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Electrical and optical properties of indium tin oxide thin films grown by pulsed laser deposition

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Abstract. Indium tin oxide (ITO) thin films (200–400 nm in thickness) have been grown by pulsed laser deposition (PLD) on glass substrates without a post-deposition anneal. The electrical and optical properties of these films have been investigated as a function of substrate temperature and oxygen partial pressure during deposition. Films were deposited at substrate temperatures ranging from room temperature to 300 °C in O_2 partial pressures ranging from 0.1 to 100 mTorr. For 300 nm thick ITO films grown at room temperature in oxygen pressure of 10 mTorr, the electrical conductivity was $2.6 \times 10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ and the average optical transmittance was 83% in the visible range (400–700 nm). For 300 nm thick ITO films deposited at 300 °C in 10 mTorr of oxygen, the conductivity was $5.2 \times 10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ and the average transmittance in the visible range was 87%. Atomic force microscopy (AFM) measurements showed that the RMS surface roughness for the ITO films grown at room temperature was ∼7 Å, which is the lowest reported value for the ITO films grown by any film growth technique at room temperature.

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Indium tin oxide (ITO) thin films have been extensively used as transparent conducting electrodes in flat-panel displays (FPDs), organic light-emitting diodes (OLEDs) and solar cells because they have high electrical conductivity, high optical transparency, and smooth surface morphology [1–3]. ITO thin films have been prepared by various deposition techniques including chemical vapor deposition (CVD), magnetron sputtering, vacuum evaporation and spray pyrolysis [1]. However, in order to obtain high-quality ITO films, these techniques require either a high substrate temperature (300–500 °C) during deposition or a post-deposition annealing treatment of the films at high temperature (400–700 °C). These high-temperature treatments generally damage surfaces of both the substrate and the film.

Recently, ITO films have also been grown by pulsed laser deposition (PLD) [2, 4–6]. PLD provides several advantages compared to other techniques. The composition of films grown by PLD is quite close to that of the target, even for a multicomponent target. PLD films may crystallize at lower substrate temperatures relative to other physical vapor deposition (PVD) techniques due to the high kinetic energies (>1 eV) of the atoms and ionized species in the laser-produced plasma [7]. Also, the surface of films grown by PLD is very smooth so that ITO films grown by PLD can be used as an anode contact in OLEDs [2].

In this paper, we present a study of the electrical and optical properties of the ITO films deposited by PLD on glass substrates without a post-deposition anneal. Film properties were measured as a function of substrate deposition temperature and oxygen deposition pressure.

1 Experiment

ITO thin films were deposited by PLD on glass substrates (Corning 7059) [7]. A KrF excimer laser (Lambda Physics LPX 305) with a wavelength of 248 nm and pulse duration of 30 ns delivered an energy of 300 mJ per pulse. The laser was operated at 10 Hz and was focused through a 50-cm focal length lens onto a rotating target at a 45° angle of incidence. The energy density of the laser beam at the target surface was maintained at $2\,\mathrm{J/cm^2}$. The target-to-substrate distance was 4.7 cm. The geometry of this PLD system produced uniform films over 1.5 cm × 1.5 cm substrate area with a thickness variation of less than 10%. The substrate was attached with a stainless steel mask to a steel block, which was heated by two quartz lamps. The temperature of the steel block was monitored with a thermocouple at all times.

The target was a 5-cm diameter In_2O_3 (95%) + SnO_2 (5% by weight). The substrates were cleaned in an ultrasonic cleaner for 10 minutes with acetone and then methanol. All substrates were blown dry with nitrogen gas before they were introduced into the deposition system. During deposition, oxygen background gas was introduced into the chamber to maintain the desired pressure using a capacitance manome-

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ter from 0.1 to 100 mTorr. During deposition, the substrate temperatures was fixed to the desired temperature (25 °C to 300 °C). After deposition, the films deposited at elevated temperature were cooled to room temperature at the same oxygen deposition pressure.

