Indium Tin Oxide Thin Films Grown on Polyethersulphone (PES) Substrates by Pulsed-Laser Deposition for Use in Organic Light-Emitting Diodes

Kyung-Hyun Kim, Nae-Man Park, Tae-Youb Kim, Kwan Sik Cho, Jeong-Ik Lee, Hye Yong Chu, and Gun Yong Sung

High quality indium tin oxide (ITO) thin films were grown by pulse laser deposition (PLD) on flexible polyethersulphone (PES) substrates. The electrical, optical, and surface morphological properties of these films were examined as a function of substrate temperature and oxygen pressure. ITO thin films, deposited by PLD on a PES substrate at room temperature and an oxygen pressure of 15 mTorr, have a low electrical resistivity of 2.9×10^{-4} Ω cm and a high optical transmittance of 84 % in the visible range. They were used as the anode in organic light-emitting diodes (OLEDs). The maximum electro luminescence (EL) and current density at 100 cd/m^2 were 2500 cd/m^2 and 2 mA/cm^2, respectively, and the external quantum efficiency of the OLEDs was found to be 2.0 %.

Keywords: Indium tin oxide (ITO), plastic substrate, pulse laser deposition (PLD), organic light-emitting diodes (OLED).

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I. Introduction

Indium tin oxide (ITO) is widely used as a transparent conducting electrode for optoelectronic devices such as liquid crystal flat panel displays (LC-FPD) and solar cell devices [1], [2]. ITO is a highly degenerate n-type semiconductor, which has a low electrical resistivity of 2×10^{-4} Ω cm to 4×10^{-4} Ω cm and a wide band gap (3.3 eV to 4.3 eV). It shows a high transmission in the visible and near infrared (IR) regions of the spectrum. ITO thin films are mainly deposited on rigid substrates, including glass and Si wafers by sputtering [3], evaporation [4], and spray pyrolysis [5] techniques. Glass substrates are difficult to use for large area displays, electronic maps, smart cards, and portable computers because they are very brittle, too heavy, and not deformable. These disadvantages can be overcome if flexible substrates could be used. The layers are robust, lightweight, and cost effective. For these reasons, flexible plastic substrates have been used in active and passive displays such as liquid crystal displays (LCD) [6] and polymeric and molecular organic light-emitting diodes (OLEDs) [7].

To apply for good optoelectronic devices, optically transparent plastic substrates must endure during the growth of the metal oxides and device fabrication. For most flexible display devices, polyethylene terephthalate (PET) substrates are used for the growth of transparent conducting oxide thin films [6], [8]. However, many researchers and OLED developers require new plastic substrates that have a higher processing temperature than PET in order to improve the

electrical and optical properties. We report here on the study of the electrical, optical, and surface morphological properties of ITO thin films grown on polyethersulphone (PES) by pulsed laser deposition (PLD) and also demonstrate the use of these films as transparent anode electrodes for OLEDs. To date, no reports on OLED fabrication with a PLD-deposited ITO on a PES substrate have been made.

II. Experiment

ITO thin films were deposited on PES substrates using a KrF excimer laser (Lambda Physik Compex 102 with a wavelength of 248 nm). The laser was operated at 10 Hz and focused through a 30 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 J/cm [9]. The target-substrate distance was 6.5 cm. Before deposition, the rotating target, which was maintained at 10 rpm during the deposition, was ablated for 1000 shots. The geometry of this PLD system produced uniform films over 2 cm × 2 cm substrate areas with a thickness deviation of less than 10%. The substrate was attached with a stainless steal shadow mask to a substrate heater, which was heated by resistance heating. The substrate temperature was maintained at a constant during the deposition using a temperature controller with input from a thermocouple imbedded in the center of the stainless steal substrate heater.

The target was a 1 inch diameter by 0.25 inch thick sintered disk containing In_2O_3 (95%) + SnO_2 (5%) by weight. The PES substrate used in this study was supplied by Sumitomo (Japan) and is heat stabilized to give an excellent dimensional stability at temperatures up to 220°C. The PES substrates were cleaned by wet and dry cleaning methods. The wet cleaning process was followed by ultrasonic cleaning for 5 min with isopropyl alcohol and deionized water. The dry cleaning requires the use of Ar or O_2 with a low RF power for 10 seconds. After the cleaning process, the PES substrate was mounted on a substrate holder, and the chamber was evacuated to a pressure of a 10^{-6} Torr. During the deposition, oxygen was introduced into the chamber to maintain the desired pressure, which was monitored with a mass flow controller (MKS) from 10 to 100 mTorr. The deposition temperature was fixed at the desired temperature (25 to 130°C). If the growth occurred at an elevated temperature, the films were cooled to room temperature under the range of 10^{-6} Torr. The oxygen pressure and substrate temperature were optimized so as to produce high quality ITO thin films with a low resistivity and high transparency. A low root-mean square (RMS) roughness is also important for application of OLEDs.

