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Tin-doped indium oxide thin film deposited on organic substrate using oxygen ion beam assisted deposition

J.W. Bae[a,*], H.J. Kim[a], J.S. Kim[a], Y.H. Lee[a], N.E. Lee[a], G.Y. Yeom[a], Y.W. Ko[b]

[a] *Department of Materials Engineering, Sungkyunkwan Univ., Suwon, Kyunggi-do 440-746, South Korea*
[b] *LCD Division, Hyundai Electronics Industries Co., Ltd. Ichon-si, Kyunggi-do 467-701, South Korea*

Abstract

Tin-doped indium oxide (ITO) thin films were deposited on polyethylene terephthalate (PET) at room temperature by oxygen ion beam assisted evaporator system and the effects of oxygen gas flow rate on the properties of room temperature ITO thin films were investigated. The increase of oxygen gas flow rate to the ion gun at a fixed rf power consistently decreased not only the oxygen ion densities in the ion gun measured by OES but also the oxygen ion flux to the substrate measured by Faraday cup while the atomic oxygen radical measured by OES showed a maximum at 6 sccm of O_2 with the increase of oxygen flow rate in our experimental conditions. The increase of oxygen flow rate to the ion gun generally increased the optical transmittance of the deposited ITO up to 6 sccm of O_2 and the further increase of oxygen flow rate appears to saturate the optical transmittance. In the case of electrical property, the resistivity showed a minimum at 6 sccm of O_2 with the increase of oxygen flow rate. Therefore, the improved ITO properties at 6 sccm of O_2 appear to be more related to the incorporation of low-energy oxygen radicals to deposited ITO film rather than the irradiation of high-energy oxygen ions to the substrate. At an optimal deposition condition, ITO thin films deposited on PET substrates showed a resistivity of 6.6×10^{-4} Ω cm and optical transmittance of above 90%.

Keywords: ITO; IBAD; Oxygen ion; Oxygen radical

1. Introduction

Transparent conductive thin films have been studied by many research workers because of their wide industrial applications. Major applications of these thin films are optical transparent electrodes in display devices. To satisfy technical requirements of applications, many new materials and various manufacturing techniques have been developed [1–3].

The most widely used material for transparent conductive thin film is tin-doped indium oxide (ITO). It has the lowest electrical resistivity ($\sim 10^{-4}$ Ω cm) and the highest optical transparency (above 85% at 550 nm). Due to these properties, ITO film is becoming increasingly important in the field of electronic devices.

Recently, there is a growing interest in applying organic substrates instead of widely used glass substrates for liquid crystal display devices. In particular, personal digital assistants (PDAs), hand held PCs (HPCs), or mobile phones are very important application fields. If the glass is substituted with organic substrate, then it could offer several advantages, such as lighter, more robust, and thinner devices.

Lower-temperature ITO thin films have been typically produced by dc (or rf)-sputtering [4–6] and vacuum/reactive evaporation [7–10]. Plasma-assisted evaporations could be promising techniques for low-temperature deposition. In particular, the ion beam assisted deposition (IBAD) technique offers advantages such as more flexibility in controlling film properties, room temperature coating on organic substrates with-

* Corresponding author. Tel.: +82-331-290-7428; fax: +82-331-290-7410.
E-mail address: jobae@nature.skku.ac.kr (J.W. Bae).

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out any post-deposition treatment, and low production cost.

In this study, the electrical and optical properties of ITO thin film deposited on PET substrates at room temperature by oxygen ion beam assisted-electron beam evaporation method were investigated.

2. Experimental conditions

The deposition of tin-doped indium oxide was carried out by an oxygen ion gun attached to an electron beam evaporator system. Polyethylene terephthalate (PET) was used as a substrate. The evaporation source material was indium oxide 90 wt.%–tin oxide 10 wt.% and the purity was 4 N. The two-grid internal type of rf inductively coupled plasma source was used as the oxygen ion source. The rf ion source can operate with any types of background gases, in particular, such as oxygen gas used in our research that can easily poison tungsten filament cathodes.

The two-grid ion gun was positioned to have the incident beam angle of the ion gun close to the normal of the substrate. To enhance the plasma density of the source, an array of permanent magnets ($\sim$ 2000 G) was applied at the bottom of the ion source.

