Research Article

Studying the Properties of RF-Sputtered Nanocrystalline Tin-Doped Indium Oxide

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Abstract

The ceramic target of Indium tin oxide (ITO) (90% In2O3-10%SnO2) has been used to prepare transparent semiconductive thin films on glass substrate by RF magnetron sputtering at room temperature. The properties of the thin films are affected by controlling the deposition parameters, namely, RF power values and deposition times. The structure, morphology, optical and electrical properties of the thin films are investigated using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), atomic force microscope (AFM), UV-Vis spectrophotometer, and four-point probe measurement. Nanoparticles of 10–20 nm are measured and confirmed using both FESEM and AFM. The main preferred orientations of the prepared thin films are (222) and (400) of the cubic ITO structure. The transparent semiconductive films have high transmittance within the visible range of values 80–90% and resistivity of about $1.62 \times 10^{-4} \, \Omega \cdot \text{cm}$.

1. Introduction

Indium-tin-oxide (ITO) thin film is n-type degenerated semiconductor with a wide band gap (Eg∼3.3 eV) [1]. It has high photoelectrolytic properties: high transparence in the range of visible spectrum (>95%), high reflectance in the infrared (IR) range (>80%) because of its high density of free electrons in ITO conduction band, and high conductivity ($10^{-4} \, \Omega \cdot \text{cm}$) similar to a metallic material [1]. It is usually deposited at temperature above 200°C, since it is difficult to obtain a thin film with a resistivity below $2 \times 10^{-4} \, \Omega \cdot \text{cm}$ at a low substrate temperature. However, low-temperature deposition, below 100°C, is necessary to deposit films on plastic substrates that have poor heat resistance, such as polycarbonate [2] polyethylene terephthalate [3] and polyethersulfone [4]. ITO coatings are the most widely used as transparent conductive oxide (TCO) coatings in various applications such as transparent conducting electrode in flat-panel displays (FPDs) [5], organic light emitting diodes (OLEDs) [6], and photovoltaic solar cells because they have high electrical conductivity, high optical transparency, and smooth surface morphology [7–10].

ITO thin films are prepared using various methods such as DC, pulsed DC, and RF magnetron sputtering [11–13], reactive evaporation [14], ion beam assisted deposition [15], sol-gel, co-precipitation [16, 17], chemical vapor deposition (CVD) [18], and spray pyrolysis [19]. Magnetron sputtering is one of the most versatile techniques for ITO thin films preparation. This technique provides a uniform fabrication of the reproduction of ITO thin films, which is advantageous for many applications in industry [20].

The optical and electrical properties of ITO coatings are sensitive to process parameters and depend on the control of films composition, structure, crystallinity, defect density, surface roughness, and dopant concentration [21, 22].

In this paper, the crystallization behavior of ITO thin films deposited at room temperature under Ar atmosphere by RF magnetron sputtering is examined as a function of RF power values and deposition time, aiming to determine the conditions that lead to the production of thin films with
an optical band gap (3.5 eV) and transparency (≥90%) in the visible region and in some cases near IR region. Also, low resistivity, good surface uniformity, highly smooth and chemically stable surfaces in various environments are essential parameters that should be investigated.

2. Experimental Details

The ITO thin films were deposited on 1 mm thick soda lime glass by RF magnetron sputtering technique using the system (HUMMER 8.1) under an Ar atmosphere. SnO2-In2O3 sintered disks of 10 cm in diameter were used as the target. Glass was precleaned with ethanol and acetone, respectively. The chamber was evacuated to a background pressure of 0.6 mTorr initially, and the working pressure during the film deposition was fixed to 7–10 mTorr by utilizing pure Ar (99.999%) gas. The RF power varied from 50 to 300 W, whereas the deposition time varied from 10 to 40 min. The deposition process is carried out at room temperature, that is, the substrate is not heated during the film deposition.

