

Properties of amorphous tin-doped indium oxide thin films deposited by O₂/Ar mixture ion beam-assisted system at room temperature

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Abstract

Highly transparent and conductive thin films of tin-doped indium oxide (ITO) on glass substrates were grown by the ion beam-assisted deposition (IBAD) technique without any substrate heating. X-Ray diffraction investigations indicated that all films have an amorphous structure and no other crystalline phases. The addition of Ar to O₂ flow and the increased energy of incident ions were found to reduce the resistivity of the grown films. Observed decrease in the resistivity was attributed to the increase in the carrier concentration. In the optimal growth conditions at room temperature, we obtained the electrical resistivity of $4.6 \times 10^{-4} \Omega\text{-cm}$, visible transmittance (at $\lambda = 550 \text{ nm}$) $\geq 90\%$, and optical direct band gap energy of $\cong 3.75 \text{ eV}$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thin films of transparent conductive oxides (TCO) are used for display devices such as liquid crystal displays (LCDs), electro-luminescent displays (ELDs), field emission displays (FEDs), and electro-chromic displays (ECDs), etc., which require high visible transmittance ($\sim 90\%$) together with a resistivity of $\sim 10^{-4} \Omega\text{-cm}$ [1–3]. In general, zinc oxide (ZnO), cadmium oxide (CdO), cadmium stannate (Cd₂SnO₄), tin oxide (SnO₂), and indium oxide (In₂O₃) have been widely studied as the possible candidates for TCO. Especially, tin-doped indium oxide (ITO) films are known to decrease resistivity significantly because substitutional tin dopants and oxygen vacancies create a high carrier concentration caused by the overlap of the Fermi level with the

conduction level at the bottom of the conduction band [4].

Most of ITO film deposition techniques including sputtering [5], chemical vapor deposition [6], evaporation [7] and spray pyrolysis [8] commonly utilize elevated growth temperature to achieve required conductivity and visible transmittance. Recently ITO films deposited on organic substrate have attracted much attention in flat panel display (FPD) technologies because they have many merits compared with those deposited on glass substrate, such as light weight, small volume and flexibility of devices [9]. Deposition on organic substrates, however, requires room temperature or near room temperature growth techniques due to their thermal instability at elevated temperature, which gives poor electrical conductivity and visible transmittance. For the successful room temperature growth, the use of reactive oxygen ion-beam is very promising because the bombardment of growing film surfaces by energetic oxygen ion-beam significantly enhances the electrical and optical properties of films by

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improving film quality as well as by compensating oxygen deficiency of the evaporated ITO flux. Recently, the bombardment of growing film surfaces by an Ar^+ ion-beam only in an oxygen atmosphere resulted in obtaining the good quality ITO films at room temperature [10].

In this paper, ITO films were deposited on glass substrates at room temperature using an e-beam evaporated ITO flux and assisted O_2/Ar mixture ion-beam with various fluxes and energies to elucidate the correlation between ion-beam parameters and structural, electrical and optical properties of the grown films.

2. Experimental procedure

The equipment used for film deposition was a conventional e-beam evaporation system equipped with an ion source for the supply of O_2/Ar mixture ion-beam and a turbomolecular pump. The ion source used in these experiments was a RF (radio-frequency) inductive-plasma type because the conventional Kaufman source containing a hot filament cannot be used in an oxygen atmosphere due to the oxidation-induced degradation of the filament. The ion source has two grids, where one is for the acceleration of the ions from 0 to 3 kV and the other is for the extraction of the ions from 0 to -1 kV.

