structure and carrier transport mechanism in a-IGZO are similar to that in sc-IGZO, which would be associated with the
electronic structure of oxide semiconductors; for which electron transport paths are made of spherical extended s orbitals and are not largely affected by local distortion of the chemical bond.

![Graph](image.png)

**Figure 16.** (a) Dependence of carrier concentration on oxygen partial pressure between a-IGZO and a-IZO films.\(^{45}\) (b) Relationship between room-temperature Hall mobility and carrier concentration for a-IGZO and sc-IGZO films.\(^{31}\)

Figure 17 shows temperature dependence of electrical conductivity for different a-IGZO films. The electrical conductivity shows thermally activated behavior when carrier concentration is less than \(10^{19}\) cm\(^{-3}\), and the behavior changes to degenerate conduction at larger concentrations. Also, the carrier conductivity \((\sigma)\) follows \(\sigma = \sigma_0 \exp[-A/T^{1/4}]\) relationship when the carrier concentration was less than \(10^{15}\) cm\(^{-3}\), suggesting hopping conduction.

Figure 18 shows the Hall mobility and carrier concentration in the temperature dependence analysis. It should be noted that although carrier concentration does not show temperature dependence at \(N_e>10^{17}\) cm\(^{-3}\), mobility shows a thermally-activated behavior at \(10^{17}<N_e<10^{19}\). This result implies that the carriers are not localized. The non-dependence temperature of carrier concentration at \(N_e>10^{17}\) suggests that Fermi level exceeds the mobility edge. Nevertheless, mobility still exhibits thermally activated behavior, suggesting the existence of potential barriers above the mobility edge.
1.3.4. Optical properties

In a crystalline semiconductor, a well-defined energy gap exists between the VB and CB. In contrast, in an amorphous semiconductor, the band edges, at valence and conduction bands, are no longer well defined cut-off energies, and there are electronic states above the VBM and below the CBM where the density of states fall sharply with energy away from the band edges. That localized states are called the tail states and they are in the gap region, as mentioned in section 1.3.2. The band edges or mobility edges separate these localized states from their extended or delocalized counterparts, and are a contribution of defects.
Examples of these defects are: broken and dangling bonds, over and under coordinated atoms, voids, pores, cracks, and other macroscopic defects.

The absorption of photons, with lower energy than the band gap energy, involves the localized tail states. Such excitation leads the absorption coefficient ($\alpha$) to depend exponentially of $h\nu$, a dependence that is called Urbach rule, given by:

$$\alpha = \alpha_0 e^{\frac{h\nu-E_g}{\Delta E}}$$  \hspace{1cm} \text{Eq. 1}$$

Where $\alpha_0$ and $E_g$ are material dependent constants and $\Delta E$, called Urbach width, is also a material dependent constant. The absorption tail behavior may be attributed to the strong internal field, for instance to ionized dopants or defects.

![Figure 19. Typical spectral dependence of the optical absorption coefficient in amorphous semiconductors.]

The optical absorption in amorphous semiconductors, near the absorption edge, is usually characterized by three types of optical transitions, corresponding to transitions between: (a) tail and tail states; (b) tail and extended states; and (c) extended to extended states. The first two correspond to $h\nu<E_g$, and the third corresponds to $h\nu\geq E_g$. Thus, the plot of absorption coefficient versus photon energy has three different regions, A, B and C,
respectively; which correspond to the three characteristic optical transitions shown in Figure 19, and described as follows:

a) In the small absorption coefficient range A (also called the weak absorption tail, WAT), where \( \alpha < 10^{-1} \text{ cm}^{-1} \), the absorption is controlled by optical transitions from tail-to-tail states. The localized tail states in amorphous semiconductors are attributed to defects. The absolute value of absorption in region A may be used to estimate the density of defects in the material.

b) In region B \((10^{-1} < \alpha < 10^{4} \text{ cm}^{-1})\), the absorption is related to transitions from the localized tail states above the valence band to extended states in the conduction band and/or from extended states in the valence band to localized states below the conduction band. The spectral dependence follows the so-called Urbach rule, giving in Eq. 1. The Urbach energy, \( \Delta E \), is related to the width of the valence and conduction band tails, and may be used to compare the widths of such localized states in different materials.

c) In region C, the absorption is controlled by transitions between extended states. The absorption coefficient, \( \alpha \), due to the interband transition near the band gap is known to be well described by the following equation:

\[
\alpha \nu = B (\nu - E_g)^2
\]

Eq. 2

Where \( \nu \) and \( E_g \) denote the photon energy and the band gap, respectively. In amorphous semiconductors, the optical gap \( E_g \) is determined by a plot of \( (\alpha \nu)^{1/2} \) vs. \( \nu \), which is known as Tauc’s plot.\(^{80}\) It has been found that the estimated band gap values (Tauc’s gaps) are 3.0 – 3.2 eV for a-IGZO and tend to be larger than 3.7 – 4 for high quality films.\(^{81, 82}\)

1.3.5. TFT application

“Semiconducting” means that the conductivity can be manipulated using electrodes, in particular a gate electrode in a transistor setup. The key application of TAOS is the transparent thin film transistor (TTFT). The TAOS serves as active layer, connected to source and drain contacts, in the TFT structure.\(^{31}\) TAOS are expected to replace a-Si:H in the near
future, due to the better performance and the cost saving through the lower processing temperatures. The field effect mobility higher than 10 cm²V⁻¹s⁻¹ of TAOS outperforms the mobility showed by a-Si:H, which is lower than 1 cm²V⁻¹s⁻¹.

TFTs are three terminal field-effect devices, whose working principles rely on the modulation of current flowing in a semiconductor placed between two electrodes (source and drain). A dielectric layer is inserted between the semiconductor and a transversal electrode (gate), being the current modulation achieved by the capacitive injection of carriers close to the dielectric/semiconductor interface (accumulation channel), which is known as field effect. Inside these, top- and bottom- gate structures exist, depending on whether the gate electrode is on top or bottom of the structure. Each of these structures present advantages and disadvantages, largely dictated by the materials used.

![Figure 20. Most conventional TFT structures.](image)

Figure 20 shows different TFT configurations. Depending if the source-drain are on opposite sides or on the same side of the semiconductor, the structures are identified as staggered and coplanar according to Weimer’s definition. The schematics in Figure 20 only shows the fundamental layers of a TFT, but other layers can also be introduced for different purposes.
TFTs are quite similar to other field effect devices in terms of operation and composing layers, such as the well-known MOS-FETs used in high performance applications (i.e. microprocessors and/or memories). However, important differences exist between these devices, some of them readily seen by inspecting their typical structures (Figure 21). The most important differences are:

a) While TFTs use an insulating substrate, normally glass, in MOSFETs the silicon wafer acts as the substrate and the semiconductor. Thus, higher performance naturally arises for MOSFETs, given that the electrons flow in a single crystalline semiconductor, rather than the polycrystalline or amorphous one.

b) The temperature involved in the fabrication of both devices is quite different. The processing temperatures exceed 1000°C in MOSFETs (for instance to create the dielectric layer); in TFTs they are limited by parameters such as the softening point of the substrate, which for most common glass substrates does not exceed 600-650°C.

c) MOSFETs have p-n junctions at source-drain regions, which are absent in TFTs. Even if both, MOSFETs and TFTs, have the field effect as the basic principle to modulate the conductance of the semiconductor (close to the interface with the dielectric); in TFTs this is achieved by an accumulation layer, while in MOSFETs an inversion region has to be formed.
The most important TFT static characteristics are extracted from the output and transfer curves (shown in Figure 22 (a) and (b), respectively) and they are: mobility ($\mu$), on/off current ratio, turn-on voltage ($V_{ON}$) and subthreshold swing ($S$).

a) **On/Off current ratio.** This is simply defined as the ratio of the maximum to minimum drain current ($I_{DS}$). The minimum $I_{DS}$ is generally given by the noise level of the measurement equipment or by the gate leakage current ($I_{GS}$), while the maximum $I_{DS}$ depends on the semiconductor material itself and on the effectiveness of capacitance injection by the field effect. On/Off ratios above $10^6$ are typically obtained in TFTs and a large value is required for their successful usage as electronic switches.

![Figure 22. Typical (a) output and (b) transfer characteristics of an a-IGZO TFT.](image)

b) **Threshold Voltage ($V_{TH}$) and Turn on Voltage ($V_{ON}$).** $V_{TH}$ correspond to the gate voltage ($V_G$) for which an accumulation layer or conductive channel is formed close to the dielectric/semiconductor interface, between the source and drain electrodes (channel region). For an n-type TFT, depending upon whether $V_{TH}$ is positive or negative, the device has an enhanced or depletion mode, respectively. Both types are useful for circuit fabrication, but generally enhancement mode is preferable, because no $V_{GS}$ is required to turn off the transistor, simplifying the circuit design and minimizing power dissipation.
V_{TH} can be determined using different methodologies, such as linear extrapolation of the I_{DS}-V_{GS} plot (for low V_{DS}) or the I_{DS}^{1/2} – V_{GS} plot (for high V_{DS}), V_{GS} corresponding to a specific I_{DS} ratio of conductance and transconductance among others. \(^{88}\)

The concept of V_{ON} is largely used in literature, simply corresponding to the V_G at which I_{DS} starts to increase as seen in a log(I_{DS}) – V_{GS} plot, or in other words, the V_G necessary to fully turn off the transistor. \(^{89}\)

c) **Subthreshold swing (S)**. The inverse of the maximum slope of the transfer characteristic, and it indicates the necessary V_{GS} to increase I_{DS} one decade:

\[
S = \left(\frac{d \log(I_D)}{d V_G}\bigg|_{max}\right)^{-1}
\]

Typically, S<<1 around 0.10 to 0.3 V/decade and small values result in higher speeds and lower power consumption. \(^{87}\)

d) **Mobility (\mu)**. Is related with the efficiency of carrier transport in a material, affecting directly the maximum I_{DS} and operating frequency of devices. \(^{90}\) In a material, mobility is affected by several scattering mechanisms, such as lattice vibrations, ionized impurities, grain boundaries and other structural defects. \(^{90, 91}\) On a TFT, since the movement of the carriers is constrained to a narrow region close to the dielectric/semiconductor interface, additional sources of scattering should be considered, such as Coulomb scattering from dielectric charges and from interface states or surface roughness scattering. \(^{91}\)

In a TFT, mobility is controlled by V_{GS}, so scattering mechanism become less relevant for particular bias conditions. Mobility can be extracted using different methodologies. \(^{91}\) Following the Schröder's nomenclature, one may have:

**Effective mobility (\mu_{eff})**: Obtained by the conductance (g_d) with low V_D:

\[
\mu_{eff} = \frac{g_d}{C_i \frac{W}{L} (V_{GS} - V_{TH})}
\]

\(^{Eq. 4}\)
Field effect mobility ($\mu_{FE}$): obtained by the transconductance ($g_m$) with low $V_D$:

$$\mu_{FE} = \frac{g_m}{W \frac{C_i}{L} V_{DS}}$$  \hspace{1cm} Eq. 5

Saturation Mobility ($\mu_{sat}$): obtained by the transconductance with high $V_D$:

$$\mu_{sat} = \frac{(\frac{d}{dV_{GS}} \frac{I_{DS}}{W})^2}{\frac{1}{2} \frac{C_i}{W L}}$$  \hspace{1cm} Eq. 6

Where $W$ and $L$ are the channel width and length, respectively. $C_i$ is the dielectric capacitance per unit area, $I_{DS}$ is the drain current, and $V_{GS}$ and $V_{DS}$ are the applied gate and drain voltages, respectively.