The film crystalline structure was investigated by X-ray diffractometer (Schimadzu-7000) using Cu-Kα radiation target. The optical transmittance was measured using a UV-Vis double beam spectrophotometer (Ultrospec 2000-Pharmacia Biotech Co.) in the wavelength range from 200 nm to 1100 nm. The surface morphology of the films was observed with a field emission scanning electron microscope (JEOL 7600) and the average surface roughness is measured under ambient conditions with an atomic force microscope (AFM) JEOL-JSPM-5400 in the noncontact mode. The resistivity of the coatings is measured using a four-point probe technique (Sigma One) and the reported value was an average of three measurements over the sample.

3. Results and Discussion

3.1. Structural Properties. Figure 1 shows the X-ray diffraction patterns of the ITO thin films deposited with various RF power values at a constant working pressure, and the deposition time is fixed at 40 min. At low deposition power of 50 W (Figure 1(a)), the ITO thin film shows no diffraction peaks, which may indicate amorphous state of the deposited film. Increasing the deposition power to 100 W (Figure 1(b)), the deposited film shows the appearance of the (222) peak of the ITO cubic structure (JCPDS Card No. 06-0416).

Starting from a deposition power of 150 W, most of the typical ITO diffraction peaks of (222), (400), (440), and (622) are detected as shown in Figure 1(c). It has been observed that the (222) preferential orientation is highly dominant at the initial growth stage for any deposition condition. This is due to the fact that during the nucleation stage of ITO thin films, indium atoms on substrate are likely to aggregate into densely packed (111) planes which are close to (222) planes in the bixbyite structure. But the dominant nature changed from (222) to (400) when there is an increase in substrate temperature and also due to an increase in film thickness due to increasing the power value [23].

A preferential orientation of (400) plane is observed as the deposition power is increased from 150 to 300 W as shown in Figure 1 ((c)–(f)). The data also shows that the peak position slightly shifts to a lower 2θ value as the power increases while the full width half maximum (FWHM) decreases, meaning that the film grain size increases [4]. It has also been noted that the intensity of the (222) diffraction peak does not increase significantly any more when the thickness is higher than a certain value, whereas the (400) diffraction intensity increases for thicker films. Thus, the growth of the (222) grains is suppressed when the thickness increases [24]. According to the literature, the predominant orientation changes from (222) to (400) as the oxygen incorporation in the structure decreases or as the deposition rate increases which is in good agreement with the presented results. On the other hand, the change in the orientation from (222) to (400) can also be influenced by the deposition rate because the (222-) oriented grains are less resistant against sputtering than the (400-) oriented grains [24].

Figure 2 shows the XRD patterns of the grown ITO thin films at a constant power of 200 W and various deposition times. The film deposited for 10 min (Figure 2(a)) reveals low-diffraction intensities of the ITO crystal structure (JCPDS Card No. 06-0416) with the preferred orientation of
the (222) plane, and changing the orientation to (400) plane will increase the deposition time to 20, 30, and 40 min (Figure 2 ((b), (c), and (d))). It is known that the thickness of the deposited film affects the X-ray spectra [24]. Thin crystallized film deposited for 10 min might represent the diffraction peak with very low intensity.

During deposition, plasma provides the sample with heat that increases temperature to about 150°C. This temperature is required in order to have a crystalline structure [6, 14, 15]. One aspect of the plasma-surface interactions is the transfer of energy. Energy transfer from plasma to solid surfaces occurs through optical radiation and fluxes of neutral particles and ions. In plasma, at a pressure below 1 Pa (7.5 mTorr), the degree of ionization is very high, the density of neutrals is much lower than that of ions, and the ions collisions are predominant [16]. During the ion bombardment, the dissipation of the kinetics and the vibration energy fractions of ions causes heating of the substrate [16]. Therefore, a deposition time up to 40 min resulted in good crystallization by the prolonged energetic bombardment, while insufficient energy for crystallization is transferred to the films when the deposition time is short [17].