Sodalime silicate glass substrates were cleaned ultrasonically in acetone, ethyl alcohol and deionized water to remove organic contaminations. Prior to deposition, the substrate surfaces were pre-cleaned using Ar^+ ion-beam bombardment for 5 min in order to further reduce impurities on the substrate surfaces. The evaporation source material used for the generation of ITO flux was a mixed ITO bulk with 90 wt.% In_2O_3 and 10 wt.% SnO_2 with a purity of 99.99%. During the deposition, the substrate was rotated without heating and deposition conditions such as RF power of ion source, P_{rf} , grid extraction voltage, V_{ex} , distance between the substrate and the ion source, and incident ion-beam angle between the ion source and the substrate were kept at 100 W, -100 V, 35 cm, and 40° , respectively. The film growth rate, R , was maintained at 1 Å/s using a quartz crystal monitor and the total film thickness was $\cong 1200$ Å. The chamber was evacuated to a base pressure of $\cong 1 \times 10^{-6}$ torr initially and the chamber pressure during deposition was maintained at $5.9 \times 10^{-5} \sim 4.4 \times 10^{-4}$ torr by fixing the oxygen flow to the RF ion source at 6 sccm and by adding Ar flow rate from 0 to 4 sccm. The energy of O_2/Ar mixture ion-beams was varied by increasing the grid acceleration voltage, V_{ac} , from 0.4 to 2 kV. The relative density of oxygen ion (O_2^+) and argon ion (Ar^+) in the ion source was analyzed by optical emission spectroscopy (OES) to investigate the effects of Ar addition to the relative

intensity of O_2^+ species in the ion source. The structural, electrical and optical properties of as-deposited ITO films were measured using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Hall-effect measurement, and UV-visible spectrometry.

3. Results and discussion

The microstructure of all as-deposited ITO films was analyzed by XRD. An amorphous structure without any other crystalline phases was observed based on the XRD spectrum. These results agree well with other reports that the ITO films deposited at room temperature and near-room temperature by various deposition techniques have an amorphous structure because the low-growth-temperature limits or freezes the motion of adatoms on the film surface and prevents them from diffusing and seeking out equilibrium lattice sites [11,12].

In order to investigate any shifts in the chemical bonding states of grown films from those of the bulk ITO, we have performed XPS measurements for the ITO films by varying O_2/Ar flow rate ratio and the bulk ITO source used for the evaporation. The results are shown in Fig. 1. From the literature [13] it can be found that the binding energies of In 3 $d^{3/2}$ and Sn 3 $d^{3/2}$ are 443.9 eV and 485 eV, respectively. When indium (In) and tin (Sn) oxidize into indium oxide (In_2O_3) and tin oxide (SnO_2), the binding energies of In 3 $d^{3/2}$ and Sn 3 $d^{3/2}$ shift to 444.3 eV and 486.7 eV, respectively. No change in the binding energies of In 3 $d^{3/2}$ and Sn 3 $d^{3/2}$ in the ITO films from those in the ITO bulk indicates that bonding states of In and Sn in the films are also the same as those of the ITO bulk.

Fig. 2 shows the resistivity, carrier concentration, and Hall mobility as a function of O_2/Ar flow rate ratio. The values of resistivity decrease with increasing Ar flow rate from 0.6 to 4 sccm in Fig. 2a. While the resistivity of the ITO films deposited using the oxygen ion-beam only was 7.7×10^{-4} Ω-c m the resistivities were decreased to 5.1×10^{-4} Ω-cm when Ar flow of 1 sccm was added to O_2 flow of 6 sccm and then saturated after showing a slight increase as Ar flow increased further up to 4 sccm. The variation of the carrier concentration in Fig. 2b shows the minimum value of 2.2×10^{20} cm^{-3} with the use of oxygen ion-beam only and then the saturated value of 4.2×10^{20} cm^{-3} after showing a slight increase with increasing Ar flow. In contrast, except for the ITO films deposited by the oxygen ion-beam only no significant variation of Hall mobility values was observed. The results indicate that the enhancement of conductivity was not caused by the increase in carrier mobility due to the nature of amorphous structure of the grown films [14]. In our experiment, the observed decrease of resistivity is pri-

marily attributed to the increase of carrier concentration.

