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Electrical, optical, and structural characteristics of ITO thin films by krypton and oxygen dual ion-beam assisted evaporation at room temperature

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Abstract

Transparent conducting tin-doped indium oxide (ITO) thin films on polycarbonate and glass substrates were deposited without substrate heating and post-deposition annealing using a dual ion-beam assisted evaporation technique, where the bombardment of the growing film surfaces during electron beam evaporation was done using krypton (varied ion flux, J_{Kr^+}, and grid acceleration voltage, V_a, of the krypton ion source) and oxygen (fixed ion flux and grid acceleration voltage of the oxygen ion source) ion beams. The electrical, optical, and structural effects of krypton ion-beam bombardment of the growing ITO thin films were investigated using Hall-effect measurements, X-ray photoelectron spectroscopy (XPS), UV-visible spectrometry, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The total film thickness and the deposition rate were 100 nm and 0.06 nm/s, respectively. All ITO films grown with $J_{Kr^+} = 1.92–3.76 \times 10^{14}$ cm^{-2} s^{-1} and $V_a = 100–500$ V showed an amorphous structure and no other crystalline phases. As J_{Kr^+} increased, the electrical conductivity and the optical transmittance of the grown films were improved compared with those of the ITO films deposited using the oxygen ion-beam only. Also, an increase of the bombardment energy by increasing V_a of the krypton ion source caused the deterioration of ITO film properties. The conductivity and the optical transmittance of ITO films deposited on polycarbonate substrates were a little lower than those of films on glass substrates. At room-temperature, using optimal growth conditions, the electrical resistivity was as low as 6.4×10^{-4} Ω cm with an electron carrier concentration $n_e = 4.3 \times 10^{20}$ cm^{-3} and a Hall mobility $\mu_H = 26.7$ cm^2 V^{-1} s^{-1}, the visible transmittance (at $\lambda = 550$ nm) was 90%, and optical direct band gap energy 3.8 eV.

Keywords: Tin-doped indium oxide (ITO); Ion bombardment; Ion-beam assisted evaporation; Room-temperature deposition

1. Introduction

Although a large variety of transparent and electrically conductive oxides (TCO) are known, such as zinc oxide (ZnO), tin oxide (SnO_2), indium oxide (In_2O_3) and cadmium stannate (Cd_2SnO_4), especially tin-doped indium oxide (ITO) thin films are very widely used as transparent conducting electrodes for solar cell, displays, organic light emitting diodes (OLEDs), and other electro/optical devices [1,2]. An ITO thin film is a highly degenerated n-type semiconductor which has a low electrical resistivity of $\cong 10^{-4}$ Ω cm and a high optical transmittance of $\cong 85\%$ in the visible region. A low resistivity of ITO films containing $5 \sim 10$ wt.% of tin oxide in indium oxide is attributed to a high electron carrier concentration caused by the overlap of the Fermi level with the conduction level at the bottom of the conduction band [3]. The electron carrier concentration of highly conductive ITO films ranges from $\cong 10^{20}$ to $\cong 10^{21}$ cm^{-3}. Moreover, ITO is a wide band gap semiconductor ($E_g = 3.5 \sim 4.3$ eV), showing high

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optical transmittance in the visible and near-IR regions of the spectrum [4].

Recently, many devices in flat panel display (FPD) technologies often demand the use of flexible substrates such as organic materials. In the case of deposition on the temperature-sensitive substrates, special techniques, such as pulsed-laser deposition [5], low-voltage sputtering [6], vacuum/reactive evaporation [7] or high-density plasma-assisted evaporation [8,9], are necessary to produce a good quality ITO film. In particular, the use of ion-beams is very suitable for obtaining film properties because the substrate is separated from the plasma-generating area and simultaneous bombardment of the growing film surfaces by the energetic ion-beam improves the electrical and optical properties of films at low deposition temperature by transferring their energy to the adatoms on the surface layer, and, in turn, modifying nucleation and growth kinetics [10].

For the successful room-temperature growth of ITO films, the use of a reactive oxygen ion-beam is very promising due to the compensation of the oxygen deficiency of the evaporated ITO flux. The additional effects of physical bombardment by inert gas ion-beams such as Ar^+ or Kr^+ is expected to improve the quality of the deposited ITO film. Recently, the bombardment of growing films by an Ar ion-beam only in oxygen atmosphere has been reported to result in a significant decrease of the film resistivity [11].

