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Preparation and characterization of indium tin oxide films formed by oxygen ion beam assisted deposition

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Abstract

Indium tin oxide (ITO) films were produced by low-energy oxygen ion beam assisted electron-beam evaporation. The dependence of surface morphology, electrical and optical properties on evaporation rate, oxygen ion beam energy and density, as well as substrate temperatures was characterized by atomic force microscopy, X-ray photoelectron spectroscopy, Hall-effect and optical transmittance measurements. The results show that high-quality ITO films (resistivity of $7.0 \times 10^{-4}\ \Omega$ cm, optical transmittance above 85% at wavelength 550 nm, surface roughness of 0.6 nm in root mean square) can be obtained at room temperature.

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Keywords: A. Indium tin oxide; D. Ion beam assisted deposition

Tin-doped indium oxide (ITO) is a n-type semiconductor. It has two basic properties: transparent in the visible and near-IR regions due to its wide band-gap (~3.8 eV at room temperature) and conductive due to the high electron degeneracy. These remarkable characteristics have made it possible to be used as transparent electrodes in opto-electronics, such as liquid crystal displays, photovoltaic cells, organic light emitting diodes, and electroluminescent displays. Although many deposition techniques, for example, d.c. and r.f. magnetron sputtering [1,2], ion beam sputtering [3], reactive evaporation [4], reactive ion plating [5], spray pyrolysis [6], pulsed laser deposition [7], have successfully been developed to produce ITO thin films, all of them require elevated substrate temperatures between 200 and 500 °C during the deposition, or post-deposition annealing [8–12], or post-deposition oxygen plasma treatment [13], in order to optimize the electrical and optical properties. For fabrication of organic luminescent devices, room-temperature deposition of ITO layers is desired because of the low thermal stability of the organic materials. However, the relatively higher resistivity and lower transparency of ITO films prepared at room temperature cannot meet the requirement of industrial applications. Their rough surfaces deteriorate the resolution of the large-area flat panel displays. Therefore, preparation of very smooth ITO films with low resistivity and high transparency at room temperature still remains a significant challenge.

Some scientists have used ion beam assisted deposition (IBAD) to prepare In_2O_3 [14] and ITO [15] films, aiming to improve the electrical and optical properties at low deposition temperatures. The substrate temperature during the deposition decreased to 90 °C [15]. This opens up the possibility to deposit ITO films on polymer substrates. Recently, we have reported room-temperature deposition of ITO films by electron-beam evaporation of ITO bulk material and irradiated at the same time by a low-energy oxygen ion beam produced in an electron cyclotron resonance (ECR) source [16]. Using this technique, crystalline ITO films can also be prepared at room temperature as long as the film

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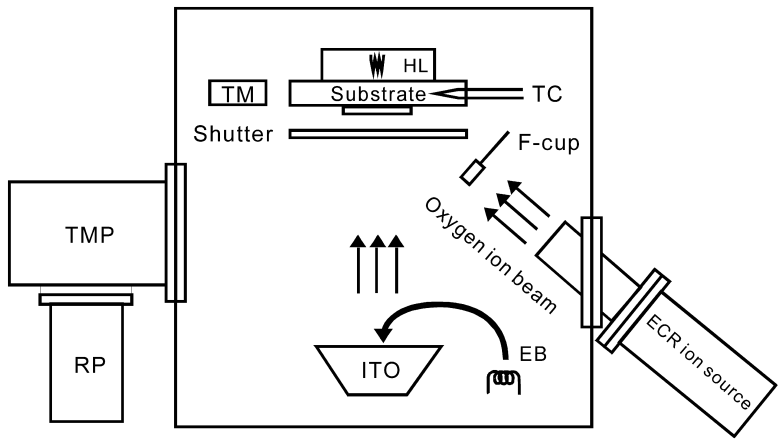

Fig. 1. Schematic demonstration of the IBAD system. EB, electron beam; TM, thickness monitor; HL, halogen lump; TC, thermal couple; TMP, turbo molecular pump; RP, rotary pump.

thickness reaches a critical value. In this paper, we focus on the influence of deposition parameters on the structural, electrical and optical properties of ITO films.