After the photolithography process of preparing a pattern for thickness measurement, the thickness of the ITO/PES film was measured with a stylus profilometer (Tencor Alpha-step 500). The electrical properties, including resistivity, sheet resistance, mobility, and carrier concentration, were measured using a Hall measurement system (HL 5500PC). Hall mobility and carrier concentration measurements were made using the Van der Pauw method at room temperature with a magnetic field of 5000 G. Optical transmission measurements were obtained using an ultraviolet (UV)-visible near-infrared spectrometer (U-3501, by Hitachi). The surface morphology of the films was determined using a non-contact mode atomic force microscopy.

The OLED structure consists of a hole transport layer, an electron transport layer, and an emitting layer. Organic layers and a cathode less than were deposited by vacuum vapor deposition at less than 3×10^{-7} Torr. A schematic diagram of an OLED structure on a PES substrate is shown in Fig. 3(a).

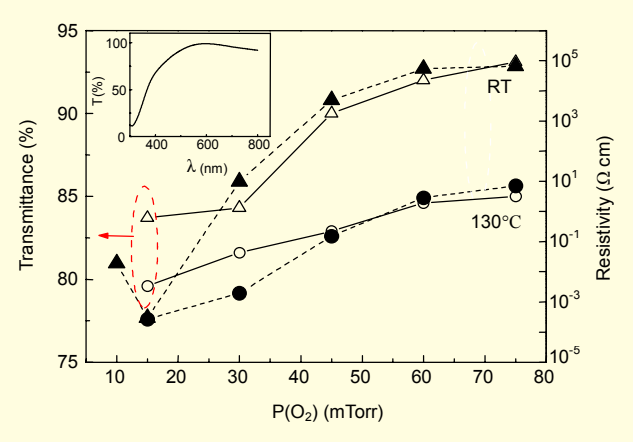

Fig. 1. Electrical resistivities and optical transmittance of ITO thin films, plotted as a function of oxygen pressure at different substrate temperatures. Optical transmittance of ITO thin films is the average value in the visible range. The inset shows the transmittance of ITO/PES grown at 15 mTorr.

III. Results and Discussion

Figure 1 shows plots of electrical resistivity and optical transmittance as a function of oxygen pressure during the deposition of ITO thin films on the PES substrate at room temperature and 130°C. It is clear that the electrical resistivity of the ITO films dramatically changes with the partial pressure of oxygen. Within the full oxygen pressure region, the resistivity of the ITO films grown at room temperature was also higher than that for a substrate temperature of 130°C. We conclude that the lower resistivity at 130°C is the result of an improved crystallinity, high oxygen vacancy concentration, and grain growth, which reduces grain boundary scattering and surface roughness. As the oxygen local pressure decreases, the resistivity of ITO also decreases. This can be explained by the change in the number of residual oxygen vacancy sites in the

Table 1. Electrical and optical properties of ITO thin films deposited on different substrates using different deposition techniques. All transmittance values were normalized by the transmission of their own bare substrates.

Deposition technique	Target	Sub.	T_s (°C)	R_s (Ω/□)	ρ (Ω cm)	T_{ave} (%) (invisible)	n (cm^{-3})	μ (cm^2/Vs)	Ref.
IAD	90:10	PET	RT	35		85	5×10^{20}	19	10
Sputter	90:10	PES	180	25	2.6×10^{-4}	80			16
PLD	95:5	PET	RT	70	7.00×10^{-4}	87			7
	95:5	PES	RT	16.3	2.94×10^{-4}	84	2.1×10^{21}	10.2	ETRI
	95:5	PES	130	14	2.7×10^{-4}	80	2.6×10^{21}	8.9	ETRI