Even if $\mu_{eff}$ includes the important effect of $V_{GS}$, it requires the determination of $V_{TH}$ and is more sensitive to contact resistance (Low $V_D$). This last issue is also verified for $\mu_{FE}$, but $\mu_{FE}$ does not required $V_{TH}$ and is easily calculate by the derivative of transfer characteristics, consequently, it is a widely used parameter. Finally, $\mu_{sat}$ does not require $V_{TH}$ and is less sensitive to contact resistance. However, it describes a situation where the channel is pinched-off, i.e., its effective length is smaller than $L$, which is intrinsically not assumed by the classical model. However, plotting Eq. 4, 5 or 6 as function of $V_{GS}$ allows for a more complete understanding of the device physics, clearly showing effects such as mobility degradation due to contact resistance or increased interface scattering as $V_{GS}$ increases.

There are several requirements that the material must satisfy to make a flexible and transparent TFT. First of all, the thin film must be formed at low temperature (<200°C). Further requirements are high mobility, high stability of transport properties, and, in general for TFT operation, reliable controllability of carrier concentration, which, for oxide materials, is related with oxygen vacancies acting as donors, since electrical conductivity is mainly controlled by such defects. The incorporation of stronger metal-oxygen bonds, like Ga$^{3+}$ or Al$^{3+}$ (stronger chemical bonds than zinc and indium), would be effective to suppress carrier generation via oxygen vacancies.

Amorphous IGZO TFTs offer several advantages over the low mobility (<1 cm$^2$V$^{-1}$s$^{-1}$) a-Si:H TFTs (widely used in flat panel displays), low temperature polysilicon (LTPS) and
polycrystalline semiconductors (POS). Table 3 shows the main properties of AOS in comparison with other TFT existing technologies.

Table 3. Comparison between TCOs TFTs and other available technologies.\textsuperscript{36, 92-96}

<table>
<thead>
<tr>
<th>TFT semiconductor material</th>
<th>a-Si:H</th>
<th>LTPS</th>
<th>Organic</th>
<th>a-IGZO (AOS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier mobility (cm(^2)V(^{-1})s(^{-1}))</td>
<td>&lt;1</td>
<td>50-100</td>
<td>0.1-10</td>
<td>1-100</td>
</tr>
<tr>
<td>Switching characteristics (V/Dec)</td>
<td>0.4-0.5</td>
<td>0.2-0.3</td>
<td>0.1-1.0</td>
<td>0.09-0.6</td>
</tr>
<tr>
<td>Source-drain leakage current (A)</td>
<td>(\sim 10^{-12})</td>
<td>(\sim 10^{-12})</td>
<td>(\sim 10^{-12})</td>
<td>(10^{-12}) max</td>
</tr>
<tr>
<td>Process temperature (°C)</td>
<td>(~250)</td>
<td>250 min</td>
<td>RT</td>
<td>RT to 350</td>
</tr>
<tr>
<td>TFT characteristics variation</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>TFT manufacturing for organic LED panels</td>
<td>4 to 5 masks</td>
<td>5 to 9 masks</td>
<td>4 to 5</td>
<td>4 to 5 masks</td>
</tr>
<tr>
<td>Manufacturing cost</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Visible transparency</td>
<td>Poor</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Long term TFT reliability</td>
<td>Low</td>
<td>High</td>
<td>Low in air</td>
<td>Unknown</td>
</tr>
<tr>
<td>Pixel TFT</td>
<td>NMOS+PMOS</td>
<td>NMOS</td>
<td>PMOS</td>
<td>NMOS</td>
</tr>
<tr>
<td>Motherglass Generation Size</td>
<td>Gen 8</td>
<td>Gen 4</td>
<td>Gen 8</td>
<td>Gen 8</td>
</tr>
<tr>
<td>Applicable displays</td>
<td>LCD, etc.</td>
<td>LCD, small organic LED</td>
<td>OLED</td>
<td>LCD, OLED, etc</td>
</tr>
</tbody>
</table>

The advantageous feature of IGZO TFTs are summarized as follows:

1. \textit{Low processing temperature}. AOS TFTs exhibit satisfactory operation characteristics even if fabricated at room temperature.

2. \textit{Wide processing temperature window and ease of fabrication} by choosing an appropriate chemical composition. AOS form stable amorphous phases with high crystallization temperature of >500°C; therefore, an appropriate temperature condition can be chosen to modify the TFT characteristics.

3. \textit{Large electron mobilities}. AOS exhibit large hall mobility and TFT mobilities of >10 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and even higher than 50 cm\(^2\)V\(^{-1}\)s\(^{-1}\) by choosing appropriate chemical compositions.

4. \textit{Low operation voltage}. Oxides have an electronic structure specific to the ionic chemical bonds, and therefore they form much fewer defect states in the band gap than conventional covalent semiconductors such as silicon. The low defect density allows small subthreshold slope values of 0.1 V/decade and low operation voltages of <5V.
5. **Large allowance in the choice of gate insulator.** The choice of a gate insulator is critical for field effect transistors including TFTs. This feature would also benefit for two reasons: (a) the unipolarity of AOS, by which only electrons are mobile; and thus (b) the valence band offset between the gate insulator and AOS is not critical; and the high ionic chemical bonding nature, which gives rise to fewer defects at the gate insulator/AOS interfaces.

6. **Excellent uniformity and surface flatness.** AOS TFTs exhibit excellent short-range uniformity and surface flatness (>0.3nm) owing to the amorphous structure.

### Table 4. Comparison of device parameters for various TFTs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Type</th>
<th>Subs.</th>
<th>Insulator</th>
<th>Gate</th>
<th>(V_{TH}) (V)</th>
<th>(V_{SD}) (V)</th>
<th>(I_{on}/I_{off})</th>
<th>(\mu_{FE})</th>
<th>REF</th>
</tr>
</thead>
<tbody>
<tr>
<td>*PLD</td>
<td>BG</td>
<td>PET</td>
<td>Y_2O_3</td>
<td>ITO</td>
<td>1.6</td>
<td>10</td>
<td>10^3</td>
<td>5.6</td>
<td>31</td>
</tr>
<tr>
<td>RFS</td>
<td>TG</td>
<td>Glass</td>
<td>Y_2O_3</td>
<td>Ti/Au</td>
<td>1.5</td>
<td>5</td>
<td>10^6</td>
<td>12</td>
<td>32</td>
</tr>
<tr>
<td>*PLD/ALD</td>
<td>BG</td>
<td>Glass</td>
<td>ATO</td>
<td>ITO</td>
<td>2</td>
<td>10</td>
<td>5x10^7</td>
<td>11</td>
<td>98</td>
</tr>
<tr>
<td>MS/PECVD</td>
<td>BG</td>
<td>Si/SiO_2</td>
<td>SiN_x</td>
<td>Ti/Au</td>
<td>7</td>
<td>7</td>
<td>~10^8</td>
<td>10</td>
<td>99</td>
</tr>
<tr>
<td>RFS/PECVD</td>
<td>TG</td>
<td>Glass</td>
<td>SiN_x</td>
<td>ITO</td>
<td>1.9</td>
<td>10</td>
<td>1.9x10^7</td>
<td>45</td>
<td>100</td>
</tr>
<tr>
<td>MS</td>
<td>BG</td>
<td>p-Si</td>
<td>SiO_2</td>
<td>Ti/Au</td>
<td>12.9</td>
<td>20</td>
<td>6.1x10^7</td>
<td>24.5</td>
<td>101,102</td>
</tr>
<tr>
<td>RFS</td>
<td>BG</td>
<td>n-Si</td>
<td>TiO_x</td>
<td>ITO</td>
<td>1.2</td>
<td>5</td>
<td>10^7</td>
<td>11.4</td>
<td>103</td>
</tr>
<tr>
<td>*PLD</td>
<td>BG</td>
<td>n-Si</td>
<td>SiO_2</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>10^9</td>
<td>-12</td>
<td>34</td>
</tr>
<tr>
<td>RFS</td>
<td>BG</td>
<td>Paper</td>
<td>paper</td>
<td>IZO</td>
<td>1</td>
<td>10</td>
<td>10^6</td>
<td>40</td>
<td>104</td>
</tr>
<tr>
<td>RFS/PECVD</td>
<td>BG</td>
<td>Glass</td>
<td>SiO_2</td>
<td>Mo</td>
<td>1.2</td>
<td>10</td>
<td>10^6</td>
<td>30</td>
<td>105</td>
</tr>
<tr>
<td>RFS</td>
<td>BG</td>
<td>p-Si</td>
<td>SiO_2</td>
<td>Ti</td>
<td>0.34</td>
<td>10</td>
<td>&gt;10^6</td>
<td>3.6</td>
<td>106</td>
</tr>
<tr>
<td>RFS</td>
<td>BG</td>
<td>Glass</td>
<td>Y_2O_3</td>
<td>Mo</td>
<td>0.7</td>
<td>3</td>
<td>1.1x10^6</td>
<td>6.9</td>
<td>107</td>
</tr>
<tr>
<td>RFS/ALD</td>
<td>BG</td>
<td>Glass</td>
<td>HOYO</td>
<td>Mo</td>
<td>1.1</td>
<td>3</td>
<td>7x10^7</td>
<td>3.3</td>
<td>107</td>
</tr>
<tr>
<td>*PLD</td>
<td>BG</td>
<td>Glass</td>
<td>ATO</td>
<td>ITO</td>
<td>-0.25</td>
<td>10</td>
<td>&gt;10^7</td>
<td>14</td>
<td>108</td>
</tr>
<tr>
<td>MS/PECVD</td>
<td>BG</td>
<td>Glass</td>
<td>SiO_2</td>
<td>Mo</td>
<td>0.13</td>
<td>10</td>
<td>10^9</td>
<td>9.5</td>
<td>109</td>
</tr>
<tr>
<td>MS/ALD</td>
<td>TG</td>
<td>Glass</td>
<td>AlO_x</td>
<td>Pt</td>
<td>2.5</td>
<td>15</td>
<td>10^10</td>
<td>12.2</td>
<td>110</td>
</tr>
<tr>
<td>MS</td>
<td>BG</td>
<td>p-Si</td>
<td>SiO_2</td>
<td>Ti/Au</td>
<td>1.6</td>
<td>20</td>
<td>10^6</td>
<td>8.9</td>
<td>112</td>
</tr>
<tr>
<td>RFS/PECVD</td>
<td>TG</td>
<td>Glass</td>
<td>SiN_x</td>
<td>Au/Ti</td>
<td>1</td>
<td>20</td>
<td>10^6</td>
<td>1.6</td>
<td>113</td>
</tr>
<tr>
<td>MS/PECVD</td>
<td>BG</td>
<td>Glass</td>
<td>SiO_2</td>
<td>Ti/Au</td>
<td>13.4</td>
<td>25</td>
<td>9x10^5</td>
<td>1.14</td>
<td>114</td>
</tr>
</tbody>
</table>

7. Notes: Type (BG: Bottom gate, TG: Top Gate), preparation method (ALD: Atomic Layer deposition, MS: Magnetron sputtering, RFS: rf-sputtering, PECVD: Plasma-enhancement chemical vapor deposition, PLD: Pulsed laser deposition)

Figure 22 shows typical operation characteristics for a-IGZO TFTs: large saturation mobility (\(\mu_{sat}\)) of 11.8 cm^2V^{-1}s^{-1}, small subthreshold swing (S) of approximately 0.1 V/decade and low operation voltage of <5V. Mobility exhibited by IGZO is sufficiently large for driving
organic light-emitting diode (OLED) displays and large-area liquid crystal displays (LCDs) and operate at low voltage (<5 V), owing to small subthreshold voltage swing approx. 0.1V/decade even of these, there are fabricated at room temperature (RT) on plastic substrates without defects passivation treatment. Among of these, there are transparent in the whole visible range, because its band gaps is larger than 3.0 eV.

