
Fabrication of ITO thin films by filtered cathodic vacuum arc deposition

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Abstract

Polycrystalline indium–tin-doped oxide (ITO) thin films have been fabricated on Si(1 1 1) and quartz substrates by filtered cathodic vacuum arc (FCVA) technique for the first time. The ITO thin films were deposited at different substrate temperature and oxygen gas flow rates into the reactor chamber. The films deposited at low temperature below 100 ◦C are amorphous. The films grown between 200 and 350 ◦C mainly oriented in the (2 2 2), (4 0 0), (4 4 0), and (6 2 2) directions both on silicon substrate and quartz substrate. The optimized ITO film has a high transmittance of about 95% in the wavelength range of 400–800 nm, the volume resistivity is 6.57 × 10−4 Ω cm and the electron carrier concentration is as high as 1.62 × 1021 cm−3. Atomic force microscopy (AFM) images show that the surface of ITO film is very smooth both on silicon and quartz substrates, the RMS average roughness is 2.24 nm for silicon substrate and 2.43 nm for quartz substrate respectively.

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1. Introduction

Indium–tin-doped oxide (ITO) is an n-type wide band-gap oxide semiconductor. ITO is well known as the most widely applied transparent conducting oxides (TCOs), which have attracted a great deal of interest due to their prospective employment in the field of optoelectronics, such as optical windows and electrodes. ITO is ubiquitous in all kinds of flat panel displays, solar cells, photodetectors and electroluminescent devices [1–5]. Different techniques are used to prepare ITO thin films, including chemical-vapor deposition, evaporation, the sol–gel process, magnetron sputtering, and pulsed-laser deposition (PLD) [6–10]. The commercially available ITO deposited by sputtering has low resistivity in the range of 6 × 10−4 Ω cm, and high transmittance of 85–90% in the visible region. The roughness of ITO surface is usually a few 10-folds angstroms. With the progress of flat panel display technology, much lower resistivity, higher transmittance and more smooth surface are needed to decrease the voltage drop and power consumption of ITO line and improve the performance of the display. The roughness of ITO thin film is especially important for organic light-emitting devices (OLEDs) [11]. In OLEDs, the organic layers are very thin, protrusions of as little as 30 nm in a 300 nm of ITO layer can cause shorts and dark spots formation [12]. Exploring new techniques and materials to produce a very planar layer (low roughness) of ITO thin film while maintaining or improving the sheet resistance and the transmittance becomes crucial for long life time organic light-emitting display.

The filtered cathodic vacuum arc (FCVA) technique is an attractive thin film deposition method, which is one of the most promising techniques for high-quality hard coating and semiconductor applications [13]. The FCVA deposition system employs a magnetic filtering technique to remove unwanted macroparticles and neutral atoms. Only ions within a well-defined energy range and certain mass can reach the substrate, thus producing films with good quality, controllability and reproducibility.

In this paper, we investigate ITO thin films deposited on Si(1 1 1) and quartz substrates by filtered cathodic vacuum arc technique. The ITO thin films were deposited at different substrate temperature and oxygen gas flow rates into the reactor chamber. The ITO thin films were characterized by surface profilometer (Alpha-step, TENCOR P-10), X-ray diffraction (XRD), optical transmittance, Hall effect

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measurement, and atomic force microscopy (AFM) at room temperature under ambient atmosphere.

2. Experimental

A schematic of the FCVA system used in this study is shown in Fig. 1. A cylindrical tin-doped indium target was mounted on a water-cooled copper plate. A spiral heater with thermal couple was used for heating the substrate. Typically, the base vacuum of the chamber was \(2 \times 10^{-6}\) Torr by a two-stage pumping system made of a mechanical roughening pump and a cryogenic pump. The pressure during the deposition was usually increased to about \(6 \times 10^{-5}\) to \(2 \times 10^{-4}\) Torr due to injection oxygen gas into the chamber. The oxygen gas was introduced into the chamber directly by a mass flow controller with constant flow rate. The substrates were (1 1 1) n-type silicon wafers with average thickness of 0.4 mm and quartz glasses of thickness of about 1 mm. Prior to loading into the chamber, the substrates were cleaned by ultrasonic bath in acetone, isopropyl alcohol, and rinsed in de-ionized water, and then dried by nitrogen gas. The arc current of 50 A was used for all the samples. A toroidal magnetic field around 40 mT was employed to produce the axial and curvilinear fields to steer the plasma.

