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Effects of oxygen radical on the properties of indium tin oxide thin films deposited at room temperature by oxygen ion beam assisted evaporation

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Abstract

In this study, ITO films were deposited by an oxygen ion beam assisted evaporation technique on glass and polycarbonate substrates at room temperature and the effects of oxygen radical on the properties of ITO thin films were investigated. To generate oxygen radicals, in addition to one oxygen ion gun irradiating oxygen ions to the substrate during the ITO deposition, a separate oxygen ion gun was used without applying any voltage to acceleration grid and extraction grid while varying rf power to the ion gun. The increase of rf power to the gun increased the number of oxygen radicals. The increase of oxygen radicals to the oxygen ion beam assisted evaporation of ITO increased the optical transmittance of the ITO deposited on both glass and polycarbonate substrates. The conductivity of the deposited ITO also increased with the increase of oxygen radicals, however, too many oxygen radicals decreased the conductivity of the ITO. Hall measurement showed that the change of the carrier concentration in the film was responsible for the change of the resistivity. The increase of optical transmittance and the change of electrical conductivity with the increase of oxygen radicals were related to the oxygen incorporation to the deposited ITO thin film. ITO deposited on the polycarbonate substrate showed a little lower optical transmittance and conductivity possibly due to the higher surface roughness of the substrate. We were able to obtain room temperature ITO thin film on glass with 5.5×10^{-4} Ωcm and above 85% transmittance (at 550 nm) and that on polycarbonate with 6.0×10^{-4} Ωcm and approximately 85% transmittance (at 550 nm).

Keywords: ITO; IBAE; Oxygen radical; Polycarbonate (PC)

1. Introduction

Indium tin oxide (ITO) thin films have been widely used for various display devices such as liquid crystal displays (LCDs), electroluminescent displays (ELDs), and field emission displays (FEDs), etc. for their high optical transmittance ($> 85\%$) and low electrical resistivity ($\sim 10^{-4}\,\Omega$cm) [1–3]. To deposit ITO thin films, glass substrates are generally used, however, the replacement to organic substrates such as polycarbonate (PC), polyethylene terephtalate (PET), and polyether sulfon (PES), etc. is under investigation because organic substrates can give advantages such as lighter-weight, thinner thickness (half the thickness of glass), and higher shock resistance (over 10 times than that of glass) that can be useful for the displays of personal digital assistants (PDAs), notebook computer, etc. However, due to the lower softening temperature of the organic substrates, low temperature ($< 100°C$) or room temperature ITO deposition techniques need to be developed.

Currently, low temperature or room temperature ITO thin film deposition techniques are under investi-

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gation using dc/rf magnetron sputtering [4–6], vacuum/reactive evaporation [7,8], ion beam assisted evaporation [9,10], etc. to obtain lower resistivity and higher optical transmittance on larger area substrates at lower temperature. Among these techniques, ion beam assisted evaporation techniques could give some advantages in depositing room temperature ITO because the incident angle, energy, and flux of ions relative to evaporating ITO flux could be changed relatively easily, therefore, the modification and optimization of film properties could be obtained easier.

However, when ITO thin films are deposited using oxygen ion beam assisted evaporation, not only the incident angle, ion energy, and flux of the ions but also the radicals emitted from the oxygen ion gun are important for the properties of the deposited ITO thin films. However, it is difficult to separate the effect of oxygen radicals with the evaporation system equipped with one oxygen ion gun due to simultaneous change of oxygen radicals with flux of the oxygen ions. Therefore, in this study, dual oxygen gun assisted evaporation has been used and the effect of oxygen radicals on the ITO film properties of oxygen ion beam assisted evaporation were investigated by using one gun as an oxygen ion beam source and by using the other gun as an oxygen radical source.

2. Experimental conditions

The deposition system used in the experiment consisted of an electron beam evaporator and two oxygen ion guns which are used for oxygen ion beam source and oxygen radical source, respectively. The schematic drawing of the deposition system is shown in Fig. 1. Both of the oxygen ion guns were driven by rf inductively-coupled plasma (13.56 MHz) and two grids were attached for the extraction and acceleration of the ions generated. To study the effect of the oxygen radicals, one of the oxygen ion guns (further called ion gun 1) was used as oxygen radical source by varying rf power from 0 W to 350 W at 4 sccm oxygen flow and without applying any voltage to the accelerator grid and the extraction grid. The other oxygen ion gun (further called ion gun 2) was found to have the incident ion-beam angle normal to the substrate and irradiated oxygen ions during the evaporation. The operation condition of the ion gun 2 was fixed at 200 W of rf power, +1.8 kV of acceleration voltage, −100 V of extraction voltage, 4 sccm of oxygen flow, and 55 cm of the distance between the ion gun and the substrate. The deposition rate and the thickness of the deposited ITO thin films were kept at 0.08 nm/s and 140 nm, respectively. No substrate heating was applied during the deposition. The pressure in the process chamber was kept at 3.1×10^{-2} Pa.