Figure 3 illustrates the XRD patterns of the ITO-deposited thin films at a constant power (200 W) where the effect of heat treatment at 400°C for 1 hr is discussed. The nonheated film (Figure 3(a)) shows that the (400) plane is the preferred orientation which may indicate that the oxygen vacancies on these planes are accommodated. On the other hand, the postannealed ITO film (Figure 3(b)) shows that the (222) plane is a preferred one which is a close-packed plane in In2O3 body-centered cubic structure. This plane does not accommodate oxygen vacancies very well, and so it is stabilized [25].

Also, heat treatment causes a decrease in lattice constant \( a \) which is calculated using (1)

\[
d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \tag{1}
\]

where \( d \) is the spacing between adjacent (hkl) lattice planes. It is decreased from 1.023 nm to 1.011 nm due to the attractive

3.2. Morphological Properties. The FESEM and AFM of ITO thin films are shown in Figures 4 and 5, respectively, to show the film morphology and roughness. Figure 4 shows that the average grain size is about 10 nm with high density accompanied by large grains of 20–30 nm with low density is observed and may be explained as: for the thick film, a change from (222) to (400) orientation and columnar grains growing perpendicular to the substrate by increasing the deposition time to 40 min. It was previously reported that the morphology and orientation of ITO films depend on the energy of particles arriving to the substrate and have been found.

Figure 5 shows the topography of the ITO thin film deposited at room temperature for 40 min. The average film roughness value calculated from this image is about 20 nm. According to the literature [27, 28], the average roughness increases with increasing the film thickness. In the same way, it has been reported for ITO films prepared by various techniques [29, 30] that the grain size enlargement is related with the increase of the film thickness.

3.3. Optical Properties. Several methods have been used to determine the optical constants of thin films based on the measurement of the intensity of the reflected, absorbed and/or transmitted light as a function of wavelength and/or the angle of incidence. Among these methods, the one given by Swanepoel is widely used because it is a simple method and does not need a complicated computer program [31].

For any \( \lambda, T_M \) has a correspondent \( T_m \) value: The refractive index is calculated by Manifacier et al. [32]

\[
n = \left[ N + (N^2 - S^2)^{1/2} \right]^{1/2}, \tag{2}
\]

![Figure 3: XRD patterns for ITO thin films deposited using RF power value 200 W for 40 min deposition time: (a) without, (b) with heat treatment at 400°C for 1 h.](image)

![Figure 4: FESEM for ITO thin films deposited using RF power value of 200 W for 40 min deposition time.](image)
where $N$ is defined as
\[ N = \frac{2S(T_M - T_m)}{T_M T_m} + \frac{(S^2 + 1)}{2}, \] (3)

where $S$ is the refractive index of the glass substrate.

If $n_1$ and $n_2$ are the refractive indices at two adjacent maxima (or minima) at $\lambda_1$ and $\lambda_2$, according to the basic equation of interference fringes,
\[ 2nt = m\lambda, \] (4)

the thickness $t$ of the film is given by
\[ t = \frac{\lambda_1\lambda_2}{2(\lambda_1n_2 - \lambda_2n_1)}. \] (5)

Table 1 shows an example of the calculated refractive indices and thicknesses of the ITO samples prepared with different RF power. With increasing the power value, the refractive index and the thickness are increased from 1.48 and 0.50 μm (power value = 50 W) to 1.506 and 1.09 μm (power value = 300 W), respectively, with increasing the deposition time, the refractive index and the thickness are increased from 1.499 and 46 μm (deposition time = 10 min) to 1.506 and 1.09 μm (deposition time = 40 min), respectively.

The measured optical transmittance as a function of the light wavelength is represented in Figures 6 and 7 for ITO thin films deposited as a function of RF deposition power and deposition time, respectively. From the results summarized in Figure 6 for various samples, it is observed that as the deposition power increases, the transmittance in the near infrared region decreases, which is explained by the increase of film’s free electron absorption [4].

