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Reactive Magnetron Sputtering of Indium Tin Oxide Films on Acrylics—Electrical Resistivity and Optical Properties

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The effects of processing parameters on the deposition rate lattice parameters, stoichiometric compositions, surface morphology, and bonding state of indium tin oxide (ITO) films on acrylics had been previously reported. This study was a continuation of the previous investigation and focused on the electrical resistivity and optical properties of ITO films.

The electrical resistivity decreased and then increased with oxygen flow rate. This was due to the effects of oxygen vacancies and impurity scattering. The resistivity of ITO films decreased with the applied bias voltage and film thickness. The transmittance of visible light increased with the oxygen flow rate and decreased with film thickness. Films deposited at oxygen flow rates having low electrical resistivity also had higher infrared radiation (IR) reflectance.

Keywords acrylics, indium tin oxide, optical properties, reactive sputtering, resistivity

1. Introduction

The potential applications of indium tin oxide (ITO) films include antireflection coatings, pilot windows, transparent electrodes, photoelectronic devices, and display devices. Therefore, their electrical and optical properties have attracted much attention over the past decade.[1–7]

Acrylics were selected as the substrate material for coating ITO films in specific applications such as pilot windows. This was due to their good impact strength and light weight. In addition, acrylics are transparent to visible light and can be easily fabricated into complex shapes. Because the softening temperature of acrylics is less than 80 °C, a low-temperature deposition technique such as physical vapor deposition is required.

In this investigation, the ITO films were deposited on acrylics by low-temperature reactive magnetron sputtering. The effects of processing parameters on the deposition rate, lattice parameters, stoichiometric compositions, surface morphology, and bonding state of films had been previously reported.[8,9] This study focused on the influence of oxygen flow rate and bias voltage on the electrical and optical properties of ITO films. The auger electron spectroscopy, four point probe, and fourier transform infrared reflectance were used in this investigation.

2. Experimental Procedures

2.1 Sample Preparation

The ITO films were deposited on acrylics by reactive direct current magnetron sputtering. The acrylics (methyl methacrylate) were machined into blocks of 15 × 15 × 7 mm, degreased, and ultrasonically cleaned in acetone and ethyl alcohol, rinsed in deionized water, and subsequently blown dry in flowing nitrogen before deposition.

The target used in this study was an In-Sn alloy (99.99% purity, 3 o.d. × 0.25 in.^{2}) with a composition of 90:10 (wt.%, Plasmaterial Inc. (CA, USA)). The sputtering was conducted in a mixed Ar-O_2 atmosphere with a target-to-substrate distance of 4 cm. A diffusion pump coupled with a rotary pump was used to achieve an ultimate pressure of 10^{-5} torr before gas mixtures of argon (99.9995%, Lien Hwa Gas Co., Hsin Chu, Taiwan) and oxygen (99.999%, Lien Hwa Gas Co.) were introduced. The pressure was measured using an ion gauge and a convection vacuum gauge. Two separate mass flow controllers (Hastings (Teledyne Hasting, VA) HFC-202) were used to monitor the gas flow rates of argon and oxygen.

The target was first sputtered for 10 min at 10 m torr in Ar for cleaning purposes. The cathode current and substrate temperature were maintained at 50 mA and 70 °C, respectively. A radio frequency power supply was used for establishing various negative substrate biases. Deposited samples were cooled in Ar atmosphere for 3 h before the system was vented.

2.2 Characterization of ITO Films

Film thickness was measured by an α step (ALPHA-STEP 200, Tencor Instruments, CA). The deposition rate was calculated *via* film thickness and deposition time.

Elemental compositions were analyzed by electron spectroscopy for chemical analysis (VG Scientific 210, Imberhorne

