Physical Properties of Sputtered Indium-doped ZnO Films Deposited on Flexible Transparent Substrates

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Indium-doped zinc oxide (IZO) polycrystalline thin films were grown on polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and as reference on 7059 Corning glass substrates at room temperature by radio frequency magnetron sputtering from a target prepared with a mixture of ZnO and In2O3 powders. The structural, optical, and electrical properties of the films were analyzed and compared. The IZO polycrystalline films showed n-type conductivity. The electrical resistivity drops significantly, and the carrier concentration increases as a consequence of In incorporation within the ZnO crystalline lattice. In both cases the changes are of several orders of magnitude. The resistivity obtained was 3.1 ± 0.5 x 103 Ω-cm for an IZO sample grown on PET with a carrier concentration of 3.1 ± 0.7 x 1020 cm-3, the best mobility obtained was 27.7 ± 0.8 cm2V-1s-1 for an IZO sample grown on PEN. From the results, we conclude that n-type IZO polycrystalline films with high transmittance, high mobility and low resistivity were obtained on flexible transparent substrates.

Keywords: Flexible transparent substrates, PET, PEN, Indium-doped zinc oxide, polycrystalline thin films.

1. Introduction

Transparent conducting oxide (TCO) materials such as indium tin oxide (ITO) have been of interest due to their high electrical conductivity and optical transparency. However, due to the scarcity of In reserves1, candidates for ITO replacements are necessary especially when In concentration is as high as 90% in commercial ITO glasses. ZnO-based transparent electrodes have been extensively investigated as potential substitutes2-3. Conductive ZnO films have aroused increasing interest due to their applications in solar cells, gas sensors, varistors and light emitting diodes4-6. However, the electrical conductivity of ZnO is low compared to most TCO electrodes. To increase ZnO conductivity, group III elements (Al, Ga, and In) have been used as substitutional dopants for Zn, with Al-doped ZnO (AZO) as one of the most extensively TCO studied materials7-8. In this regard, Indium is an attractive dopant for n-type ZnO because has less reactivity and greater oxidation-resistance relative to Al. Therefore, Indium-doped zinc oxide (IZO) films are a promising alternative for ITO films. Nevertheless, the literature about IZO films9-11 is not as abundant as in the case of AZO films.2,4 On the other hand, in energy conversion technology the deposition on flexible substrates will be a reliable solution12. Some advantages of these substrates are: cost, they are cheaper than glass, flexibility and lighter weight13,14, besides plastic substrates are compatible with low temperature manufacturing processes; for instance, the thin film transistor manufacture, for the development of flexible large-area electronics15,16, where TCOs deposited at low temperature and with high mobility are required17. Plastic materials which have been used for substrate purposes are: acrylic, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polycarbonate, etc.;12,15,17-19. Due to their good optical and mechanical properties and easy processability, PEN and PET materials stand out as substrates for applications in flexible electronics. For this work, we deposited IZO thin films on PEN, PET, and as reference on alkali-free borosilicate glass substrates by radio frequency (rf) magnetron sputtering. We investigated the structural, optical, and electrical properties of the sputtered thin films grown at room temperature (RT). The electrical resistivity of IZO thin films decreases by four orders of magnitude; meanwhile its carrier concentration increases three to four orders of magnitude as compared with an undoped ZnO reference film. Furthermore, the IZO film deposited on a PEN substrate has excellent transmittance in the visible range and very high mobility figures.

2. Experimental Details

Indium-doped zinc oxide (IZO) films were deposited onto, PET, PEN, and as reference a ZnO film and an IZO
The ZnO target used for the growth of the ZnO reference film, was composed only with 5.2 grams of zinc oxide powder, target was compressed at 15 Tons for 8 hours. The ZnO and IZO reference films deposited on glass were labeled as ZnO and IZO, respectively. IZO films grown on PET and PEN were labeled IZO2 and IZO3 respectively (see Table 1). The growths were performed under identical experimental conditions to evaluate the structural, optical, and electrical properties of IZO films deposited on plastic substrates. The crystalline structure of the films was determined by X-ray diffraction (XRD) using a SIEMENS D-5000 equipment, with the Cu-Kα line (1.5406 Å). The film thicknesses were estimated by a KLA Tencor P15 profiler. The optical transmittance spectra of the films were measured in an UNICAM 8700 spectrophotometer in the 200-1000 nm range. IZO thin films and plastic substrates roughness measurements were obtained with an Atomic Force Microscopy (AFM) equipment model Autoprobe CP from Veeco Metrology Group. Atomic concentration measurements of the samples were evaluated by Energy Dispersive Spectroscopy (EDS) with an X-Flash 5010 detector from Bruker installed in a Jeol Scanning Electron Microscope model JSM-3600. To determine the elemental atomic concentration of O, Zn, and In in the films, a set of ZnO and IZO samples were deposited on silicon substrates to avoid oxygen contribution from the PET, PEN, and glass in the EDS measurements. The silicon substrates were placed aside of the PET, PEN, and glass substrates in each growth. The resistivity, carrier concentration, mobility and type of conductivity of the films were measured at RT using the Van der Pauw method in a Hall effect equipment. To perform electrical measurements, high purity Silver Paint (Alfa Aesar >99 %) electrodes were deposited on the films.