The film thickness was measured by a stylus profilometer (Tencor Alpha-Step 250). The sheet resistance (R_s) measurements were performed using a four-point probe. By assuming that the thickness of the films is uniform, the film resistivity (ϱ) was determined using the simple relation $\varrho = R_s d$, where d is the film thickness. Hall mobility and carrier density measurements were made using the Van der Pauw method [8] at room temperature with magnetic field strength of 5 kG. The optical transmittance and reflectance measurements were made using a UV-visible-near IR spectrophotometer (Perkin-Elmer Lambda 9). All transmittance and reflectance values were normalized by the values of the bare substrate. The badgap (E_g) was determined by extrapolations of the straight regions of the plots of square of the absorption coefficient α^2 vs. photon energy ($h\nu$). The absorption coefficient α was determined by the equation, $\alpha = \ln(1/T)/d$, where T is optical transmission and d is the film thickness. Refractive indices of the films were determined from the reflectance maxima data using the following relation: $nd = k\lambda/4$, where n is the refractive index, d is the film thickness [nm], λ is the wavelength [nm], and k is the interference order (an odd integer) [9]. X-ray diffraction (XRD) (Rigaku rotating anode X-ray generator with Cu K_α radiation) was used to characterize the crystal structure of the films. From an analysis of the diffraction pattern, we determined the lattice parameter, preferred orientation and average grain size of the deposited films. Scanning electron microscope (SEM) [LEO-1500] and atomic force microscopy (AFM) (Digital Instrument, Dimension 3100 series) were used to evaluate the surface morphology of the films.

2 Results and discussion

We have studied the electrical properties of the ITO films as a function of target composition with SnO_2 content (0–15 wt. %) and found that the 5 wt. % of SnO_2 in the target was the optimum composition to achieve the maximum film conductivity [10]. Hence, the 5-wt. % SnO_2-doped In_2O_3 target was used to deposit ITO films in this work. We have also performed the Hall measurements for the ITO films and all of the ITO films grown by PLD were observed to be n-type semiconductors. The substrate temperature and oxygen background gas pressure are typical deposition conditions that can be controlled during deposition to obtain ITO films of high electrical conductivity and optical transparency.

The substrate deposition temperature was found to have a significant effect on the electrical and optical properties of the ITO films. Figure 1 shows the variation of electrical conductivity (σ) and average optical transmittance (T_a = % transmittance from 400–700 nm) as a function of substrate deposition temperature for the ITO films (∼300 nm). Deposition conditions other than substrate deposition temperature were maintained constant for each film. The conductivity of the ITO films increases from 2.6×10^3 to $5.2 \times 10^3\ \Omega^{-1}\text{cm}^{-1}$ as the substrate deposition temperature is increased from 25 °C to 300 °C. The increase in conductivity with increase

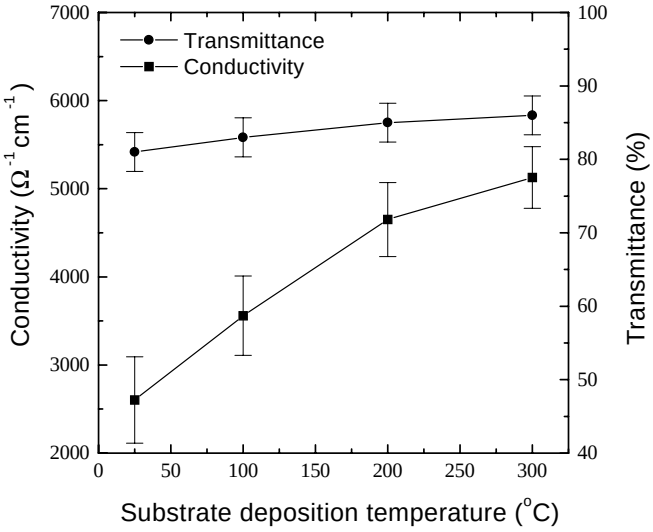

Fig. 1. Variation of electrical conductivity (σ) and average optical transmittance (T_a) as a function of substrate deposition temperature for the ITO films. Film thickness was about 300 nm for all films. Oxygen pressure was kept in 10 mTorr during deposition. All transmittance values were determined as an average in visible range from 400 nm to 700 nm