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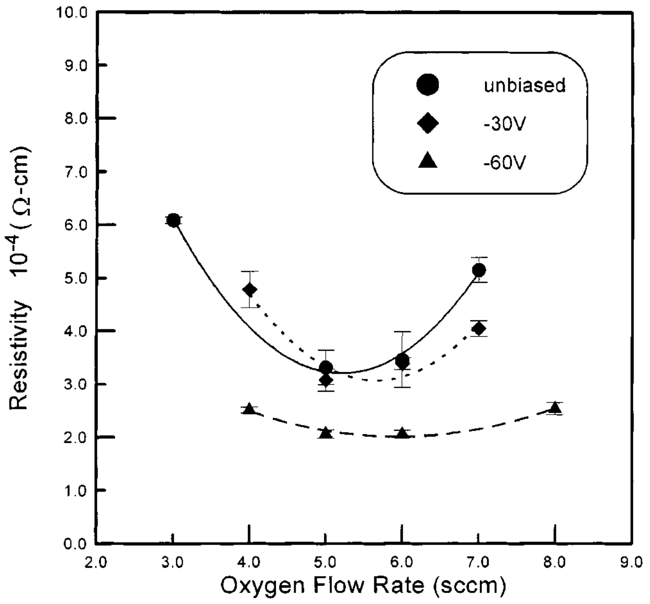

Fig. 1 Resistivity vs oxygen flow rate for ITO films under various bias voltages

Lane, East Grinstead, West Sussex, United Kingdom) with Mg source at 12 keV, 17 mA under 10^{-9} torr.

2.3 Electrical Resistivity

The four-point probe (model RT-7, Napson, Tokyo, Japan) was used for determining the electrical resistivity from the measured current (I), voltage (V), and film thickness. The resolution was controlled in less than 1%. Sheet resistance (R) of films can be calculated from the electrical resistivity and film thickness.

2.4 Optical Properties

The transmittance and reflectance of films in the visible light and infrared radiation (IR) regions were determined by the fourier transform infrared reflectance (Bomem DA8.3FTS MB 100FT-IR, Canada) and the affiliated near infrared ray source.

3. Results and Discussion

3.1 Resistivity

The resistivity of ITO film deposited under different oxygen flow rates and bias voltages is shown in Fig. 1. Results indicated that the resistivity decreased initially with the increase in flow rate. However, when the oxygen flow rate became higher than critical values of 5 to 6 sccm, the resistivity increased again. This trend was not so evident at a high bias voltage of −60 V.

Indium tin oxide is an n-type semiconductor due to oxygen vacancies and the presence of tin dopant with a higher valence than indium. The generation of the *n*-type charge carriers, *i.e.*, the electron in ITO films, can be described as follows:[10]

$$O_o \rightarrow V_o^{\bullet\bullet} + 2e' + \tfrac{1}{2}O_{2(g)} \qquad \text{(Eq 1)}$$

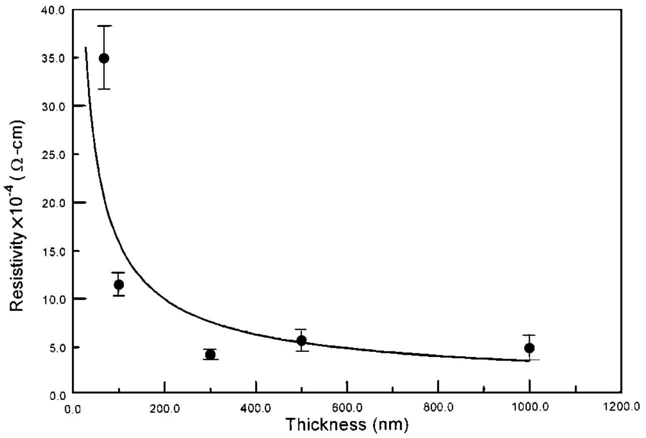

Fig. 2 Resistivity vs thickness of ITO films. Samples were prepared at an oxygen flow rate of 4 sccm without bias voltage

$$2SnO_{2(s)} \xrightarrow{In_2O_3} 2Sn_{In} + 3O_o + 2e' + 1/2O_{2(g)} \qquad \text{(Eq 2)}$$

It had been previously reported that the chemical compositions of ITO films under the experimental conditions were not stoichiometric,[8] and the change in carrier concentration was the dominant factor for determining the resistivity.[10] When the oxygen flow rate was lower than 4 sccm, the oxygen vacancies and associate electron carriers increased with oxygen flow rate and lowered the electric resistivity. At high oxygen flow rates, the impurity scattering was enhanced with oxygen flow; the mobility of electrons was therefore decreased and resulted in the increase of resistivity.[11]

Results in Fig. 1 also indicated that the resistivity of films decreased with the applied bias voltages. The high-energy particles at −60 V may knock out oxygen atoms, resulting in the presence of oxygen vacancies in the films. The oxygen vacancies may act as doubly ionized donors and contribute two electrons to electrical conductivity.[10] The effects of bias voltage on the resistivity could therefore overshadow that of oxygen flow rate at high bias voltages. A low resistivity of 2.05×10^{-4} was obtained at an oxygen flow rate of 6 sccm and a bias voltage of −60 V.