Reported results on a-IGZO TFTs are compiled in Table 4. Various materials have been reported as gate dielectric, among them SiO$_2$, SiN$_x$, Al$_2$O$_3$, HfO$_2$, multilayers, and organic materials. In order to keep the gate leakage current at acceptable level (typically <1 nA), the thickness of the gate insulator is chosen sufficiently thick, typically at least 100 nm. Therefore the gate voltages are mostly in the range of 10 V or more; similarly, source and drain voltages are often in this range. Apart from issues of large power consumption, such large voltages are unpractical for operation in water (e.g. for biological applications) or the integration with silicon CMOS electronics. Until now, not much work has been done by PLD and, also, using HfO$_2$ as gate dielectric.

1.4. Thin film deposition techniques

A thin film is defined as a low dimensional material created by condensing, one by one atomic, molecular or ionic species of matter. Thin film technology make use of the fact that the properties can be controlled by the thickness, which, to be considered as a thin film, range from a fraction of nanometer to several nanometers.$^{115}$

<table>
<thead>
<tr>
<th>Table 5. Classification of thin film deposition methods.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical methods</strong></td>
</tr>
<tr>
<td>Sputtering</td>
</tr>
<tr>
<td>Magnetron sputtering</td>
</tr>
<tr>
<td>Radio frequency sputtering</td>
</tr>
<tr>
<td>Ion-beam sputtering</td>
</tr>
<tr>
<td>Ion-assisted deposition</td>
</tr>
<tr>
<td><strong>Chemical methods</strong></td>
</tr>
<tr>
<td><strong>Gas Phase</strong></td>
</tr>
<tr>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>Laser induced CVD</td>
</tr>
<tr>
<td>Plasma enhanced CVD</td>
</tr>
<tr>
<td>Metal-organic CVD</td>
</tr>
<tr>
<td>Low pressure CVD</td>
</tr>
<tr>
<td>Electroplating</td>
</tr>
</tbody>
</table>
The properties of the thin films are extremely sensitive to the method of preparation/deposition. Several techniques have been developed depending on the desired film properties. This techniques are classified in two types:116, 117 (a) Physical methods, and (b) Chemical methods. Physical methods covers the deposition techniques which depends on the evaporation or ejection of the material from a source, i.e. electron beam evaporation and sputtering. Chemical methods depend on physical properties. Table 5, summarizes the thin film deposition techniques.

Each technique has its advantages and disadvantages, and no one deposit technique covers all the desired aspects such as cost of equipment, deposition conditions and nature of the substrate material, among others. Hence, choice and selection of deposition process plays a vital role in the formation of good quality thin films. The aspects to be considered when selecting a deposition technique are listed below:

- Able to deposit the desired material.
- Film microstructure and deposition rate should be controlled.
- Process temperature.
- Film adhesion to the substrate.
- Abundance of deposit materials.
- Process scaling up.
- Substrate masking.
- Control of defects created in the film.

Liquid phase chemical methods are accepted as cheaper deposition techniques, but an intensive work must be done to grow the desired material. Evaporation methods are widely used for studying the deposition parameters. Physical methods are a good way for IGZO study since it has been widely reported by sputtering (Table 4), but not much work has been done by PLD.

Table 6 and Table 7 shows a comparison of the main IGZO deposition methods. PLD has the capability of stoichiometry transfer of complex materials from target to substrate, deposit in a controlled atmosphere, low temperature process and uniform film deposition with a stable amorphous microstructure, among others. All of these make the PLD technique a good choice for IGZO study despite its main disadvantage: cost effectiveness.
Table 6. Physical methods for IGZO deposition.

<table>
<thead>
<tr>
<th>TECHNIQUE</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPUTTERING</td>
<td>- Dense films</td>
<td>- Relatively slow</td>
</tr>
<tr>
<td></td>
<td>- Good uniformity</td>
<td>- Cost</td>
</tr>
<tr>
<td></td>
<td>- Wide range of inorganic materials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Low substrate temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Very good uniformity</td>
<td></td>
</tr>
<tr>
<td>PLD</td>
<td>- Stoichiometric transfer</td>
<td>- Highly cost</td>
</tr>
<tr>
<td></td>
<td>- Complex materials</td>
<td>- Difficult scale up</td>
</tr>
<tr>
<td></td>
<td>- Controlled deposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Atmospheric</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Low temperature process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Highly uniform film</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Chemical methods for IGZO deposition.

<table>
<thead>
<tr>
<th>TECHNIQUE</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD</td>
<td>- Good control of coating chemistry</td>
<td>- Difficult to scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Often uses hazardous liquid or gases</td>
</tr>
<tr>
<td>SOL-GEL</td>
<td>- Wide range thicknesses</td>
<td>- Low wear resistance</td>
</tr>
<tr>
<td></td>
<td>- Low temperature</td>
<td>- High permeability</td>
</tr>
<tr>
<td></td>
<td>- Economic</td>
<td>- Porosity difficult to control</td>
</tr>
<tr>
<td></td>
<td>- Wide range of inorganic materials</td>
<td></td>
</tr>
</tbody>
</table>

1.4.1. Pulse laser (PLD) for IGZO deposition

The technique of PLD has been used to deposit high quality films of materials. High-power laser pulses are used to melt, evaporate and ionize material in a shallow depth of the target (source material). This “ablation” event produces a transient, highly luminous plasma that expands rapidly away from the target surface and is collected on an appropriately placed substrate upon which it condenses and the thin film grows. The depth involved is either the optical absorption depth, $1/\alpha_r$ ($\alpha_r$ is the optical absorption coefficient), or the thermal diffusion length, $\Lambda$. For AOS, a transparent material, $1/\alpha_r$ would be a good approximation.\textsuperscript{118}

The PLD technique was first used by Smith and Turner in 1965\textsuperscript{119} for the preparation of semiconductors and dielectric thin films and was established due to the work of Dijkkamp et. al on high temperature superconductors in 1987.\textsuperscript{120} Since then, PLD has been intensively used for all kinds of oxides, nitrides, or carbides, and also for preparing metallic systems and even polymers or fullerenes. The technique of PLD was found to have significant benefits over other film deposition methods, including:

Rodolfo Antonio Rodríguez Dávila
a) The capability for stoichiometric transfer from target to substrate, i.e. the extra chemical composition of a complex material such as YBCO or IGZO, can be reproduced in the deposited film.

b) Relatively high deposition rates, typically ~100Å, can be achieved at moderate laser fluences, with film thickness controlled in real time by simply turning the laser on and off.

c) The fact that the laser is used as an external energy source results in an extremely clean process without filaments. Thus deposition can occur in both inert and reactive background gases.

d) The use of a carousel, housing a number of target materials, enables multilayer films to be deposited without the need to break vacuum when changing between materials.

In spite of these significant advantages, industrial uptake of PLD has been slow and to date most of the applications have been confined to the research environment. There are basically three main reasons for this:

a) The plasma created during the laser ablation process is highly forward directed, therefore the thickness of material collected on a substrate is highly non-uniform and the composition can vary across the film. The area of deposited material is also quite small, typically ~1cm², in comparison to that required for many industrial applications which require area coverage of ~7.5x7.5 cm².

b) The ablated material contains macroscopic globules of molten material. The arrival of these particulates at the substrate is obviously detrimental to the properties of the film being deposited.

c) The fundamental process, occurring within the laser-produced plasma, is not fully understood; thus deposition of novel materials usually involves a period of empirical optimization of the deposition parameters.
The first two problems have been solved. Films of uniform thickness and composition can be produced by *rastering* the laser spot across the target surface and/or moving the substrate during deposition. The particulate material was initially removed from the plasma using a mechanical velocity filter, although recently more elaborate techniques, involving collision between two plasmas or off-axis deposition, have been used to successfully grow particulate-free films. The third problem will be resolved with the development of computer simulations to describe PLD.

![Figure 23. (Left) Geometry and process of pulsed-laser vaporization. (Right) Rotations available in PLD system.](image)

Figure 23 (left) shows the geometry for pulsed laser evaporation. The beam enters the vacuum chamber through a quartz window and is directed at the target of source material at an oblique angle so that the substrate can be placed directly facing the target surface. This is done because most of the evaporant is directed in a narrow lobe oriented closely perpendicular to the target. As was mentioned before, the beam is scanned in a raster pattern so that the target erodes evenly, also the substrate has a rotation mechanism as shown in Figure 23 (right). A spinning hexagon with different source materials on each face is used for alternate-layer structures or multi-element compositions.

The possibility of additionally changing laser features, such as wavelength, repetition rate, pulse length, fluences and target-to-substrate distance, and the deposition conditions, such as substrate temperature and substrate orientation with respect to the deposited material, further demonstrates the enormous versatility of PLD.
1.5. Justification

The importance of the electronic industry relies in the fact that we have common daily contact with it; for example liquid crystal displays, portable audio/video players, cellphones, and computers, among others. Silicon has been the key material for electronic industry progress since 1950, but it is well known that its properties are not enough for the current demanding applications. Some of these applications are: displaying video imagery when required on windows, while simultaneously converting solar energy into electricity; or transmitting visual information like speed, navigation directions and alerts directly on an automobile windshield. That kind of applications open the door to the field of transparent electronics.

In the search of transparent materials, amorphous oxide semiconductors (AOS) have been attracting much attention. AOS have good uniformity and reasonably high mobilities, even when deposited at room temperature on plastic substrates.\cite{31} AOS are preferred over POS TFTs for applications that require large area deposition at low temperatures. This new class of materials, represent a revolutionary idea and exhibit a stimulating combination of high optical transparency, high electron mobility and amorphous structure.\cite{38,39}

A series of amorphous oxide semiconductors was found, following the Hosono’s hypothesis. However, since 2004\cite{31} the ternary oxide system of $\text{In}_2\text{O}_3 – \text{Ga}_2\text{O}_3 – \text{ZnO}$ (In:Ga:Zn=1:1:1) has shown promising electrical performance for active layer on TFTs. Mobility exhibited by IGZO is sufficiently large for handle organic light-emitting diode (OLED) displays and large-area liquid crystal displays (LCDs). TFTs made of IGZO operate at low voltage (<5 V). Also, they show a small subthreshold swing of approximately 0.1 V/dec even if these are fabricated at room temperature (RT) on plastic substrates. In addition, it is transparent in the whole visible range (band gap is larger than 3.0 eV).

Regarding to the amorphous structure of IGZO, it becomes difficult to understand its transport properties and optimize it for TFT applications. Also, most of the work made until now is related with the composition In:Ga:Zn=1:1:1, with enough electronic mobility for flat panel displays but not enough for high performance transparent devices, in example. However, the main issue of this composition is the difficulty of carrier control due to the high
content of indium and zinc. Hence, a post deposition treatment should be performed to improve the electrical characteristics of the devices.

This research proposal addresses the study of IGZO thin films with a composition of In:Ga:Zn=4:4:1 obtained by pulsed laser deposition. The increase of gallium and indium content (in relation with previous studies), is related to the control of the carrier concentration (gallium effect) and improve of the mobility (indium effect). A study of the effect of thickness and oxygen pressure during deposition on the film properties is proposed. An important issue of the present research is the investigation of the Hall effect as a function of the temperature. It has the objective of determining the transport properties of the films as a function of the deposition pressure. This issue has not been addressed previously, and is of great importance for the understanding of the electronic transport and, therefore, the control of the electrical properties of the semiconductor.

