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Study of Indium Tin Oxide Thin Films Deposited on Acrylics Substrates by Ion Beam Assisted Deposition Technique

Li-Jian Meng[1, 2, *], Erjun Liang[3], Jinsong Gao[4], V. Teixeira[2], and M. P. dos Santos[5]

[1] *Departamento de Física, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal*
[2] *Centro de Física, Universidade do Minho, 4700 Braga, Portugal*
[3] *School of Physical Science and Engineering, Zhengzhou University, Zhengzhou 450052, China*
[4] *Center of Optical Technology, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China*
[5] *CeFITec, Universidade Nova de Lisboa/Departamento de Física, Universidade de Évora, 7000, Portugal*

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Indium tin oxide (ITO) thin films have been deposited onto acrylics (PMMA) substrates by ion beam assisted deposition technique at different oxygen flows. The structural, optical and electrical properties of the deposited films have been characterized by X-ray diffraction, transmittance, FTIR, ellipsometry and Hall effect measurements. The optical constants of the deposited films have been calculated by fitting the ellipsometric spectra. The effects of the oxygen flow on the properties of the deposited films have been studied. It has been found that 40 sccm oxygen flow is an optimum value for getting the films with good transmittance and low electrical resistivity.

Keywords: ITO, Optical Properties, Thin Film, PMMA, Ion Beam Assisted Deposition, Indium Tin Oxide.

1. INTRODUCTION

Indium tin oxide (ITO) is a tin-doped In_2O_3 based n-type degenerate wide bandgap semiconductor. The degeneracy is caused by both oxygen vacancy and substitutional tin created during deposition. ITO material in thin film form has attracted much attention from both basic scientific research and industrial applications for many years because of its low resistivity, high transmittance in visible and near infrared regions, stable physical and chemical properties, as well as good adhesion to many kinds of substrates.[1] It has been widely used in the optoelectronic area such as flat panel display, solar cell devices and organic light emitting diodes as transparent conducting electrode.[2] ITO thin films can be deposited by many techniques such as evaporation, sputtering, chemical vapour deposition, laser ablation, sol–gel process, and ion beam assisted deposition.[3–10] However, in order to obtain ITO films with low resistivity and high transmittance, most of these deposition techniques require or a high substrate temperature or a post annealing treatment (over than 300 °C). Recently, the interest in deposition of ITO film in flexible optoelectronic devices has grown up.[11] It is necessary for ITO films to be deposited at very low substrate temperature due to the poor thermal endurance of polymer substrates. Ion beam assisted deposition (IBAD) has been considered as a low temperature deposition technique and has been used to deposit ITO films. Several transparent organic substrates such as polycarbonate (PC),[12] polypropylene adipate (PPA),[13] polyimide (PI),[3] polyethylene terepthalate (PET)[4] have been used to deposit ITO films. Many reports can be found on ITO films deposited onto PC and PET substrates. However, it is hardly to find the report on ITO films deposited onto polymethyl methacrylate (PMMA) substrate. In this study, the ITO films were deposited onto PMMA substrate at room temperature by ion beam assisted deposition technique. The effects of the oxygen flow on the structural, optical and electrical properties were reported.

2. EXPERIMENTAL DETAILS

ITO films were deposited onto the commercial acrylics (PMMA) substrates at room temperature by ion beam

*Author to whom correspondence should be addressed.

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assisted deposition technique using a vacuum coater equipped with electron beam gun and a Kaufman ion source. ITO powder pellet with a composition of 90 wt% In_2O_3 and 10 wt% SnO_2 was used as the evaporation source material. A 120 mm diameters Kaufman ion source was used to generate oxygen ion beam. The oxygen gas flow was controlled by a mass flow controller. The deposition rate and the film thickness were monitored and controlled by a quartz crystal sensor which has been linked to e-beam power supply for automatic controlling. The nominal deposition rate and the thickness were preset at 0.2 nm/s and 200 nm, respectively. The substrate holder was rotated at a speed of 0.3 rounds/s. The angle between the incident oxygen ion beam and the normal of the substrate holder was fixed at 45°. Before the deposition, the chamber was evacuated until a pressure of 1×10^{-3} Pa. After that, the oxygen gas was introduced into the chamber. The oxygen flow was set to be 50, 40, 30 and 20 sccm, respectively. And the dynamic pressure in the chamber was about 2.9×10^{-2}, 2.3×10^{-2}, 1.8×10^{-2} and 1.4×10^{-2} Pa, respectively. For all deposition processes, the ion beam current, the accelerating voltage and the screen voltage were kept constants of 100 mA, 250 V and 300 V.

