Device quality InO$_x$:Sn and InO$_x$ thin films deposited at room temperature with different rf-power densities

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The influence of tin doping on the electrical, optical, structural and morphological properties of indium oxide films produced by radio-frequency plasma enhanced reactive thermal evaporation is studied, as transport properties are expected to improve with doping. Undoped and tin doped indium oxide thin films are deposited at room temperature using both pure In rods and (95–80) % In:(5–20) % Sn alloys as evaporation sources and 19.5 mW/cm$^2$ and 58.6 mW/cm$^2$ as rf-power densities. The two most important macroscopic properties – visible transparency and electrical resistivity – are relatively independent of tin content (0–20%). Visible transmittance of about 75% and electrical resistivity around 5 x 10$^{-4}$ Ω·cm can be observed in the films. The structural features are similar for all samples. Nevertheless, the surface morphology characterization shows that the homogeneity of the films varies according to the tin content. Moreover this variation is a balance between the rf-power and the tin content in the alloy: i) films with small and compact grains are produced at 58.6 mW/cm$^2$ from a 5% Sn alloy or at 19.5 mW/cm$^2$ from a 15% Sn alloy and consequently, smooth surfaces with reduced roughness and similar grain size and shape are obtained; ii) films showing the presence of aggregates randomly distributed above a tissue formed of thinner grains and higher roughness are produced at the other deposition conditions.

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1. Introduction

Transparently conductive oxides (TCO) have been known and employed technologically since the 60s. The excellent physical properties (visible transparency and electrical conductivity) of the TCO films constitute an important advantage and render these materials as the most interesting for several technological applications like solar cells [1], heat-reflecting films [2], gas sensors [3] and thin film transistors [4].

The most widely used TCO films, both in research and device applications, are In$_2$O$_3$, SnO$_2$ and ZnO which are usually impurity doped with Sn, F and Al, respectively. In the near past, most of these films were deposited by techniques based on high substrate temperature to maximize visible transmittance and electrical conductivity. Several methods such as spray pyrolysis [5], sol–gel processing [6], sputtering [7], electron beam [8] and reactive thermal evaporation [9] have been used to prepare such films. Recently, the deposition on flexible polymer substrates is gaining great interest as they provide lighter weight and roll to roll processing. However, the major drawback of these techniques is the lack of room temperature (RT) condition which limits their further applications, as polymers do not withstand high deposition substrate temperatures. Meanwhile, different room temperature techniques have been reported [10].

In this work, undoped (InO$_x$) and tin doped (InO$_x$:Sn) indium oxide thin films with different Sn concentrations were deposited at room temperature by radio-frequency plasma enhanced reactive thermal evaporation (rf-PERTE) [11,12]. We report and discuss the influence of Sn content on the optical, electrical, structural and morphological properties of these films.

2. Experimental details

Two series of InO$_x$ and InO$_x$:Sn thin films were deposited by rf-PERTE of either pure In rods or 95–80:5–20 In:Sn (wt.%) alloys in the presence of oxygen at room temperature. Thermal evaporation was used and simultaneously rf-plasma was applied to the mixture of oxygen and evaporating gases by adapting an rf generator to a conventional evaporation arrangement: rf-power density, $P_d = 19.5$ mW/cm$^2$ (series A) and $P_d = 58.6$ mW/cm$^2$ (series B). This deposition parameter was previously optimized in order to produce device quality TCO films, exploring the rf-power density range of 1.95–78.1 mW/cm$^2$. As substrates, alkali free glass for AFM and electrical measurements and window glass plus quartz for thickness and optical measurements were used, respectively. The rf-power generator (13.6 MHz) is an Advanced Energy RFX-600. A Balzers tungsten crucible (ref. BD 482 200) was
used for the In/In–Sn evaporation heated with an electrical current of 200 A. The substrate was kept at ground potential and the source–substrate distance is around 30 cm. Oxygen (99.99% purity) is introduced into the deposition system through a calibrated leak valve. In order to enhance the reaction of the In/In:Sn evaporating species with oxygen, oxygen plasma is generated by a radio-frequency electrode (metallic grid of 16 × 16 cm²) placed into the deposition chamber, between the resistance-heated crucible of tungsten and the substrate holder, at 10 cm from the substrates [13]. The process starts with the evacuation of the deposition chamber to a vacuum pressure of 10⁻³ Pa. Then, prior to evaporation, a 4.5 sccm oxygen flow was imposed and a gate valve was used to control the pressure in the chamber (6 × 10⁻² Pa and 8 × 10⁻² Pa for series A and B, respectively). In the beginning of evaporation, until the alloy is completely melted, a shutter between the substrates and the crucible is used to prevent contaminants from the heated crucible to reach the substrates. During evaporation, the reaction (in the gas phase) of the metal with the oxygen atoms, results in a pressure decay down to 4 × 10⁻² Pa and 5 × 10⁻² Pa for series A and B, respectively. The substrate temperature was around 25 °C. The thickness of the films was kept constant around 100 nm and the average deposition rate was r=0.11 nm/s for series A and 0.17 nm/s for series B. The InOx and InOx:Sn thin film deposition parameters are summarized in Table 1.