In this paper, the correlation between the Kr ion-beam parameters and the electrical, optical, and structural properties of the grown films is investigated to improve the conductivity and transmittance of the deposited ITO films and the effects of physical bombardment by inert gas ions on their physical properties. For this purpose, ITO films were deposited at room-temperature on polycarbonate and glass substrates, at the same time using the *e*-beam evaporated ITO flux and the assisting krypton ion-beam with various ion flux, J_{Kr^+}, and grid acceleration voltage, V_a, while keeping the condition of reactive oxygen ion-beam bombardment constant, and various film properties were measured.

2. Experimental

ITO films were prepared by the dual ion-beam assisted evaporation technique (DIBAE) on polycarbonate and sodalime silicate glass substrates without substrate heating. Bulk ITO with the composition of 90 wt.% In_2O_3 and 10 wt.% SnO_2 (purity, 99.99%) was evaporated by the *e*-beam evaporator. During evaporation, krypton and oxygen ions extracted from the separated ion sources with a filamentless rf (radio-frequency) inductive-plasma type, were directed onto the substrates. Especially, the ion sources had two grids, where one is for the acceleration of the ions from 0 to $+3$ kV and the other one is for the extraction of the ions from 0 to -1 kV.

The krypton ion flux, J_{Kr^+}, produced from the krypton ion source was varied from 1.92 to 3.76×10^{14} cm^{-2} s^{-1} by changing the rf-power, P_{rf}, and the energy of krypton ions was varied by changing the grid acceleration voltage, V_a, from $+100$ to $+500$ V. During film deposition, the condition of the oxygen ion-beam was kept constant by fixing the oxygen ion beam source condition at an rf-power of 200 W, the grid acceleration voltage at $+1$ kV, the grid extraction voltage at -100 V, and the oxygen flow rate at 3 sccm. The fluxes of ions were calculated from the ion current densities measured by a Faraday cup. The distance between the substrate and the krypton (oxygen) ion source, and the incident ion-beam angle between the krypton (oxygen) ion source and the substrate to the normal of the evaporator were kept at 40 (45) cm and 45° (40°), respectively. All substrates were cleaned ultrasonically in ethyl alcohol and de-ionized water, and then dried by nitrogen flow. The ITO evaporation rate, R, was maintained at 0.06 nm/s by using a quartz crystal monitor and the total film thickness of the deposited ITO films measured using a step profilometer was $\cong 100$ nm in these experiments. The chamber was evacuated to a background pressure of $\cong 8\times10^{-4}$ Pa initially and the chamber pressure during film deposition was maintained at $1.4–2.0\times10^{-2}$ Pa.

Various electrical, optical, and structural properties of as-deposited ITO films without post-annealing were measured using Hall-effect measurements, X-ray photoelectron spectroscopy (XPS), UV-visible spectrometer, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

3. Results and discussion

Throughout the present experiments, the conditions of krypton ions incident on the growing film were varied by changing the parameters of the krypton ion source. The krypton ion-beam flux, J_{Kr^+}, was varied by changing the rf-power, P_{rf}, of the beam source, while keeping the grid acceleration voltage, $V_a = +200$ V, the grid extraction voltage, $V_e = -50$ V, and the krypton flow rate of 1 sccm constant. The resulting Kr^+ flux was calculated from the electrical current densities measured by a Faraday cup. The J_{Kr^+} values varied linearly from 1.92×10^{14} to 3.76×10^{14} cm^{-2} s^{-1} by changing P_{rf} of the krypton ion source from 100 to 300 W, as shown in Fig. 1. The flux and grid acceleration voltage of the oxygen ion-beam extracted from the oxygen ion source were fixed at 2.68×10^{16} cm^{-2} s^{-1} and $V_a = +1$ kV, respectively.