The resistivity of films deposited at 4 sccm without bias voltage was plotted versus film thickness, as shown in Fig. 2. The resistivity first decreased dramatically and then slowly with the increase in film thickness. The scattering of charge carriers by impurity was more prominent for films with smaller thickness due to relatively greater defects per unit volume.[12] The resistivity was therefore decreased with the film thickness.

3.2 Transmittance and Reflectance in the Visible Light and IR Regions

The transmittance of ITO films prepared at different oxygen flow rates is shown in Fig. 3. Transmittance of greater than 70% was detected in most test samples, as shown in Fig. 3. In addition, a trend of increase in transmittance of visible light at high oxygen flow rates was observed.

It was previously reported that the morphology and orientation of ITO films depend on the energy of particles arriving at

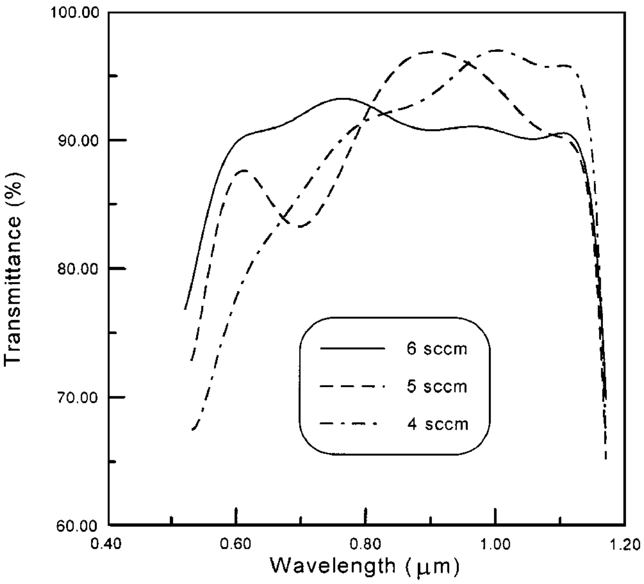

Fig. 3 Transmittance of ITO films prepared at various oxygen flow rates without bias voltage

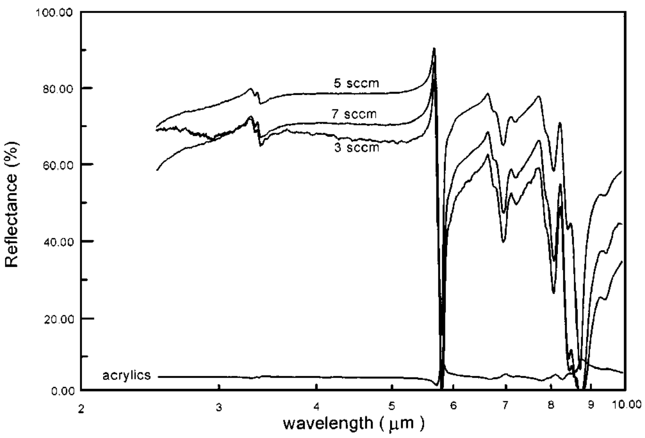

Fig. 4 Infrared reflectance of ITO films prepared at various oxygen flow rates without bias voltage

the substrate.[8,13,14] The effects of oxygen partial pressure on the preferred texture were also discussed by Higuchi *et al.*[15] and Dutta and Ray.[16] The atomic force microscope was used to examine the surface morphology and determine the average roughness of ITO films with the oxygen flow rate by Huang and Jah.[9] Columnar grains growing perpendicular to the substrate were initially observed. However, the grain size appeared to increase, the grain diameter became wider, and the surface morphology appeared flatter and denser with the increase of oxygen flow. The increase in transmittance of visible light with oxygen flow rate was probably due to the flatter surface resulting from the fulfillment of voids between columnar grains at high oxygen flow.

Transmittance of ITO films with thicknesses of 100, 300, and 500 nm were measured. Results indicated that the transmittance decreased with thickness.