in growth temperature can be explained by the fact that the grain size increases significantly with increasing the growth temperature, thus reducing the grain boundary scattering and increasing the conductivity. It is also observed that the average optical transmittance (T_a) increases slightly from 83% to 87% with increasing the substrate temperature from 25 °C to 300 °C. This increase in optical transmittance is also related to the increase in grain size of the films with increasing the substrate temperature.

The substrate deposition temperature also affects other properties of the film such as the direct bandgap, the plasma wavelength and the refractive index. Figure 2 shows the variation of direct bandgap (E_g), plasma wavelength (λ_p) and refractive index (n) as a function of the substrate deposition temperature for the ITO films deposited in 10 mTorr of oxygen. The direct bandgap of the ITO films increases from 3.89 eV to 4.21 eV as the substrate deposition temperature increases from 25 °C to 300 °C. This shift of the bandgap can be explained by the Burstein-Moss effect [11, 12] in which the absorption edge shifts towards higher energy with an increase of carrier concentration [10]. The plasma wavelength (or cutoff wavelength) (λ_p), which is defined at Transmittance=Reflectance, where the dielectric-like transmission equals the metallic-like IR reflectance, is observed to initially decrease with increasing the substrate deposition temperature up to 100 °C and then slightly increase up to 300 °C. In Fig. 2, it is also observed that the refractive index (at 550 nm of wavelength) decreases from 2.14 to 1.81 with an increase in the substrate deposition temperature from 25 °C to 300 °C.

The oxygen deposition pressure was also found to affect the electrical and optical properties of the ITO films. Figure 3 shows the variation of electrical conductivity (σ) and average optical transmittance (T_a) as a function of oxygen deposition pressure for the ITO films (∼200 nm). Deposition conditions other than oxygen pressure were maintained constant for each film. The conductivity of the ITO films deposited at 25 °C is very sensitive to oxygen pressure. High-conductivity

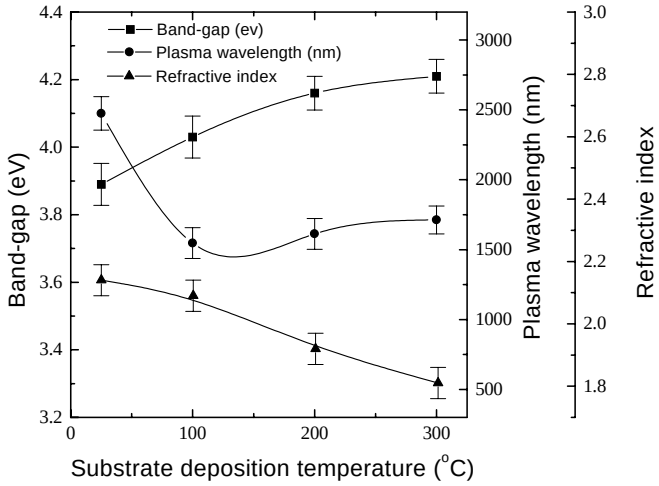

Fig. 2. Variation of direct bandgap (E_g), plasma wavelength (λ_p) and refractive index (n) as a function of substrate deposition temperature for the ITO films deposited in 10 mTorr of oxygen