ITO films deposited at room-temperature as a function of J_{Kr^+} showed an amorphous structure with no characteristics of the crystallinity judged from XRD

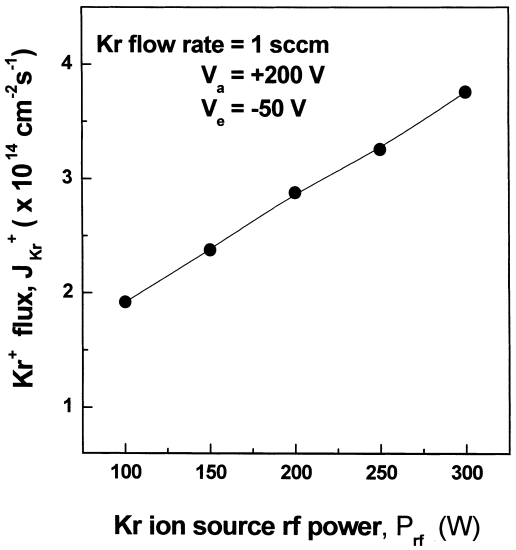

Fig. 1. The Kr ion flux, J_{Kr^+}, as a function of Kr ion source rf power, P_{rf}, measured by a Faraday cup.

measurements. The amorphous nature of as-deposited ITO films is primarily attributed to the low adatom mobility due to the very low film deposition temperature where the adatoms on the growing film surface are not activated enough to find the crystalline lattice sites. These results are well consistent with other experimental reports that ITO films deposited near room-temperature show an amorphous structure [12,13].

In order to investigate the effects of energetic Kr^+ bombardment on the electrical properties of as-deposited ITO films, the resistivity, electron carrier concentration, and Hall mobility were obtained from Hall effect measurements. Fig. 2 shows the measured results obtained for ITO films deposited on glass and polycarbonate substrates as a function of J_{Kr^+}. As shown in Fig. 2a, the as-deposited ITO film on polycarbonate bombarded by the oxygen ion-beam only without any Kr^+ bombardment showed a high resistivity of $\cong 3\times10^{-3}$ Ω cm. The simultaneous bombardment of the film surfaces with the oxygen and krypton ion-beam, however, decreased the resistivity down to $\cong 6\times10^{-4}$ Ω cm as J_{Kr^+} is increased from 0 to 3.26×10^{14} cm^{-2} s^{-1}, and then the resistivity saturated near 6×10^{-4} Ω cm at $J_{Kr^+}\geq 3.26\times10^{14}$ cm^{-2} s^{-1}. The observed decrease in the resistivity of the ITO films is primarily due to the simultaneous increase in the electron carrier concentration and Hall mobility as clearly seen in Fig. 2b,c, respectively. The electron Hall mobility and carrier concentration of the ITO films under oxygen ion bombardment only were $\cong 2\times10^{20}$ cm^{-3} and $\cong 14$ cm^2 V^{-1} s^{-1} and increased to $\cong 4\times10^{20}$ cm^{-3} and $\cong 26$ cm^2 V^{-1} s^{-1} as J_{Kr^+} was increased to 3.26×10^{14} cm^{-2} s^{-1}. Further increase in $J_{Kr^+}\geq 3.26\times10^{14}$ cm^{-2} s^{-1} did not change the electron Hall mobility and carrier concentration values consistent with the trend in the resistivity values as shown in Fig. 2a. These results may indicate that the physical bombardment by the Kr^+ beam can increase the electrical conductivity by improving physical properties of the films such as atomic packing density and phase stability, and optimizing the film stoichiometry caused by the change in oxygen incorporation in the growing films by Kr^+ bombardment.

The difference in the electrical resistivity of the films deposited on different substrates using the same deposition conditions (i.e. deposited simultaneously) is clearly seen in Fig. 2a. It can be seem from Fig. 2b,c that the difference in the electrical resistivity values is caused by the difference in the Hall mobilities (see Fig. 2c) rather than by that in the carrier concentration (see Fig. 2b). The Hall mobilities of the ITO films deposited on polycarbonate substrates (indicated as P-ITO in Fig. 2) were lower than those of the ITO films deposited on

