Research Article

Thickness Dependence of Optoelectrical Properties of Mo-Doped In2O3 Films Deposited on Polyethersulfone Substrates by Ion-Beam-Assisted Evaporation

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Indium molybdenum oxide (IMO) films were deposited onto the polyethersulfone (PES) substrates by ion-beam-assisted evaporation (IBAE) deposition at low temperature in this study. The effects of film thickness on their optical and electrical properties were investigated. The results show that the deposited IMO films exhibit a preferred orientation of B(222). The electrical resistivity of the deposited film initially reduces then subsequently increases with film thickness. The IMO film with the lowest resistivity of $7.61 \times 10^{-4}$ ohm-cm has been achieved when the film thickness is 120 nm. It exhibits a satisfactory surface roughness $R_{sv}$ of 8.75 nm and an average visible transmittance of 78.7%.

1. Introduction

Transparent conductive oxides (TCOs) possessing excellent visible transmittance and a high electrical conductivity are widely applied to organic light-emitting devices (OLEDs) [1–3], liquid crystal displays (LCDs) [4–6], plasma display panels (PDPs) [7, 8], and thin-film solar cells (TFSCs) [9–11]. Some semiconductive oxide systems with wide band gaps (3–4.5 eV), such as In$_2$O$_3$, ZnO, and SnO$_2$, were highly considered as TCO materials [12, 13]. Among them, the indium tin oxide (ITO) consisting of In$_2$O$_3$ doped with 5–10% SnO$_2$ is tremendously used in display industry. An electrical resistivity of $2 \times 10^{-4}$ ohm-cm can be easily achieved for ITO films deposited on glass with a substrate temperature of 400°C [14].

Recently, the high electrical conductive indium molybdenum oxide (IMO) drew interests as an alternative to ITO. The IMO also presents a crystal structure of bixbyte (B) In$_2$O$_3$, where In$^{3+}$ is partially substituted by Mo$^{6+}$ and increases more free charge carriers than that of ITO. For example, the IMO film with a lower electrical resistivity of $1.7 \times 10^{-4}$ ohm-cm with a carrier mobility of 100 cm$^2$/Vs and a visible transmittance of 80% has been achieved by Meng et al. [15] via reactive thermal evaporation (RTE) method at a lower substrate temperature of 350°C. Most of IMO deposition works were demonstrated by using a variety of deposition techniques, such as magnetron sputtering [16–18], spray pyrolysis (SP) [19, 20], high density plasma evaporation (HDPE) [21], pulsed laser deposition (PLD) [22], and channel spark ablation (CSA) [23].

In all the aforementioned deposition techniques, the required deposition temperatures for glass substrates were too high for common polymeric substrates which have far lower glass transition temperatures. Polymeric substrates and
the deposited film might be damaged at those reported temperatures. Besides the deposition temperature, the other way to lower down the electrical conductivity for TCO films on glass substrates is increasing film thickness. The thicker film usually shows a higher crystallinity and an electrical resistivity [24–26]. However, the accumulated residual stress which is proportional to the film thickness would cause a distortion of flexible polymeric substrate. In our previous study, to deposit IMO films with a resistivity of \(1.59 \times 10^{-3}\) ohm-cm and a transmittance of 82\% on PES substrates under a deposition temperature of 130°C has been successfully achieved by applying an ion-beam-assisted evaporation (IBAE) [27]. It is demonstrated that the low energy ion beam source can provide an additional energy to adatom migration thus enhances film crystallinity. In this paper, the film thickness was varied under constant working pressure to investigate its influence on the optical and electrical properties.

2. Experimental Procedures

As shown in Figure 1, the IBAE system is composed of vacuum pumps, an electron gun evaporator module, sample holder, a deposition rate monitor, a quartz lamp heater, thermal couple, and a 3 cm diameter end-Hall ion source. In addition to argon gas, oxygen gas was introduced through the mass flow controller (MFC) for reactive evaporation deposition. The deposition temperature and gas pressure were adjusted by quartz lamp power and throttle valve, respectively. Source material was a mixture of 97 wt% In\(_2\)O\(_3\) and 3 wt% MoO\(_3\). The substrate samples were 20 × 20 mm PES squares with a thickness of 200 \(\mu\)m. The glass transition temperature of PES substrate material is 225°C.

Prior to the deposition process, the base pressure was ultimately pumped down to \(2 \times 10^{-2}\) Pa by using a cryopump, and a subsequent 5 min ion cleaning was performed to remove the contamination on the substrate surface. Argon gas was then introduced into the deposition chamber to maintain a constant working pressure of \(4 \times 10^{-2}\) Pa. A closed-loop control technology was used to trigger the argon MFC automatically for ensuring a constant working pressure. Oxygen gas flow was kept at 3 sccm from run to run. The Veeco Mark-I end-Hall ion source is usually sensitive to the pressure, and its appropriate working pressure is between \(2\sim8 \times 10^{-2}\) Pa. The working pressure was carefully controlled for facilitating a stable plasma ion source. The ion beam discharge voltage and discharge current were 110 V (ion beam energy 66 eV) and 0.5 A, respectively. The relation between ion beam energy and discharge voltage has been described in literatures [28, 29].