As the substrates, sodalime silicate (SLS) glass and polycarbonate were used to compare the effect of the different substrates on the properties of ITO. The evaporation source material was ITO composed of tin oxide 10 wt.% and indium oxide 90 wt.% with the purity of 99.99%.

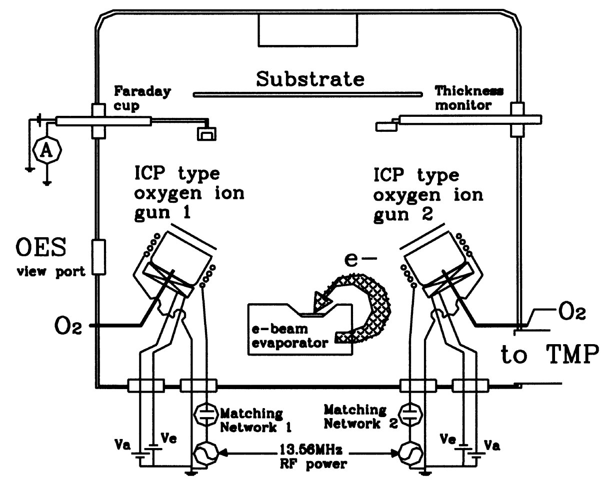

Fig. 1. A schematic diagram of the IBAE system used in the experiment.

Optical emission spectroscopy (OES) was used to investigate the plasma species in the oxygen ion source chamber as a function of rf power to ion gun 1. The properties of the deposited ITO films such as resistivity, optical transmittance, carrier concentration and mobility, stoichiometry, and surface roughness were measured using van der Pauw method, UV-spectrophotometer, Hall probe, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM), respectively. The deposited thickness was measured using a step profilometer in addition to the thickness monitor.

3. Results and discussion

The flux ratio of ion beam and evaporation was one of the most important parameters in determining the properties of the deposited material in the ion beam assisted evaporation method. When oxygen ion beam assisted evaporation was used to deposit ITO thin films, not only oxygen ions but also oxygen atomic radicals are extracted from the ion beam source differently from Ar ion beam assisted evaporation. Therefore, in addition to oxygen ions, these oxygen atomic radicals will affect the properties of deposited ITO.

To study the effects of oxygen radicals, the ion gun 1 was operated without applying any voltages to the acceleration and extraction grids while varying rf power to the gun. We measured the optical emission spectra inside of the chamber of the ion gun 1 with OES while varying rf power from 200 W to 350 W at the oxygen flow of 4 sccm, and the results are shown in Fig. 2. As shown in the figure, optical emission peaks from O (for example; 616 nm) and O_2^+ (for example; 563 nm) were observed and the intensities of the peaks were increased with the increase of the rf power. Because no voltage was applied to the gun, the increased O_2^+ will not deliver any significant energy to the substrate not only because of low energy possessed by the O_2^+ in the plasma but also due to the charge transfer collision occurring during the travel to the substrate. Therefore, the increase of rf power to the ion gun 1 will generally perform its function as the increase in the reactive oxygen radicals which will react with the substrate. [11–14]

ITO thin films were deposited on glass and polycarbonate substrates at room temperature by varying the rf power of ion gun 1 from 0 W to 350 W while maintaining same evaporation rates of ITO and oxygen ion beam condition of ion gun 2. The operation condition of ion gun 2 was rf power 200 W, acceleration voltage 1.8 kV, extraction voltage −100 V, and oxygen flow rate 4 sccm. The deposition rate of ITO was 0.08 nm/s. Fig. 3 shows the transmittance spectra of ITO films deposited on glass substrate (a) and polycarbonate substrate (b). The thickness of the deposited ITO was 140 nm and, to rule out the different absorptions from the different substrates, the absorption spectra of the respective substrates were measured and subtracted after the measurements of optical transmittances of the deposited ITO films. As shown in the figure, the optical transmittance of the ITO film increased almost linearly with the increase of rf power of ion gun 1 for both glass substrate and polycarbonate substrate. The increase of optical transmittance of the deposited ITO thin films appears to be from the increased oxygen radical emitted from the ion gun 1, therefore, by supplying more reactive oxygen atoms to the depositing ITO thin films during the evaporation.