Optical emission spectroscopy (OES) was used to observe the condition of plasma in the source chamber. OES enables a quick determination of the species contained in a plasma. The current density of the ion beam in the process region was measured using a Faraday cup located near the substrate holder. The surface composition of deposited ITO film was investigated using X-ray photoelectron spectroscopy. The pressure in the chamber during the deposition process was changed from 1×10^{-4} torr to 2.3×10^{-4} torr by varying the oxygen flow to the rf ion source from 3 sccm to 7 sccm as a discharge gas.

The thickness of ITO thin film was measured using a thin film thickness monitor during the deposition and was also measured using a step profilometer after the deposition. The thickness of the deposited ITO thin films was varied in the range from 800 Å to 2500 Å while maintaining the deposition rate was 0.6 Å/s. Other deposition conditions such as rf power to ion gun, bias voltage to the extraction grid, voltage to the acceleration grid, and the distance between ion gun and the substrate were also kept at 100 W, -900 V, 2.1 kV and 65 cm, respectively. The sheet resistance of the deposited ITO was also measured using a four-point probe. An UV-spectrophotometer was used to measure the optical transmittance of the film.

3. Results and discussion

In the ion beam assisted deposition, one of the most important factors affecting the properties of the deposited films is known to be the relative ratio between ion beam flux and evaporated vapor flux. However, in the case of reactive ion beam, not only the ion beam flux to the substrate but also reactive radicals generated in the ion gun can affect the properties of the deposited film. To investigate the effect of reactive radicals on the film properties, the characteristics of the plasma inside of the ion gun were measured using optical emission spectroscopy (OES). Fig. 1 shows one of the OES spectra of oxygen plasmas measured in the ion gun. Optical emission peaks related to the positive molecular oxygen ions (O_2^+) and atomic oxygen radicals (O) could be identified. Among these emission peaks, the O_2^+ peak at 565 nm and the O peak at 616 nm were selected for further investigation.

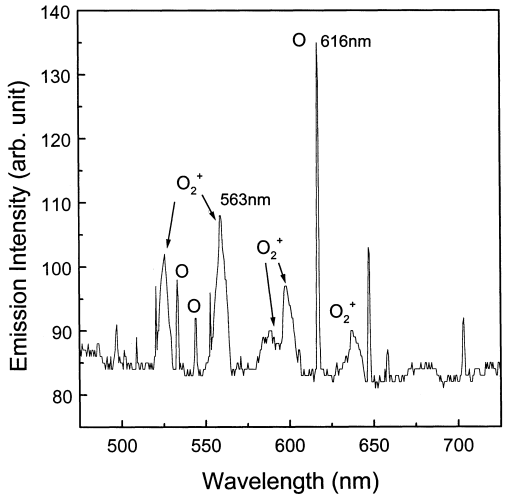

Fig. 1. Optical emission spectrum of oxygen plasma in the ion source chamber measured by optical emission spectroscopy (rf power: 100 W; oxygen flow rate: 6 sccm).

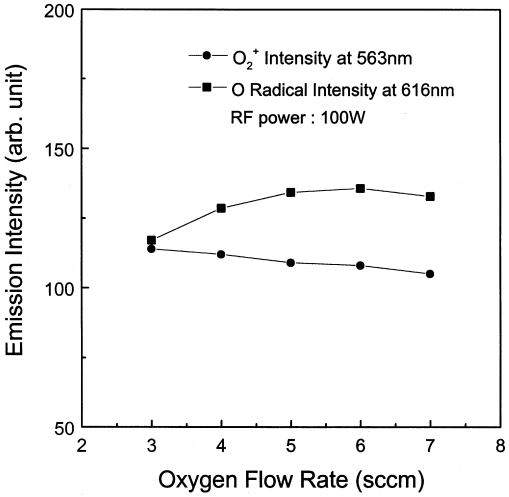

Fig. 2. Optical emission intensities of ionic molecular oxygen at 563 nm and atomic oxygen radical at 616 nm as a function of oxygen flow rate at 100 W of rf power.