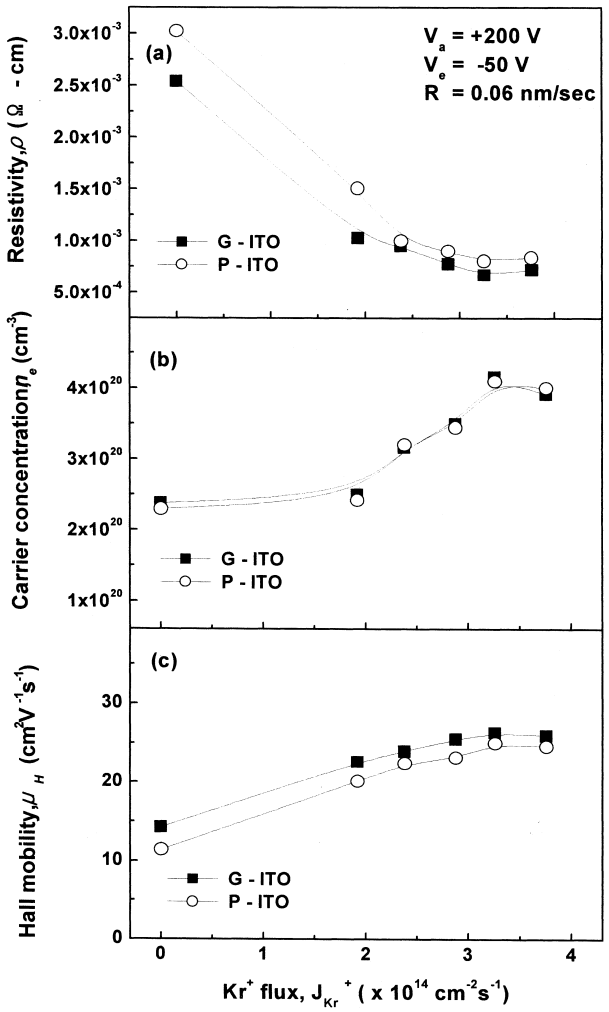

Fig. 2. (a) Resistivity, ρ; (b) electron carrier concentration, n_e; and (c) Hall mobility, μ_H, of G-ITO and P-ITO films deposited as a function of the Kr ion flux, J_{Kr^+}, measured by Hall measurement. (G-ITO: ITO film deposited on glass; P-ITO: ITO film deposited on polycarbonate.)

glass substrates (indicated as G-ITO in Fig. 2). In the present experiments, the decreased Hall mobility of the electrons in the ITO films on polycarbonate substrates may be due to the scattering of carriers by the increased surface roughness of the grown ITO films caused by the larger surface roughness of the original polycarbonate substrates [14].

The supporting results indicating the enhanced incorporation of oxygen into the growing ITO films were confirmed by XPS analyses of as-deposited ITO films on glass substrates. The relative atomic composition ratios, Sn/In and O/(In + Sn), obtained from the analysis of various XPS narrow scan spectra, are plotted as a function of the krypton ion flux, J_{Kr^+}, in Fig. 3. As a reference, the relative atomic composition ratios of the bulk ITO target are indicated. The reduced Sn/In and O/(In + Sn) ratios of as-deposited ITO films compared with those of the bulk ITO are due to the difference in the vapor pressures of In and Sn and due to the oxygen deficiency in the grown films caused by preferential evaporation of oxygen in the ITO flux. The results in Fig. 3 show that the Sn/In ratio values were not changed much with increasing J_{Kr^+} but the O/(In + Sn) ratio values were increased by 17% when J_{Kr^+} was increased from 0 (bombarded only with the oxygen ion beam) to 3.76×10^{14} cm^{-2} s^{-1}. An interesting observation in the current results is that pure physical bombardment of growing ITO film surfaces by the inert Kr^+ beam enhances the incorporation of oxygen supplied by the separate oxygen ion source into the growing films. This may be explained by recoil implantation of oxygen atoms on the surface by the incoming Kr^+ flux [15,16].

In general, the electrical conductivity of ITO thin films is determined by the balance between the concentration of oxygen vacancy and Sn dopant in the ITO film. It is well known that an excess deficiency of oxygen in the ITO film decreases the electrical conductivity by reducing the electron carrier concentration, while an excess of oxygen in the ITO film decreases the concentration of oxygen vacancy and, as a result, increases the resistivity. Therefore, it is necessary to optimize the oxygen concentration to obtain highly conductive ITO films [17]. In the case of as-deposited ITO thin films in the present experiments, the significant change in the oxygen concentration rather than in the Sn concentration as a function of J_{Kr^+} affected the observed change in the electrical resistivities indicated in Fig. 2a. This change in oxygen concentration is correlated with the change in the concentration of oxygen vacancy and, in turn, in the concentration of the electron carriers in the films. The oxygen concentration in the present experiments is in the regime where the electron concentration increases with the increasing oxygen concentration in the film. This increase in the oxygen concentration in the grown films, therefore, is expected to increase the carrier concentration of the films causing the decrease in the electrical resistivities, as observed in Fig. 2a,b.