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The optical transmittance spectra of the films were recorded by Perklin-Elmer Lambda 900 UV/VIS/NIR spectrometer and the infrared reflectance was measured by Perklin-Elmer Spectrum GX at angle of incidence of 60°. The ellipsometric parameters IS and IC were measured using a Jobin-Yvon UVISEL ellipsometer acquired at 70.25° of incidence angle over the spectral range 300–800 nm in steps of 5 nm. The X-ray diffraction was done by SHIMADZU XRD-6000 performed between the 2θ values of 20°–70° with a step of 0.05°. Atomic force microscopy (AFM) measurements were made using equipment from Digital Instruments Veeco Metrology Group. The Hall effect was measured using Lake Shore 665 with a 5 kG magnetic field intensity at room temperature.

3. RESULTS AND DISCUSSION

The X-ray diffraction measurements show that the films deposited at different oxygen flows are all amorphous. It means that the ion beam energy used in this work (300 V screen voltage) is not enough to form the polycrystalline ITO film, although it is supposed that the additional heat energy and increased surface mobility of adatom by ion bombardment can result in polycrystalline ITO growth.[14] In order to form the polycrystalline ITO films, it is necessary to increase the ion beam energy to a certain level. Our work has shown that the polycrystalline ITO films will be produced only when the screen voltage, which is related directly with ion beam energy, is higher than 500 V.[17] The specular transmittance of ITO films deposited at different oxygen flows are shown in Figure 1. It can be seen clearly

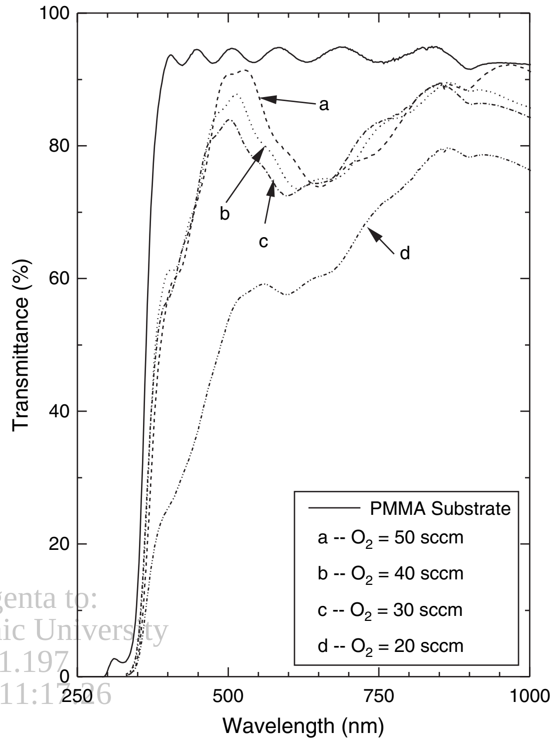

Fig. 1. Specular transmittance of ITO films deposited at different oxygen flows.

that the transmittance increases with oxygen flow. When In_2O_3 and SnO_2 mixed oxides pellet are evaporated, the oxygen will be lost and a metal-like, brownish and less transparent film of lower oxide will be formed. It has been found that the ITO film deposited in this work without oxygen flow is opaque which indicates the importance of the oxygen ion bombardment during the deposition process for forming transparent ITO films. At low oxygen flow, the oxidation is incomplete and leads to a low transmittance. At high oxygen flow, the stoichiometric ITO film will be formed and results in a high transmittance. For comparison, the transmittance of bare PMMA substrate is also shown in Figure 1. The PMMA substrate used in this work has been treated to increase its surface hardness. The small fringes in the transmittance of PMMA substrate come from this treatment. This treatment also improves its transmittance. The transmittance of conventional PMMA substrate in the visible region is about 91%.[15] But the transmittance of our PMMA substrate in the visible region is about 95%. The highest transmittance, 91% at 500 nm wavelength, has been reached for ITO films prepared at 50 sccm oxygen flow.

For getting the optical constants (refractive index n and extinction coefficient k) and the film thickness of the ITO films deposited at different oxygen flows, the ellipsometric measurements have been performed for all samples as shown in Figure 2. The ellipsometric spectra have been fitted using the Lorentz oscillator model (classical model).