Also, the transmittance band edge is shifted to higher wavelengths as the RF power increases. Figure 7 shows the optical transmittance for the grown ITO thin films deposited at various deposition times. The optical transmission decreases as the ITO film thickness increases, which is attributed to the optical scattering arising from longer optical paths and also to the increased carrier concentration in the films [25, 27, 28]. The higher the carrier concentration value, the lower the ITO transmittance in the longer wavelength region.

Table 1: Resistivity, thickness and refractive index of ITO thin films deposited using various RF power for 40 min deposition time.

<table>
<thead>
<tr>
<th>RF power (W)</th>
<th>Thickness (μm)</th>
<th>Refractive index</th>
<th>Resistivity (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.50</td>
<td>1.48</td>
<td>$7.71 \times 10^{-4}$</td>
</tr>
<tr>
<td>100</td>
<td>0.59</td>
<td>1.49</td>
<td>$9.98 \times 10^{-4}$</td>
</tr>
<tr>
<td>150</td>
<td>0.63</td>
<td>1.5</td>
<td>$3.96 \times 10^{-4}$</td>
</tr>
<tr>
<td>200</td>
<td>1.09</td>
<td>1.506</td>
<td>$1.62 \times 10^{-4}$</td>
</tr>
<tr>
<td>250</td>
<td>1.17</td>
<td>1.505</td>
<td>$2.32 \times 10^{-4}$</td>
</tr>
<tr>
<td>300</td>
<td>1.29</td>
<td>1.509</td>
<td>$2.38 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Figure 6: Optical transmittance for ITO thin films deposited for 40 min deposition time with various RF power.

Figure 7: Optical transmittances for ITO thin films deposited using RF power value of 200 W and various deposition times.
After heat treatment, the preferred orientation changed from (400) to (222) which is a result of the concentration of oxygen vacancy and the rearrangement of atoms in close-packed plane of In$_2$O$_3$ having a body-centered cubic structure.

References


### Table 2: Resistivity, thickness and refractive index of ITO thin films deposited using RF deposition power value of 200 W for various deposition times.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Thickness (µm)</th>
<th>Refractive index</th>
<th>Resistivity (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.46</td>
<td>1.499</td>
<td>$5.18 \times 10^{-4}$</td>
</tr>
<tr>
<td>20</td>
<td>0.52</td>
<td>1.501</td>
<td>$4.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>30</td>
<td>0.63</td>
<td>1.503</td>
<td>$1.92 \times 10^{-4}$</td>
</tr>
<tr>
<td>40</td>
<td>1.09</td>
<td>1.506</td>
<td>$1.62 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Such higher free carrier density for thicker layers can be associated to the observed crystallite-size enhancement with increasing the film thickness that should reduce the number of donor sites trapped at the dislocations and grain boundaries [28].

### 3.4. Electrical Properties. Table 1 shows that the resistivity decreased from $77.15 \times 10^{-4}$ Ω·cm at 50 W to reach its minimum value of $1.62 \times 10^{-4}$ Ω·cm at 200 W then increased to $2.38 \times 10^{-4}$ Ω·cm at 300 W. Table 2 shows the resistivity of the ITO thin films deposited at a power of 200 W and various deposition times. At the deposition time of 10 min, the transmittance value is 79% with a high resistivity of $5.18 \times 10^{-4}$ Ω·cm. At a high deposition time (40 min), the transmittance values increased to about 91%, and the resistivity decreased to $1.62 \times 10^{-4}$ Ω·cm.

In the process of Ar sputtering (no oxygen), the oxygen concentration of the ITO film is lower than that of the target itself because a part of the oxygen sputtered from the target will not be incorporated into the film [17]. That is, the films without oxygen flow show metal-like characteristics with low transmittance, low resistivity, and higher oxygen vacancy concentration. On the other hand, as the power increases, the concentration of oxygen vacancies is drastically decreased resulting in a higher transmittance and resistivity like an oxide-insulating thin film [33, 34].