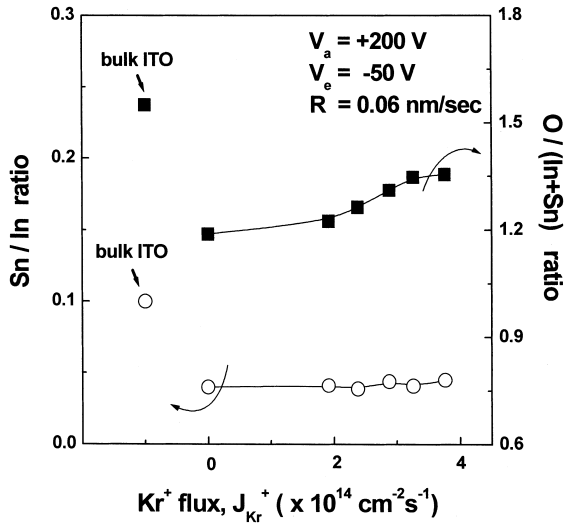

Fig. 3. The relative chemical composition ratios of bulk ITO and G-ITO films deposited as a function of the Kr ion flux, J_{Kr^+}, measured by X-ray photoelectron spectroscopy (bulk ITO: 90 wt.% In_2O_3 ~ 10 wt.% SnO_2).

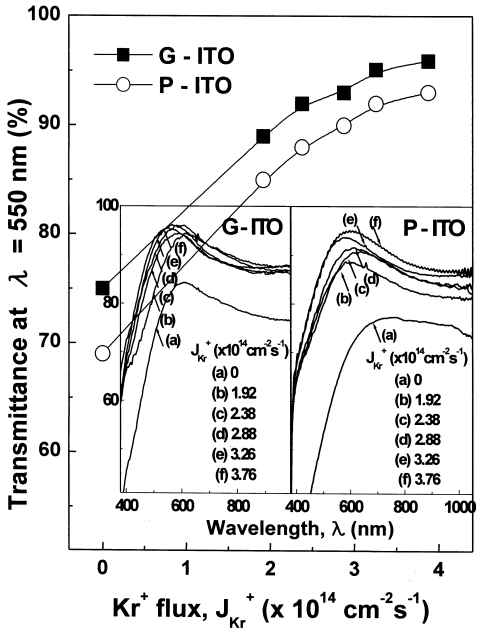

Fig. 4. The optical transmittance of G-ITO and P-ITO films deposited as a function of the Kr ion flux, J_{Kr^+}, measured using a UV-visible spectrometer ($V_a = +200$ V, $V_e = -50$ V, $R = 0.06$ nm/s).

Optical transmittances at the wavelength λ = 550 nm were measured and are shown in Fig. 4 for the ITO films grown as a function of J_{Kr^+} on glass substrates (G-ITO films) and polycarbonate substrates (P-ITO films). Detailed spectra measured by a UV-visible spectrometer as a function of λ are also included in Fig. 4.

