Dependence of the sheet resistance of indium-tin-oxide thin films on grain size and grain orientation determined from X-ray diffraction techniques

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Abstract

ITO thin films (100–200 nm) are deposited on glass and plastic (PET and polycarbonate) substrates by r.f. sputtering. Process parameters such as oxygen partial pressure, r.f. power, and post deposition annealing parameters are varied to determine the dependence of the sheet resistance on process parameters. The microstructure of these thin films is determined using an X-ray diffractometer (XRD) and a transmission electron microscope (TEM). The experimentally observed dependence of the sheet resistance on the grain size and grain orientation of these films is correlated to the dependence of the electron mobility on grain boundary scattering. Larger grain sizes (<25 nm) in ITO films result in lower sheet resistance (250 V/A). This type of large grain size microstructure is produced with moderate r.f. power (<100 W) and low oxygen partial pressure (<10%). There is a unique correspondence between grain size and grain orientation. ITO films with a strong peak intensity ratio of (400) orientation to all other orientations (<0.35) have the largest grain size (<25 nm) resulting in the lowest sheet resistance (250 V/Ω) and high transmission (~86.7%) at λ = 550 nm. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Indium-tin-oxide (ITO) is a transparent conducting oxide used in several optical and optoelectronic applications which include transparent electrodes, transparent resistive heaters, transparent heat reflecting mirrors, antireflective coatings, electromagnetic shield coatings and anti-static coatings for instrumental panels [1–3]. Most of these applications require high electrical conductivity and high visible transparency. To be able to use ITO films as transparent electrodes for high quality flat panel displays, the electrical conductivity has to be > 1 × 10^6 Ω^−1 m^−1 and the visible transmission must be greater than 90% [4]. Out of many deposition techniques including sputtering, thermal or electron-beam evaporation, chemical vapor deposition, spray pyrolysis, and sol-gel process, sputtering has emerged as the most viable technique for depositing high quality ITO thin films [5,6]. In our previous work on ITO thin films, we determined the optimum theoretical values of conductivity and transparency based on the energy band diagram of ITO [7,8]. We have recently published the experimental results on ITO thin films deposited on plastic and glass substrates, e.g. sheet resistance, percentage transmittance and the microstructure [9,10]. In this paper, we have analyzed the microstructure of the ITO thin films in detail to explain the dependence of the electrical properties on the grain size and grain orientation. In general, the grain size and orientation of thin films dictate the electrical and optical properties of thin films of different materials such as ITO [11], ZnO [12], PbTiO3 [13] and poly-silicon [14].

2. Samples

Table 1 shows six samples selected among many others that were fabricated on different substrates using an r.f. deposition system. The details of the system used and fabrication are described elsewhere [15]. Three different types of substrates used in this investigation were PC (polycarbonate), glass (Corning® glass no. 11/2), and PET (polyethylene terephthalate). The water cooled sputtering target is pressed In2O3 with 10 wt.% SnO2. The target to substrate distance is fixed at 5 cm. The system is pumped to a background pressure of 10^−7 Torr (=10^−5 Pa). Oxygen is mixed with the argon inside the system and the desired
partial pressure of oxygen is obtained by controlling the flow rates of oxygen and argon. These partial pressures of oxygen for different samples are given in Table 1. Though the substrates were not heated intentionally (plastic substrates melt around 150°C), the temperature of the substrate is expected to rise to about 100°C with r.f. power held at 100 W. The thickness of the ITO film is not measured directly. Using the transmittance spectra, the deposition rate for 100 W r.f. power is estimated to be 8 nm/min. Hence, the thickness of the ITO thin films is estimated to be 100–200 nm.

3. Experimental results

The sheet resistance of the ITO films is measured using a standard four-point probe technique. Using proper correction factors based on sample geometries, the sheet resistance (average of several measurements at different positions on the samples) is evaluated and listed in Table 1 [15]. The resistance values are affected by the surface smoothness of the substrate (PC substrates are significantly rougher compared to glass and PET substrates), oxygen partial pressure used and the r.f. power used. We have reported the importance of substrate surface roughness in determining the sheet resistance in a previous paper [10].

A HP8451A UV–visible diode array spectrophotometer is used to measure the optical transmission data of ITO samples. The transmission percentages listed in Table 1 are calculated by dividing the measured percent transmission of ITO sample by the measured percent transmission of a corresponding bare substrate at λ = 550 nm. The dependence of the percentage transmission on the substrate type and the process parameters are explained [9].