3. Experimental Results and Discussion

Fig. 1 exhibits a diffractogram of an IZO representative sample. The XRD pattern indicates the films are polycrystalline with hexagonal wurtzite structure. A preferred orientation along the (002) direction is observed. The right inset in Fig. 1 shows, both, the (002) interplanar distance (ID) of the samples estimated from the XRD patterns and the Bragg angle as a function of the deposited sample. ZnO corresponds to the bulk standard data taken from literature, and the ZnO sample is the undoped reference film grown on a glass substrate. Based on the ZnO standard position in the graph, note that the (002) reflection corresponding to the studied samples shifts to lower 2θ angles while the ID values increase. Similar tendency is observed for the (102) and (103) XRD reflections showed in the left inset in Fig. 1, the 2θ values of the (102) and the (103) diffraction peaks decrease in the samples. This behavior suggests expansion in the ZnO lattice. In the case of the ZnO reference sample a larger ID value compared

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Thickness(nm)</th>
<th>Grain Size(GS) (nm)</th>
<th>rms roughness (Å)</th>
<th>$E_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>glass</td>
<td>134 ± 10</td>
<td>16.4±1.2</td>
<td>8.20</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>IZO1</td>
<td>glass</td>
<td>130 ± 8</td>
<td>13.2±0.9</td>
<td>108</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>IZO2</td>
<td>PET</td>
<td>131 ± 5</td>
<td>13.0±0.5</td>
<td>49.1</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>IZO3</td>
<td>PEN</td>
<td>128 ± 11</td>
<td>16.0±0.7</td>
<td>49.6</td>
<td>3.2 ± 0.1</td>
</tr>
</tbody>
</table>
with the ZnO standard is related with the difference in the linear expansion coefficient between the film and substrate (corning glass). The linear expansion coefficient for bulk zinc oxide \(^{21}\) is about two orders of magnitude larger than that corresponding to the glass substrate. In despite the growth is performed at RT, due to plasma and the rf power in the magnetron sputtering system the temperature increases about 5 °C. Therefore, after growth, when the film and the substrate thermalize the ZnO film lattice remains expanded. For the IZO samples the difference in ID values can be explained in terms of the difference in the atomic radii between Zn and In atoms. The In atomic radii (81 pm) is larger than the Zn one (74 pm). Thus, the substitution of Zn atoms by In atoms in the films increases the lattice parameters.

From the full width at half maximum (FWHM) of the (002) XRD diffraction peak, the grain size (GS) of the films was estimated using the Debye-Scherrer formula: \( GS = \frac{\lambda}{\beta \cos \theta} \), where \( GS \) refers to grain size, \( \epsilon \) is a constant with a value of 0.94, \( \lambda \) is the Cu-K\( \alpha \) wavelength of the XRD source, \( \beta \) is the FWHM of the diffraction peak measured in radians, and \( \theta \) is the Bragg angle\(^{8}\). The films have grain size between 13 and 16.4 nm. It was previously reported that small grain size could be due to the fact that samples were grown at RT without a post-growth thermal annealing\(^{9}\). GS values and thickness of the IZO films are displayed in Table 1. A detailed analysis of the surface morphology of the samples was made by AFM. 2 \( \mu \)m × 2 \( \mu \)m images of ZnO and IZO samples prepared at RT are depicted in Fig. 2. There is an evident change of roughness in the IZO\(_1\), IZO\(_2\), and IZO\(_3\) samples compared to ZnO. The ZnO sample presents root mean square (rms) roughness of 8.20 Å while the samples IZO\(_1\), IZO\(_2\), and IZO\(_3\) have rms values of 108, 49.1, and 49.6 Å, respectively (see Table 1). This higher value in roughness for IZO samples could be probably due to the incorporation of indium in the films. Figure 3 compares the optical transmittance of the films and the PEN, PET and glass substrates. The average transmittance in the 400-1000 nm wavelength range of the undoped ZnO film was 78% while for the IZO\(_1\), IZO\(_2\), and IZO\(_3\) films average transmittance values were 79%, 80%, and 82%, respectively. It is worth to mention that sample with the highest transmittance is the sample with the largest GS. It is well known that samples with reduced GS have poor transparency due to light scattering from grain frontiers\(^{7}\). The ripples observed in the transmission signal for the IZO\(_2\) sample are effect of the structure of the PET substrate, as corroborated from the PET transmission