1.6. Objectives

1.6.1. General objective

Study the effect of the oxygen pressure and thickness on the overall properties of IGZO thin films, deposited by pulsed laser deposition (PLD).

1.6.2. Specific objectives

1. Deposit the IGZO thin films at room temperature using the PLD technique and different oxygen deposition pressures.

2. Evaluate the structural, morphological, chemical, electrical and optical properties of the deposited films.

3. Correlate the properties of the films with the preparation conditions.

4. Evaluate the behavior of the films obtained with different thicknesses as active layer in TFTs.
Chapter 2

Experimental methods

Through this chapter, materials and experimental methods are described (Figure 24). The main process is divided in: cleaning and substrate selection, film deposition, processing after film deposition, characterization and sample storage.

![Fabrication process, overview.](image)

### 2.1. Substrate

Substrate was selected in agreement to the characterization technique and purpose, as shown in Figure 25. Since mechanical silicon wafer is cheaper than the highly doped silicon wafer, were used for different purposes. For structural and morphological characterization is not necessary to handle high conductivity, allowing to use cheap substrates. However, for the fabrication of thin film transistors (TFTs) with common gate and electrical characterization of films, the conductivity of the substrate is important.
The structure and purpose of the substrate are described as follow:

1. Mechanical p-type doped silicon $<100>$ ($t = 500-550 \, \mu m$) with resistivity in the range of 1 to $100 \, \Omega \cdot cm$, was selected for structural and morphological characterization (Figure 26b).

2. Highly p-type doped silicon $<100>$ ($t = 500-550 \, \mu m$) with resistivity higher than $10^{-3} \, \Omega \cdot cm$ was selected for:

   - Thin film transistors with common gate. It is necessary a low resistivity substrate with a coating of 30nm of hafnium oxide ($\text{HfO}_2$), in order to form a metal-dielectric-semiconductor (MIS) capacitor (Figure 26a).

   - Circular transmission line method for acquire the semiconductor’s resistivity and the contact resistance. A coating of 500nm of silicon dioxide ($\text{SiO}_2$) for isolate the semiconductor from the substrate, and 30nm of hafnium oxide to reproduce the IGZO growth of a TFT (Figure 26c).

3. Corning glass substrates of 1 x 1 cm were used for transmittance characterization (Figure 26b) and Hall effect (Figure 26d) due to easy fabrication and operation of the samples.

![Figure 25. Substrate assigned for each characterization technique.](image)

The substrate cleaning is of key importance, since it affects the adhesion of the film and it has the function of removing all contaminants from the substrates surface. The substrate cleaning starts with an ultrasonic bath and a succession of solvents; acetone, isopropyl
alcohol (IPA) and deionized water (DIW), for 5 min each. Samples were dried with nitrogen gas and heated for 2 min at 115°C in order to remove the remaining water.

2.2. Dielectric deposition

Hafnium oxide (HfO2), deposited by atomic layer deposition (ALD), was used as dielectric. Table 8 shows the precursor parameters. The carrier nitrogen gas flow rate was set to 20 sccm, and the substrate temperature to 100°C. The process chamber pressure was in the range of 200 mTorr to 500 mTorr. A total of 217 cycles were used in order to grow 30 nm thick films.

Table 8. Precursor parameters used to deposit Hafnium oxide.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Process Temp (°C)</th>
<th>Pulse time (s)</th>
<th>Pump time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrakis(dimethylamido)hafnium (TDMA-Hf)</td>
<td>75</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Water (H2O)</td>
<td>RT</td>
<td>0.03</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 26. Schematic representation of the substrate used.
2.3. PLD deposition

2.3.1. Target

The InGaZnO (IGZO) target, purchased at Testbourne Ltd, has a composition of \( \text{In}_2\text{O}_3: \text{Ga}_2\text{O}_3: \text{ZnO} = 2:2:1 \) at.% and purity of 99.99%. Target dimensions were 25.4 mm in diameter and 6.35 mm in thickness.

2.3.2. Experimental set-up

Four pressures and three thickness, within the range of 10 to 80 mTorr and 25 to 100 nm, respectively, were selected giving a total of 12 samples. All deposits were performed at room temperature (RT). The study was divided into: (a) film properties and (b) application. For the film properties study, the thickness of the film were fixed at 100 nm and the effect of the deposition pressure were study (Figure 27). For the application study, all pressures and all thickness were study as active layer in common gate thin film transistors (Figure 28).

Figure 27. Film properties study overview.

Figure 28. Application study overview.

Figure 29 shows the PLD system overview and the physical equipment used for the IGZO deposition. A KrF excimer laser with a wavelength of 248 nm, a frequency range from 1 to 25 Hz and high voltage between 18 to 23 kV were used. The laser is redirected through mirror 1 (Figure 29-1) to mirror 2, which controls the laser spot size. Later, laser is focused into the chamber, with a controlled atmosphere (as mentioned before), through a quartz
window with 1” of thickness (Figure 29-2). Inside the chamber, the laser impacts with the target, evaporating material in form of molecules and macromolecules in direction to the substrate. The target-substrate distance was set to 50mm. The laser raster the target from the edge to the center, while rotating in the same fashion than the substrate (Figure 30). Raster and rotations have controlled velocity. The parameters used are in Table 9.

Figure 29. (Left) Schematic overview of PLD system. (Right) Equipment used for PLD deposition.

Figure 30. Rotations available in PLD system

Figure 31. Holder distribution.

Figure 31 shows the substrate distribution in the sample holder, which has a diameter of 2”. In order to make the experiment reproducible, the energy density must be reported; which is defined as the amount of energy stored per unit area. Table 10 shows the energy density measured in function of the IGZO thickness. A laser energy sensor and a special paper were used for measuring the laser energy and spot size, respectively. Laser energy is
controlled through the high voltage, but a common problem is that the sacrificial window gets dirty, decreasing the energy inside the chamber. HCl at 5% in DIW was used to clean oxides (i.e. IGZO) from the sacrificial window.

Table 9. Parameters used for IGZO deposition by PLD.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Background Pressure (Torr)</td>
<td>&lt;1x10^-6</td>
</tr>
<tr>
<td>2 Subs (°C)/Ramp Temp.(°C/min)</td>
<td>RT/NA</td>
</tr>
<tr>
<td>3 Subs/Tgt/Raster Vel. (deg/s)</td>
<td>60/60/60</td>
</tr>
<tr>
<td>4 Raster Type</td>
<td>Target 3 (-7,+7)</td>
</tr>
<tr>
<td>5 Pre-abilation</td>
<td>2000 at 10Hz</td>
</tr>
<tr>
<td>6 Laser Voltage</td>
<td>22kV</td>
</tr>
</tbody>
</table>

Table 10. Energy density measured in function of the IGZO thickness.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>25 nm</th>
<th>50 nm</th>
<th>100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (J/cm²)</td>
<td>1.14±0.16</td>
<td>0.97±0.05</td>
<td>0.98±0.04</td>
</tr>
</tbody>
</table>

The routine used for IGZO deposition is described as follows:

1. Evacuate the chamber to less than 1x10^-6 Torr.

2. Feed the chamber with oxygen (99.99%) in order to adjust the pressure inside the chamber with the selected value (Figure 27).

3. Clean the target’s surface (pre-ablation) with 2,000 shots. Note: Shutter must be closed.

4. Shoot pulses in agreement to the thickness expected. Previous to the experimental procedure, shown in this section, the relationship between the number of shots and the film thickness was studied. For 25, 50 and 100 nm the number of shots used were 2700, 5600 and 13000 respectively.

5. Vent with nitrogen and take off the sample.
2.4. Process after deposition

2.4.1. TFTs fabricated by shadow mask process

Thin film transistors with common gate were fabricated by shadow mask process (Figure 34). A shadow mask, made of metal film, was used to grow rectangular shapes on the semiconductor’s surface which serve as source (S) and drain (D) electrodes. The length (L) and width (W) used for the application study were 40 and 1000 μm, respectively. Figure 33 shows the true dimensions of the source and drain contacts. The dimensions were measured by an optical microscope.

Fabrication process start with substrate and shadow mask cleaning, which was described in section 2.1. Substrate is composed of highly p-type doped silicon, 30 nm of HfO₂, and the IGZO. Following, the shadow mask is placed on the substrate surface (IGZO) and attached to it using kapton. Note: the edges of the substrate must be covered with kapton to avoid short circuit between the top contacts and the bottom contact. Aluminum, with a purity of 99.999%, was evaporated by e-beam in order to grow 100 nm through the shadow mask, as shown in Figure 34. Deposition rate was set to 0.2 Å/s for the first 200 Å, but for the following 800 Å was changed to 0.8 Å/s. Before deposition, the chamber was evacuated to <2x10⁻⁶ Torr. After deposition, the center part of the bottom side of the substrate was cleaned with HF and a cotton swab, in order to remove native oxides and expose the highly doped silicon. Then, 100 nm of aluminum were deposited as gate contact with the same deposition conditions described before.
In order to determine the resistivity of the semiconductor and the contact resistance, circular transmission line method was performed. The method consists on a conduct circular region of radius “L”, a gaps of width “d”, and a conducting outer region (Figure 35). Ten
different gaps were used, taken from 5 to 50, and 2 different values of radius: 150 and 300 μm (Figure 26c).

Figure 35. Schematic representation of the circular transmission line method.

Figure 36. Schematic representation of lift-off process.

The process used for metal pattern was lift-off, and is described as follows (Figure 36):

1. Rinse the IGZO wafer with acetone (5 min), followed by IPA (5 min) and DIW (30 s). Blow with nitrogen gas and dry in the hot plate at 115°C for 1 min.

2. Place wafer in the spinner plate, and cover the entire surface with photoresist S1813. Then, a thin film of the photoresist is created by operating the spinner at 2000 rpm at 3000 acc (RPM/s) for 60 s. Bake at 115 °C for 1.5 min.
3. Expose the wafer to UV light using a dose of 130 and the CTLM mask (Figure 26c). An inverse pattern is created on substrate surface. Note: The exposure time is the ratio of dose and lamp power.

4. Develop in MF-319 for 55 s immediately rinse with DIW and dry with nitrogen. Bake at 115°C for 1 min.

5. Deposit aluminum in the same fashion described in section 2.4.1.

6. Wash out photoresist (sacrificial layer) together with aluminum (target material), through an ultrasonic bath in acetone for 2.5 min, followed by IPA (2 min) and DIW (30 s). Dry with nitrogen and bake at 115 °C for 1.5 min.

2.5. Characterization techniques

Film characterization was divided into three categories: the first one comprising structural, morphological and chemical characterization; the second one optical characterization: and the third one electrical characterization. Each category is described as follow:

1. **Structural, morphological and chemical characterization:**

   a. The structure of the IGZO films was investigated using grazing incidence X-ray diffraction (XRD) by a Rigaku Ultima III X-ray diffractometer. A monochromatic copper anode (Cu Kα1 1.54056 Å), operated with an acceleration voltage of 40 kV and an emission current of 44 mA, was used as radiation source. The grazing angle and the step size were fixed at 0.5 degree and 0.05 deg/s, respectively.

   b. The composition and chemical bonding state of the IGZO films were investigated using X-ray photoelectron spectroscopy (XPS) with a PHI 5800 XPS system. The tool used is equipped with an Al Kα (hν = 1486.6 eV) monochromatic X-ray source (15 kV and 23 mA) and a hemispherical
electron analyzer. The XPS measurements were taken on the surface and after cleaning with Ar ion sputtering for 2 min.

c. The surface morphologies and surface roughness level of the films were determined by tapping mode scanning probe microscopy (SPM, VEECO Dimension 5000 SPM) with a scan area of 3 μm x 3 μm.

d. Plane view and cross sectional view micrographs of the IGZO thin films were acquired by a Zeiss Supra-40 scanning electron microscope (SEM) operated at 15 kV and low vacuum. Also, a qualitative and semi-quantitative compositional analysis of the samples was carried out by EDX.

e. Spectroscopic ellipsometry (SE) was used for studying the thickness and refractive indices of the thin films. The spectrum response range was 400 to 850 nm with an incident angle of 70 degrees.