3. Results and discussion

The thickness of all the ITO films obtained with surface profilometer ranged from 30 to 50 nm. The crystalline phase and crystal orientation were evaluated using X-ray diffractometer with Cu Kα radiation wavelength of 0.154 nm at 40kV and 40 mA. Fig. 2 shows the X-ray diffraction patterns of ITO thin films on quartz glass substrate (a) and (1 1 1) silicon substrate (b) at different substrate temperatures of 200, 250, 300 and 350 °C. The XRD patterns indicate that the films exhibit a polycrystalline body-centered cubic crystal structure (\(a = b = c = 1.0118\) nm). Five peaks appear at 2\(\theta\) = 30.6°, 35.4°, 50.9°, 60.6°, and 63.8°, which correspond to the (2 2 2), (4 0 0), (4 4 0), (6 2 2), and (4 4 4) directions of the body-centered cubic crystal structure, respectively. The ITO films deposited at room temperature are almost amorphous as no preferred orientations peaks are observed. When the substrate temperature is increased to 200 °C, the films tend to crystal. The crystalline peaks
Fig. 2. X-ray diffraction patterns of ITO thin films on quartz glass substrate (a) and (111) silicon substrate (b) at different substrate temperatures. The diffraction patterns become sharper when the substrate temperature is increased to 350°C. Compared Fig. 2a and b, it can also be seen that there are similar XRD patterns at the same substrate temperature.

The transmittance of the ITO films on quartz glass substrate was characterized by UV-Vis scanning spectrophotometer (UV-2501PC). Shown in Fig. 3 are the respective transmittances of the samples deposited under substrate temperatures of 200, 300 and 350°C with oxygen flow rates of 5 sccm (standard cubic centimeters per minute) and 15 sccm, respectively. The transmittance of the ITO films is dependent on grown temperature and oxygen flow rates. The films, deposited at lower temperature of 200°C and oxygen flow rates of 5 sccm, looks blackish as much less oxygen was incorporated in the film. The absorption edge of the ITO is at approximately 300 nm. The overall transmittance of the films deposited at higher temperature of 350°C and oxygen flow rates of 15 sccm is over 95% in the wavelength range of 400–800 nm.

Room temperature Hall effect measurements were performed for the samples based on quartz glass substrates grown at different temperature and oxygen flow rates. The results are given in Table 1. From the table, it can be seen that the volume resistivity is increased with the increase of the substrate temperature, when the oxygen flow rate is the same. While the volume resistivity is decreased with the increase of oxygen flow rate, when the substrate temperature is the same. The low volume resistivity is due to high carrier concentrations in the ITO films. The sample, deposited at temperature of 300°C and oxygen flow rate of 15 sccm, has the lower volume resistivity of 6.57 × 10^{-4} Ω cm and higher carrier density of 6.2 × 10^{21} cm^{-3}. The resistivity is comparable to the best reported results by other techniques [14]. The high carrier density in the order of 10^{21} cm^{-3} is close to that of ITO films derived by pulsed laser deposition and sputtering [7,8], where ions are involved in the deposition process.

The low resistivity of ITO film is due to the large free carrier density. It is generally accepted that these free carriers are generated by two mechanisms: (1) tin atom substitution of indium atom and giving out one extra electron, and (2) oxygen vacancies acting as two electron donors [15]. The films deposited at room temperature appeared dark, indicating the incorporated oxygen of the films comes not only from the ionized oxygen because of ionization of oxygen at the arc source and the collision of indium and tin atoms with oxygen, but also from the reaction of the indium and tin with oxygen on the film surface. With fixed temperatures of 300°C, increasing the oxygen flow rate from 5 to 15 sccm helps to slow down the indium and tin ions towards the substrate, more oxygen can be incorporated into the film, thus resulting in a lowering of the resistivity. With fixed flow rate of 15 sccm, increasing the temperature facilitate more oxygen incorporation, but too much oxygen resulting in reduced oxygen vacancies. Thus the resistivity is increased.

