



Effects of oxygen ion beam plasma conditions on the properties of Indium tin oxide thin films

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Abstract

Tin-doped indium oxide (ITO) films were deposited at room temperature by ion beam-assisted evaporation and the effects of oxygen ion beam conditions on the properties of room-temperature ITO thin films were investigated. It is well known that high conductivity of ITO is caused by intrinsic defect (oxygen vacancy) and dopant (tin). One of the techniques to obtain highly conductive ITO film at room temperature is to cause electron degeneracy in the band gap by introducing non-stoichiometry in the ITO film using oxygen ion beam plasma while evaporating ITO films using an electron beam evaporation. In this study, flux and energy of oxygen ion beam plasma were varied to modify depositing ITO thin films by controlling gas flow rates and grid bias potential. The structure of deposited ITO thin film was amorphous for all of the experimental conditions. The increase of oxygen ion beam flux increased the optical transmittance of the deposited ITO film, however, at a given ITO evaporation rate, the resistivity showed a minimum in a certain range of ion beam flux. The increase of oxygen ion beam energy up to 900 V decreased the resistivity and increased the optical transmittance of deposited ITO thin films. Using the oxygen ion beam-assisted method, ITO thin films with the resistivity of $5.2 \times 10^{-4} \Omega \text{ cm}$ and optical transmittance of above 90% could be deposited at room temperature. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: ITO; Oxygen ion beam; Evaporation

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, photovoltaic cells, and opto-electronic devices [1–3]. To satisfy technical requirements of each specific applications, many new materials and various manufacturing techniques have been developed [4–6].

The most widely used materials for transparent conductive thin films are semiconducting oxides such as zinc oxide (ZO), tin oxide (TO), and indium oxide (IO). Compared to TO, ZO, and IO, tin-doped indium oxide (ITO) has the lowest electrical resistivity ($\sim 10^{-4} \Omega \text{ cm}$) 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.

The development trends for ITO coating technique can be integrated into decrease of operation temperature for using various substrate materials. ITO has been produced by a number of techniques such as chemical vapor deposition (CVD) [7], pulsed laser deposition (PLD) [8], DC (or rf)-sputtering [9], and evaporation [10–12]. Among these techniques, DC (or rf)-sputtering techniques are the most widely applied to industrial applications, however, plasma assisted-evaporations could be promising techniques for low-temperature deposition. In particular, ion beam-assisted electron beam evaporation (IBAE) technique offers several advantages such as more flexibility in controlling film properties and room-temperature coating on organic substrates without any post deposition treatment. In this IBAE technique, the establishment of parameters of ion beam plasma is very important. Those are the flux and energy of the ion beam, the uniformity of the beam, and the distance between ion gun and substrate.

In this study, the effects of the interaction between oxygen ion beam plasma and the surface of substrate during ITO film growth on the physical, electrical, and optical properties of the films were investigated

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by varying oxygen ion beam energy and flux to the substrate.

2. Experimental conditions

The deposition of tin-doped indium oxide was carried out by an oxygen ion gun attached electron beam evaporator system. Sodaslime silicate (SLS) glass was used as the substrate. Evaporation source material was indium oxide 90 wt%–tin oxide 10 wt% and the purity was 4N. Rf inductively coupled plasma was used as the oxygen ion source. 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. Also rf source offers several advantages such as long-life operation and clean plasma production.

The schematic diagram of the deposition system used in our experiment is shown in Fig. 1. The rf ion gun is contained in the vacuum chamber and the incident beam angle of the ion gun could be varied from 0 to 60° from the normal of the substrate. To enhance the plasma density of the source, permanent magnets were applied around the wall of the ion source.

The current density and energy of the ion beam in the process region were measured using a Faraday cup located near the substrate holder. To measure the ion beam energy as a function of acceleration voltage of ion gun, positive bias voltage in the range from 0 to 1 kV was applied to the grid of the Faraday cup. The pressure in the chamber during the deposition process was changed from 8×10^{-5} T to 2.6×10^{-4} T by varying the oxygen flow to the rf ion source from 2 to 10 sccm as a discharge gas. The energy of the oxygen ion beam was varied by increasing the acceleration voltage from 400 to 900 V.

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 deposition. The thicknesses of the deposited ITO thin films were kept same as 1000 \AA and the deposition rate was maintained at 0.6 \AA/s . Other deposition conditions such as rf power to ion gun, extraction grid bias voltage, and the distance between ion gun and the substrate were also kept at 100 W, -200 V , and 60 cm, respectively.