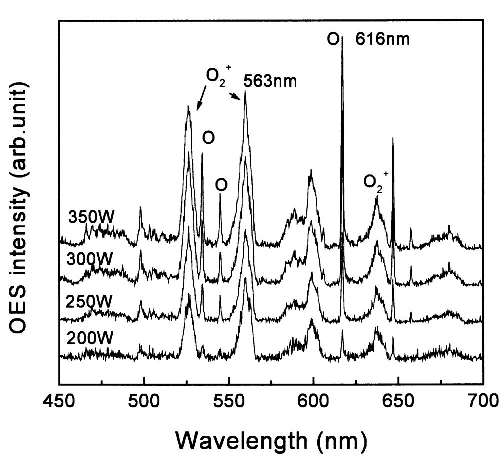

Fig. 2. Optical emission spectra of oxygen plasmas in the ion source chamber (ion gun 1) measured by optical emission spectroscopy as a function of rf power (oxygen flow rate: 4 sccm).

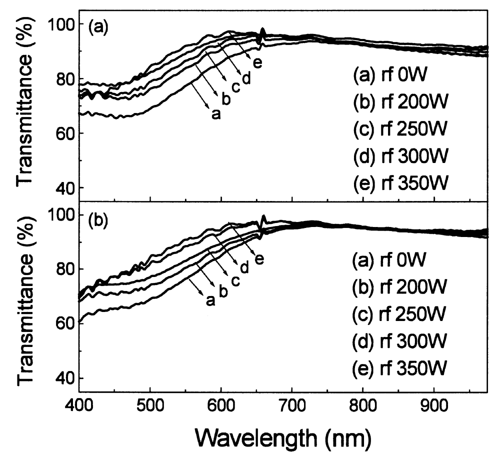

Fig. 3. Variation of the optical transmittance of ITO thin films deposited on (a) glass and (b) polycarbonate substrates as a function to rf power of ion gun 1 (oxygen flow rate: 4 sccm).

At 550 nm, above 85% of optical transmittance could be obtained by applying 200 W of rf power for the glass substrate, however, in the case of polycarbonate substrate, to obtain 85% of optical transmittance, more than 250 W of rf power was required. Therefore, higher transmittance was obtained for the ITO deposited on the glass substrate compared to that on the polycarbonate substrate for the same deposition condition.

Resistivities of ITO thin films deposited on the glass and polycarbonate substrates were also measured as a function of rf power of ion gun 1 using the van der Pauw method. The results are shown in Fig. 4. The resistivities of the ITO thin films deposited on both glass and polycarbonate substrates were initially decreased with the increase of rf power and, when rf power to ion gun 1 was higher than approximately 250 W, the resistivities were increased with the increase of rf power. The minimum resistivity measured for the ITO deposited on the glass substrate was approximately 5.5×10^{-4} Ωcm and that on the polycarbonate substrate was approximately 6.0×10^{-4} Ωcm. Therefore, the resistivity of the ITO deposited on the polycarbonate substrate was slightly higher than the ITO deposited on the glass substrate.

Using the Hall measurement method, carrier concentrations and mobilities were measured for those ITO thin films, and the results are shown in Fig. 5. The carrier concentrations of the ITO thin films on both glass and polycarbonate substrates were similar to each other and increased with the increase of the rf power to ion gun 1. They reached a maximum of approximately 3.5×10^{20} cm^{-3} at approximately 250 W of rf power and the further increase of the rf power decreased the carrier concentration. However, the Hall mobilities were remained similar with the variation of the rf power even though the mobilities of ITO on the glass substrate was a little higher than those on the

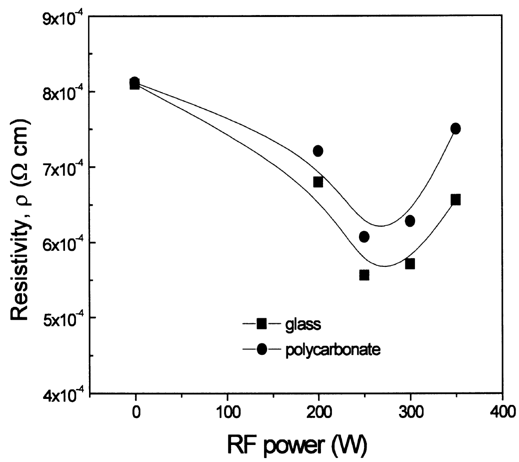

Fig. 4. Variation of resistivity of ITO thin films deposited on glass and polycarbonate substrates as a function of rf power to ion gun 1 (oxygen flow rate: 4 sccm).