Fig. 2 shows the variation of peak intensities of O_2^+ and O as a function of oxygen gas flow rate to the ion gun. The rf power to the ion gun was maintained at 100 W. As shown in the figure, the increase of oxygen gas flow rate decreased the O_2^+ peak intensities, therefore, possibly decreased the O_2^+ ion densities in the ion gun. Lee et al. [11] has reported that, in the case of an ion gun using inductively coupled plasma type, positive ions in the plasma are generally decreased with the increase of pressure from the pressure range of approximately a few 10s of mtorr especially for oxygen plasma, and our results of oxygen ion density on gas flow rate at a fixed rf power appear to agree with the report by Lee et al. In the case of oxygen radicals, the increase of oxygen gas flow rate increased the density of oxygen radicals until 6 sccm of oxygen gas was flown to the ion gun, however, the further increase of oxygen flow decreased the density of oxygen radicals.

To compare the oxygen ion density estimated from the optical emission peaks of O_2^+ in the ion gun, with the actual oxygen ion flux to the substrate, positive ion beam flux extracted through the ion gun grid was measured using a Faraday cup located near the substrate holder at 100 W rf power, −900 V extraction voltage, and 2.1 kV acceleration voltage while varying the oxygen flow rate from 2 sccm to 7 sccm. The result is shown in Fig. 3 and, as shown in the figure, the increase of oxygen flow rate to the ion gun decreased the flux of ions at the substrate similar to the data of oxygen ion density measured by OES. When rf power was increased to 200 W, the similar trend was obtained, however, when rf power was increased to 300 W, the increase of ion flux with the increase of oxygen flow was observed at the low gas flow, and when rf power was increased further to 400 W, the ion flux increased with the increase of oxygen flow rate until 5 sccm of oxygen was flown to the ion gun (not shown). Therefore, there appears to be a certain operational parameter space where the increase of oxygen gas flow rate to the ion gun decreases the ion density in the ion gun.

ITO thin films were deposited on PET substrates at room temperature while varying the oxygen flow rate to the ion gun from 4 sccm to 7 sccm. Other deposition conditions such as rf power to the ion gun, acceleration voltage, extraction voltage, and the distance between the ion gun and the substrate were maintained at 100 W, 2.1 kV, −900 V and 65 cm, respectively. The optical transmittance of the deposited ITO was investigated as a function of oxygen gas flow rate and the results are shown in Fig. 4. As shown in the figure, the increase of oxygen gas flow increased the transmittance of the deposited ITO, however, the transmittance after 6 sccm of oxygen gas flow appeared to saturate. In general, the optical transmittance of ITO thin film increases with the increase of oxygen incorporation into oxygen-deficient ITO thin film. When the ITO thin films were

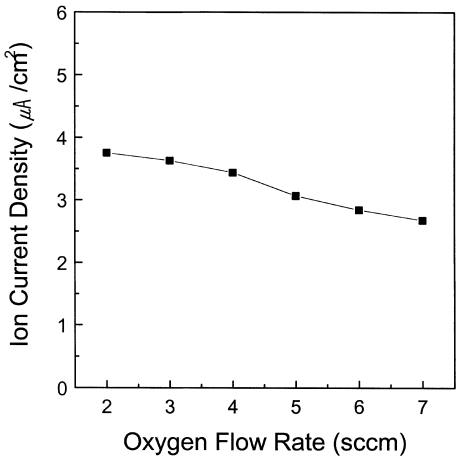

Fig. 3. Ion current density measured by a Faraday cup as a function of oxygen flow rate at 100 W of rf power.

deposited without the assistance of the oxygen ion gun, metallic colored, therefore, oxygen excessively deficient ITO thin films were obtained and, by applying the oxygen ion gun, more transparent ITO thin films were obtained. When oxygen ion gun is applied to ITO deposition, not only the oxygen ion flux extracted from the ion gun but also the atomic oxygen radical dissociated from oxygen molecule in the ion gun can affect the incorporation of oxygen in the deposited ITO film. From Figs. 2 and 3, the ion flux to the substrate decreases with the increase of oxygen gas flow rate, therefore, the increase of optical transmittance in Fig. 4 appears not to be significantly related to the oxygen ion flux to the substrate. Instead, the variation of atomic oxygen radicals with the increase of oxygen gas flow appears to be more responsible for the variation of optical transmittance. The variation of atomic oxygen radical with the increase of oxygen gas flow changed the atomic oxygen radical flux to the substrate, there-