2. Optical characterization:

a. The optical transmission measurement of the IGZO thin films was conducted by UV-VIS spectroscopy (Ocean optics QE65 Pro). The analysis was carried out for wavelengths ranging from 300 to 900 nm by ultraviolet/visible/near infrared spectroscopy.

3. Electrical characterization:

a. The electrical characteristics of the IGZO films were investigated by way of an 8400 series AC/DC Hall effect measurement system with a magnetic field of 1.7 T; by a four-point probe van der Pauw method in the temperature range from room temperature (RT) to 8K in dark. Evaporated aluminum electrodes were used for the ohmic contacts.

b. An Alessi 4-point probe with 1 mm of spacing between the tungsten carbide probes tips was used to characterize the resistivity of the films. The measurement is provided by a Keithley 2400 4-wire digital meter.
c. Circular transmission line method (CTLM) and thin film transistors (TFTs) were measured with a Keithley 4200 semiconductor parameter analyzer taking precautionary measures to avoid ambient light.

2.6. Sample storage

After characterization, samples were stored inside a glove box with a controlled nitrogen atmosphere.

2.7. A few words before results

The presented study was divided into two categories: (a) film properties and (b) application. In the film properties section (chapter 3) the effect of the oxygen pressure during film deposition on the IGZO properties was study using a fixed thickness of 100nm; but, in the application section (chapter 4), the effect of the film thickness was added, and also, the oxygen pressure were studied on the overall properties of thin film transistors.
Chapter 3

Film properties: Results and discussion

Through this chapter the physical, chemical, optical and electrical properties of the IGZO films are discussed. It starts with the morphological and structural properties, followed by chemical, optical and electrical properties. As a reminder, only those films deposited at different pressures and fixed thickness (100nm) will be discussed throughout this chapter.

3.1. Structural and morphological properties

The thickness were plotted versus oxygen pressure in Figure 37a. Also, the average thickness and relative error (as a function of the thickness expected) were calculated and results are shown in Table 11. Results confirm that the expected thickness adjust with the measured thickness by using the number of shots selected.

The deposition rate was calculated from the slope of thickness against number of shots and by using Eq. 7. The calculated deposition rates were 0.91, 0.96, 0.91 and 0.90 Å/s for 10,
20, 30 and 80 mTorr, respectively. A tendency was not found, but the deposition rate is around 0.9 Å/s.

\[ R_k = \frac{t}{s_{\text{hot}}} * \frac{1}{f} = \frac{m}{f} \]

Eq. 7

Figure 37b shows the refractive index (\( n \)) over oxygen pressure. The increase in oxygen pressure decreases \( n \), promoting the propagation of light through the film, giving the point of view that the transmittance increase with the increase in the oxygen pressure. This will be discussed in section 3.3.

Figure 37. (a) Thickness versus deposition pressure, (b) Refractive index at \( \lambda = 632.8 \text{nm} \) versus deposition pressure.

<table>
<thead>
<tr>
<th>Shots</th>
<th>Expected Thickness (nm)</th>
<th>Measured thickness (nm)</th>
<th>Relative error (%)</th>
<th>Deposition time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13300</td>
<td>100</td>
<td>92.3±5.16</td>
<td>-7.7</td>
<td>1330</td>
</tr>
</tbody>
</table>

Table 11. Summary of the thickness study.

In order to study the film structure, X-ray diffraction technique were used. Figure 38 shows the XRD data plotted over 2 theta versus the intensity in counts per second (cps). Two wide peaks, originate from the film, were observed at around 32.6 and 56.2 degrees. No sharp peak feature were found for all pressures, indicating an amorphous structure. The change in
the intensity of the peak around 32 degrees, for all pressures, is related with the change in the thickness of the films, as showed in section 3.1.

![XRD spectra for IGZO deposited at different oxygen pressures.](image)

*Figure 38. XRD spectra for IGZO deposited at different oxygen pressures.*

![AFM images, surface morphology and cross section for different oxygen pressures.](image)

*Figure 39. AFM images, surface morphology and cross section for different oxygen pressures.*
The surface morphology of IGZO thin films, grown at various oxygen pressures, were studied by using AFM in a scanning area of 3x3 \( \mu \text{m}^2 \). Figure 39 depicts the AFM images for all deposition pressures. The roughness change from 0.18 nm to 1.76 nm as deposition pressure increase from 10 to 80 mTorr. The change in the film roughness is explained as follows: With increasing oxygen pressure, the collision between ablated species and oxygen molecules increase (Mean free path decrease), therefore the kinetic energy of the ablated species would decrease. This in turn reduces the migration ability of the adsorbed atoms (adatoms) on the surface of the substrate, leading to the aggregation of the adatoms or clusters on the surface with increasing deposition pressure.\(^{121, 122}\)

The analysis of the surface root mean square (RMS) roughness, from AFM images, confirms the general tendency of the evolution of the RMS that increases with increasing deposition pressure, as shown in Figure 40, although the RMS changes rapidly at lower deposition pressure and seems to be saturated at higher deposition pressures, in the same fashion that oxygen flow does.

![Figure 40. Roughness and oxygen flow over deposition pressure.](image)

The cross sectional view and the surface morphology of a-IGZO films at different deposition pressures are shown in Figure 39. As shown, there is no aggregates or crystallites throughout the film. Featureless contrast (typical of an amorphous film) is seen over the whole morphology, further indicating that the films shows amorphous structure, which have been verified by XRD pattern.\(^{123}\) As shown from the surface morphology (Figure 39), the film display very smooth surface for all deposition pressures, and is accord with AFM results.
3.2. Chemical composition

Energy dispersive x-ray spectroscopy (EDX) were used for elemental analysis and elemental mapping. Elemental mapping, depict in Figure 41, shows that the distribution of all elements is quite uniform for all samples. Composition expected form target and for films is 11.1 at% of Zn, 44.4 at% of In, and 44.4 at% of Ga as mentioned in section 2.3.1. From elemental analysis (Table 12), results show that samples composition is 11.3±1.5 at% of Zn, 45.6±3.3 at% of Ga and 43.8±4.7 at% of In. Also, the target composition is 13.1±3.9 at% of Zn, 41.9±1.5 at% of Ga, and 45.0±4.6 at% of In. Films composition is highly consistent with expected and measured target composition.

Figure 41. Elemental mapping for a-IGZO films deposited at different oxygen pressures.
The discrepancy between the results showed en Table 12 and Figure 41, with respect to Ga, is related with the following: Figure 41 shows the atomic dispersion on the sample, and is related with the weight percent (wt%); while, Table 12 shows the atomic percent (at%).

**Table 12. Zn, Ga and In atomic content (%) for target and films deposited at different pressures.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn</th>
<th>Ga</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>13.10 ±3.87</td>
<td>41.94 ±1.47</td>
<td>44.96 ±4.60</td>
</tr>
<tr>
<td>10 mTorr</td>
<td>7.70 ±0.87</td>
<td>42.29 ±1.54</td>
<td>50.02 ±2.32</td>
</tr>
<tr>
<td>20 mTorr</td>
<td>10.55 ±2.05</td>
<td>41.14 ±1.57</td>
<td>48.30 ±3.54</td>
</tr>
<tr>
<td>30 mTorr</td>
<td>11.30 ±1.49</td>
<td>46.67 ±6.55</td>
<td>42.03 ±7.79</td>
</tr>
<tr>
<td>80 mTorr</td>
<td>11.67 ±1.50</td>
<td>52.39 ±3.41</td>
<td>34.68 ±5.05</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopy (XPS) was performed in order to find out the composition and bonding state of elements on the IGZO samples. The core level XPS spectra, for In 3d$_{5/2}$, Ga 2p$_{3/2}$, Zn 2p$_{3/2}$, and O 1s, are displayed in Figures 42 to 44 for the surface of the films and after 2 min of argon ion sputtering (bulk). The binding energies (BE) were taken as the peak center energy obtained by fitting using pseudo-Voigt (mixed Gaussian-Lorentzian) functions and at least squares method. All binding energies were calibrated by using Carbon 1s peak at 284.5 eV as reference, and by aligning the Zn 2p$_{3/2}$ core level because is deep as ~1022 eV and would not be affected by chemical bonding effects.$^{124}$

The In 3d$_{5/2}$, Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$ spectra shows symmetric shape, suggesting a single state (Figures 42 and 43). The BE obtained for those peaks were shifted to higher BE compared to the metallic state, as shown in figures.$^{125-129}$ Furthermore, the BE match with In$^{3+}$, Ga$^{3+}$ and Zn$^{2+}$ in their oxidized state. The shift of In 3d$_{5/2}$ to lower BE might be attributed to the decrease in the In-(In, Ga, Zn) distance due to the high indium content (section 1.3.1), thus, the cations would pack more densely and the open spaces in the film would be eliminated. Also, the shift might be attributed to the In$^{3+}$ in an oxygen deficient region, due to In$_2$O$_3$ has the lowest formation energy, compared with Ga$_2$O$_3$ and ZnO.

Figure 44 shows the O1s core levels on the bulk and surface for samples. The asymmetry of the O1s region indicates the presence of multiple components. At the surface of the film, the O1s region could be divided into three Gaussian peaks: p0, p1 and p2, while into two peaks, p0 and p1, for the bulk.
The component on the low BE, p0, can be attributed to O$^{2-}$ ions surrounded by Zn, Ga and In atoms on the IGZO compound system.\textsuperscript{130-132} In other words, the intensity of this component is a measure of the amount of oxygen atoms in a fully oxidized environment.

**Figure 42.** Core level XPS spectra for (a) In 3d$^{5/2}$, (b) Zn 2p$^{3/2}$ and (c) Ga 2p$^{3/2}$ on the surface.

**Figure 43.** Core level XPS spectra for (a) In 3d$^{5/2}$, (b) Zn 2p$^{3/2}$ and (c) Ga 2p$^{3/2}$ on the bulk.

**Figure 44.** Core level XPS spectra for O1s on the surface and bulk for different pressures.

Rodolfo Antonio Rodríguez Dávila

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The mid energy component, p1, is typically associated with the presence of oxygen-deficient regions in the IGZO structure. Therefore, the change in the intensity of this component may be connected with the change in the concentration of oxygen vacancies. The high binding energy component, p2, is usually attributed to the presence of loosely bound oxygen on the surface of the film, belonging to a specific specie, e.g., –CO₃, adsorbed H₂O or adsorbed O₂. It should be that the signal intensities of the p2 disappear with after sputtering, suggesting that it belong to the surface of the films.