The transmittance, T(λ), in the UV–VIS–NIR wavelength range (200–2500 nm) was recorded using a Shimadzu UV-3100 spectrophotometer, without a bare substrate across the reference beam. The direct optical gap values, E_{opt}, of the films are inferred from the transmittance data by plotting (αhν)² vs. hν, where α is the absorption coefficient and hν the photon energy, through an extrapolation of the linear portion of the plot (Tauc plot). The sheet resistance, R_s, of the films was measured using a Veeco FPP-5000 four point probe. Quantitative measurements of topographical features of the films were performed by atomic force microscopy (AFM). A Dimension 3100 microscope with a Nanoscope IIIa controller from Digital Instruments (DI) was used for AFM measurements. These were performed in tapping mode under ambient conditions. A commercial tapping mode etched silicon probe from DI and a 90 μm × 90 μm scanner were used. Glancing incidence X-ray diffraction (GIXRD) measurements were performed using a Bruker AXS D-5000 diffractometer. The diffraction patterns were recorded for Cu-Kα radiation incident at an angle of 1° to the sample’s surface. Phase analysis was carried out using the JCPDS database cards [14].

### 3. Results and discussion

Fig. 1 shows the transmittance spectra, T(λ), of series A (Fig. 1a) and series B (Fig. 1b) samples as a function of the wavelength in the UV–VIS–NIR range (200–2500 nm). The spectrum of the quartz substrate is also presented for comparison purposes. As can be seen, in series A, all samples show a good visible transparency. Although, the thickness of sample A3 is slightly lower, its transparency decreases. In series B the visible transparency is even better than in series A except for two samples (B4 and B1) which have a slight decrease in thickness. In these samples occurs the same situation as in series A: samples with lower thickness show a lower transmittance, contrary to what was expected. The average transmittance in the visible range varies from 55 to 78% for series A, showing the highest value for the undoped film (A5); for series B, the corresponding variation is 64 to 78%, decreasing significantly as tin doping increases. The direct optical gap values, E_{opt}, of the films were determined to be within the 3.9 to 4.1 eV range. The results are summarized in Table 2.

The sheet resistance as a function of indium content (wt.%) in the alloy is plotted in Fig. 2. Their values, for all the samples, fall in the range of 40–60±1 Ω/sq (equipment uncertainty), showing no particular dependence on alloy composition. The slight variability observed may be just due to statistical fluctuations characteristic of the deposition system or thickness variations. Comparing the sheet resistance values with data from literature [10,15–16], the films now studied show to be of very high quality, taking into account the room temperature deposition conditions used. Moreover, these samples are very stable since measurements performed six months later have shown no significant changes in the transport values.

Glancing incidence XRD patterns were recorded from selected films from both series of experiments (Fig. 3). As can be seen, the spectra overlap showing that they are insensitive to Sn-doping. Phase analysis carried out by comparing the recorded spectra with the JCPDS database led to the assignment of the observed patterns.

### Table 1

Deposition conditions of InOx and InOx:Sn thin films with 100 nm nominal thicknesses, prepared by rf-PERTE.

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>Evap. source alloy (% In:Sn)</th>
<th>Rf-power density (mW/cm²)</th>
<th>Dep. duration (s)</th>
<th>Evaporation pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>80:20</td>
<td>19.5</td>
<td>900</td>
<td>~4 × 10⁻²</td>
</tr>
<tr>
<td>A2</td>
<td>85:15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>90:10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>95:5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A5</td>
<td>100:0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>80:20</td>
<td>58.6</td>
<td>600</td>
<td>~5 × 10⁻²</td>
</tr>
<tr>
<td>B2</td>
<td>85:15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>90:10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>95:5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B5</td>
<td>100:0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1](image-url)
Table 2
Transmittance <T>, optical gap (E_{opt}), sheet resistance (R_s) and average roughness (R_a) determined by AFM measurements of samples of series A and B deposited by rf-PERTE at room temperature.