The structure of the film was characterized by X-ray diffractometry (XRD). The electrical properties of the film such as resistivity, carrier concentration, and mobility were analyzed by using Hall measurement. The resistivity was also measured using a four point probe. An UV-spectrophotometer was applied to measure the optical transmittance of the film.

3. Results and discussion

The structure of the ITO thin films deposited in our experiments was investigated using XRD and the typical result is shown in Fig. 2. All of the deposited ITO thin films showed an amorphous structure as shown in the figure. In fact, many researchers have reported that the structure of ITO thin films deposited at room temperature are amorphous and, especially due to their structural defect, Bellingham et al. [13] reports that the mobility of the electrons in the amorphous ITO thin films cannot contribute the enhancement of the electrical conductivity significantly. Therefore, to increase the electrical conductivity, rather than trying to enhance the mobility of the electrons, the density of carriers should be increased. That is, to improve the electrical conductivity of our ITO thin films, the control of oxygen vacancy concentration and tin-dopant concentration is very important.

To improve the electrical and optical properties of ITO thin films, gas flow rate of oxygen ion beam plasma

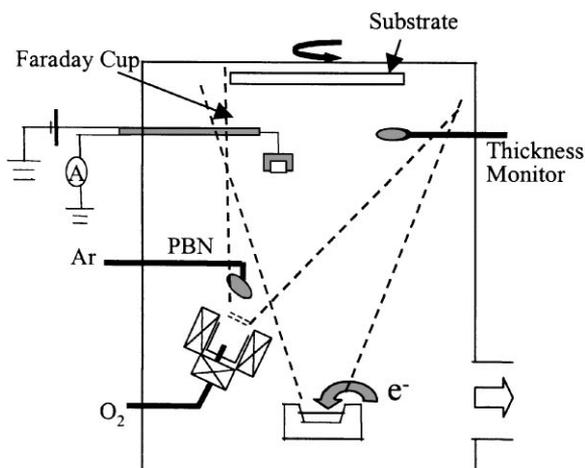


Fig. 1. A schematic diagram of the IBAE system used in the experiment.

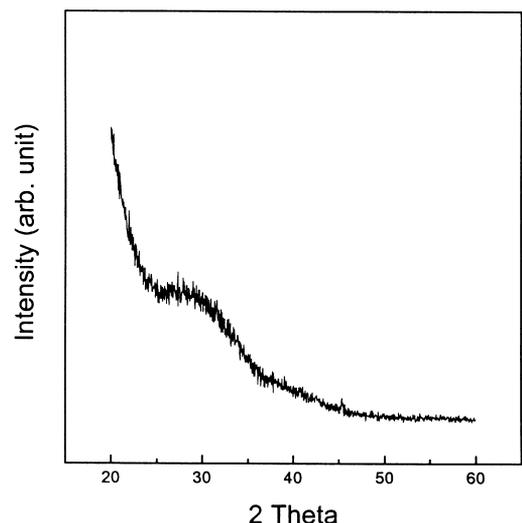


Fig. 2. XRD of ITO thin film deposited at room temperature.

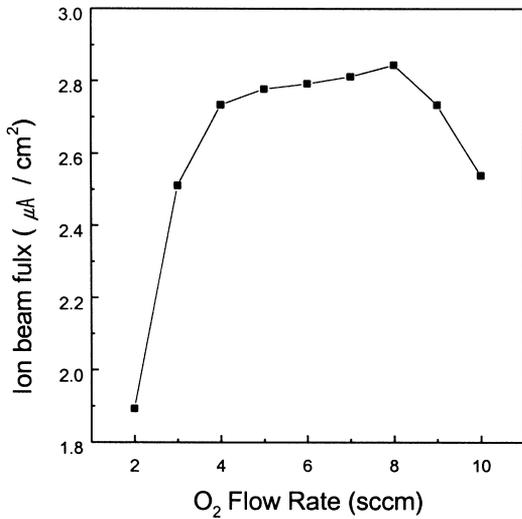


Fig. 3. Variation of oxygen ion beam flux as a function of oxygen gas flow rate (RF power: 100 W, V_c : -200 V, V_a : 800 V).