From the results mentioned above, the resistivity of ITO film is correlated with the free carrier density and the mobility of the free carriers. In general, the higher the free carrier density, the lower the resistivity [16,17]. On the other hand, the mobility of the free carriers are dependent on various scattering mechanisms in the film, for example, ionized impurity scattering and grain boundary scattering [16]. From Table 1, it can be seen that the mobility, in general, increases with the increase of the substrate temperature, indicating a reduced grain boundary scattering with the increase of temperature, which is consistent with XRD result that increasing
substrate temperature helps to improve crystallinity (Fig. 2). This result is in agreement with the result previously reported [8]. Also seen from Table 1, the increase of the flow rate, thus reducing the energy of ions reaching the substrate surface, also helps to increase the mobility. The reason is that there are less ionized impurities generated with smaller energy ions bombardment on the growing ITO film, hence, less ionized impurity scattering.

The surface morphology of the ITO thin films deposited on silicon and quartz glass substrate was investigated by AFM technique. Fig. 4a and b show the AFM images of ITO films deposited on silicon and quartz glass substrates respectively. The top two figures of Fig. 4 show the 3D surface morphologies, while the bottom top figures show line scans of surfaces. The samples were deposited under the condition of 300 °C substrate temperature and 15 sccm oxygen flow rates. For a scanning area of 1 × 1 μm², Fig. 4 shows smooth surface morphologies for both silicon substrate and quartz glass substrate. For the silicon substrate in Fig. 4a, the width of the marked peaks is 591.80 nm and the RMS value of the line scan is 2.838 nm. The RMS average value is of 2.243 nm for the whole area of the 1 × 1 μm². For the quartz glass substrate in Fig. 4b, the width of the marked peaks is 554.89 nm and the RMS value of the line scan is 2.105 nm, while the RMS average value is of 2.435 nm for the whole area of the 1 × 1 μm². Overall, the surface morphology and roughness of the ITO films based on silicon substrate are similar to that of quartz substrate. The surface roughness is slightly better than commercial ITO glass that has a RMS roughness of around 2.8 nm from our own measurement. The smooth surface morphology of ITO films derived from FCVA technique is believed to come from the high energy and high density of ions involved in FCVA deposition [13]. Due to the bombarding of ions, the film becomes denser and amorphous, and etching of the growing film is also expected. The etching rate is higher for peaks on the films than for pits. Eventually the surface of the growing ITO thin film is smoothened. The smooth surface of ITO thin films can be used to fabricate highly reliable OLED for advanced applications [11].

Table 1
Summary of electrical properties of ITO thin films on quartz substrates grown at different temperature and oxygen flow rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Temperature (°C)</th>
<th>Oxygen flow rate (sccm)</th>
<th>Resistivity (×10⁻⁴ Ω cm)</th>
<th>Hall mobility (cm² V⁻¹ s⁻¹)</th>
<th>Carrier density (×10²¹ cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200</td>
<td>5</td>
<td>13</td>
<td>4.68</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>300</td>
<td>5</td>
<td>15.2</td>
<td>3.52</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>300</td>
<td>15</td>
<td>6.57</td>
<td>5.86</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>350</td>
<td>15</td>
<td>27.4</td>
<td>7.62</td>
<td>0.29</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. AFM images of ITO films based on different substrate: (a) on silicon substrate and (b) on quartz glass substrate.
4. Conclusions

ITO films have been successfully fabricated on Si (1 1 1) and quartz substrates by filtered cathodic vacuum arc technique. The properties of ITO thin films are dependent of the substrate temperature and oxygen gas flow rates. The optimized ITO film has a high transmittance of about 95% in the wavelength range of 400–800 nm, the volume resistivity is $6.57 \times 10^{-4} \Omega \cdot \text{cm}$ and the electron carrier concentration is as high as $1.62 \times 10^{21} \text{cm}^{-3}$. AFM images show that the surface of ITO film is very smooth both on silicon substrate and quartz substrate. These films are promising for OLED applications.

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