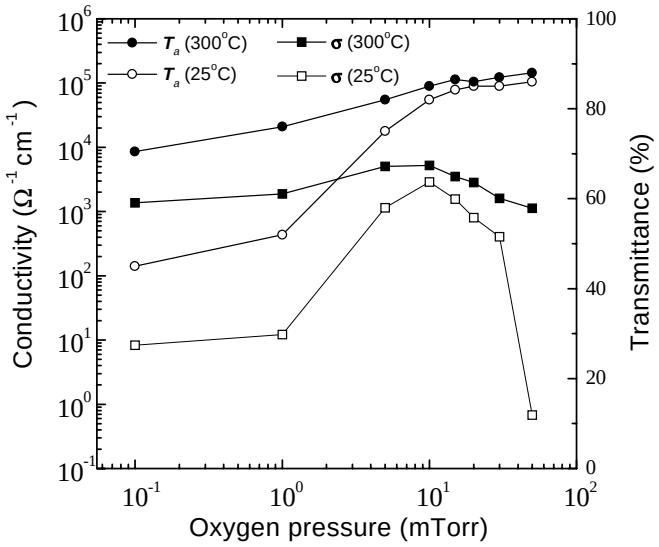

Fig. 3. Variation of electrical conductivity (σ) and average optical transmittance (T_a) as a function of oxygen pressure for the ITO films grown at 25 °C and 300 °C. Film thickness was about 200 nm for all films. All transmittance values were determined as an average in visible range from 400 nm to 700 nm ■ (σ, 300 °C); □ (σ, 25 °C); ● (T_a, 300 °C); ○ (T_a, 25 °C)

ITO films are obtained only between 5 and 15 mTorr of oxygen. However, the conductivity of the ITO films deposited at 300 °C is less dependent on the oxygen pressure. The increase in the conductivity with a decrease in oxygen pressure from 50 mTorr to 10 mTorr can be explained by the number of oxygen vacancies in the ITO films. Decreasing the oxygen pressure increases the number of oxygen vacancies in the film and thus increases the carrier concentration and increases the film conductivity. However, this increase in carrier concentration also leads to a decrease in the optical transmittance due to an increase in free carrier absorption. Figure 3 shows this inverse relationship between the conductivity and transmittance of the ITO films. The optical transmittance increases with increasing oxygen pressure from 10 mTorr to 50 mTorr for the ITO films grown at both 25 °C and 300 °C. This is related to the improvement of the film crystallinity with increasing

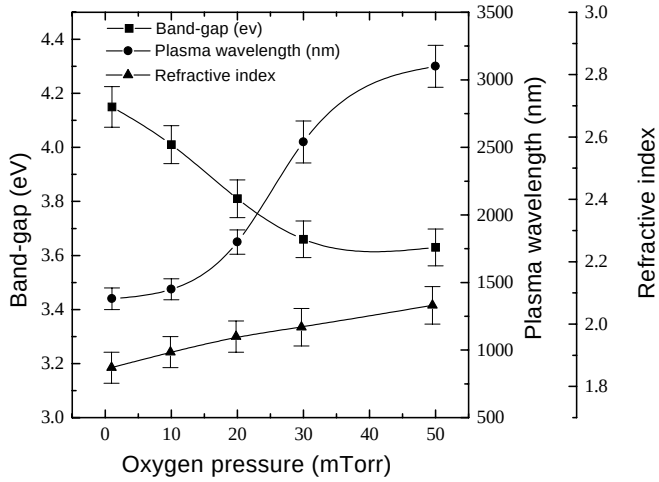

Fig. 4. Variation of direct bandgap (E_g), plasma wavelength ($lambda_p$) and refractive index (n) as a function of oxygen pressure for the ITO films deposited at 300 °C. Film thickness was about 400 nm for all films in this figure

the oxygen pressure since the width of the (222) XRD peak decreased and the intensity of the (222) peak increased with increasing the oxygen pressure.

The oxygen pressure also affects the direct bandgap, the plasma wavelength and the refractive index of the films. Figure 4 shows the variation of direct bandgap (E_g), plasma wavelength (λ_p) and refractive index (n) as a function of oxygen pressure for the ITO films (∼400 nm) deposited at 300 °C. The direct bandgap of the ITO films decreases from 4.14 eV to 3.63 eV as the oxygen pressure increases from 1 mTorr to 50 mTorr. This decrease in the direct bandgap with an increase in oxygen pressure is due to a decrease in carrier concentration. This is also explained by the Burstein-Moss shift [11, 12], which is related to the carrier concentration of the film. The plasma wavelength of the ITO films increases from 1380 nm to 3100 nm with increasing oxygen pressure from 1 mTorr to 50 mTorr. It is also observed in Fig. 4 that the refractive index of the ITO films at 550 nm increases from 1.86 to 2.06 with increasing oxygen pressure from 1 mTorr to 50 mTorr.