ITO film. In the case where the deposition was carried out at a low oxygen pressure or at a high substrate temperature, the ITO had an almost metallic resistivity because of the large number of oxygen vacancies. However, when the oxygen pressure is below 10 mTorr, resistivity increases in a reverse fashion [7]. The origin of increasing resistivity of the ITO film has a couple of possibilities. First, if many free electrons exist in ITO films, the mobility is rapidly decreased by scattering with carriers or with crystal defects. Second, if a change in chemical composition or micro-crystal structure of an ITO film occurs, resistivity can increase. Resistivities of $2.7 \times 10^{-4}\Omega$ cm and $2.9 \times 10^{-4}\Omega$ cm were reproducibly obtained for ITO films deposited at 130°C and 25°C, respectively. Figure 1 also shows that the optical transmittance of the ITO films changes with oxygen pressure and a strong correlation with electrical resistivity. As resistivities increase, the optical transmittance of ITO thin films increase with oxygen pressure. Therefore, optical transmittance is also closely related to oxygen vacancies, which are associated with free electrons in ITO films. We conclude that many electrons or disordered lattice structures in ITO films are scattered by incident light, thus reducing the transparency of the ITO thin film. Table 1 shows data on the resistivity, sheet resistance, mobility, carrier concentration, and transmittance of ITO films grown on various substrates at room temperature. A lower sheet resistance of 16.3 Ω/□ and a higher optical transmittance of 84 % were obtained, compared to other reports [7], [9], [10], [12], and [13].

Figure 2 shows four 3D-AFM images (5 μm × 5 μm × 0.04 μm) of ITO films deposited by PLD at different substrate temperatures and using different oxygen pressures. The films in Figs. 2(a) and 2(b) are deposited in 15 mTorr and 75 mTorr at 130°C. The films in Figs. 2(c) and 2(d) are carried out at 15 mTorr and 75 mTorr at 25°C. The RMS surface roughness for each ITO thin film was 9Å, 12Å, 6Å, and 19Å, respectively. RMS roughness of the base PES substrate is about 2 Å (not shown here). This indicates that the RMS surface roughness of this ITO/PES is much lower than that of sputtered ITO films [12]. However, the surface morphology of the PLD ITO films

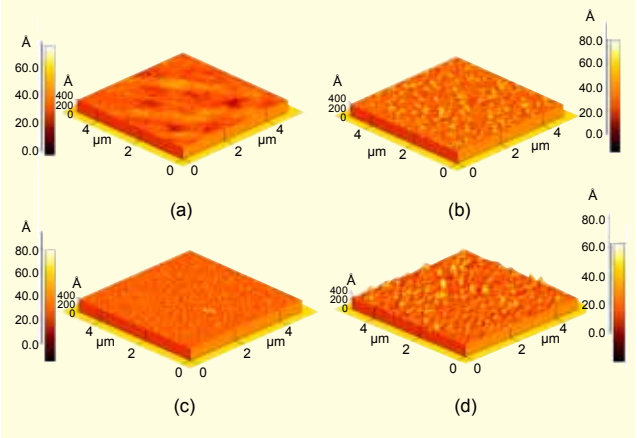

Fig. 2. 3D-AFM images (5 μm × 5 μm × 0.04 μm) of the ITO films grown on polyethersulphone (PES) substrates in (a) 15 mTorr and (b) 75 mTorr at 130°C, and (c) 15 mTorr and (d) 75 mTorr at 25°C.

grown on PET [6] or polycarbonate [16] has a higher RMS value than ours. The RMS surface roughness of the ITO/PES has a low value at a relatively higher deposition temperature and low oxygen pressure. Eventually, the average surface roughness of an ITO is dependent on the oxygen pressure and deposition temperature. The flat surface morphology of thin ITO films could protect against cathode-to-anode electrical shorts in OLEDs.

Figure 3(a) shows current-voltage-luminescence (J-V-L) output profiles for an OLED using an ITO anode grown on PES at room temperature by PLD. The device structure included a 60 nm thick N, N'-bis-[1-naphthyl (N,N'-diphenyl-1,10-biph-enyl-4,4'-diamine)] (NPB) as a hole transport layer; a 60 nm thick tris-[8-hydroxyquinoline] aluminum (Alq) as an electron transport layer, and a cathode. The cathode included a 12 Å thick LiF and a 1,000 Å thick Al layer.