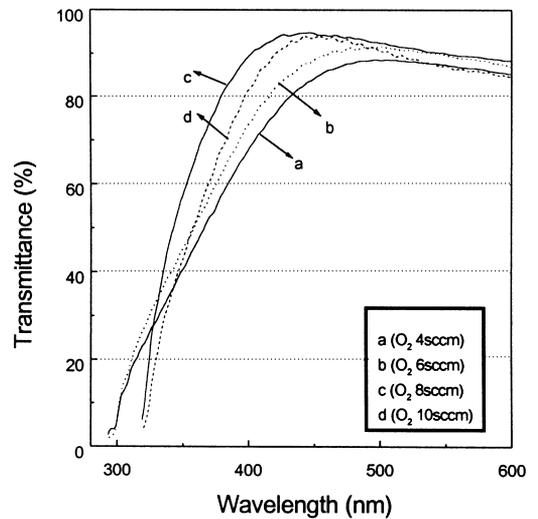


Fig. 4. Variation of the optical transmittance of ITO thin films as a function of oxygen gas flow rate (RF power: 100 W, V_c : -200 V, V_a : 800 V).

source was varied while maintaining other deposition parameters. The deposition rate was kept at 0.6 Å/s, rf power at 100 W, extraction grid voltage at -200 V, and acceleration grid voltage at +800 V. The effect of gas flow rate of the ion beam plasma source on the ion beam flux to the substrate was measured using a Faraday cup located near the substrate and the result is shown in Fig. 3. The increase of gas flow rate of ion beam plasma source increased the ion beam flux to the substrate until 8 sccm of oxygen was reached. The increase of ion beam flux with the increase of gas flow rate is related to the increase of plasma density in the ion beam source. However, the decrease of ion beam flux at the high gas flow rate appears to be related to be the energy loss due to the formation of ion–electron pairs as reported by Lee et al. [14].

Optical transmittances of the ITO thin films deposited by varying the oxygen gas flow rate at the conditions described above are shown in Fig. 4. As shown in the figure, the optical transmittance increased with the increase of oxygen gas flux up to 8 sccm of oxygen gas flow and the further increase of oxygen gas flow decreased the optical transmittance in general. The increase and decrease of optical transmittance appears to be due to the change of the flux ratio between the oxygen ion flux and evaporated ITO flux. When oxygen ion flux is low at a given ITO evaporation rate, the deposited ITO thin film showed a deep brownish color and the optical transmittance decreased drastically showing the lack of oxygen in the film. Therefore, even though the ITO evaporation source itself has stoichiometric oxygen content in the material, oxygen deficient films were obtained on the substrate under no or low-oxygen ion flux conditions.

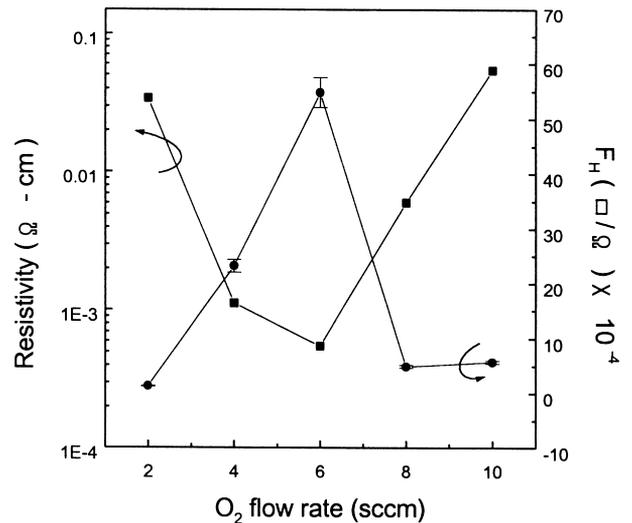


Fig. 5. Variation of resistivity and figure of merit as a function of oxygen gas flow rate (RF power: 100 W, V_c : -200 V, V_a : 800 V).

Fig. 5 shows the variation of resistivity of the ITO thin films deposited with the same conditions described in Fig. 4. The resistivity showed a minimum value at 6 sccm of oxygen gas flow. The increase of oxygen gas flow, that is, the increase of oxygen ion beam flux, increased the oxygen incorporation into the oxygen-deficient ITO film, and which reduced the resistivity of the film by compensating too high oxygen vacancies in the evaporated ITO thin film. However, the increase of oxygen flow higher than 6 sccm decreased oxygen vacancies in the film more than the required amount, therefore, increased the resistivity of the film. As shown in Fig. 4, the ITO thin film

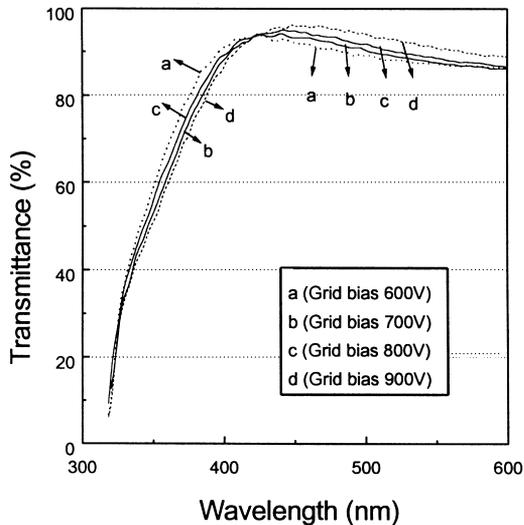


Fig. 6. Variation of the optical transmittance of ITO thin films as a function of acceleration voltage (RF power: 100 W, V_c : -200 V, oxygen flow rate: 6 sccm).