An XDS 2000 diffractometer is used to obtain the X-ray diffraction (XRD) data on the deposited ITO films. The X-ray radiation source used is Cu Kα radiation (λ = 0.154 nm). The angles at which the peak intensities occur (see Fig. 1) are related to the inter-planar distances of the atomic structure of In2O3 and related by Bragg’s law:

\[ \lambda = 2d \sin \theta \]

where \( \lambda \) is the wavelength of X-ray radiation used, \( \theta \) is the peak position angle and \( d \) is the inter-planer distance. The full width at half maximum (FWHM) of each peak is the width (in degrees) at half the maximum peak intensity. The FWHM of a peak can be related to the average grain size of a polycrystalline film. An estimate of the average grain size, \( \delta \), of samples is made using Eq. (2) and the FWHMs of the XRD peaks for different orientations. This estimate excludes the effects of peak broadening due to the instrument used and any effect of residual stresses in the ITO films.

\[ \delta = 0.9\lambda / \text{FWHM}(\cos \theta) \]  

Table 2 shows the detailed structural information on samples 2–6 obtained from the XRD patterns shown in Fig. 1. Though peaks are seen for four different orientations, namely (222), (400), (440) and (622), the calculations are shown only for (222) and (400) orientations because they are the most predominant orientations in ITO thin films. These estimated values are compared with the standard values given for the lattice constants of In2O3 (JCPDS card 6-416). The microstructure of the ITO thin film (sample 1) is obtained using a transmission electron microscope (TEM) and is described in a previous paper [9]. Just for comparison purposes, the electron diffraction ring patterns of sample 1 are shown in Fig. 2. There are four strong diffraction lines and an obscure line. The four strong lines correspond to (211), (222), (440) and (622) planes of the In2O3 lattice structure while the obscure line for (400) orientation is embedded in the strong (222) diffraction line (these orientations are obtained by calculating the inverse of the distances from the center of the pattern to the center of a particular ring). From the plan view of the ITO film of sample 1 (not shown here but can be found in ref. [9]) an estimate of the grain size is made and that value is given in Table 2.

4. Discussion of results

4.1. Effects of grain size on sheet resistance

The sheet resistance, \( R_s \), of a thin film is given by

\[ R_s = 1 / \sigma t \]

where \( \sigma \) is the conductivity of the film and \( t \) is the thickness of the film. The conductivity is expressed as:

\[ \sigma = n q \mu \]
where \( n \) is the free electron concentration, \( q \) is the electron charge and \( \mu \) is the electron mobility. The electron mobility depends on several scattering mechanisms including lattice scattering, neutral impurity scattering, and grain boundary scattering [16]. The grain boundary scattering is expressed as [16]:

\[
\mu_g = \left( \frac{q}{2 \pi m^*_e kT} \right)^{1/2} \exp\left(-\frac{\phi_b}{kT}\right)
\]

Here \( \delta \) is the grain size, \( m^*_e \) is the electron effective mass, \( \phi_b \) is the grain boundary potential barrier, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. If the grain boundary scattering is assumed to be the predominant scattering mechanism, then the sheet resistance \( R_s \) can be expressed as

\[
R_s = \frac{1}{n q \mu_g t} = \frac{1}{M \delta}
\]

where

\[
M = \left( \frac{n q^2 t}{2 \pi m^*_e kT} \right)^{1/2} \exp\left(-\frac{\phi_b}{kT}\right)
\]

Thus, one would expect an inverse relationship between the sheet resistance and the grain size of the thin film. A plot of sheet resistance of ITO thin films versus grain size is shown in Fig. 3. It is evident from this plot that the sheet resistances are approximately inversely related to the grain sizes. The solid curve (theoretical curve) is based on Eq. (6) with appropriate values for the material parameters. \((m^*_e = 0.3 m_0, \quad n = 1 \times 10^{26} \text{ m}^{-3}, \quad t = 100 \text{ nm}, \quad \phi_b = 0.1 \text{ eV and } T = 300 \text{ K})\). Using the values given above one obtains \( \mu_g \approx 4.0 \times 10^{-14} \text{ m}^2/\text{Vs} \) from Eq. (5) which is a reasonable value in our samples studied using Hall effect experiment [16].

Apart from the grain size, the substrate surface appears to have a significant impact on the sheet resistance values. Using an atomic force microscope (AFM) we have observed larger surface roughness in PC substrates compared to PET.
or glass substrates. The dependence of the sheet resistances on surface roughnesses for very thin films (<50 nm) will be discussed in another paper.