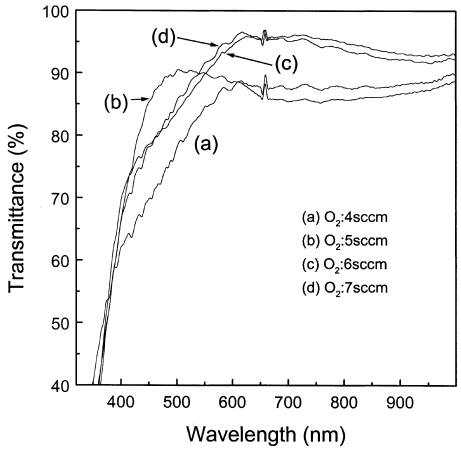

Fig. 4. Variation of the optical transmittance of ITO thin films as a function of oxygen flow rate (rf power: 100 W; Ve: −900 V; Va: 2.1 kV).

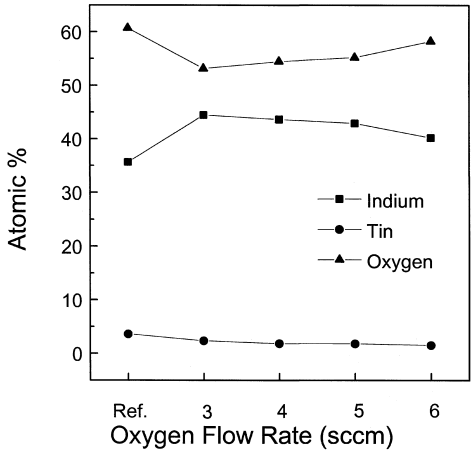

Fig. 5. Variation of the atomic composition of ITO thin films as a function of oxygen flow rate. To remove the native oxygen, the each samples are pre-sputtered at 2 keV for 1 min (rf power: 100 W; Ve: −900 V; Va: 2.1 kV).

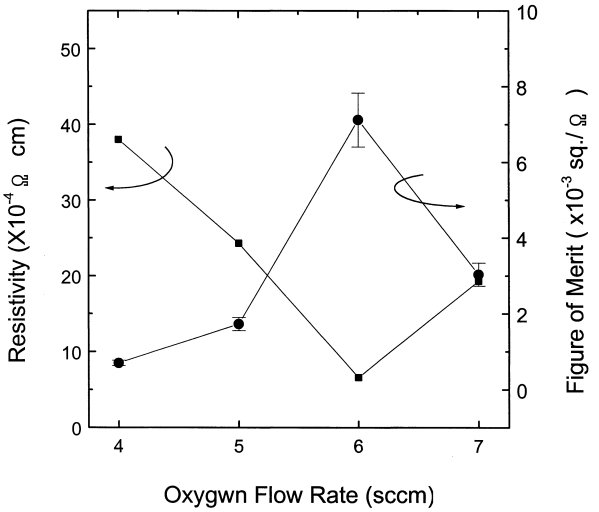

Fig. 6. Variation of sheet resistance and figure of merits as a function of oxygen flow rate (rf power: 100 W; Ve: −900 V; Va: 2.1 kV).

fore, changed the amount of oxygen incorporation to the deposited ITO.

The surface composition with the increase of oxygen flow rate to the ion gun was investigated using X-ray photoelectron spectroscopy and the result is shown in Fig. 5. The surface composition of ITO evaporation source itself was investigated and also included in the figure as a reference. As shown in the figure, ITO thin films deposited at a low oxygen flow rate showed oxygen-deficient films compared to the reference, however, as the oxygen gas flow rate increased to 6 sccm, the increased incorporation of oxygen close to the reference in the deposited ITO could be obtained.

The resistivities of the ITO thin films described in Fig. 4 were measured and the results are shown in Fig. 6. In the figure, the figure of merits defined by Haacke [12] to describe the quality of the transparent thin films was also included on the right-hand side of the figure. As shown in the figure, the resistivity of ITO thin film deposited on PET decreased with the increase of oxygen gas flow up to 6 sccm of oxygen flow and the further increase of oxygen flow increased the resistivity. The trend of the resistivity with oxygen flow was similar to that of atomic oxygen radicals in the ion gun. Therefore, the decrease of electrical resistivity of the deposited ITO thin film appears to be more related to the increased oxygen incorporation of oxygen radical to the ITO thin film for the conditions used in our experiment.