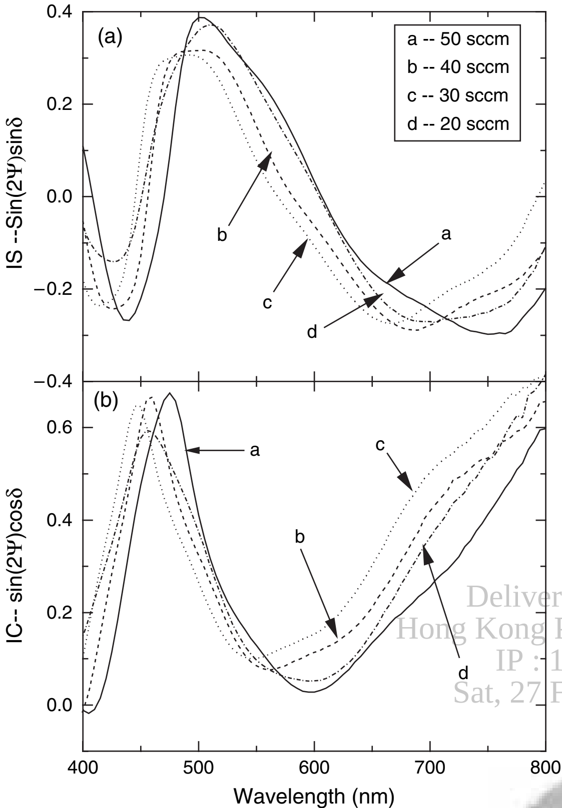

Fig. 2. Ellipsometric spectra of ITO films deposited at different oxygen flows, (a) IS; (b) IC.

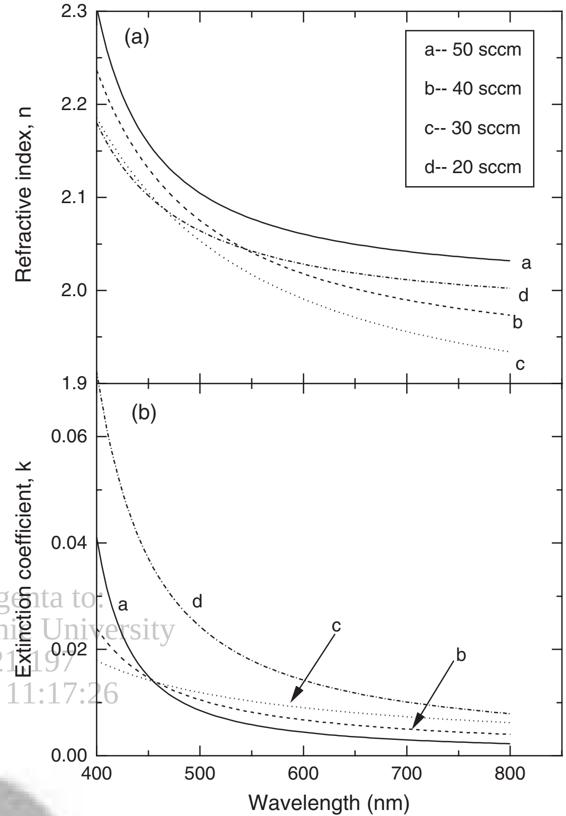

Fig. 3. (a) Refractive index and (b) extinction coefficient of ITO films deposited at different oxygen flows.

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The dielectric function in the visible region for classical model can be described as follows:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_t^2}{\omega_t^2 - \omega^2 + i\Gamma_0\omega}$$