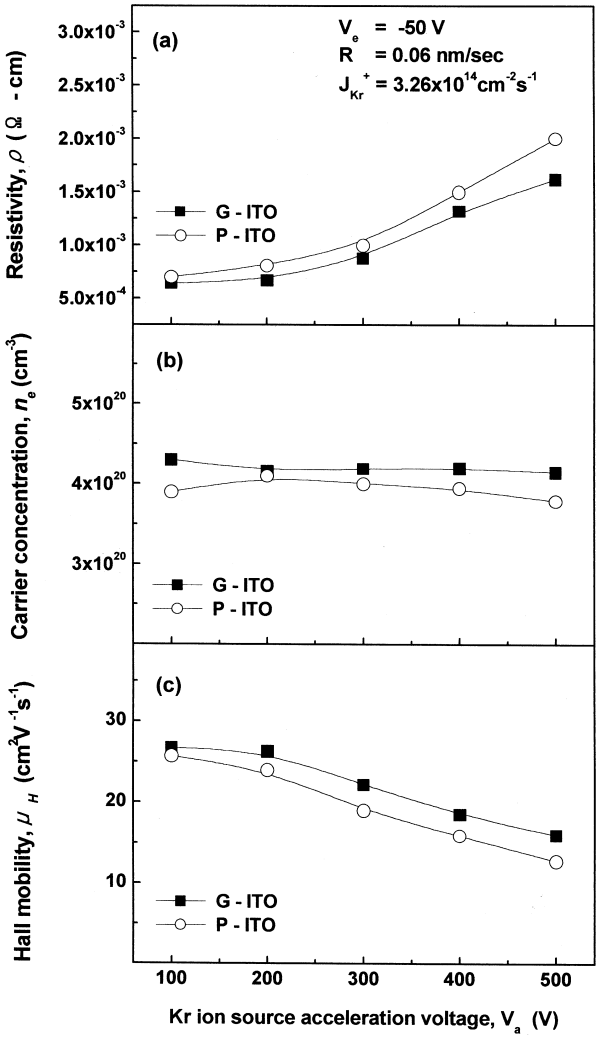

Fig. 5. (a) Resistivity, ρ; (b) electron carrier concentration, n_e; and (c) Hall mobility, μ_H, of G-ITO and P-ITO films deposited as a function of the grid acceleration voltage, V_a, of the Kr ion source measured by Hall measurement.

The measured values in Fig. 4 show that the optical transmittances of G-ITO and P-ITO films increase with increasing J_{Kr^+} and the optical transmittances of G-ITO films are higher than those of P-ITO films. These results are consistent with the fact that an increased oxygen concentration with increasing J_{Kr^+}, as observed in Fig. 3, increases the optical transmittance [18]. The smaller optical transmittances observed for the P-ITO films compared with those of the G-ITO films are attributed to the larger surface roughness observed by scanning electron microscopy (SEM) observations of the grown ITO film surfaces. It is well known that increased surface roughness decreases the optical transmittance due to increased optical scattering of incident light on the film surface [13].

In addition to the effects of J_{Kr^+} on the physical bombardment of growing ITO thin films, the effects of the incident energy of krypton ions on the ITO film properties were also investigated. For this purpose, the acceleration voltage, V_a, of the krypton ion-beam source was varied from +100 to +500 V with the fixed $J_{Kr^+} = 3.26 \times 10^{14}$ cm^{-2} s^{-1} by keeping the rf-power, $P_{rf} = 250$ W, and the extraction voltage, $V_e = -50$ V, constant. The electrical results measured by the Hall effect are shown in Fig. 5. Fig. 5a shows that the electrical resistivity increases as V_a increases from +100 to +500 V. This increase in the resistivity is caused by the decrease in Hall mobility (see Fig. 5c) rather than the change in the carrier concentration in the films (see Fig. 5b). These results indicate that the oxygen incorporation was not significantly affected by changing the energy of the incident krypton ions.

Optical transmittances at $\lambda = 550$ nm in the visible region measured for the same samples grown as a function of V_a are shown in Fig. 6. The results indicate that the optical transmittances decrease significantly as V_a increases above +400 V. This can be explained by the increased damage in the film as well as the increased surface roughness of the as-deposited ITO films. An increased surface roughness is expected to decrease the Hall mobility of carriers, as can be seen in Fig. 5c, by increased surface carrier scattering and also decrease the optical transmittance as seen in Fig. 6 by increased optical scattering of light. The increased surface roughness of ITO films deposited with higher krypton ion energy on polycarbonate substrates was confirmed by SEM observation of as-deposited ITO films, as shown in Fig. 7. The SEM images of the ITO films deposited with $V_a = +500$ V indicate the substantially increased surface roughness compared with the

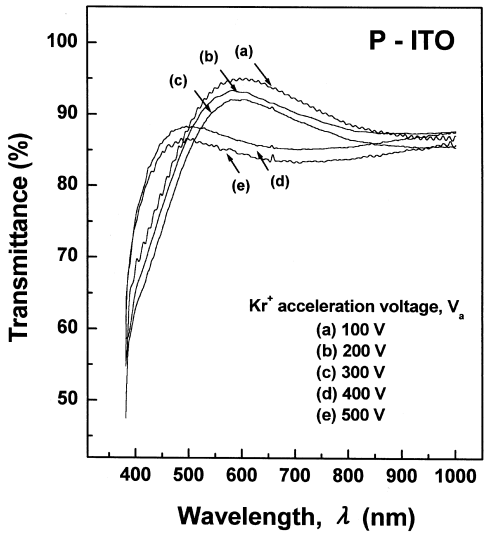

Fig. 6. The optical transmittance of P-ITO films deposited as a function of the grid acceleration voltage, V_a, of the Kr ion source measured using a UV-visible spectrometer ($J_{Kr^+} = 3.26 \times 10^{14}$ cm^{-2} s^{-1}, $V_e = -50$ V, $R = 0.06$ nm/s).