deposited at 8 sccm of oxygen gas flow showed the transmittance higher than 93%, however, the resistivity was very high and was close to the insulator. In Fig. 5, the figure of merit (F_H) defined by Haacke [15] is also shown. F_H is one of the indices used to compare among the various transparent conducting thin films. F_H is defined by $F_H = T^x/R_{\square}$, and where T is transmittance, R_{\square} is sheet resistance, and x is a value depending on the transmittance of the material (at 90, 95, and 99% of optical transmittance, x is 10, 20, and 100, respectively) [16]. It is known that higher the F_H , better quality of the material is represented. Therefore, from Fig. 5, the optimum oxygen flow is 6 sccm, where F_H is the highest, if other deposition parameters are maintained same as described above.

As another deposition parameter to improve the quality of the film, the ion beam acceleration voltage was varied while other parameters such as evaporation rate, rf power, extraction voltage, and oxygen gas flow rate are fixed at 0.6 \square/s , 100 W, -200 V, and 6 sccm, respectively. Fig. 6 shows the optical transmittance of the ITO thin films deposited with the above condition while varying the acceleration voltage, therefore, oxygen ion energy to the substrate. As shown in the figure, the increase acceleration voltage increased the optical transmittance, however, the degree of increase was small. Therefore, it appears that the effect of ion beam energy on the optical transmittance of the deposited ITO thin films is small if an adequate flux ratio between oxygen ion beam flux and ITO evaporation flux is maintained.

Fig. 7 shows the resistivity and F_H measured as a function of acceleration voltage with the same conditions

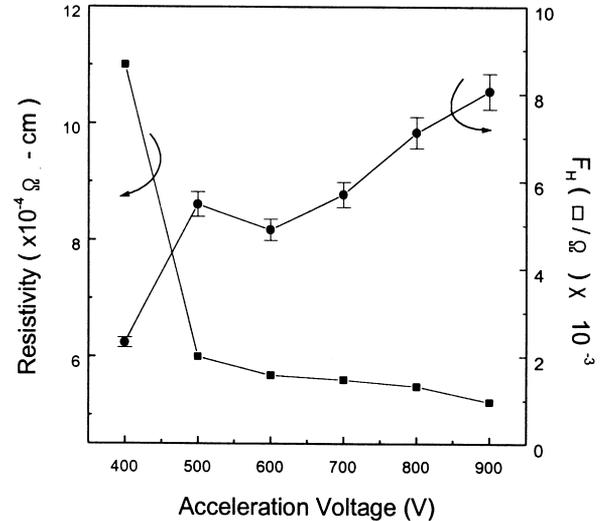


Fig. 7. Variation of resistivity and figure of merit as a function of acceleration voltage (RF power: 100 W, V_c : -200 V, oxygen flow rate: 6 sccm).

described in Fig. 6. The resistivity decreased rapidly until the acceleration voltage is reached to 500 V and the further increase of acceleration voltage slowly decreased the resistivity of the deposited ITO thin films. The rapid decrease of resistivity with the acceleration voltage up to 500 V appears to be more related to the rapid increase of ion beam flux. Because, in our experimental condition, the distance between the oxygen ion gun and the substrate is 60 cm apart, some of the ion beam flux may not be able to reach the substrate due to the scattering. The oxygen ion beam flux which arrives at the substrate can be estimated by measuring ion beam flux reaching the Faraday cup located near the substrate. Fig. 8 shows the ion beam flux measured using the Faraday cup as a function of acceleration voltage while other conditions are maintained as described above. As shown in Fig. 8, the ion beam flux increased until 500 V of acceleration voltage was reached and the further increase of acceleration voltage saturated the ion beam flux to the Faraday cup. The slow decrease of resistivity with the increase of acceleration voltage above 500 V, therefore, appears to be more related to the improvement of crystallinity such as improvement of the density of the deposited ITO thin films by supplying energy to the atoms depositing on the substrate. In Fig. 7, the figure of merit is also shown and F_H increased with the increase of acceleration voltage, therefore, the increase of ion beam energy increased the quality of the deposited ITO thin films for the experimental conditions investigated. Finally, with 6 sccm of oxygen gas flow and 900 V of acceleration voltage, we were able to obtain a room temperature ITO thin film with the resistivity of $5.2 \times 10^{-4} \Omega \text{ cm}$ and the optical transmittance of above 90%.