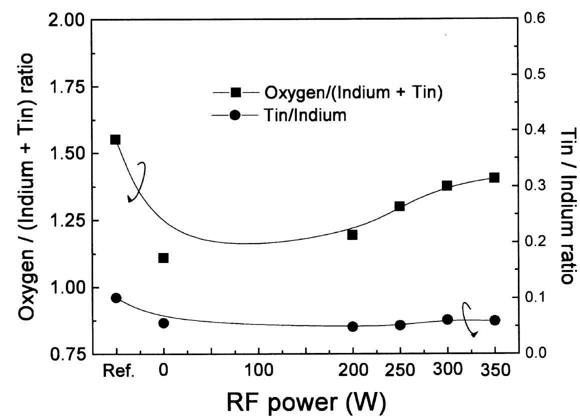

Fig. 6. Variation of the atomic composition of ITO thin films as a function of rf power to ion gun 1 deposited on polycarbonate substrate (oxygen flow rate: 4 sccm).

polycarbonate substrate. The Hall mobilities of ITO on the glass wafer were approximately 30 cm^2 V^{-1} s^{-1} and those on the polycarbonate substrates were approximately 25 cm^2 V^{-1} s^{-1}.

The variation of resistivities of ITO thin films as a function of rf power shown in Fig. 4 appears to be related to the variation of carrier concentration in the film shown in Fig. 5. The variation of carrier concentration as a function of the rf power to ion gun 1 was related to the variation of oxygen radicals shown in Fig. 2, therefore, possibly to the incorporation of oxygen atoms into the growing ITO thin films. To investigate the degree of incorporation of oxygen atoms into the ITO film with the increase of the rf power, the component ratios of the ITO such as oxygen/(indium + tin) and tin/indium deposited on the polycarbonate substrate were measured using XPS as a function of the rf power and the result is shown in Fig. 6. The component ratio of ITO source itself was measured as a reference.

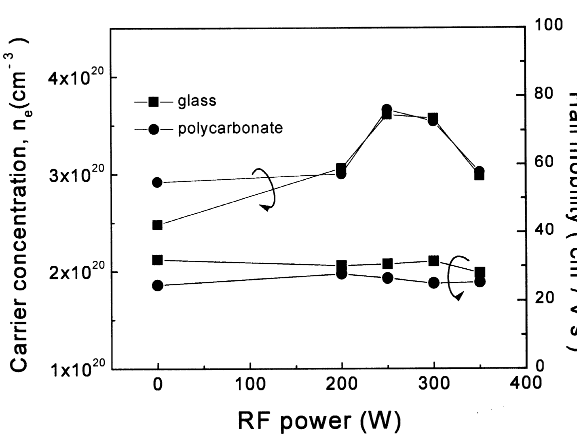

Fig. 5. Variation of electron concentration and Hall mobility of ITO thin films deposited on glass and polycarbonate substrates as a function of rf power to ion gun 1 (oxygen flow rate: 4 sccm).

As shown in the figure, all of the deposited ITO thin films were oxygen and tin deficient. The increase of the rf power did not change the tin/indium ratio, and the deficiency of tin in the film appears to be from the higher vapor pressure of In compared to that of Sn during the ITO evaporation, therefore, the deposited ITO thin films contains less Sn compared to the source material.

Oxygen deficiency in the film originates from the preferential removal of oxygen by the vacuum system during the evaporation as generally observed on various oxides deposited by evaporation. In our experiment, some of deficient oxygen atoms in the film were provided by the oxygen ion gun 2 through the oxygen ion beam irradiation to the substrate, however, as shown in Fig. 6, it appeared to be not enough for the condition we used. With the addition and increase of oxygen radicals using ion gun 1 in addition to ion gun 2, the oxygen incorporated in the film increased from 1.1 [the ratio of oxygen/(indium + tin)] to 1.4 which was close to 1.5 (the ratio of ITO source). The increase of oxygen in the film close to the stoichiometric compound will decrease the number of defects in the film. The increase of optical transmittance with the increase of the rf power shown in Fig. 2 is from the decrease of oxygen vacancy related defects in the film by the increase of oxygen incorporation [15,16].