To prevent the chamber temperature disturbance, especially caused by thermal radiation of ion source and electron gun, a quartz lamp heater was used to accurately control the chamber and specimen temperature at 130 ± 5°C.

PES substrate was predeposited with a very thin (50 ± 3 nm) silicon dioxide (SiO\(_2\)) film as a barrier layer to avoid outgassing. Film thickness was carefully controlled by an \textit{in situ} ULVAC CRTM-6000 monitor and was inspected after words by using Ambios-XP2 surface profilometer. A Mikropack Nanocalc-2000 spectroscopic reflectometer, based on spectral reflectance theory, was also used for film thickness measurement. The film structural characterization was done using a Mac Science MXP3 X-Ray diffractometer with a Cu K\(_\alpha\) radiation. The crystallite size (\(D\)) of IMO films with different thicknesses was calculated from the fringe width at half maximum (FWHM) of the B(222) peak using Scherrer formula [30],

\[
D = \frac{0.9\lambda}{\beta_{2\theta} \cos \theta},
\]

where \(\beta_{2\theta}\) is the FWHM and \(\lambda\) is the wavelength of Cu K\(_\alpha\) radiation. Surface and cross-sectional morphology of the IMO film was observed by using a HITACHI S4800 cold field.
emission scanning electron microscope and a SEIKO SPA400 atomic force microscope. The electrical resistivity was measured by using a Quatek QT-50 four point probe, while the carrier concentration and the mobility were determined by an Ecopia HMS-3000 Hall measurement system with Van der Pauw technique at room temperature. The transmittance of the IMO-deposited PES was measured by using a Shimadzu 1601 UV-Vis spectrometer. The obtained spectra were used to estimate the transmittance spectrum and the optical band gap of each deposited IMO layer. The optical band gap $E_g$ is relevant to the absorbency coefficient $\alpha$ as described in

$$\alpha \propto (h\nu - E_g)^{1/2}, \quad (2)$$

where $h\nu$ is the incident photon energy. The diagram of $\alpha^2$ versus photon energy gives a linear plot. By extrapolation of the $\alpha^2$ value to zero and the intercept at photon energy, the optical band gap of the deposited IMO can be obtained.

3. Results and Discussion

3.1. Microstructure. Figure 2 shows X-ray diffraction (XRD) patterns of the deposited IMO films with various thicknesses. The B(222) peak corresponding to the cubic bixbyite phase appears in each film. Peaks of other phases and PES substrates are not observed. It is also noticeable that the peak intensity of preferred B(222) orientation increases with the film thickness. This somewhat indicates that crystallinity of IMO films is enhanced with the film thickness. It coincides with the results for IMO films on high-density polyethylene (HDPE) substrates [21]. This implies that the film microstructure is insensitive to substrate material. In fact, the preferred orientation of the deposited IMO films is usually more sensitive to process techniques rather than substrate material, because the preferred orientation of IMO films produced by evaporation deposition is very different from those produced by sputtering deposition [31, 32]. It should be associated with the particle energy involved in a deposition process. The same situation has also been
reported in other TCO systems [33, 34], where a same B(222) preferred ITO film was obtained by using an IBAE system. Figure 3 shows the FE-SEM cross-sectional images of the deposited IMO films with various thicknesses. There is a same thick darker SiO2 layer beneath the brighter IMO layer of each sample. All IMO layers present a columnar feature, and the thicker layer exhibits coarser columnar domains. The grown columnar domain size of each IMO film can also be compared from surface morphology images in Figure 4. Each domain is covered with nanogranules. The calculated crystallite sizes of 75 nm, 95 nm, 120 nm, 150 nm, and 170 nm thick IMO films are 14.4 nm, 15.34 nm, 15.6 nm, 15.8 nm, and 16.0 nm, respectively, which also increases with the film thickness. This trend confirms the enhancement of film crystallinity with the thickness. These calculated values are much larger than the surface nanogranules but a bit smaller than the domain. It demonstrates that the change of domain size can relatively indicate the crystallite size change.

3.2. Electrical Properties. Figure 5 shows the dependence of electrical resistivity and surface roughness on the film thickness. The resistivity decreases from $1.10 \times 10^{-3}$ ohm-cm to a minimum of $7.61 \times 10^{-4}$ ohm-cm with increasing the film thickness from 75 nm to 120 nm. However, it subsequently increases to $1.47 \times 10^{-3}$ ohm-cm when the film thickness reaches 170 nm. It is unlike the results on the glass substrate, where the resistivity is found to be continuously decreasing as the film thickness is increasing [25]. The internal stress accumulated with increasing the film thickness might be a reason for the increase of electrical resistivity. The microscopic defects, such as cracks or wrinkles [35, 36] in the deposited films caused by the internal stress, are detrimental to the electrical conductivity. The extended deposition time may also make thicker films receive more radiation or heat, which brings instability in substrate and changes the stress state of the growing film.