where ε_s is static dielectric constant, ε_∞ is high-frequency dielectric constant, ω_t is the characteristic frequency of the main oscillator, Γ_0 is the damping factor. After fitting, the dispersions of the refractive index and the extinction coefficient have been obtained as shown in Figure 3. The fitting parameters have been listed in Table I. It can be seen that the extinction coefficient decrease with oxygen flow. The ITO film prepared at low oxygen flow has high extinction coefficient. As the ITO film in the visible region is a non-absorption media, the variation of the extinction coefficient can be related with light scattering. The main light scattering centres are impurities, grain boundaries and oxygen vacancies. In addition, the surface roughness will also produce light scattering. AFM measurements show that the surface rms roughness for the ITO films deposited at different oxygen flows is on the order of one nanometer and no regular variation can be found with oxygen flow. The AFM image for ITO film prepared at 40 sccm oxygen flow is given in Figure 4. So it is not the main light scattering reason for these ITO films. XRD measurements have shown that the all ITO films are amorphous, the grain boundary scattering can be neglected. As the evaporation materials are same for all processes, the impurity in all the films should not have a big difference. Therefore, the main scattering source should be the oxygen vacancies in our ITO films. It is known that the film prepared at low oxygen flow has many oxygen vacancies. These oxygen vacancies supply the electrons for conductivity. But in the same time the light will also be scattered by these vacancies. As the oxygen flow is increased, the number of the oxygen vacancies goes down; the loss of the scattering light decreases and leads to a low extinction coefficient. It has been found that the film prepared at high oxygen flow has high refractive index. As the oxygen flow is increased,

Table I. Properties of ITO films deposited at different oxygen flows.

	PMMA1	PMMA2	PMMA3	PMMA4
Oxygen flow (sccm)	50	40	30	20
d (nm)	245	240	236	242
ε_∞	3.59	2.57	3.12	3.38
ε_s	4.03	3.72	3.49	3.91
ω_t	3.58	4.26	4.79	3.90
γ_0	0.12	0.12	0.14	0.42
$R_{(\Omega/\text{square})}$	150	27	25	67
ρ ($\times 10^{-3}$ Ω-cm)	15.8	2.8	2.5	7.0
μ(cm^2/VS)	28.6	31.8	30.4	10.2
n ($\times 10^{20}$ cm^{-3})	0.6	3.0	3.4	3.8

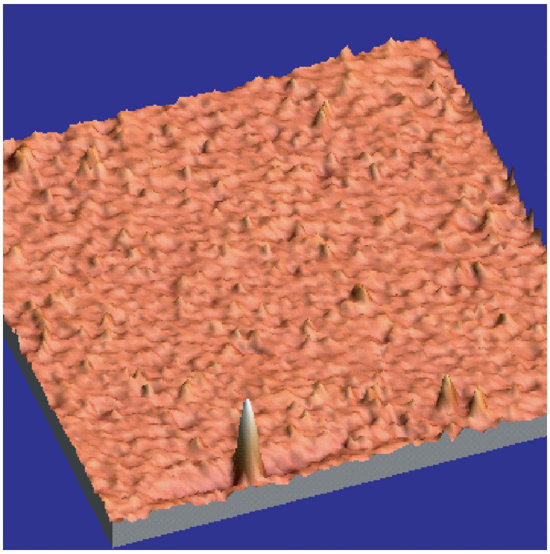

Fig. 4. AFM image of ITO film on PMMA substrate prepared at 40 sccm oxygen flow.

the ITO film approximates its stoichiometry and leads to an increase of the refractive index.

The electrical properties of ITO films deposited at different oxygen flows have been characterized by Hall effect measurement. The Hall mobility, electron concentration, sheet resistance and electrical resistivity of these ITO films have been given in Table I and plotted in Figure 5. It can be seen that ITO films prepared at 30–40 sccm oxygen flow have low resistivity. From Figure 5(b) it can be seen that the electron concentration decreases as the oxygen flow is increased. It is known that the one origin of the electron in ITO film is from the oxygen vacancies, as the oxygen flow is increased, the number of the oxygen vacancy decreases and results in the decreasing of the carrier concentration. Although the electron concentration is decreased with oxygen flow, the Hall mobility gets high value at 30–40 sccm oxygen flow and then leads to a low resistivity.

The infrared reflectance spectra of ITO films deposited at different oxygen flows are given in Figure 6. The variation of the reflectance is related with the electrical properties of the films. Frank et al.[16] showed that the infrared reflectance R for high reflection level can be expressed by

$$R = 1 - \frac{4\varepsilon_0 c_0}{e} \cdot \frac{1}{dn\mu}$$

where ε_0 (the permittivity of electron in vacuum) $= 8.85 \times 10^{-12}$, c_0 (velocity of light in vacuum) $= 3 \times 10^8$ m/s, e (electronic charge) $= 1.6 \times 10^{-19}$ C, n is the carrier concentration, d is the film thickness and μ is the carrier mobility.