Since the organic thin films employed in OLEDs are directly deposited on the ITO anode, the surface roughness of the ITO affects the device performance. Figure 5 shows AFM image (2 μm × 2 μm) of an ITO film deposited on silica substrate at room temperature in 10 mTorr of oxygen. Prior to AFM measurements, the film was washed with methanol and then blown dry with nitrogen gas. The r.m.s. surface roughness for the ITO film is ∼7 Å, which is the lowest value ever reported for the ITO films grown by any other technique at room temperature. For comparison, the r.m.s. surface roughness for the bare silica substrate is 12.5 Å. The grain size of the film shown in Fig. 5 is observed to be 20–40 nm.

3 Summary

High-quality ITO films have been deposited on glass substrates by PLD. The electrical and optical properties of the ITO films have been investigated as a function of substrate deposition temperature and oxygen deposition pressure. All

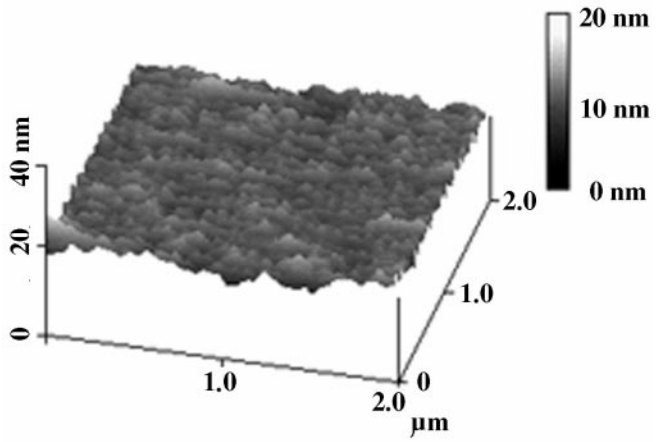

Fig. 5. AFM image (2 µm × 2 µm) of the ITO film grown by PLD on silica substrate at room temperature in 10 mTorr of oxygen. Note that the scale in the *z*-direction (20 nm/div.) is greatly expanded with respect to the scales in the *x*- and *y*-directions (1.0 µm/div.) and therefore, in fact, the crystallites are flat and broad in the lateral direction

of the ITO films grown by PLD were found to be *n*-type semiconductors. Decreasing oxygen pressure up to 10 mTorr created more oxygen vacancies and thus increased conductivity of the films. However, this increase in oxygen vacancies also leads to a decrease in the optical transmittance due to an increase in free carrier absorption. The bandgap, the plasma wavelength and the refractive index for the ITO films were strongly affected by deposition conditions such as substrate deposition temperature and oxygen deposition pressure. An increase in the bandgap was observed by increasing the substrate deposition temperature and/or by decreasing the oxygen pressure. The change is due to an increase in carrier concentration in the films. A reduction of the refractive index for ITO films can be achieved by raising the electron density in the films, which can be obtained by increasing deposition temperature or decreasing oxygen pressure. The plasma wavelength of the ITO films was controlled by changing the substrate deposition temperature and oxygen pressure. For 300 nm thick ITO films grown at room temperature in oxygen pressure of 10 mTorr, the electrical conductivity was $2.6 \times 10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ and the average transmittance in the visible range was 83%. For 300 nm thick films deposited at 300 °C in 10 mTorr of oxygen, the conductivity was $5.2 \times 10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ and the average transmittance in the visible range was 87%. ITO films deposited by PLD at room temperature have the surface roughness of 7 Å, which is approximately 1 order of magnitude smaller than commercial ITO films grown by sputtering.

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