From the practical viewpoint, a smooth IMO surface is necessary for an anode layer over the top of multilayered flexible OLEDs. A smooth anode layer can significantly reduce the probability of the short circuit in OLEDs. The surface roughness of the deposited IMO films taken by AFM on an area of $2 \times 2 \mu m$ shows a very smooth surface.
with an $R_{pv}$ (Peak-to-valley roughness) of 8.75 nm. With increasing film thickness, the $R_{pv}$ increases to 13.58 nm due to the enlarged domain size of the deposited films. Higher $R_{pv}$ indicates more spikes on the film surface which may cause the leakage current to occur [37, 38]. The measured $R_{pv}$ of the 120 nm-thick film in this study is 10.32 that is lower than the reported value of $R_{pv}$ 15.4 nm deposited by channel spark ablation [23]. Apparently, the additional ion bombardment on the growing film surface in an IBAE system significantly improves the film roughness. The carrier mobility and carrier concentration of the deposited IMO films with different thicknesses are compared in Figure 6. The carrier concentration of the IMO films is relatively independent and falls into the range between $2.385 \times 10^{20}$ cm$^{-3}$ and $2.455 \times 10^{20}$ cm$^{-3}$. There is more complicated dependency of the carrier mobility on the film thickness.
The mobility initially climbs up from 27.84 cm²/Vs of the 75 nm-thick film to 31.02 cm²/Vs of the 120 nm thick film, a maximum value, and thereafter sharply decreases to 22.60 cm²/Vs for the 170 nm-thick film. It is believed that the thinner films have a larger surface-to-volume ratio, and therefore thin films may contain more defects than thicker films. Besides, the smaller domain size in IMO thinner films tends to scatter charges in the more domain boundaries. The greater scattering of carriers, therefore, results in a low mobility [39]. Nevertheless, the potential internal-stress-induced microscopical cracks in the thicker films also could result in the charge scattering. Thus, a maximum mobility is found at the thickness of 120 nm in this study. This result agrees quite well with those reported ITO material systems [40, 41].

3.3. Optical Properties. Figure 7 shows transmittance spectra of different IMO deposited PES. Due to the differences between PES, SiO₂, and IMO layers, all transmittance spectra present interference fringes [42]. It is difficult to compare the transmittance of specific wavelength of each IMO layer. The average transmittance for visible region (400–700 nm) of all samples were, therefore, calculated. The average transmittance of the samples with 75 nm, 95 nm, 120 nm, 150 nm, and 170 nm thick IMO films is 71.3%, 75.0%, 77.4%, 78.7%, and 79.3%, respectively. The 75 nm thick film presents a brown color and a lowest average transmittance. The average transmittance proportionally increases as the film thickness increases. It might be due to the lesser grain boundary scattering effect in higher crystalline thicker films [43]. However, the constructive or destructive interference caused by the thickness difference between high refractive index IMO film, a low refractive index SiO₂ film, and lower refractive index PES significantly affect the transmittance [44]. The refractive index of IMO layer might also increase due to the accumulated internal stress with the film thickness. The reasons of increased transmittance with coated thickness remain in suspense.

The estimated optical band gap of the deposited IMO films is presented in Figure 8. The band gap approximately increases from 3.44 eV to 3.58 eV, as the film thickness is increased. The similar trend of band gap in Figure 8 and the carrier concentration in Figure 6 indicates that free carrier concentration difference might facilitate the absorption edge shift to the higher energy, as the Burstein-Moss band-filling effect [45]. However, this supposition still requires other complementary characterizations.

4. Conclusions

In this paper, the influence of film thickness on optical and electrical properties of low-temperature IBAE-deposited IMO thin films onto PES substrates was investigated. The deposited IMO films are crystalline and exhibits a preferred orientation along B(222) of bixbyite B-In₂O₃ phase. It demonstrates that Mo₆⁺ ions are solid solved and partially substitute In³⁺ sites in the B-In₂O₃. A columnar structure of IMO film is observed. The columnar domain size and crystallite size both increase with the film thickness. A very low electrical resistivity of the deposited IMO film is mainly due to the increased carrier mobility. However, the potential defects induced by accumulated internal stress in films might cause the film discontinuity and increase the electrical resistivity when the film thickness is over 170 nm. The lowest electrical resistivity of 7.61 × 10⁻⁴ ohm-cm with an average transmittance of 78.7% and surface roughness Rₚ of 8.75 nm has been achieved on the 120 nm thick IMO film. This satisfies the requirement for a flexible transparent conductive polymer substrate.

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