Sintered ITO bulk (In_2O_3:SnO_2 = 95 wt%:5 wt%) was used as the evaporation source material. ITO films were deposited at room temperature and 200 °C onto micro slide glass (Matsunami Glass Co.) and fused silica (SiO_2) by electron-beam evaporation and oxygen-ion-beam irradiation. The schematic demonstration of the deposition system was drawn in Fig. 1. The distance between the evaporating source and the substrates was 65 cm. An ECR ion source is used to produce low-energy oxygen ions. The energy of the oxygen ion beam was varied in this study from 50 to 300 eV. The angle between the incident oxygen ion beam and the normal of the substrates was fixed at 45°. A biased moveable Faraday cup was equipped near the substrate to measure the current density. After measuring the beam current, it moved out to let the whole beam bombard the substrate. Before the deposition, the vacuum in chamber was generally pumped to 10^{-4} Pa. The flow rate of pure oxygen (99.99%) was set to be 4 sccm. During the deposition, the dynamic vacuum was kept around 10^{-2} Pa. The thickness of the deposited films was monitored by a quartz crystal sensor (CRTM6000, Ulvac) and the evaporation rate was changed from 0.04 to 0.23 nm/s.

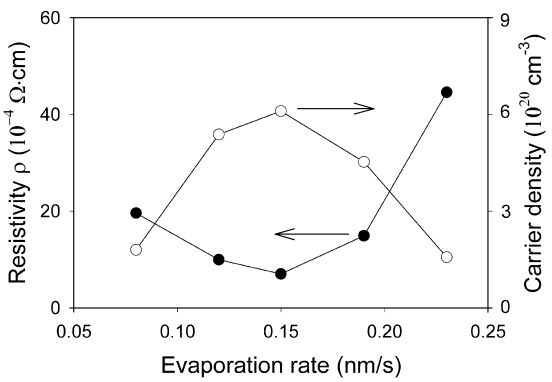

Fig. 2. Dependence of resistivity (left) and carrier density (right) of the ITO films on the evaporation rate. The films were deposited on glass at room temperature with the same thickness of 100 nm by oxygen IBAD (100 eV, 60 μA/cm^2).

The electrical properties of the ITO films, such as resistivity, carrier density and mobility, were measured by Hall-effect with a van der Pauw geometry (Resitest 8300, Toyo Co.). An UV-spectrophotometer (UV-1600PC, Shimadzu) was applied to measure the optical transmittance of the films in atmosphere. Chemical bonding analysis was performed using an X-ray photoelectron spectroscopy (XPS, ESCA 5300, Perkin–Elmer) equipped with an Mg Kα X-ray source (15 kV 24 mA) and an hemispherical analyzer. All binding energies were referenced to the C1s hydrocarbon peak at 285 eV. Overlapping peaks were resolved with a non-linear least-squares algorithm using a mixture of Gaussian and Lorentzian peak shapes. The surface morphology was studied by an AFM (SPA 300, Seiko Instrument).

Evaporation rate, substrate temperature, oxygen ion beam energy and density are key parameters to control the quality of ITO films in our deposition system. Among them, evaporation rate plays the most important role. In general, a high evaporation rate is desired to avoid decomposition of ITO on the way from crucible to the substrates. Since the composition of ITO films was determined by the arriving ratio of indium, tin, and oxygen, it is crucial to find an optimum evaporation rate to match a preset oxygen ion beam. Fig. 2 shows the dependence of resistivity (left) and carrier density (right) of the ITO films on the evaporation rate. All ITO films in this figure have the same thickness of 100 nm. At low evaporation rate (less than 0.05 nm/s), it is easy to incorporate more oxygen atoms in the deposited films and form crystalline structure [16]. Due to shortage of oxygen vacancies that contribute to carriers, the resistivity of the deposited films lies around 10^{-2} Ω cm (not shown in Fig. 2). On the other hand, if the evaporation rate is higher