In order to verify the relationship between the carrier concentration and the variation of the oxygen vacancy concentration and the substituent Sn in the films, we measured Sn/In and O/(In + Sn) as a function of O₂/Ar flow rate ratio by computing the area of XPS peaks (In 3 *d*^{5/2}, Sn 3 *d*^{5/2} and O) in Fig. 1 using Eclipse software with the sensitivity factor. As seen in Fig. 3, the concentration of dopant Sn was not changed significantly with increasing Ar flow rate, but the oxygen concentration reached a minimum at the Ar flow rate of 1 sccm and slightly increased with increasing Ar

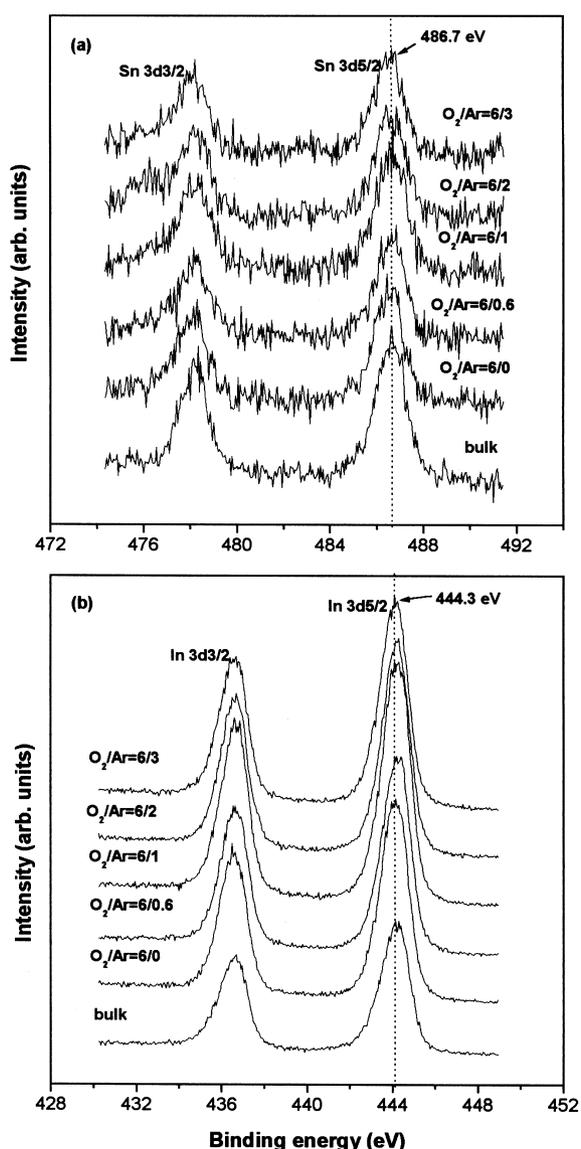


Fig. 1. XPS spectra of the ITO source (90 wt.% In₂O₃ ~ 10 wt.% SnO₂) and the ITO films deposited as a function of O₂/Ar flow rate ratio. (a) Sn 3 *d*^{5/2}: 485 eV and Sn-O₂: 486.7 eV. (b) In 3 *d*^{5/2}: 443.9 eV and In₂O₃: 444.3 eV ($P_{\text{rf}} = 100$ W, $V_{\text{ex}} = -100$ V, $V_{\text{ac}} = 0.8$ kV, $R = 1 \text{ \AA/s}$).