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**Figure 2.** AFM images of ZnO and IZO films deposited on different substrates at RT by rf magnetron sputtering.
The direct optical band gap $E_g$ was calculated using Cody’s relationship:\[^{22}\] $\alpha^2 = A(h\nu - E_g)$ where $\alpha$ is the optical absorption coefficient, $h\nu$ is the photon energy, $A$ is a constant, and $E_g$ the band gap energy. Absorption coefficients of the films for different wavelength have been calculated from the transmittance and reflection data. Table 1 summarizes the energy band gap $E_g$ of the films studied in this work. The data were measured several times at different points on the surface of the samples and the standard deviation values were calculated as reported. Despite the expansion of the lattice, $E_g$ conserves the zinc oxide value in bulk. The analysis of the chemical composition measured by EDS (Table 2) indicates that indium atoms were incorporated into the ZnO films at 4.5 at. % for IZO sample, 5.2 at. % in IZO\(_2\), and 4.1 at. % for IZO\(_3\) sample, the In incorporation in the ZnO lattice was of the same order in despite of the type of substrate. Fig. 4 and Table 2 show the behavior of the resistivity, carrier concentration, and mobility of the IZO samples studied in this work as a function of the substrate and GS. Note the incorporation of indium into the IZO films has a strong effect in the electrical measurements. The undoped ZnO film has a resistivity of $74 \pm 2 \ \Omega\cdot\text{cm}$ (not shown in the graph but in the Table 2) while samples IZO\(_1\), IZO\(_2\), and IZO\(_3\) have resistivity of $1.8 \times 10^3$, $3.1 \times 10^3$, and $2.9 \times 10^3 \ \Omega\cdot\text{cm}$, respectively. After indium doping process, every In\(^{3+}\) contributes with an extra electron to the number of charge carriers\(^7\) although, resistivity of the IZO samples decreases compared with the undoped ZnO film. The resistivity for IZO\(_1\), IZO\(_2\), and IZO\(_3\) films drops four orders of magnitude, compared with that of the ZnO reference film deposited on glass. On the other hand, the carrier concentration, according to the graph in Fig. 4 and results in Table 2, varies from $9.5 \times 10^{16} \ \text{cm}^{-3}$ in ZnO to $3.1 \times 10^{20} \ \text{cm}^{-3}$ in IZO\(_3\) film grown on the PET substrate. The ZnO and IZO films are $n$-type. The Hall mobility $\mu$ increases after In doping and shows a maximum value of $27.7 \ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ in sample IZO\(_3\), which was deposited on PEN. This higher Hall mobility was measured in the sample with a lower carrier concentration. Mobility trend can be explained as follows: low doping levels decrease the carrier concentration in the IZO films with a consequent reduction in electron scattering effects\(^3\), thus the Hall mobility increases. Fig. 4 also indicates that if the GS decreases, $\rho$ decreases while $n$ increases, which means that higher doping levels decrease the grain size in the samples for the experimental conditions reported in this work. It has been observed that the planarity of surface strongly influences the physical properties of deposited material\(^{23,24}\). Although, the rms roughness of the surface of substrates was determined by AFM: glass $0.36 \pm 0.04 \ \text{nm}$, PET $2.3 \pm 0.6 \ \text{nm}$, and PEN $2.5 \pm 0.4 \ \text{nm}$. In our experiments, the GS of IZO samples decreases when rms roughness of the substrate also decreases affecting $\mu$ figures, which, according with the above discussion, corroborates the influence substrate surface has on physical properties.
of deposited films. Doping efficiency for the IZO samples was calculated considering the inset in Fig. 4, the unit cell parameters were taken from reference\textsuperscript{21}. The ZnO unit cell volume (V) calculated was $V=4.76 \times 10^{-23}$ cm$^3$. For $n$-type doping, indium occupies zinc sites. The percentage of Indium in the IZO sample is 4.5 at.\%. By assuming that all the In atoms enter substitutionally in the ZnO lattice, that is, the number of In atoms in interstitials positions and in antisites is neglected. Then, the number of atoms that the In should occupy for a 100% doping efficiency is, (an electron per each In atom), $~0.045 \times 4.2 \times 10^{22}$ cm$^{-3}$. Assuming also that all the donors are ionized at room temperature, this number would be the expected majority carrier density. However, only $2.5 \times 10^{20}$ cm$^{-3}$ active carriers were measured in the Hall experiments. Thus, the doping efficiency calculated for IZO is $2.5 \times 10^{20}/1.8 \times 10^{21} = 0.132 = 13.2\%$. For IZO the efficiency results 14.2\%, and for IZO 7.6\%. Note doping efficiency is better for PET substrates and in post-growth annealed samples (see Table 3)\textsuperscript{25-31}.