The effect of ITO thickness on the optical transmittance was investigated for the deposition condition with 6 sccm oxygen flow and the results are shown in Fig. 7. Other deposition parameters were kept the same. As shown in the figure, the increase of ITO thickness generally decreased the optical transmittance, however, at the thickness of 2500 Å, the optical transmittance at 550 nm was still higher than 85% which is the required optical transmittance of transparent electrodes for display devices. Therefore, the room temperature ITO deposited on PET in our experiment appears to have a quality applicable to display devices as a transparent electrode.

4. Conclusions

In our experiment, ITO (TO-10 wt.%) thin films were deposited on PET at room temperature using oxygen ion beam assisted electron beam evaporation technique. Oxygen gas flow to the ion gun was varied while other deposition parameters were fixed. The characteristics of the plasma such as atomic oxygen radical density and positive O_2^+ ion density in the ion

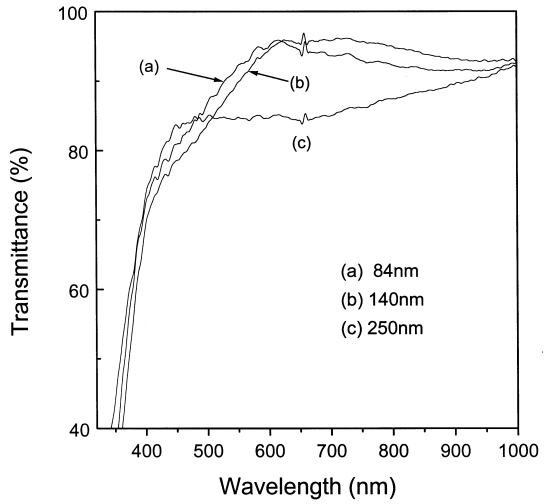

Fig. 7. Variation of the optical transmittance of ITO thin films as a function of thickness (rf power: 100 W; Ve: −900 V; Va: 2.1 kV).

gun were investigated using optical emission spectroscopy and the oxygen ion flux arriving at the substrate was studied using a Faraday cup.

The increase of oxygen flow rate to the ion gun decreased the ion density in the ion gun and also decreased the ion flux to the substrate. However, atomic oxygen radicals measured using optical emission spectroscopy showed a maximum at 6 sccm of oxygen flow with the increase of oxygen flow. The optical transmittance of deposited ITO increased with the increase of oxygen flow rate and appeared to saturate at 6 sccm of oxygen flow rate. In the case of electrical resistivity, the resistivity was the minimum at 6 sccm of oxygen flow. Therefore, from the above results, in increasing the optical transmittance and the electrical conductance of the ITO, not only the oxygen ion beam flux to the substrate but also the atomic oxygen radicals appear to play an important role. At an optimal condition, ITO thin films with a resistivity of 6.6×10^{-4} Ω cm and 90% optical transmittance at 550 nm could be deposited on PET at room temperature.

References

[1] M. Sawada, M. Higuchi, Thin Solid Films 317 (1998) 157.
[2] J.L. Yao, S. Hao, J.S. Wilkinson, Thin Solid Films 189 (1990) 227.
[3] T. Minami, T. Kakumu, K. Shimokawa, S. Takata, Thin Solid Films 317 (1998) 318.
[4] W.F. Wu, B.S. Chiou, Thin Solid Films 298 (1997) 221.
[5] B.S. Chiou, S.T. Hsieh, Thin Solid Films 229 (1993) 229.
[6] A. Mukherjee, Vacuum 39 (1989) 537.
[7] J.A. Dobrosdski, F.C. Ho, D. Menagh, R. Simpson, A. Walderf, Appl. Optics 26 (24) (1987) 5204.
[8] J. Ma, S.Y. Li, J.Q. Zhao, H.L. Ma, Thin Solid Films 307 (1997) 200.
[9] S. Laux, N. Kaiser, A. Zoller, R. Gotzelmann, H. Lauth, H. Bernitzti, Thin Solid Films 335 (1998) 1.
[10] A. Salehi, Thin Solid Films 324 (1998) 214.
[11] C. Lee, M.A. Lieberman, J. Vac. Sci. Technol. A13 (2) (1995) 368.
[12] G. Haacke, J. Appl. Phys. 47 (1976) 4086.