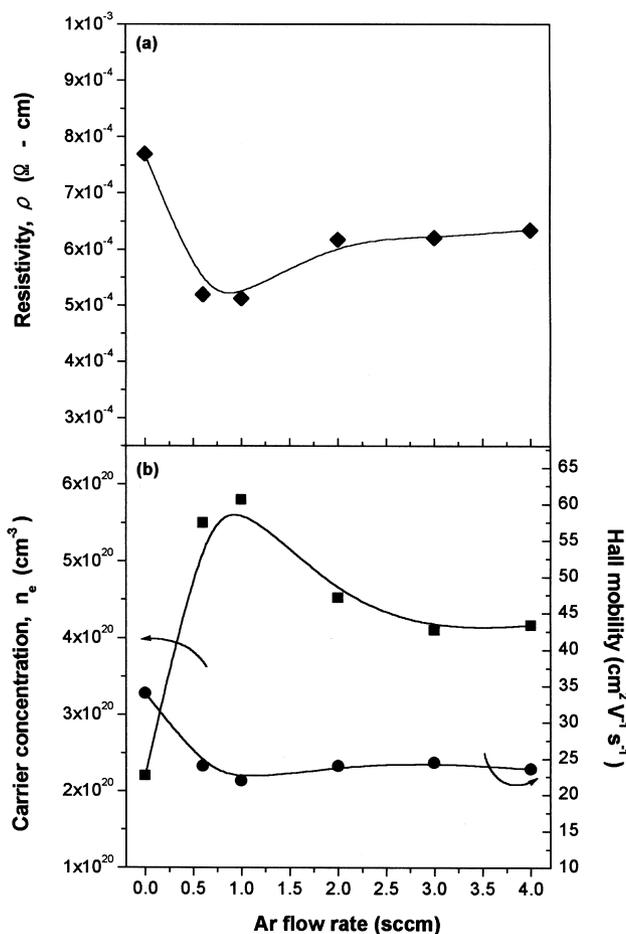


Fig. 2. Variations of (a) resistivity and (b) electron carrier concentration and Hall mobility of ITO thin films deposited as a function of O₂/Ar flow rate ratio measured by Hall measurement ($P_{\text{rf}} = 100$ W, $V_{\text{ex}} = -100$ V, $V_{\text{ac}} = 0.8$ kV, $R = 1 \text{ \AA/s}$).

flow rate. These results indicate that the decrease of resistivity caused by the increase of carrier concentration in the films is primarily due to the increase in the concentration of oxygen vacancies which can contribute two electrons to the conduction band rather than due to the variation of the dopant Sn which can render one electron to the conduction band.

Fig. 4 shows the relative emission intensities of O₂⁺ and Ar⁺ ions in the ion source measured by OES. The relative emission intensity of O₂⁺ decreased slightly with increasing Ar flow rate but that of Ar⁺ increased gradually. If we assume that the ion flux extracted from the ion source is proportional to that in the ion source, this result agrees well with the fact that the oxygen concentration in the films decreased with increasing Ar flow rate.

The visible transmittances of the ITO thin films deposited by varying the O₂/Ar flow rate ratio are shown in Fig. 5. All transmittance values were normalized using the transmittance of a bare glass substrate as a reference. As shown in the Fig. 5, the visible trans-

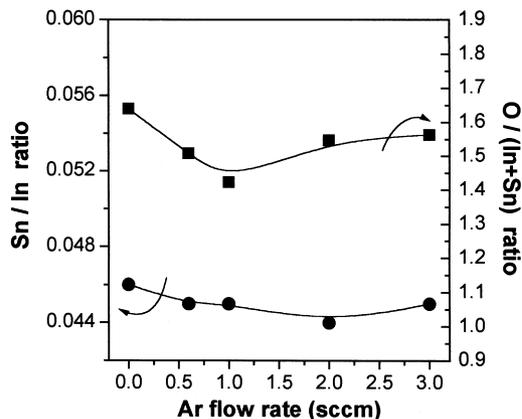


Fig. 3. Chemical composition of ITO thin films deposited as a function of O_2/Ar flow rate ratio measured by XPS ($P_{rf} = 100$ W, $V_{ex} = -100$ V, $V_{ac} = 0.8$ kV, $R = 1$ Å/s).

mittance (at $\lambda = 550$ nm) was typically larger than 90% in all ITO films. Especially, the visible transmittance of the ITO film deposited by the oxygen ion-beam only was higher than that of the films deposited with additional of Ar. The values of optical direct band gap energy, E_g , were extracted by extrapolating the straight regions of the plots of the squared absorption coefficient, α^2 , vs. photon energy, $h\nu$. The absorption coefficient, α was determined by the relation, $(\alpha h\nu)^2 = h\nu - E_g$. Based on this relationship, E_g was ≈ 3.75 eV.