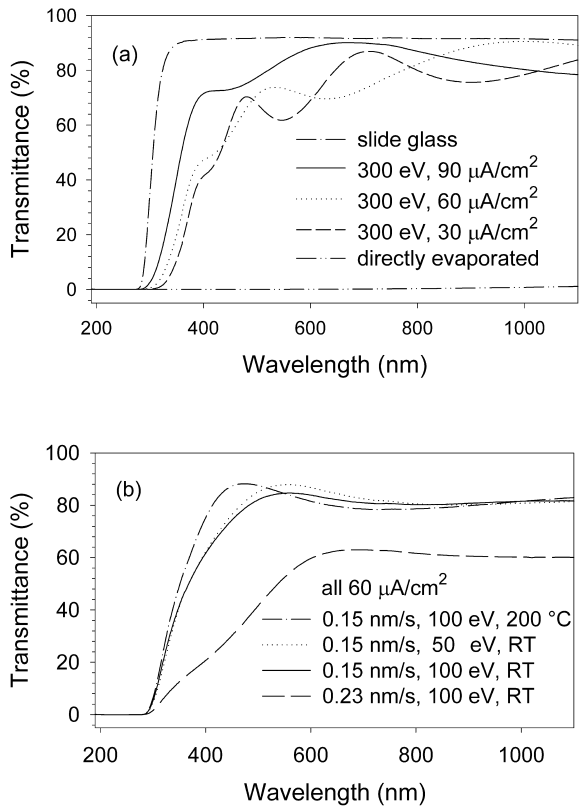

Fig. 3. Transmission spectra of ITO films on glass (a) deposited at room temperature with a thickness of 380 nm at different oxygen ion density; (b) deposited at different conditions but with the same thickness of 100 nm. The transmittance of the directly evaporated ITO film without any irradiation of oxygen ions was also included in (a) for comparison.

than 0.2 nm/s, the oxygen content in the deposited films is so low that the films become metal-like, brownish and less transparent (see Fig. 3(b)). Therefore, the optimum evaporation rate is around 0.15 nm/s at our geometry.

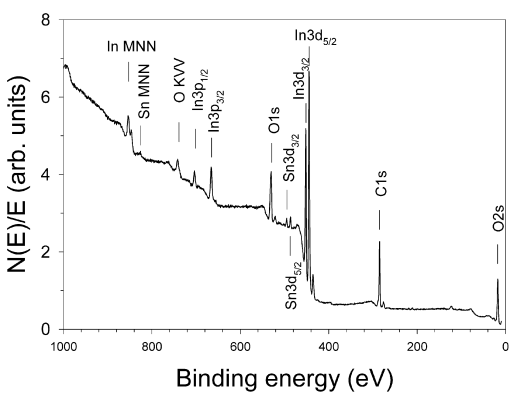

Fig. 4. A XPS survey spectrum of the ITO film on glass with a thickness of 100 nm. The film was prepared at 200 °C by oxygen IBAD (100 eV, 60 μA/cm^2).

Under the optimum condition, 100 nm thick ITO film has a resistivity of 7.0×10^{-4} Ω cm and a carrier density of 6.1×10^{20} cm^{-3}.

The influence of oxygen ion beam density on the optical transmission is presented in Fig. 3(a). For comparison, the transmission spectra of the glass substrate and the directly evaporated ITO film without any oxygen ion irradiation in the same dynamic vacuum environment are also included. It is quite clear that the ITO film prepared by the direct evaporation is not transparent at all. This shows the importance of the oxygen ion beam irradiation during the deposition. Under the oxygen ion beam irradiation, the film becomes transparent, suggesting high reactivity of the oxygen ion beam produced in the ECR source. At the same ion energy, irradiation with a higher ion beam density improves the transparency and shifts the band edge absorption to higher energy region, indicating the ratio of O/(In + Sn) approaching the sesquioxide's. One the other hand, however, adequate oxygen content in the deposited ITO films suggests directly an insufficient oxygen vacancies, resulting in a low conductivity since oxygen vacancies and tin-dopants contribute to the carriers. Fig. 3(b) shows the transmission spectra of ITO films with a thickness of 100 nm at different evaporation rates, ion energies, and substrate temperatures. The ITO film deposited with an evaporation rate of 0.15 nm/s at room temperature under the bombardment of 100 eV, 60 μA/cm^2 oxygen ions shows a transmittance of 85% (including the glass substrate) at a wavelength of 550 nm. If the ion energy decreases to 50 eV, the transmittance increases to 88%. If the glass substrate is taken as background, the transmittance reaches 97%. This indicates the importance to use low-energy oxygen ion beam and agreed with the results of Ref. [14] in which irradiation with a lower energy oxygen ion beam results in a lower resistivity and a higher mobility of the ITO films. When the glass substrate was heated to 200 °C, the transmission in a region from ultraviolet to green light has been much improved, while the transmission in the other wavelengths remains nearly the same. As discussed earlier, a high evaporation rate is desired to prevent the oxygen escape from the evaporated flux. However, it should match the oxygen beam density. At the evaporation rate of 0.23 nm/s, the ITO film lost transparency due to a very low oxygen content, although its resistivity lies around 5×10^3 Ω cm.

It is very important to verify whether the impurities contained in the glass substrates diffuse into the deposited ITO layer at the elevated substrate temperature, because the impurities, mainly alkali metals and Zn, are acceptors in ITO films. They compensate the electron concentration and make the electrical properties undesirable. Fig. 4 shows the XPS survey spectrum of the ITO film deposited at 200 °C. Only the elements of In, Sn, O and C can be found in the spectrum. Thus, it can be concluded that no impurities diffuse into the ITO layer during the deposition at 200 °C.