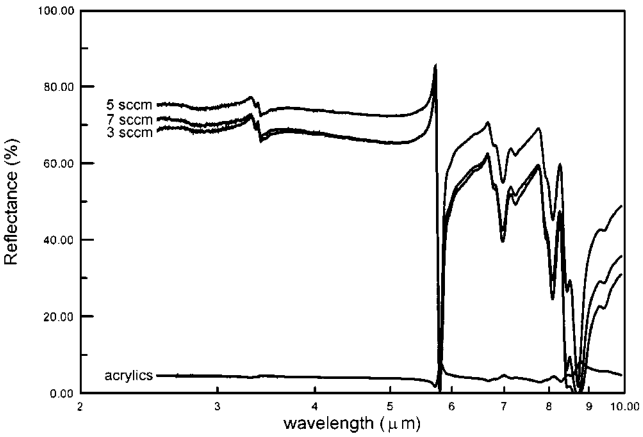

Fig. 5 Infrared reflectance of ITO films prepared at a bias voltage of −30 V with different oxygen flow rates

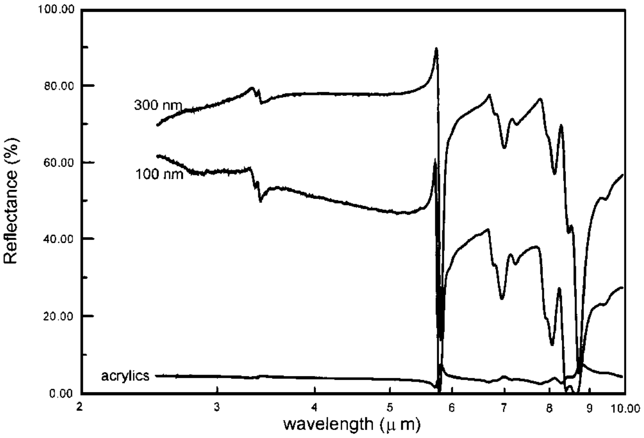

Fig. 6 Infrared reflectance of ITO films with different thickness. Samples were prepared at an oxygen flow rate of 5 sccm without bias voltage

The reflectance of ITO films in the IR region prepared at different oxygen flow rates and without bias voltage is shown in Fig. 4. The reflectance of acrylics without ITO deposition was also measured for comparison. Results indicated that the reflectance increased from less than 10% to more than 70% after ITO deposition.

According to Frank *et al.*,[17] the IR reflectance can be expressed by

$$R = 1 - 4(\varepsilon_0 C_0/e)\,(1/Nd\mu) \qquad \text{(Eq 5)}$$

where R is the reflectance, e is the electron charge, C_0 is the velocity of light, ε_0 is the dielectric constant, N is the carrier concentration, d is the thickness of the films, and μ is the mobility of the free carriers. An interesting correlation between the resistivity in Fig. 1 and that in Fig. 4 was noticed. The resistivity of ITO films under various oxygen flow rates without bias voltage was on the order of $3 > 7 > 5$ sccm, as indicated in Fig. 1. Films deposited at oxygen flow rates having lower resistivity also had higher IR reflectance, as shown in Fig. 4.

This was probably because films deposited at oxygen flow rates having low resistivity also had larger product of carrier concentration and carrier mobility ($N\mu$), hence higher IR reflectance according to Eq 5.[10] A similar trend was observed in samples prepared with bias voltages (Fig. 5).

Infrared reflectance of ITO films with thicknesses of 100 and 300 nm, prepared at an oxygen flow rate of 5 sccm without bias voltage, were measured as shown in Fig. 6. Results indicated that the reflectance increased with the film thickness d, as expressed in Eq 5. This was possibly due to the lower resistivity in relatively thick films, as discussed in Fig. 2.

4. Summary and Conclusions

1. The resistivity decreased and then increased with oxygen flow rate. This was due to the effects of oxygen vacancies and impurity scattering. However, this trend was not so evident at a relatively high bias voltage of -60 V. A low resistivity of 2.05×10^{-4} was obtained at an oxygen flow rate of 6 sccm and a bias voltage of -60 V.
2. The resistivity of ITO films decreased with the applied bias voltage. The resistivity first decreased dramatically and then slowly with film thickness.
3. The transmittance of visible light increased with the oxygen flow rate and decreased with film thickness.
4. Films deposited at high oxygen flow rates having low electrical resistivity also had higher IR reflectance. This could be explained by the product of carrier concentration and carrier mobility. Similar results were observed in samples prepared with and without bias voltages. The IR reflectance increased with film thickness

Acknowledgments

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