4. Conclusion

In summary, the structural, optical, and electrical properties of IZO films deposited under identical growth conditions at RT by rf magnetron sputtering on glass, PET and PEN substrates were investigated. IZO samples showed hexagonal phase, with (002) preferential crystalline orientation. The optical transmission was around 80% in the 400-1000 nm wavelength range. The lowest resistivity measured was $1.8 \pm 0.3 \times 10^{-5}\Omega\cdot$cm in the sample grown on glass substrate. The carrier concentration was $3.1 \pm 0.7 \times 10^{20}$ cm$^{-3}$ obtained in the sample grown on PET substrate. A very high Hall mobility of 27.7 cm$^2$V$^{-1}$s$^{-1}$ was observed in the IZO film deposited on a PEN substrate. Our results showed IZO samples grown on flexible substrates are suitable for flexible TCO electrodes and applications in flexible optoelectronic devices.

5. Acknowledgements

The authors are grateful to M. Guerrero and R. Fragoso for their helpful technical assistance. This work was financially supported by CONACyT, México.

Table 2. Elemental atomic composition and electrical parameters of ZnO and IZO samples studied in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn(at%)</th>
<th>O(at%)</th>
<th>In(at%)</th>
<th>Resistivity($\rho$) (Ω-cm)</th>
<th>Carrier Concentration($n$) (cm$^{-3}$)</th>
<th>Hall Mobility($\mu$) (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Doping efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>48.2 ± 2.0</td>
<td>51.8 ± 3.2</td>
<td>--</td>
<td>74 ± 2</td>
<td>9.5 ± 0.8 x10$^{16}$</td>
<td>4.3 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>IZO$_1$</td>
<td>23.3 ± 1.5</td>
<td>72.3 ± 3.0</td>
<td>4.5 ± 0.5</td>
<td>$1.8 \pm 0.3$ x10$^{-3}$</td>
<td>2.5 ± 0.9 x10$^{20}$</td>
<td>12.9 ± 0.4</td>
<td>13.2</td>
</tr>
<tr>
<td>IZO$_2$</td>
<td>22.4 ± 2.7</td>
<td>72.4 ± 4.1</td>
<td>5.2 ± 0.7</td>
<td>$3.1 \pm 0.5$ x10$^{-3}$</td>
<td>3.1 ± 0.7 x10$^{20}$</td>
<td>6.4 ± 0.4</td>
<td>14.2</td>
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<tr>
<td>IZO$_3$</td>
<td>22.6 ± 3.1</td>
<td>73.4 ± 4.1</td>
<td>4.1 ± 0.4</td>
<td>$2.9 \pm 0.7$ x10$^{-3}$</td>
<td>1.3 ± 0.2x10$^{20}$</td>
<td>27.7 ± 0.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 3. Comparison between data of IZO samples from scientific literature, prepared with different conditions and substrates and the results reported in this work.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Resistivity ($\Omega$cm)</th>
<th>Transparency (% at 550 nm)</th>
<th>Substrate</th>
<th>Growth Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Pyrolysis</td>
<td>19.4</td>
<td>80</td>
<td>Soda Lime</td>
<td>400</td>
<td>25</td>
</tr>
<tr>
<td>Spray Pyrolysis</td>
<td>$3.0 \times 10^3$</td>
<td>78</td>
<td>Soda Lime</td>
<td>475</td>
<td>26</td>
</tr>
<tr>
<td>Thermal Evap.</td>
<td>$2.8 \times 10^{-4}$</td>
<td>83</td>
<td>Glass</td>
<td>300*</td>
<td>27</td>
</tr>
<tr>
<td>Sol Gel</td>
<td>$2.8 \times 10^{-2}$</td>
<td>82</td>
<td>Glass</td>
<td>400*</td>
<td>28</td>
</tr>
<tr>
<td>DC Magn. Sputt.</td>
<td>$3.8 \times 10^{-4}$</td>
<td>85</td>
<td>Glass</td>
<td>RT</td>
<td>29</td>
</tr>
<tr>
<td>RF Magn. Sputt.</td>
<td>$4.0 \times 10^{-4}$</td>
<td>82</td>
<td>PES</td>
<td>RT</td>
<td>30</td>
</tr>
<tr>
<td>Pulsed Laser Dep.</td>
<td>$5.4 \times 10^{-4}$</td>
<td>75</td>
<td>Corning</td>
<td>400</td>
<td>31</td>
</tr>
<tr>
<td>RF Magn. Sputt.</td>
<td>$3.1 \times 10^{-3}$</td>
<td>80</td>
<td>PET</td>
<td>RT</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Thermal annealing
6. References


20. XRD reference card 01-089-1397.