The chemical composition can be quantitatively calculated from the relative integrated area of In, Ga, Zn and O peaks, and using the following Equation:

\[
C_x = \frac{l_x/S_x}{\sum l_i/ S_i}
\]

\text{Eq. 8}

Where S is defined as the atomic sensitive factor and I as the integrated area of the peak. Table 13 shows the atomic percent of elements present in the IGZO structure. The atomic composition is comparable with that obtained by EDX (section 3.2). Due to knock off effect, the intensities of In and Zn peak slightly decrease while Ga slightly increases after sputtering.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Surface of the films</th>
<th>After 2min of Ar-ion sputtering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Ga</td>
</tr>
<tr>
<td>10</td>
<td>11.2</td>
<td>10.4</td>
</tr>
<tr>
<td>20</td>
<td>11.3</td>
<td>9.8</td>
</tr>
<tr>
<td>30</td>
<td>11.6</td>
<td>7.7</td>
</tr>
<tr>
<td>80</td>
<td>10.0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The oxygen-vacancy formation process is closely related with the generation of charge carriers, according to the following equation:

\[
O_2^x = \frac{1}{2} O_2(g) + V_0^- + 2e^- \]

\text{Eq. 9}
Here, $O_2$ is lost from the oxide sublattice ($O_2^+$) to create a doubly charged oxygen vacancy ($O_2^-$) and two free electrons. The ratio of the peak $p_0$ and $p_1$ indicates the relative quantity of the oxygen-related defects. The ratio was calculated as follows:

$$r_N = 100 \frac{N}{O_{bonding}^2 + O_{defect}^2} \% = 100 \frac{N}{Area(p_0) + Area(p_1)} \%$$  \hspace{1cm} \text{Eq. 10}$$

As shown in Figure 45, the ratio of oxygen vacancies decrease as deposition pressure increase in the same fashion than oxygen flow does. The lower ratio of oxygen vacancies and surface absorbed oxygen is related to charge trapping and increases the electrical stability of TFT devices.

![Graph showing oxygen ratio versus oxygen pressure for film surface and bulk.](image)

**Figure 45.** Oxygen ratio versus oxygen pressure for film surface and bulk.

### 3.3. Optical properties

Figure 46 shows the optical transmittance spectra in the 300 to 950 nm range for all samples. The transmittance of each sample was normalized with respect to that of the glass substrate. If we define the averaged transmittance in a region from 380 to 780 nm (visible range) as transparency, the inset in Figure 46 shows the evolution of optical transparency as a function of oxygen deposition pressure.

It was found that with increasing oxygen pressure, the transparency increases until ~95%, for 80 mTorr, and seem to be saturated with further increasing oxygen pressure. Also,
the absorption edge shifts to low wavelength. This might be attributed to the change in concentration of oxygen deficiencies which is highly related with the carrier concentration. This behavior has been interpreted as the band filling effect, which lead to a widening of the optically observed band gap.

![Transmittance spectra for IGZO deposited at different pressures. Inset: Average transmittance in the visible range versus oxygen pressure.](image)

Figure 46. Transmittance spectra for IGZO deposited at different pressures. Inset: Average transmittance in the visible range versus oxygen pressure.

The optical band-gap were determined by using the Tauc model in the strong absorption region:

\[ (\alpha \cdot h\nu) = B(h\nu - E_g)^n \]

Eq. 11

Where \( h\nu \) is the photon energy, \( E_g \) is the optical band-gap (or Tauc gap) and the constant “n” is usually equal to 2 for amorphous semiconductors (indirect transition). The absorption coefficient (\( \alpha \)) can be obtained from the transmittance data by using the next relation:

\[ \alpha_{h\nu} = \frac{1}{d} \ln \frac{1}{T_{h\nu}} \]

Eq. 12

Where “d” and “\( T_{h\nu} \)” are the thickness and the transmittance of the film at certain photon energy, respectively. Consequently, \( E_g \) can be obtained by extrapolating from the linear region onto the photon energy axis in the Tauc plot.
Figure 47 shows the relationship between \((\alpha \cdot h\nu)^{1/2}\) and \(h\nu\). The calculated optical band gap for 10, 20, 30 and 80 mTorr were 3.08, 3.23, 3.33 and 3.41 eV, respectively. The increase in the band gap could be explained as follows: At low deposition pressure, a number of oxygen vacancies might occupy the bottom of the conduction band, leading to a decreased band gap. With increasing oxygen pressure, the reduction of oxygen vacancies suppress the defective states near to the conduction band, which increase the optical band-gap.\(^{143}\)

![Image](image.png)

**Figure 47.** (Right) Relationship between \((\alpha \cdot h\nu)^{1/2}\) and \(h\nu\) for a-IGZO at various deposition pressures. (Left) Variation of the band gap and Urbach energy with the deposition pressure.

Figure 48 shows the optical absorption spectra obtained by using Eq. 11. The strong absorption in the >3eV region is in good agreement with the Tauc relation (Eq. 11 and taken \(n=2\)). Small absorption tails were found, following the Urbach relation:

\[
\alpha = A \cdot \exp\left(\frac{h\nu}{E_u}\right)
\]

**Eq. 13**

Where “A” is a constant and \(E_u\) is the Urbach energy. The Urbach tail \((E_u)\) is a convolution of the conduction band tail and the valence band tail (width of the tail state) in the sub-gap region. It is defined as a measure of the structural disorder (Figure 49).

For 10 mTorr, \(E_u\) has a value of 0.59 eV, higher than other pressures. This is related, mainly, with the high oxygen vacancies content (due to the low roughness). \(E_u\) increases from 0.35 to 0.45 eV, as pressures increases from 20 to 80 mTorr (Figure 47). As was mentioned before, \(E_u\) is also related with structural and morphological defects. Hence, this behavior could
be related with the change in roughness (due to the decrease in the oxygen vacancies content), as shown in section 3.1.

Figure 48. Absorption coefficient versus photon energy

Figure 49. Band tails at the sub-gap region (Localized states)
3.4. Electrical properties

The electrical conductivity is the ability of a material to transport electrical charges. It is strongly dependent on the number of free charges available for conduction (carrier concentration) and how quickly that charges can move through the material (mobility), according to the relationship:

\[
\sigma = \frac{1}{\rho} = n|e| \mu_e + p|e| \mu_p
\]

Eq. 14

The resistivity \((\rho)\) is the reciprocal of conductivity; “n” and “p” are the number of free electrons and holes per unit volume, respectively; \(|e|\) is the absolute magnitude of the electrical charge; and finally \(\mu_e\) and \(\mu_p\) are the mobility of electrons and holes in a given material, respectively. Resistivity is an intrinsic property and is important for devices because it contributes to the device series resistance, capacitance, and threshold voltage, among others parameters. In order to measure the resistivity of the films, 4-point probe technique, circular transmission line method and Van Der Pauw (VDP) technique were used.

The 4-point probe technique consist in an arrangement of 4 aligned contacts. A current is applied through the two outer probes and the voltage drop is measured on the two inner probes. This arrangement allows to measure the materials resistance, with enough accuracy since it excludes the contact resistance. Table 14 shows the resistivity results obtained by this method. Only IGZO deposited at 10mTorr could be measured by this technique and tool. From results, it is suppose that the films deposited at 20, 30 and 80 mTorr possess high sheet resistance, which may be due to a low carrier concentration, low mobility of both.

Table 14. Measured resistivity for IGZO samples deposited at various deposition pressures.

<table>
<thead>
<tr>
<th>Pressure (mTorr)</th>
<th>100nm</th>
<th>4-point</th>
<th>VDP</th>
<th>CTLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6x10^{-3}</td>
<td>2x10^{-2}</td>
<td>1.8x10^{-2}</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.9x10^{0}</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6x10^{7}</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
VDP is a technique commonly used to measure resistivity of uniform samples.\textsuperscript{144} An arbitrary shape is used, containing four very small ohmic contacts placed on the periphery, preferably in the corners. Current is applied through two contacts and voltage is measure by the remaining two. As well as 4-points probes, only IGZO deposited at 10mTorr could be measured by this technique and tool. Although the method removes the effect of contact resistance, it is suppose that aluminum is not a good ohmic contact for a-IGZO, due to the high content of oxygen vacancies at the film surface (section 3.2). Table 14 shows the results obtained by this technique.

CTLM was performed for all samples in order to provide some understanding of the specific contact resistance between aluminum (metal contact) and a-IGZO (semiconductor) and enhance results obtained about resistivity of the films. Figure 50 shows the relation of resistance versus gap. All regression values are bigger than 0.99. The film deposited at 80 mTorr cannot be measured by this technique since current was out of measurement range.

With change in oxygen pressure, the concentration of oxygen defects also change (section 3.2), which is closed related with resistivity of the film, as showed in Eq. 14. The resistivity of the films increase from $1.9 \times 10^{-2} \ \Omega \cdot \text{cm}$ to $1.6 \times 10^{7} \ \Omega \cdot \text{cm}$, with the increase in the oxygen deposition pressure from 10 to 30 mTorr. The specific contact resistance for IGZO increase from $1.1 \times 10^{-2} \ \Omega \cdot \text{cm}$ to $23 \times 10^{2} \ \Omega \cdot \text{cm}$ with increasing oxygen pressure from 10 to 20 mTorr. For IGZO deposited at 30 mTorr, contact resistance was less than zero, hence specific contact resistance cannot be extracted.

The specific contact resistance and transfer length are less than $10^{-6} \ \Omega \cdot \text{cm}^{2}$ and 1 \ \mu m, respectively, for a good ohmic contact.\textsuperscript{91} Transfer length can be though as the distance over which most of the current is transfer from the metal into the semiconductor. $L_T$ is high than 1
μm and the specific contact resistance is much higher than $10^{-6} \ \Omega \cdot \text{cm}^2$, for all samples. Therefore, aluminum is not a good ohmic contact for a-IGZO, but for use as source and drain in TFTs, where the active layer has high resistivity, the specific contact resistance obtained should not be a major problem, as will be shown in chapter 4.

From resistivity values, it is possible to found some applications for the films obtained. Resistivity low than $10^{-5} \ \Omega \cdot \text{cm}$ is necessary for materials used as conductors. The film deposited at 10 mTorr has a resistivity less than $10^{-2} \ \Omega \cdot \text{cm}$, which is not in the range of conductors, but it is useful in order to make a good ohmic contact with IGZO in TFT applications. Film deposited at 20 mTorr has a mid-range resistivity, useful for LEDs, TFT, diodes, etc. Application as active layer in TFTs requires a semiconductor with high resistivity ($\rho > 10^5 \ \Omega \cdot \text{cm}$), which was obtained for those films deposited at 30 and 80 mTorr.

3.4.1. Hall Effect

The carrier concentration and mobility were obtained at room temperature by measuring the hall voltage using the Van der Pauw method, with a magnetic field of $1.7 \ T$. Figure 51 illustrates the dependence of the electrical properties including resistivity, carrier concentration, and mobility on deposition pressure. The hall coefficient was measurable only for the a-IGZO films deposited at 10 mTorr because of the measurement limit related to a large resistance or due to the high contact resistance. In that case, a new series of pressures (5, 15 and 17.5 mTorr), were introduced in order to provide some understanding on the change in electronic transport with deposition pressure.

All of the a-IGZO film were found to be n-type. The data shows that the Hall mobility decreases as well as carrier concentration, while resistivity increases. A maximum of $n_e (4.3 \times 10^{19} \ \text{cm}^{-3})$ and $\mu_{\text{Hall}} (10.6 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1})$, and a minimum $\rho$ were found for IGZO deposited at 10 mTorr. This results suggest that the electrical properties are very sensitive to oxygen deposition pressure in the PLD process. As mentioned in section 3.2, with increasing oxygen deposition pressure, the number of oxygen vacancies in the film decreases, therefore the number of free carriers in the film reduces, leading to decreasing carrier concentration and increasing resistivity.$^{145,146}$ The oxygen vacancies in a-IGZO films can act as shallow donors, effectively supplying conduction electrons; in the meantime, they can also act as scattering centers, effectively reducing charge carrier conduction to a certain extent.$^{45,147}$
“Study of amorphous InGaZnO thin film deposited by pulsed laser deposition for flexible electronic applications”

Figure 51. Dependence of Hall mobility (\(\mu\)), carrier concentration (\(N_e\)) and resistivity on deposition pressure.