<table>
<thead>
<tr>
<th>Sample ref.</th>
<th>&lt;T&gt; (450–550 nm) (%)</th>
<th>E_{opt} (eV)</th>
<th>R_s (Ω/sq)</th>
<th>R_a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 (20% Sn)</td>
<td>65.0</td>
<td>4.1</td>
<td>47</td>
<td>1.35</td>
</tr>
<tr>
<td>A2 (15% Sn)</td>
<td>65.0</td>
<td>4.0</td>
<td>47</td>
<td>1.20</td>
</tr>
<tr>
<td>A3 (10% Sn)</td>
<td>54.5</td>
<td>4.1</td>
<td>40</td>
<td>1.20</td>
</tr>
<tr>
<td>A4 (5% Sn)</td>
<td>75.3</td>
<td>3.9</td>
<td>54</td>
<td>1.30</td>
</tr>
<tr>
<td>A5 (0% Sn)</td>
<td>77.9</td>
<td>4.0</td>
<td>45</td>
<td>1.45</td>
</tr>
<tr>
<td>B1 (20% Sn)</td>
<td>63.7</td>
<td>4.0</td>
<td>58</td>
<td>1.60</td>
</tr>
<tr>
<td>B2 (15% Sn)</td>
<td>75.8</td>
<td>4.0</td>
<td>50</td>
<td>1.40</td>
</tr>
<tr>
<td>B3 (10% Sn)</td>
<td>77.9</td>
<td>3.9</td>
<td>58</td>
<td>1.25</td>
</tr>
<tr>
<td>B4 (5% Sn)</td>
<td>73.0</td>
<td>4.0</td>
<td>40</td>
<td>1.05</td>
</tr>
<tr>
<td>B5 (0% Sn)</td>
<td>74.6</td>
<td>4.0</td>
<td>54</td>
<td>1.70</td>
</tr>
</tbody>
</table>

The deposition of InOx:Sn thin films can be due to the non activation of substitutional Sn dopant atoms, in contrast with the conventional RTE technique where activation is achieved by using high substrate temperatures during film growth (~180 °C). This is corroborated by the high quality properties of the rf-PERTE room temperature InOx:Sn films in contrast with non-transparent and low conductivity films grown by RTE at room temperature. Thus, the rf-PERTE method devaluates the role of tin on the InOx:Sn physical properties. In contrast, tin is the main actor on the topographical properties of the films as will be demonstrated hereafter.

Fig. 4 shows top view images of the topography measured by AFM for both series of samples. All the images are obtained from 2 × 2 μm² scans and the height color scale is 10 nm. The sample (B4) prepared at 58.6 mW/cm² from 5% Sn alloy shows a relatively uniform grain structure and the lowest mean roughness of series B (R_a = 1.05 nm). In the undoped film (B5) as well as in the most doped films an increase of the mean roughness was observed and the measurements show the presence of aggregates emerging from the surface or clusters of small grains. It was also observed that the surface looses homogeneity as showed in the two phase sample B2 (15% Sn alloy). For the lower rf-power density, series A, the most uniform surface is observed in sample A2 showing an identical topography to that of B4 and displaying also the lowest mean roughness value of the series (R_a ≈ 1.16 nm). The formation of aggregates is observed in the films prepared from lower Sn content alloys: 10% Sn, 5% Sn and pure In. At an alloy tin concentration of 20%, the formation of sporadic aggregates, although slightly, is also observed. The trend in the morphological properties, for series A, for both higher and lower doping is in agreement with that observed in series B — surface similarities can be established by comparing B3 to A1, B4 to A2 and B5 to A3. Therefore, both series seem to indicate that the uniformity of the surface depends on the tin content and the rf-power density: higher power densities require lower tin content alloys.

This behavior may be explained by the surface mobility of the species, due to tin incorporation, inhibiting aggregation and nucleation center formation. This surface mobility depends on the balance between tin content in the alloy and power density. Conducting transparent samples can be produced by rf-PERTE using oxygen plasma to guarantee transparency and high conductivity while “tailoring” the topography surface by incorporation of tin for the specific application.

4. Conclusions

Two series (A and B) of InO_x and InO_x:Sn thin films were deposited, with a technique recently developed in our laboratory, at room temperature by rf-PERTE. As evaporation sources both pure In rods and (95–80):(5–20) In:Sn (wt.%) alloys were used for each series,
respectively. In series A, the rf-power density is \( P_d = 19.5 \text{ mW/cm}^2 \) and in series B, \( P_d = 58.6 \text{ mW/cm}^2 \). Under these deposition conditions:

a) the electrical resistivity is independent of the tin content; b) the visible transparency is slightly affected; and c) the surface topography is strongly affected by tin content and rf-power density. Results show that all the samples display a visible transmittance in the order of 75% and a sheet resistance of about \( 50 \Omega/\text{sq} \). Thus, we must emphasize that the effect of oxygen plasma could be not only an enhancement of the reaction with indium (and tin) atoms in the gas phase, but also the availability of more energy for the condensing species, with a result similar to heat treatment or substrate heating. This is another advantage of this technique.

AFM clearly shows that similar topographies can be obtained at higher power densities and lower doping content alloy or vice-versa. This behavior allows the fabrication of enhanced homogeneous films with both high and low doping contents: from 15% Sn alloy at an rf-power density of 19.5 mW/cm\(^2\) (series A) or from 5% Sn alloy at an rf-power density of 58.6 mW/cm\(^2\) (series B). Both films show a smooth surface with reduced roughness and compact grains with similar size and shape, promoting their application in microelectronic processes.

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