The conductivity of ITO is known to be from the oxygen vacancies in the film and one vacancy will generate two electrons on the conduction band (therefore, n-type) to satisfy charge neutrality. Therefore, a certain degree of oxygen deficiency in the film was required to improve conductivity, however, too many oxygen vacancies in the film will act as defects without donating electrons and will decrease the conductivity by decreasing conduction electrons. Therefore, the lowest resistivity near 250 W of the rf power shown in

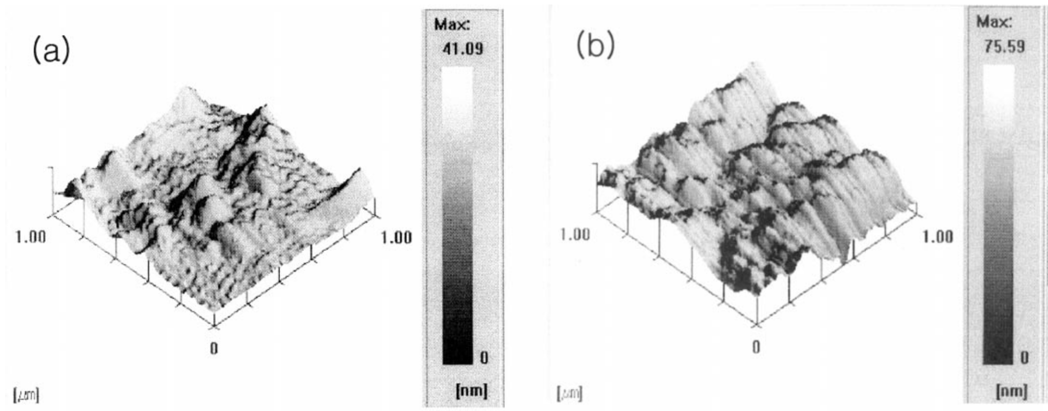

Fig. 7. AFM images (1 μm × 1 μm) of ITO thin films deposited on (a) glass and (b) PC substrate.

Fig. 4 appears to be related the optimum number of oxygen vacancies in the film which gives the largest carrier concentrations as shown in Fig. 5. In fact, the ITO thin films deposited at room temperature generally have amorphous structure. In the case of amorphous structure, it is known that Hall mobility does not change significantly, however, in the case of polycrystalline structure, Hall mobility changes significantly with grain size due to the electron scattering at the grain boundaries. Therefore, the lack of variation in Hall mobility with the change of oxygen deficiency of the film appears to be partially from the amorphous nature of our ITO thin films structure [17].

In our experiments, ITO thin films deposited on polycarbonate substrates showed a little lower transmittance and higher resistivity. The exact reason was not clear, however, when the surface roughness of the deposited ITO was measured using AFM, the roughness of ITO on glass substrates (8 nm) was lower than that on polycarbonate substrates (13 nm) as shown in Fig. 7 possibly due to the differences in the surface roughness of the substrate itself (not measured). The rougher surface and interface will scatter more electrons and photons, therefore, will decrease the optical transmittance and the conductivity by decreasing mobility [18]. Therefore, the decreased optical transmittance and conductivity with polycarbonate substrates in our experiment might be related to the roughness of the deposited ITO surface and interface.

4. Conclusions

In this study, ITO thin films were deposited at room temperature using an oxygen ion beam assisted e-beam evaporation system and the effects of oxygen radicals on the properties of ITO thin films were investigated. Oxygen radicals were generated by using a separate oxygen ion gun without applying any voltage to acceleration grid and extraction grid while varying rf power to the ion gun. The increase of rf power to the gun increased the number of oxygen radicals.

The increase of oxygen radicals to the oxygen ion beam assisted evaporation of ITO increased the optical transmittance of the ITO deposited on both glass and polycarbonate substrates due to the increased incorporation of oxygen atom to the oxygen deficient ITO film. The increase of oxygen radicals also increased the conductivity of the deposited ITO initially, however, too many oxygen radicals decreased the conductivity. The variation of conductivity of the deposited ITO was not related to the variation of mobility but to the variation of carrier concentration of the film. We were able to obtain room temperature ITO thin film on glass with 5.5×10^{-4} Ωcm and above 85% transmittance (at 550 nm) and that on polycarbonate with 6.0×10^{-4} Ωcm and approximately 85% transmittance (at 550 nm).

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