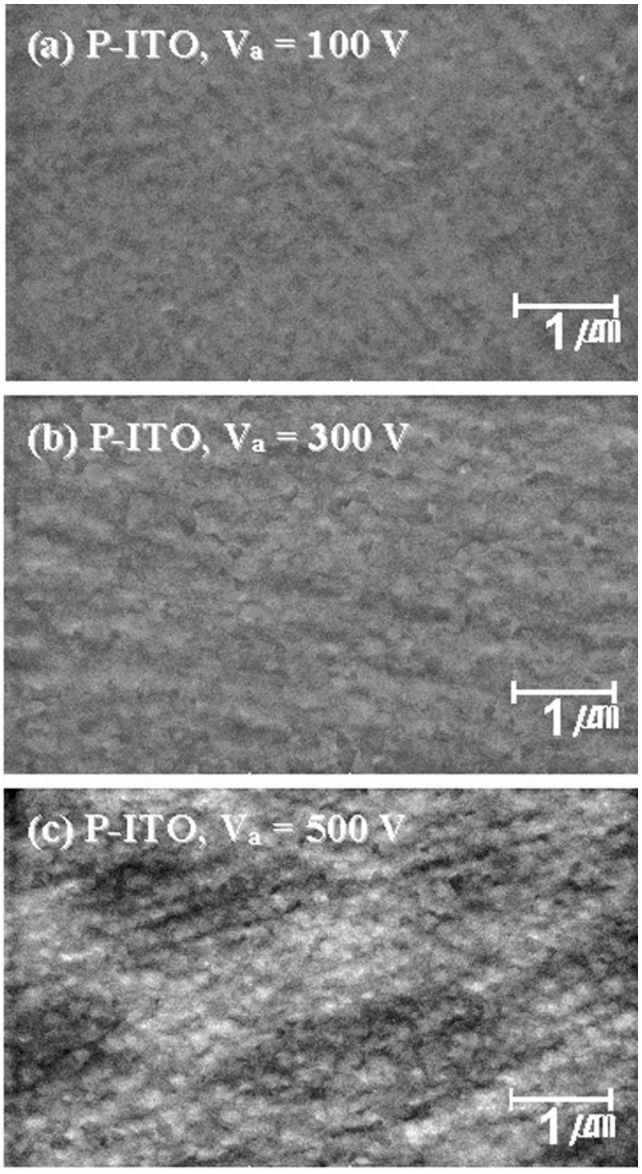

Fig. 7. SEM images of P-ITO films deposited as a function of the grid acceleration voltage, V_a, of the Kr ion source ($J_{Kr^+} = 3.26 \times 10^{14}$ cm^{-2} s^{-1}, $V_e = -50$ V, $R = 0.06$ nm/s).

SEM images of the films with $V_a = +100$ V. From these results, it can be concluded that the excessive ion energy is not favorable because the high ion energy can increase surface roughness and as a result deteriorate the electrical and optical properties of the grown ITO films.

In the present experiments, ITO thin films grown on glass and polycarbonate substrates showed an optical band gap energy, E_g, of 3.6–3.8 eV, calculated from the relation $(\alpha h\nu)^2 = h\nu - E_g$, where α is the optical absorption coefficient and $h\nu$ is the incident photon energy. These values are well consistent with other values measured for ITO film deposited by a variety of methods [19].

4. Conclusion

The electrical, optical, and structural properties of ITO thin films deposited on glass and polycarbonate substrates at room-temperature were investigated as a function of the flux and energy of the krypton ion-beam under fixed conditions of the oxygen ion-beam. As-deposited ITO films showed amorphous structures. An additional physical bombardment by an inert Kr^+ beam increased the electrical conductivity and optical transmittance of as-deposited ITO films as the Kr^+ flux increases at the constant ion energy. The bombardment of the growing film using an increased Kr^+ energy, however, increased the surface roughness of the film and, as a result, decreased the electrical conductivity and optical transmittance. The results of the present experiments indicate that the physical bombardment of the growing film surfaces by an inert gas ion-beam in addition to the bombardment by reactive oxygen ions is useful in improving the film properties. Furthermore, the results of this experiment suggest that the use of a higher flux with lower ion energy is preferable to the use of a lower ion flux with higher ion energy to transfer the same energy input to the growing film surfaces.

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