According to this equation, as ITO films deposited at different oxygen flows have a similar thickness (Table I), the film which has both high electron concentration and Hall mobility will has high reflectance. Our experimental results are agreeable with it. The films prepared at 30 and

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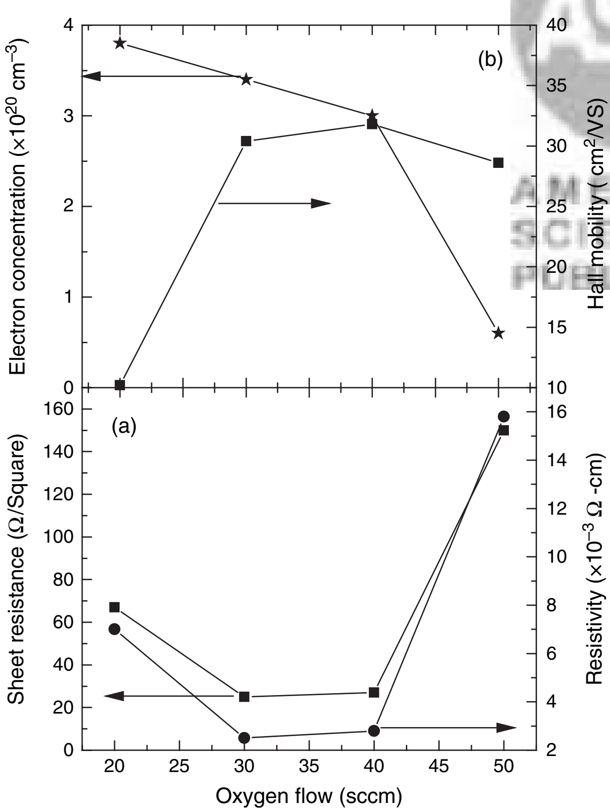

Fig. 5. (a) Sheet resistance and electrical resistivity and (b) electron concentration and Hall mobility with oxygen flow.

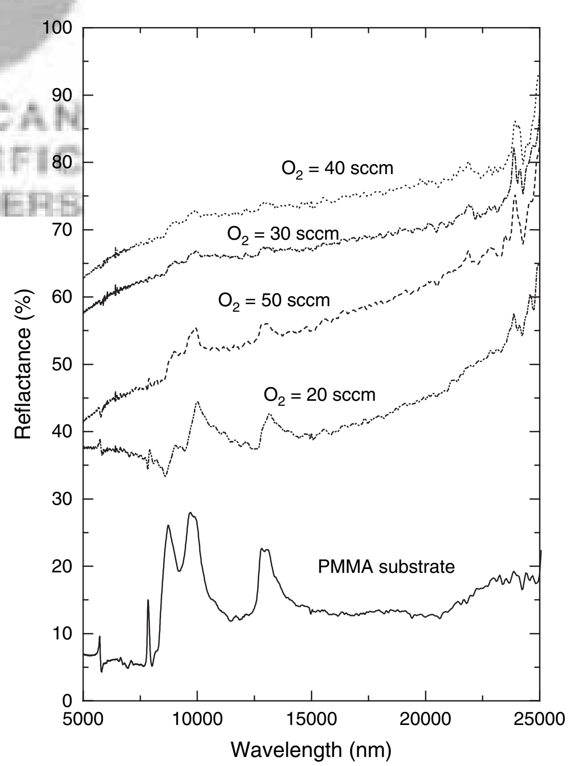

Fig. 6. FTIR spectra of ITO films deposited at different oxygen flows.

40 sccm oxygen flows have high electron concentrations and Hall mobilities and give high reflectance as shown in Figure 6.

4. CONCLUSIONS

ITO films have been deposited onto PMMA substrates at room temperature using ion beam assisted deposition technique. The oxygen flow is varied from 20 to 50 sccm. All the films show amorphous structure. The film prepared at high oxygen flow gives high optical transmittance, high refractive index and low extinction coefficient. Although the maximum transmittance (91% at 500 nm) is obtained for ITO film deposited at 50 sccm oxygen flow, it gives a high electrical resistivity (15.8×10^{-3} Ω-cm). By considering both the transmittance and the electrical resistivity, It has been found that 40 sccm oxygen flow is the optimum value for depositing ITO films. At this condition, the ITO films with 87% transmittance at 500 nm and 2.8×10^{-3} Ω-cm electrical resistivity have been obtained. It shows that ion beam assisted deposition technique is a suitable technique to deposit high quality ITO films at low substrate temperature.

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