Figure 52 shows the temperature dependence Hall mobility (\(\mu\)) and carrier concentration (\(N_e\)) of the a-IGZO films at various deposition pressures. It should be stressed that although \(N_e\) does not show temperature dependence, \(\mu\) shows thermally activated behavior at \(N_e < 2.7 \times 10^{19} \text{ cm}^{-3}\) or pressures higher than 15 mTorr. Carrier concentration did not show a temperature dependence, which implies that the Fermi level exceeds the mobility edge for \(N_e > 2.7 \times 10^{19} \text{ cm}^{-3}\). In that case, the semiconductor exhibit properties that are more metal-like than semiconductor-like; then the film shows a degenerate behavior. For pressures higher than 15 mTorr, the film shows a semiconductor behavior.

Figure 52. Temperature dependence of \(\mu_{\text{Hall}}\) and \(N_e\) for a-IGZO deposited at different oxygen pressures.
Figure 54 shows schematically the semi-logarithmic plot of the conductivity against the reciprocal temperature, where through the extrinsic range, $\sigma$ exhibit a broad “S” due to the temperature dependence of the drift mobility. The larger carrier concentration in a degenerate semiconductor is due to its heavy doping. For example, as the donor concentration in an n-type semiconductor is increased, at sufficiently high doping levels, the donor atoms become so close to each other that their orbitals overlap to form a narrow energy band that overlaps and become part of the conduction band. $E_c$ is slightly shifted down and $E_g$ becomes slightly narrower. In a degenerate n-type semiconductor, the fermi level is therefore within the CB, or above $E_c$ just like $E_F$ is within the band in a metal.

The $N_e$ value where carrier transport change to degenerate conduction is known as threshold value, $N_{th}$. Mobility exhibit thermally-excited behavior for $N_e < N_{th}$ while $N_e$ did not, which suggest existence of potential barriers above the mobility edge. It was confirmed, from section 3.3, that non-localized tail-states are formed in the vicinity of the conduction band bottom with potential barriers due to the structural randomness. Therefore carrier conduction is limited by the potential barriers when the fermi level is located in the tail-states, while carrier transport is not affected by potential barriers anymore and large mobilities are obtained if the fermi level exceeds the potential barriers ($N_e > 2.7x10^{19} \text{cm}^{-3}$).

Figure 53. Schematic illustration of Hall effect measurement, using Van der Pauw configuration.

Figure 54. Schematic illustration of the temperature dependence of electrical properties for a doped semiconductor.
Figure 55a shows the temperature dependence of electrical conductivity for the a-IGZO films deposited at 10, 15 and 17.5 mTorr. The figure shows that $\sigma$ does not follow a simple thermally activated behavior since the Arrhenius plots (Eq. 16) exhibit large deviation from a straight line, especially at $T \leq 160$ K for samples that have $N_e < N_{th}$ and do not exhibit degenerate conduction.

Better straight lines are obtained in the log $\sigma$ vs $T^{-1/4}$ plot in the whole temperature region (Figure 55b). It is shown that $\sigma$ obeys the Eq. 15, for $N_e < N_{th}$, which behavior is often interpreted as variable-range hopping (VRH) caused by localized states in disordered or highly doped semiconductors including doped or solid-solution oxides. However, It should be stress that the definite hall voltage were observed for all the films, which implies that the VRH mechanism does not likely dominate the carrier transport in spite of the fact that the temperature dependence of $\sigma$ fits well with that of the VRH model.

$$\sigma = \sigma_0 \exp \left[ \frac{-E_a}{k_BT} \right]$$

Eq. 15

$$\sigma = \sigma_0 \exp \left[ \frac{-A}{T^{1/4}} \right]$$

Eq. 16

A consistent model to explain all the above-described observation is that the conduction mechanism is controlled by percolation conduction. As it is known that a percolation conduction model also yield the $T^{-1/4}$ behavior if the potential barrier height has
Gaussian-type distributions.\textsuperscript{149} This situation is similar to the Anderson localization, where structural disorder forms localized tail states just below the conduction band edge.\textsuperscript{60} However, the present case of a-IGZO is essentially different because the carriers are \textit{not-localized} and contributed to electronic conduction even though $\sigma$ shows the VRH-like behavior.

From these results, we can deduce a more specific model for electronic structure. There is a threshold energy ($E_{th}$) that separates the carrier conduction mechanism for percolation to degenerate conduction at $N_{th}$. If we approximate that temperature smearing of the Fermi-Dirac distribution is negligible, a simple model can be built in which electrons with energies ($E$) less than Fermi energy ($E_F$) fill the tail state and thereby $E_F$ is determined solely by $N_e$ and the function of density of states $D(E)$. Therefore, $N_e$ reflects the total density of electrons in the tail state (Eq. 17). The activation energy of the electrical conductivity ($E_\sigma$) correspond to the energy difference between a threshold energy ($E_c$) and the fermi level ($E_F$), while the carrier concentration measured by Hall effect measurements correspond to the total occupied density of states.

$$N_{\text{tail state}} = \int_{E_V}^{E_F} D(\varepsilon) d\varepsilon$$  \hspace{1cm} \textit{Eq. 17}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure56.png}
\caption{Relationship between log($N_e$) and $E_\sigma$.}
\end{figure}

It should be noted that the activation energy of $E_\sigma$ corresponds to that of the mobility because $N_e$ shows almost no temperature dependence, and the energy difference between the threshold energy $E_c$ roughly correspond to the energy level of the conduction band bottom.
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Figure 56 summarizes the relationship between \( \log N_e \) and \( E_{\sigma} \), showing a good straight line and provides an exponential decay of the tail density of states:

\[
D(E) = \frac{N_{th}}{E_0} \exp \left[ \frac{E_{c} - E}{E_0} \right]
\]

Eq. 18

With \( N_{th} = 2.7 \times 10^{19} \text{ cm}^{-3} \) and \( E_0 = 0.549 \text{ meV} \).

Figure 57 schematically illustrate the electronic structure deduced. In the compound, it is though that there is tail state having the exponential density of states and the distribution in the height of the potential barrier around the conduction band edge, leading to percolation hopping conduction and low electron mobilities when \( N_e \) is lower than \( N_{th} \) as seen in Figure 55a. In the range of \( N_e < N_{th} \), the carriers still need to flow over potential barriers as \( E_F \) is below \( E_{th} \), leading to the thermally activated percolation behaviors in \( \mu \) and \( \sigma \). When \( E_F \) exceeds \( E_{th} \) at \( N_e > N_{th} \), the carriers are not affected by potential barriers anymore and exhibit the temperature-independent or degenerate behavior.

![Figure 57. Schematic energy diagram near the conduction band edge and the density of states for amorphous IGZO](image)

### 3.5. Summary

Figure 58, shows a summary of the tendency observed for roughness, optical band gap, Urbach energy, transparency and oxygen content. XRD results indicate that all films has an amorphous structure.

The RMS roughness increases with increasing oxygen deposition pressure, and is explained as follows: With the increasing oxygen pressure, the collisions between ablated
species and oxygen molecules increase, therefore the kinetic energy of the ablated species would decrease. This in turn reduces the migration ability of the adatoms on the surface of the substrates, leading to the aggregation of the adatoms or clusters on the surface with increasing deposition pressure.

![Graphs showing the relationship between roughness, oxygen flow, and pressure](image_url)

**Figure 5.** Summary morphological, optical and chemical properties of IGZO.

The In 3d$_{5/2}$, Ga 2p$_{3/2}$ and Zn 2p$_{3/2}$ spectra shows symmetric shape and the BE suggest a single oxidize state.$^{125-128}$ The asymmetry of the O1s region of the XPS spectra indicates the presence of multiple components. The O1s region, at the surface of the film, was divided into three Gaussian peaks: p0, p1 and p2, while in two peaks, p0 and p1, for the bulk. The component on the low BE, p0, can be attributed to O$^{2-}$ ions surrounded by Zn, Ga and In atoms on the IGZO compound system.$^{130-132}$ The mid energy component, p1, is associated with the presence of oxygen-deficient regions in the IGZO structure.$^{14,129,132-135}$ The high binding energy component, p2, is usually attributed to the presence of loosely bound oxygen on the surface of film belonging to a specific specie, e.g., $-\text{CO}_3$, adsorbed H$_2$O or adsorbed O$_2$.$^{129,136-138}$

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From the chemical analysis (EDX and XPS), the In, Ga and Zn content are highly consistent with expected and measured target composition. Due to knock off effect, the In and Zn peak intensities slightly decrease while Ga and O slightly increase after sputtering. The ratio of vacancies decrease as deposition pressure increase in the same fashion than oxygen flow does. The lower ratio of oxygen vacancies and surface absorbed oxygen is related to charge trapping and increases the electrical stability of TFT devices.

The transparency of IGZO increases from 87% until ~95% as deposition pressure increase, and seem to be saturated with further increasing oxygen deposition pressure. Also, the absorption edge shifts to low photon energy. It has been interpreted as the band filling effect, which lead to a widening of the optically observed band gap. The observed energy gaps were within the range of 3.08 to 3.41 eV. The change in the band gap is explained as follow: At low deposition pressure, a large number of oxygen vacancies might occupy the bottom of the conduction band, leading to a decreased band gap. With increasing oxygen pressure, the reduction of oxygen vacancies suppress the defective states near the conduction band, resulting in increasing bandgap with increasing oxygen pressure.

A good modulation of electrical properties were obtained by change the deposition pressure. From the resistivity measures, a change from $10^{-3}$ to $10^7 \ \Omega\cdot cm$ was found with increasing oxygen pressure from 10 to 30 mTorr, and for 80 mTorr is expected to be higher. CTLM results suggest that aluminum is not a good ohmic contact for a-IGZO, but for use as source and drain in TFTs, where the active layer has high resistivity, the specific contact resistance obtained should not be a major problem.

From Hall effect measurements, all of the a-IGZO film were found to be of n-type. The data shows that the Hall mobility decreases as well as carrier concentration, while resistivity increases. A maximum for $n_e (4.3 \times 10^{19} \ cm^{-3})$ and $\mu_{\text{Hall}} (10.6 \ cm^2 V^{-1} \ s^{-1})$ and a minimum $\rho$ were found for IGZO deposited at 10 mTorr. As mentioned in section 3.2, with increasing oxygen deposition pressure, the number of oxygen vacancies in the film decrease, therefore the number of free carriers decrease, leading to decreasing carrier concentration and increasing resistivity. The oxygen vacancies in a-IGZO films can act as shallow donors, effectively supplying conduction electrons; in the meantime, they can also act as scattering centers, reducing the charge carrier conduction to a certain extent.
From temperature dependent Hall effect, percolation conduction was observed when $N_e$ was lower than $N_{th} = 2 \times 10^{19}$ cm$^{-3}$ while carrier transport changes to degenerate conduction at $N_e > N_{th}$. However, such behavior is associated with an insulator-metal transition due to distribution of potential barriers formed around the conduction band edge. The carriers, in the potential barriers, contributed to electronic conduction and exhibit percolation hopping conduction. However, introduction of electron density $> N_{th}$ is necessity to obtain large mobility and high performances in drift carriers devices using TAOS.