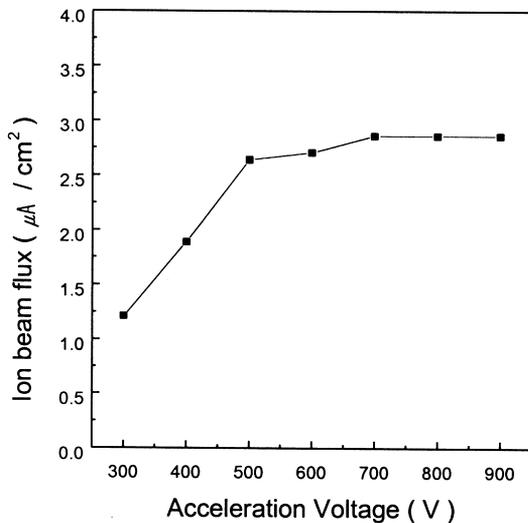


Fig. 8. Variation of oxygen ion beam flux as a function of acceleration voltage (RF power: 100 W, V_c : -200 V, oxygen flow rate: 6 sccm).

4. Conclusions

In this study, electron beam evaporation assisted by rf oxygen ion beam plasma has been used to deposit room-temperature ITO thin films and the effects of oxygen gas flow and acceleration grid voltage of the ion gun on the physical, electrical, and optical properties of deposited ITO thin films were investigated.

The structure of the deposited ITO thin films was amorphous, therefore, the electrical properties of the deposited ITO thin film were more affected by carrier density controlled by the oxygen vacancy than the mobility of the electrons. The deposited ITO thin films with no or low-oxygen ion flux to the substrate showed low optical transmittance and the increase of the oxygen ion flux increased the optical transmittance of the deposited ITO thin films. However, the deposited ITO thin films showed a minimum resistivity at a certain range of the oxygen ion flux at a given ITO evaporation rate, therefore, there appeared to be an optimum ratio between

oxygen ion flux and ITO evaporation flux to satisfy optimum oxygen vacancy concentration in the deposited ITO thin film. The increase of the oxygen ion energy from 400 to 900 V increased both the optical transmission and conductivity of the deposited ITO thin film. The increase of optical transmission with the increase of oxygen ion energy appeared to be more related to the increase of ion flux reaching the substrate and the decrease of resistivity with the increase of oxygen ion energy appeared to be more related to the increase of quality of the ITO thin films by supplying energy to the depositing atoms on the substrate. From the experimental conditions investigated, the ITO thin films with the resistivity of $5.2 \times 10^{-4} \Omega \text{ cm}$ and the optical transmission of above 90% could be obtained.

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References

- [1] Green M, Smith WC, Weiner JA. *Thin Solid Films* 1976;38:89.
- [2] Hagerott M, Jeon H, Nurmikko AV, Xie W, Grillo DC, Kobayashi M, Gunshor RL. *Appl Phys Lett* 1992;60:2825.
- [3] Goodman LA. *Thin RCA Rev* 1974;35:613.
- [4] Sawada M, Higuchi M. *Thin Solid Films* 1998;317:157.
- [5] Yao JL, Hao S, Wilkinson JS. *Thin Solid Films* 1990;189:227.
- [6] Minami T, Kakumu T, Shimokawa K, Takata S. *Thin Solid Films* 1998;317:318.
- [7] Badawy WA, Afify HH, Elgiar EM. *J Electrochem Soc* 1990;137:1592.
- [8] Zheng JP, Kwok HS. *Thin Solid Films* 1993;232:99.
- [9] Ichihara K, Inoue N, Okubo M. *Thin Solid Films* 1994;245:152.
- [10] Quaas M, Eggs C, Wulff H. *Thin Solid Films* 1998;332:277.
- [11] Coutal C, Azema A, Roustan JC. *Thin Solid Films* 1996;288:248.
- [12] Rauf IA. *Mater Lett* 1993;18:123.
- [13] Bellingham JR, Phillips WA, Adkins CJ. *Thin Solid Films* 1991;195:23.
- [14] Lee C, Lieberman MA. *J Vac Sci Technol A* 1995;13(2):368.
- [15] Haacke G. *J Appl Phys* 1976;47:4086.
- [16] Knickerbocker SA, Kulkarni AK. *J Vac Sci Technol A* 1995;13(3):1048.