As another deposition parameter, the ion-beam grid acceleration voltage, V_{ac} , which determines the energy of bombarding ions on the growing surface was varied in order to improve the quality of grown films. For this purpose, V_{ac} was varied from 0.4 to 2 kV while other parameters such as RF power, grid extraction voltage

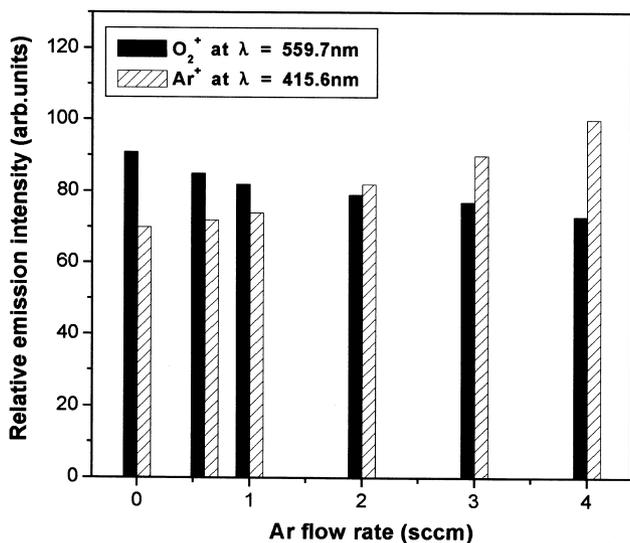


Fig. 4. Relative emission intensities of O_2^+ and Ar^+ in the ion source as a function of O_2/Ar flow rate ratio measured by OES at $P_{rf} = 100$ W.

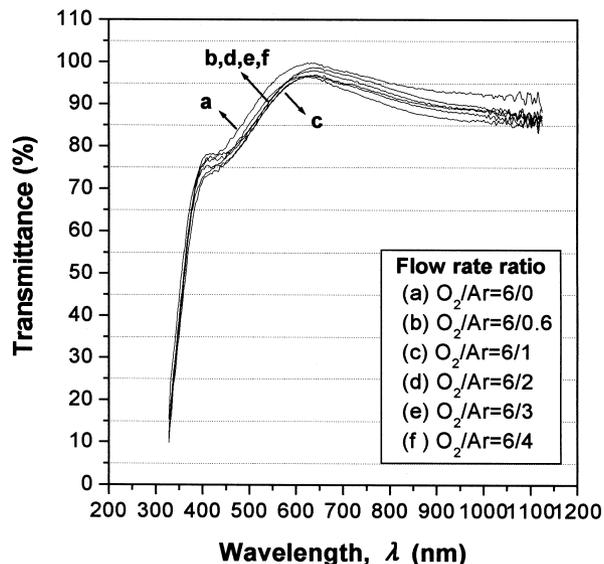


Fig. 5. Variations of the optical transmittance of ITO thin films deposited as a function of O_2/Ar flow rate ratio measured by UV-visible spectrometer ($P_{rf} = 100$ W, $V_{ex} = -100$ V, $V_{ac} = 0.8$ kV, $R = 1$ Å/s).

V_{ex} , deposition rate R , and O_2/Ar flow rate ratio were fixed at 100 W, -100 V, 1 Å/s, and $6/1$, respectively. Fig. 6 exhibits the variation of resistivity, carrier concentration, and Hall mobility as a function of V_{ac} . The resistivity decreased rapidly until V_{ac} reached 0.8 kV and the further increase of V_{ac} slowly decreased the resistivity of the deposited ITO thin films. The slow decrease in resistivity with the increase of $V_{ac} \geq 0.8$ kV appears to be related to the improvement of crystallinity due to, e.g. the improvement of the film density by the increased supply of energy to the atoms depositing on the substrate. This is plausible because the Hall mobility slowly increased while the carrier concentration was maintained at $\approx 5.7 \times 10^{20}$ cm^{-3} with V_{ac} increasing from 0.8 to 2 kV. The rapid increase of resistivity at the $V_{ac} = 0.4$ kV appears to be caused by the rapid decrease of ion-beam flux.