The luminance and color chromaticity of the devices were measured with a Minolta LS100 luminance meter and Minolta CS1000 spectrophotometer. A Keithley 238 electrometer was used to measure the current-voltage characteristics. Both I-V and L-V curves of the OLED show a typical diode behavior,

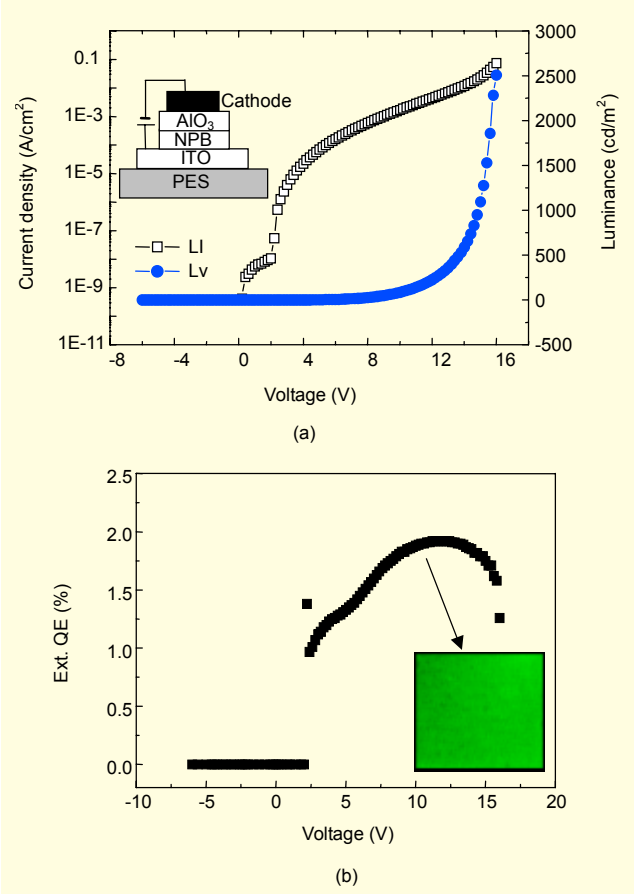

Fig. 3. (a) Current-voltage-luminescence (I-V-L) curves of an OLED and (b) its measured external quantum efficiency. The inset of (a) is an OLED structure and the inset of (b) is the emission image of a 2 mm × 2 mm active area at 11 V.

with current and power output observed in the forward bias. Compare to our OLED with a control device, which was made on glass using a commercial ITO, they have a similar leakage current and current density at 100 cd/m^2. Current density of the control device and our OLED are 2.2 mA/cm^2 and 2 mA/cm^2, respectively. Figure 3(b) shows that the external quantum efficiency (η_{ext}) of the device is about 2.0%. This value is comparable to the reported external quantum efficiency (η_{ext}: 1.5% to 2.5%) using a commercial ITO from different substrates as the anode [14]-[15]. The inset of Fig. 3(b) is the emission image of a 2 mm × 2 mm active area of the OLED. This external quantum efficiency value and uniform emission image indicate that PLD ITO thin films, grown on a PES substrate at room temperature are of acceptable quality.

IV. Conclusion

High-quality ITO thin films were grown on flexible PES substrates by PLD without post annealing. For a 180 nm thick room-temperature grown ITO thin film, the electrical resistivity was 2.9 × 10^{-4} Ω cm, and the average value of optical transmittance was 84 % in the visible range. In addition, the RMS surface roughness of an ITO grown by PLD is much lower than other commercial ITO films. These properties of PLD-ITO grown on PES are impressive when compared with considerable values of other ITO films. ITO thin films were used as the anode in OLEDs and the device performance was measured. Electro-luminescence is slightly higher than that of an ITO/PET substrate [7], and the external quantum efficiency is similar to that of commercial ITO films [11]-[13]. This indicates that a low temperature grown ITO film by PLD is a good candidate for use as an anode in high performance OLEDs.

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References

[1] I.Hamberg and C.G. Granqvist, "Evaporated Sn-doped In_2O_3 Films: Basic Optical Properties and Applications to Energy-Efficient Windows," *J. Appl. Phys.* vol. 60, 1986, pp. R123-R160.

[2] K. Zhang, F. Zhu, C. Huan, and A. Wee, "Indium Tin Oxide Films Prepared by Radio Frequency Magnetron Sputtering Method at a Low Processing Temperature ," *Thin Solid Films*, vol. 376, 2000, pp.255-263.

[3] M. Buchanan, J.B. Webb, and D.F. Williams, "Preparation of Conducting and Transparent Thin Films of Tin-doped Indium Oxide by Magnetron Sputtering," *Appl. Phys. Lett.* vol. 37, 1980, pp. 213-215.