In summary, IGZO film have been prepared at various oxygen pressures by PLD technique. Various physical properties of the films were investigated and found that, under optimal deposition condition, the amorphous IGZO film could exhibit flat surface and high transparency in visible range, even if the films are deposited at room temperature. Also, oxygen pressure has no significant effect on the morphological and structural properties of the film, but has a large effect on the vacancies formation, which greatly modifies the electrical and optical properties. Thin films deposited at pressures higher than 30 mTorr could be used as active layer in thin film transistors due to the film resistivity criteria.
Chapter 4

Application: Results and discussions

In 2004, Nomura et al. reported the first transparent flexible TFT using a-IGZO as active layer.\textsuperscript{31} Since then, research in developing of high performance a-IGZO TFTs has progressed rapidly. In this chapter, a-IGZO TFTs were fabricated and characterized, focus on investigate the impact of the channel layer thickness (semiconductor) and the deposition pressure on the TFT electrical performance. As a highlight, three different thicknesses (25, 50 and 100nm) and 4 different pressures (10, 20, 30 and 80 mTorr) were used for this study, as described in section 2.3.2.

4.1. Common gate, pulsed laser deposition (PLD) a-IGZO TFT

To investigate the effect of oxygen pressure and active layer thickness, TFT with common gate were fabricated. The thickness obtained for all the films is in accordance with the thickness expected, as illustrated in Figure 59. The common top gate staggered TFT structure serves as the most convenient test vehicle for studying the fundamental TFT properties, because it is easy to fabricate and eliminate most of the processing induced variations.
4.1.1. TFT fabrication and experimental set-up

Figure 60 highlights the metallization process. A heavily p-type doped silicon wafer with 30 nm of HfO₂, deposited by ALD, serves as gate electrode and gate dielectric layer, respectively. Different thick of a-IGZO deposited at different oxygen pressure and room temperature were used as active layer. 100 nm of aluminum, deposited by e-beam, were used as source, drain and gate electrodes. The channel length (L) and width (W) were 40 µm and 1000 µm, respectively (Figure 60).

![Figure 59. Thickness versus deposition pressure](image1)

![Figure 60. Metallization process in order to fabricate a common gate TFT.](image2)

The performance of the TFT were measured in air, at room temperature, with a probe station system located in a light tight box. The electrical properties of the TFTs were measured by a Keithley 4200 semiconductor parameter analyzer. Figure 61 summarizes the transfer
characteristics using a $V_{DS} = 6\text{V}$. As shown, the thickness of the active channel and the deposition pressure has a strong impact on the TFT performance.

4.1.2. TFT analysis

Transistor behavior was observed only for those films deposited at pressures higher than 30 mTorr (Figure 61). From section 3.4, a change in deposition pressure is related with change in resistivity of the films. High resistivity ($> 10^5 \ \Omega\cdot\text{cm}$) and low carrier concentration ($<10^{17} \ \text{cm}^{-3}$) are required for TFT operation, which are obtained for those films deposited at pressures higher than 20 mTorr.

Figure 61. Transfer characteristic for TFTs made of different thicknesses of a-IGZO deposited at different oxygen pressures.

In a TFT, the electrons, coming from the S/D, must go through the bulk of the semiconductor to reach the accumulation channel, which is formed at the dielectric-semiconductor interface (Figure 62). Then, the total series resistance ($R_T$) is actually the combination of contact resistance and bulk semiconductor (a-IGZO) resistance, under the S/D electrodes.\textsuperscript{150} Hence, the resistivity of the active layer is not the only parameter related with the total current ($I_{SD}$); also, the TFT dimensions are closely related with $I_{DS}$, i.e. width, length and thickness of the active layer.

The total on-resistance ($R_T$) can be broken down into the sum of S/D series resistance ($R_{SD}$) and intrinsic TFT channel resistance (Figure 62):
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\[ R_T = \frac{V_{DS}}{I_{DS}} = R_{ch} \cdot L_{eff} + 2R_{SD} \quad \text{Eq. 19} \]

Where the channel resistance per unit length (Ω/μm), \( R_{ch} \), has an inverse relation with mobility and threshold voltage:

\[ R_{ch} = \frac{L}{\mu_{FE}W C_i (V_{GS} - V_{th})} \quad \text{Eq. 20} \]

In order to extract the TFT parameters, a deposition pressure of 30 mTorr was selected. This is due to (a) transistor behavior was observed for all thickness; and (b) large \( I_{on/off} \) ratio than those deposited films deposited at 80 mTorr.

From \( I_{DS}^{1/2} \) vs \( V_{GS} \) (Figure 63) it is possible to calculate the \( V_{th} \) and \( \mu_{FE} \). By extra plotting the linear portion to the \( V_{GS} \) axes, the threshold voltage (\( V_{TH} \)) can be obtained, and from the slope (Eq. 21), the field effect mobility (\( \mu_{FE} \)). Moreover, the current on/off ratio could be calculated from the \( I_{DS} \) vs \( V_{GS} \) (Figure 63).

\[ \mu_{FE} = \frac{2L(V_{GS} - V_{th})^2}{W C_i} \quad \text{Eq. 21} \]

Figure 64 shows \( V_{th} \) and \( \mu_{FE} \) over thickness. With the increase in thickness, from 25 to 100 nm, the field effect mobility decrease. Due to the accumulation channel is farther from the...
surface (~10 nm with the semiconductor/dielectric interface), the trap density increase as thickness increases (scattering centers). Also, the field effect mobility on IGZO films depend on carrier concentration, since the carrier transport is governed by percolation conduction over traps states (section 3.4.1), and it is enhanced at high carrier concentration, by filling the trap states.

![Figure 63. $I_{DS}$ and $I_{DS}^{1/2}$ vs. $V_{GS}$ for different thickness of IGZO deposited at 30 mTorr and RT.](image)

![Figure 64. Electrical characteristics of a-IGZO TFT by changing the channel thickness. TFT analysis as deposited.](image)

The increase in $V_{th}$ is related with the increase in the channel resistance, due to the increase in the distance from S/D to the accumulation channel. From Eq. 20, threshold voltage is inverse proportional to the channel resistance. However, the threshold voltage is positive
(V_{th} > 2.5V) showing that the TFT operates in the enhancement mode (normally-off characteristics).

Figure 64 shows the relation of subthreshold swing and $I_{on/off}$ ratio with thickness. An $I_{on/off}$ ratio > $10^6$ was obtained for all thickness, which is an expected value for a switching device. The subthreshold swing, which is a measure of the interfacial trap density, increase with film thickness. It is indeed the film thickness which determines the subthreshold swing change. The field effect mobility and the subthreshold swing of the semiconducting thin films are mainly affected by the presence of defects that cause electron trapping. From the value of the subthreshold swing, the sheet trap density $N_{SS}$ (cm$^2$) can be estimated by:

$$\sqrt{\varepsilon_s \cdot N_{BS} + eN_{SS}} = \frac{-\varepsilon_i}{e \cdot t_{ox}} \left[ \frac{S}{\ln(10) \cdot kT/e} - 1 \right]$$

Eq. 22

Where $N_{BS}$ and $N_{SS}$ are the bulk state and surface state density of traps, respectively, $k$ is the Boltzmann constant, $T$ is the temperature, $e$ is the absolute value of the electron charge, $\varepsilon_i$ and $\varepsilon_s$ are the insulator and semiconductor dielectric constant, respectively, and $t_{ox}$ is the insulator thickness. Eq. 22 does not permit the separate determination of $N_{BS}$ and $N_{SS}$, but can be used to find out the upper limits: $N_{BS,\text{max}}$ and $N_{SS,\text{max}}$ by assuming $N_{SS}= 0$ and $N_{BS}= 0$, respectively.

The degradation of the subthreshold swing (with the increase in thickness), is due to the combination of the following effects:

a) An increase in $I_{off}$.

b) An increase in sheet trap density $N_{ss}$.\textsuperscript{152}

With the increase in semiconductor thickness, the distance between the channel layer and IGZO/HfO\textsubscript{2} interface increase; then, a semiconductor capacitance is inserted in series with the gate insulator capacitance, reducing the effective capacitance and leading to an increase in subthreshold swing. Suppose that the channel layer trap density $n_{ss}$ is constant across the entire film. Then, $N_{ss}$ is proportional to IGZO film thickness, which leads to an increase in $N_{ss}$ for a thicker film.\textsuperscript{152} The increases in the threshold voltage and subthreshold
swing, with a decrease in the field effect mobility by the increase in the channel layer thickness, suggest that the TFT transport properties are mainly attributed to an increase in the trap density.

Figure 65 shows the typical source-to-drain current ($I_{DS}$) – voltage ($V_{DS}$) output characteristics. The applied $V_{GS}$ and $V_{DS}$ range from 0 to 6 V. The current $I_{DS}$ markedly increases as $V_{DS}$ increases at a positive gate bias ($V_{GS}$), indicating that the channel is n-type. The $I_{DS}$ reaches ~0.1 mA at $V_{DS}$ and $V_{GS}$ of 6V. The $I_{DS}$-$V_{DS}$ shows a clear pinch off and current saturation, confirming that the TFT operation follows the standard field-effect transistor theory. A change in saturation current with the change in the a-IGZO thickness was found, which is related to the change in channel resistance, as was analyzed before.

![Figure 65. TFT output characteristic for different thickness of IGZO deposited at 30 mTorr.](image)

![Figure 66. Time dependent analysis for TFT performance.](image)
A time dependent analysis were performed (1 week after fabrication), in order to study the effect of time in the electrical properties of the TFTs (Figure 66). A small improve in mobility, threshold voltage, I_{on/off} ratio and subthreshold slope were observed, which might be attributed to trap filling due to: (a) diffusion of oxygen in air and/or (b) structural relaxation. Then, a post deposition annealing treatment, in oxygen, would be required to improve the electrical properties.

The fabricated devices show better performance than the TFTs made of organic semiconductors or a-Si:H (Table 3). The best performance was found for 25nm thick of a-IGZO deposited at 30mTorr. The field effect mobility and threshold voltage yield 2.09 cm²V⁻¹s⁻¹ and 2.52 V, respectively. Very sharp subthreshold slope of ~0.1 V/dec, off current less than 10⁻¹¹ A, and current on-off ratio exceeding 10⁶. Combining the performance and the ability of large area deposition, a-IGZO TFTs are very suitable to replaces a-Si:H. However, the performance is not enough for future flat panel display applications.
Conclusions

The structural, morphological, chemical, electrical and optical properties of a-IGZO films, deposited by PLD, were investigated as function of the oxygen pressure at room temperature. All the samples show amorphous structure and higher uniformity, (roughness less than 2nm). The oxygen deposition pressure has no significant effect on the morphological and structural properties of the film, but has a large effect on the vacancies formation, which greatly modifies the electrical and optical properties. It was found from the temperature dependence hall study that a pressures higher than 15mTorr \((N_e=2\times10^{-19}\text{cm}^{-3})\) the electron transport change from degenerate conduction to variable range hopping conduction.

The transistor behavior was found on those films deposited at pressures higher than 30 mTorr. Those films deposited at lower pressures did not show a transistor behavior, due to its high conductivity. The increase in thickness increase the channel resistance and the trap density, which decrease the carrier mobility and increase the subthreshold slope and \(V_{th}\).

TFTs demonstrate field effect mobilities and threshold voltage around 2.4 cm²V⁻¹s⁻¹ and 2.5 V, respectively, as well as subthreshold slopes of 0.1V/dec and low off currents in the range of \(10^{-10} \sim 10^{-11}\) A. This device achievements imply that transparent a-IGZO have the potential to overtake a-Si:H, and it is a promising material for the transparent flexible electronics.
Future Work

In order to fully understand the transport properties of a-IGZO, with the selected composition, temperature dependence Hall effect must be finished. However, a good ohmic contact is required before the study. Also, Increase the substrate temperature and/or a post deposition annealing (in oxygen), within the range of flexible electronic applications, could be a good way to improve the electrical properties of TFTs.
References


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