4.2. Effects of grain orientation on sheet resistance

The sheet resistances of ITO samples studied here decrease with the increasing peak intensity ratios of (400) orientation to all orientations. Fig. 4 shows a plot of sheet resistance versus ratio of peak intensity (area under the peak) of (400) orientation to all orientations (total area under all the peaks). A possible reason for the reduction in the sheet resistance with increasing texture (strong growth in a particular orientation, (400) in this case) is the increase of grain size with improved film texture. Fig. 5 shows that the average grain size of ITO films increases with improvements in the texture of the film.

4.3. Dependence of grain size and grain orientation on process parameters

Changes in the preferred orientations of ITO films from (222) to (400) due to changes in process parameters have been reported by several investigators [17–20]. The preferred orientation in the (400) direction is shown to be due to increased r.f. power (15 to 100 W) [17], decreasing oxygen partial pressure (12 to 1 mPa) [19] or increasing film thickness [20]. Kamei et al. have attributed the change in the ITO film texture from (222) orientation to (400) orientation to the energetic ion bombardment of the film at higher r.f. power [20]. The resputtering rate of the sputter deposited ITO films is strongly dependent on the crystallographic planes of ITO and increases in the order (400), (222) and (440). Hence, the (400) plane is more resistant to the energetic ion bombardment compared to the (222) plane and becomes the preferred orientation of sputtered ITO films.

T.J. Vink et al. and Wu et al. have reported an increase in grain size with increasing oxygen content of the ITO film [18,21]. This increase in grain size is attributed to the improved stoichiometry of sputtered films. As shown in Tables 1 and 2, an increase in oxygen partial pressure (from 5 to 10%) has resulted in an increase of grain size in samples 5 and 6 versus 2 and 3. On the contrary, the presence of oxygen reduces the oxygen vacancies, in turn decreasing the free electron concentration (each oxygen

Table 2
Structural information of ITO samples obtained from XRD patterns

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orientation</th>
<th>In₂O₃ lattice constant (nm)</th>
<th>FWHM (°)</th>
<th>Average grain size (nm)</th>
<th>Peak intensity ratio (400)/ALL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(222)</td>
<td>1.0227</td>
<td>0.703</td>
<td>11.8</td>
<td>0.109</td>
</tr>
<tr>
<td>2</td>
<td>(400)</td>
<td>1.0229</td>
<td>0.600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(222)</td>
<td>1.0157</td>
<td>0.749</td>
<td>12.2</td>
<td>0.198</td>
</tr>
<tr>
<td>4</td>
<td>(400)</td>
<td>1.0196</td>
<td>0.592</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(222)</td>
<td>1.0206</td>
<td>1.080</td>
<td>25.5</td>
<td>0.361</td>
</tr>
<tr>
<td>6</td>
<td>(400)</td>
<td>1.0239</td>
<td>0.301</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(222)</td>
<td>1.0211</td>
<td>0.616</td>
<td>54.7</td>
<td>0.348</td>
</tr>
<tr>
<td>6</td>
<td>(400)</td>
<td>1.0225</td>
<td>0.098</td>
<td>15.7</td>
<td>0.256</td>
</tr>
<tr>
<td>(JCPDS) card for In₂O₃</td>
<td>(222)</td>
<td>1.0119</td>
<td>0.145</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(JCPDS) card for In₂O₃</td>
<td>(400)</td>
<td>1.0248</td>
<td>0.445</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* From TEM data
vacancy contributes two free electrons). However, the decrease in sheet resistance due to increasing oxygen partial pressure (see Table 1) is attributed to enhanced electron mobilities in stoichiometric ITO thin films having larger grain sizes. Ichihara et al. have reported an increase of electron mobility from 2 to $5 \times 10^{-4}$ m$^2$/Vs for a corresponding increase in oxygen flow rate from 0 to 2 cc/min [22].

5. Conclusions

The sheet resistances of ITO thin films decrease with an increase in the average grain size determined from X-ray diffraction measurements. This dependence of the sheet resistance on the grain size is explained quantitatively assuming the dependence of the sheet resistance on the grain boundary scattering limited mobility. The grain boundary scattering mechanism can be the predominant scattering mechanism if the grain size is small and grain boundary potential is large ($<0.1$ eV). The grain sizes are correlated with highly oriented growth of ITO thin films along the (400) direction observed in X-ray diffraction patterns.

Dependence of grain size and grain orientation on process parameters such as oxygen partial pressure and r.f. power used during deposition is compared to the experimental results of other investigators. There appears to be an agreement between our experimental observations (preferred growth along (400) orientation due to increased r.f. power and increase in grain size with increasing oxygen content of the ITO film) and the observations of other investigators.

References