[4] P. Nath, R.F. Bunshah, B.H. Basol, and O.M. Staffsud, "Electrical and Optical Properties of In_2O_3: Sn Films Prepared by Activated Reactive Evaporation," *Thin Solid Films*, vol. 72, 1980, pp. 463-468.

[5] V. Vasu and A. Subrahmanyam, "Reaction Kinetics of the Formation of Indium Tin Oxide Films Grown by Spray Pyrolysis," *Thin Solid Films*, vol. 193-194, 1990, pp. 696-703.

[6] N.D. Young, R.M. Bunn, R.W. Wilks, D.J. McCulloch, S.C. Deane, M.J. Edwards, G. Harkin, and A.D. Pearson, "Thin-Film-Transistor- and Diode-Addressed AMLCDs on Polymer Substrates," *J. Soc. Inf. Disp.* vol. 5/3, 1997, pp. 275-281.

[7] H. Lim, W.J. Cho, C.S. Ha, S. Ando, Y.K. Kim, C.H. Park, and K. Lee, "Flexible Organic Electroluminescent Devices Based on Fluorine-Containing Colorless Polyimide Substrates," *Adv. Mater.*, vol. 14, 2002, pp.1275-1279.

[8] H. Kim, J.S. Hortwitz, G.P. Kushto, Z.H. Kafafi, and D.B. Chrisey, "Indium Tin Oxide Thin Films Grown on Flexible Plastic Substrates by Pulsed-Laser Deposition for Organic Light-Emitting Diodes," *Appl. Phys. Lett.*, vol. 79, 2001, pp. 284.

[9] N.M. Park, S.H. Kim, and G.Y. Sung, "Band Gap Engineering of SiCN Film Grown by Pulsed Laser Deposition," *J. Appl. Phys.* vol. 94, 2003, pp. 2725-2728.

[10] Nae-Man Park, Sang Hyeob Kim, and Gun Yong Sung, "Amorphous Silicon Carbon Nitride Films Grown by the Pulsed Laser Deposition of a SiC-Si_3N_4 Mixed Target," *ETRI J.*, vol. 26, no. 3, 2004, pp.257-261.

[11] Y. Yang, Q. Huang, A.W. Metz, J. Ni, S. Jin, T.J. Marks, M.E. Madsen, A. Divenere, and S.T. Ho, "High-Performance Organic Light-Emitting Diodes Using ITO Anodes Grown on Plastic by Room-Temperature Ion-Assisted Deposition," *Adv. Mater.,* vol. 16, 2004, pp. 321-324.

[12] M.S. Hwang, H.J. Lee, H.S. Jeong, Y.W. Seo, and S.J. Kwon, "The Effect of Pulsed Magnetron Sputtering on the Properties of Indium Tin Oxide Thin Films," *Surf. and Coat. Tech.*, vol. 171, 2003, pp. 29-33.

[13] J. Ma, S.Y. Li, J.Q. Zhao, and H.L. Ma, "Preparation and Properties of Indium Tin Oxide Films Deposited on Polyester Substrates by Reactive Evaporation," *Thin Solid Films*, vol. 307, 1997, pp. 200-202.

[14] J. Kido and Y. Iizumi, "Fabrication of Highly Efficient Organic Electroluminescent Devices," *Appl. Phys. Lett.*, vol. 73, 1998, pp.2721-2723.

[15] H. Murata, C.D. Merritt, H. Mattoussi, and Z.H. Kafafi, "Dye-Doped Molecular Light-Emitting Diodes with Enhanced Performance," *Proc. SPIE* , vol. 3476, 1998, pp.88-95.

[16] H. Izumi, T. Ishihara, H. Yoshida, and M. Motoyama, "Electrical Properties of Crystalline ITO Films Prepared at Room Temperature by Pulsed Laser Deposition on Plastic Substrates," *Thin Solid Films*, vol. 411, 2002, pp. 32-35.

[17] S.K. Park, J.I. Han, W.K. Kim, and M.G. Kwak, "Deposition of Indium–Tin-Oxide Films on Polymer Substrates for Application in Plastic-based Flat Panel Displays," *Thin Solid Films*, vol. 397, 2001, pp. 49-55.

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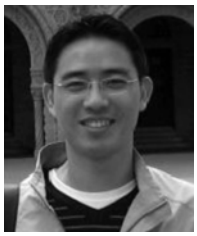

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