Fig. 5 shows a section of the XPS spectrum (open dots)

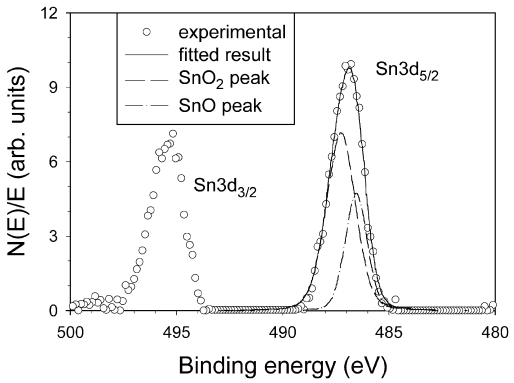

Fig. 5. A section of the XPS spectrum of Fig. 4 in Sn 3d region.

displayed in Fig. 4 in the Sn 3d region for the ITO film prepared at 200 °C. The solid line presents the fitting result for the Sn $3d_{5/2}$ peak using two Gaussian–Lorentzian profiles. As the amount of tin is very small in the sample, around 1% atomic concentration as measured by both Rutherford backscattering and particle induced X-ray emission, the statistics of the acquisition is not as good as enough to make an accurate curve fitting. The best fitting was achieved with two components at binding energies of 486.8 and 486.0 eV. The former is assigned to SnO_2 and the latter to SnO [17]. The area ratio of the former to the latter is 2.1. This ratio decreases to 1.3 when the deposition was carried out at room temperature with the same conditions. Generally, tin exists in SnO_2 with valence 4, while in SnO with valence 2. Since indium has valence 3 in In_2O_3, the presence of SnO_2 results in n-type doping, contributing one electron to the conduction band. In contrast, the presence of SnO leads to a compensation of the electron density [18]. Even the deposition was performed at room temperature, more than the half of Sn works as n-type dopants in our deposited samples.

The surface topography of the ITO films was studied by an AFM in a non-contact mode. A typical image is presented in Fig. 6 for a 200 nm thick ITO sample on SiO_2 prepared at room temperature. Its root mean square (rms) value, together with those of other ITO samples prepared at

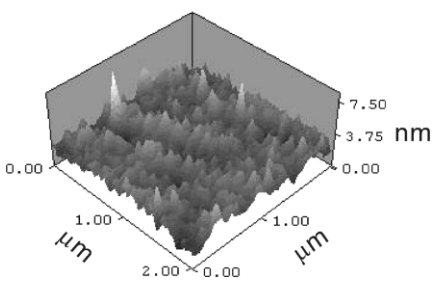

Fig. 6. AFM surface morphology (2 μm × 2 μm) of the ITO film with a thickness of 200 nm. The film was deposited on SiO_2 at room temperature with an evaporation rate of 0.15 nm/s by oxygen IBAD (100 eV, 60 μA/cm^2).

Table 1
Surface roughnesses (root mean square) of the ITO films on SiO_2 with different thicknesses prepared by oxygen IBAD (100 eV, 60 μA/cm^2) at room temperature (RT) and 200 °C

Temperature	RT	RT	RT	200 °C
Thickness (nm)	100	200	380	100
Roughness (nm)	0.6	0.7	1.7	0.5

different temperatures with different thicknesses, is listed in Table 1. As examined by X-ray diffraction, the samples with the thicknesses of 100 and 200 nm are amorphous, but have very smooth surfaces (rms ≤ 0.7 nm). Such a low rms value is one order smaller than those prepared by other deposition methods [19,20]. When the thickness reaches 380 nm, the film becomes crystalline [16]. The surface roughness increases to 1.7 nm. If the substrate was heated to 200 °C during the deposition, the rms decreases to 0.5 nm, in spite of the crystal structure of the film that usually leads to an increase of the surface roughness due to the crystallinity [21]. Meanwhile, the average grain size increases quite obviously with the substrate temperature, resulting in an improvement of the mobility. It comes a conclusion from Table 1 that very smooth ITO samples can be prepared over a wide experimental conditions using low-energy oxygen IBAD.

Under the optimum growth conditions, the room temperature prepared ITO film shows a resistivity of 7.0×10^{-4} Ω cm, carrier density of 6.1×10^{20} cm^{-3}, optical transmittance above 85% (including the substrate) at wavelength of 550 nm, and surface roughness of 0.6 nm. Deposition with a lower ion energy results in a higher transmittance and better electrical properties. Deposition at elevated substrate temperatures improves not only the surface morphology, but also the transmittance in the region from ultraviolet to green light.

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