The visible transmittances of the ITO films deposited as a function of V_{ac} , measured by UV-visible spectrometer, were close to 93% from 0.8 kV to 2 kV without a significant variation. The optical direct band gap energies, E_g , were ≈ 3.8 eV, similarly to the values of the ITO films deposited at $V_{ac} = 0.8$ keV with the variation of other deposition parameters.

4. Conclusions

In this study, the influence of various conditions of O_2/Ar mixture ion-beams on the structural, electrical, and optical properties of ITO thin films deposited onto unheated glass substrates was investigated. The resistiv-

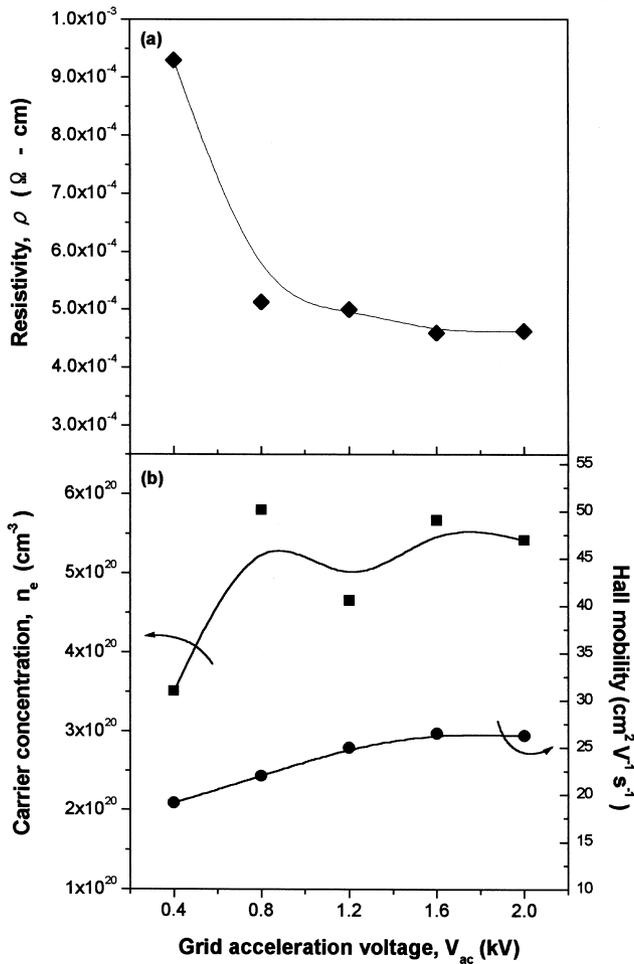


Fig. 6. Variations of (a) resistivity and (b) electron carrier concentration and Hall mobility of ITO thin films deposited as a function of grid acceleration voltage, V_{ac} , for ion source measured by Hall measurement ($P_{rf} = 100$ W, $V_{ex} = -100$ V, $R = 1 \text{ \AA/s}$, O_2/Ar flow rate ratio = 6/1).

ity of the ITO films deposited by an additive Ar flow was decreased compared with that of the ITO films deposited using the oxygen ion-beam only. Also, the

increase of the ion energy by increasing the grid acceleration voltage from 0.4 to 2 kV reduced the electrical resistivity. Because of the amorphous nature of the grown films at room temperature, the decrease in resistivity was primarily attributed to the increase of carrier concentration rather than the increase of carrier mobility. In the optimal growth conditions with $P_{rf} = 100$ W, $V_{ex} = -100$ V, $V_{ac} = 1.6$ kV, O_2/Ar flow rate ratio = 6/1, and $R = 1 \text{ \AA/s}$, we obtained the ITO films with the resistivity of $4.6 \times 10^{-4} \text{ \Omega-cm}$ and the visible optical transmittance $\geq 90\%$.

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