

Indium tin oxide thin films grown on flexible plastic substrates by pulsed-laser deposition for organic light-emitting diodes

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Transparent conducting indium tin oxide (ITO) thin films were grown by pulsed laser deposition (PLD) on flexible polyethylene terephthalate (PET) substrates. The structural, electrical, and optical properties of these films were investigated as a function of substrate deposition temperature and background gas pressure. ITO films (200 nm thick), deposited by PLD on PET at 25 °C and 45 mTorr of oxygen, exhibit high optical transparency ($\sim 87\%$) in the visible (400–700 nm) with a low electrical resistivity of $7 \times 10^{-4} \Omega \text{ cm}$. ITO films grown by PLD on PET were used as the anode contact in organic light-emitting devices. A luminous power efficiency of $\sim 1.6 \text{ lm/W}$ was achieved at 100 cd/m^2 , slightly higher than that ($\sim 1.5 \text{ lm/W}$) measured for the control device based on a sputter-deposited ITO on glass. © 2001 American Institute of Physics. [DOI: 10.1063/1.1383568]

Indium tin oxide (ITO) thin films deposited on rigid glass substrates have been widely used as transparent conducting electrodes in many optoelectronic and electro-optic devices such as solar cells and flat panel displays because they combine attractive properties with respect to visible transparency and electrical conductivity.¹ However, glass substrates are unsuitable for certain applications such as electronic maps, smart cards, and portable computers where flexibility, weight, and/or safety issues are important. Glass is very brittle, cannot be easily deformed, and is too heavy, especially for large area displays. These disadvantages can be overcome using flexible substrates, which are robust, lightweight, and cost effective. For these reasons, flexible plastic substrates have been used in passive and active matrix displays such as liquid crystal displays² and polymeric and molecular organic light-emitting diodes (OLEDs).^{3–6}

Optically transparent plastics with high glass transition temperatures are desired for many optoelectronic devices. In addition, they need to withstand the growth conditions of metal oxides while maintaining their mechanical and optical properties. Polyethylene terephthalate (PET) has been widely used as substrate materials for the growth of transparent conducting oxide thin films.^{7–9} A resistivity of $10 \times 10^{-4} \Omega \text{ cm}$ was reported by Minami *et al.*⁷ for ITO films grown by dc magnetron sputtering on PET followed by annealing at 150 °C for 100 h. Ma *et al.*⁸ obtained a resistivity of $7 \times 10^{-4} \Omega \text{ cm}$ for the ITO films deposited on PET at a substrate temperature of 180 °C using reactive evaporation. Kulkarni *et al.*⁹ reported a resistivity of $12\text{--}25 \times 10^{-4} \Omega \text{ cm}$ for ITO films coated on PET using rf sputtering. We report here a study of the electrical, optical, and structural properties of ITO films deposited by pulsed laser deposition (PLD) on flexible PET substrates as a function of substrate temperature and oxygen deposition pressure. We

demonstrate the use of these PLD grown ITO films on PET as transparent anode electrodes for OLEDs with improved luminous power efficiency.

ITO thin films were deposited on PET substrates using a KrF excimer laser (Lambda Physics LPX 305, 248 nm and pulse duration of 30 ns). Details of the film growth conditions have been published elsewhere.^{10–13} The laser was operated at a pulse rate of 10 Hz and the laser beam quality was improved by passing it through a spatial filter. The laser beam 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 1.2 J/cm^2 . The target–substrate distance was 5.8 cm. The target was a 2-in.-diam by 0.2-in.-thick sintered oxide ceramic disk (95 wt% In_2O_3 and 5 wt% SnO_2 , 99.99% purity) supplied by Target Materials, Inc. The PET substrate used in this research was supplied by Dupont (Melinex ST505), which is heat stabilized to give excellent dimensional stability at temperatures up to 150 °C.

The OLED structure consists of a hole transport layer of N,N'-diphenyl-N, N-bis (3-methylphenyl)1,1'-diphenyl-4,4'-diamine, and an electron transport and emitting layer of tris (8-hydroxyquinolinolato) aluminum (III). The cathode contact deposited on top of the electron transport layer is an alloy of Mg:Ag (ratio=12:1 by weight). Details of the device fabrication are described elsewhere.^{14,15} After the deposition of the organic layers, the Mg/Ag alloy was deposited through a shadow mask by co-evaporation from separate sources. The active emissive area of the device is $\sim 2 \text{ mm} \times 2 \text{ mm}$. The current–voltage–luminance ($I\text{--}V\text{--}L$) data were taken in N_2 atmosphere using a Keithley 238 current/voltage source and a luminance meter (Minolta LS-110).

Figure 1 shows a plot of the ITO electrical resistivity as a function of oxygen partial pressure (P_{O_2}) during deposition for films grown on PET substrates held at two different temperatures, T_s , (25, 100 °C). It is clear that the ITO resistivity is very sensitive to the oxygen partial pressure. Low values of film resistivity can be obtained only in a small range of oxygen pressures between 40 and 45 mTorr. The decrease in resistivity with a decrease in P_{O_2} , from 70 to 40 mTorr, can

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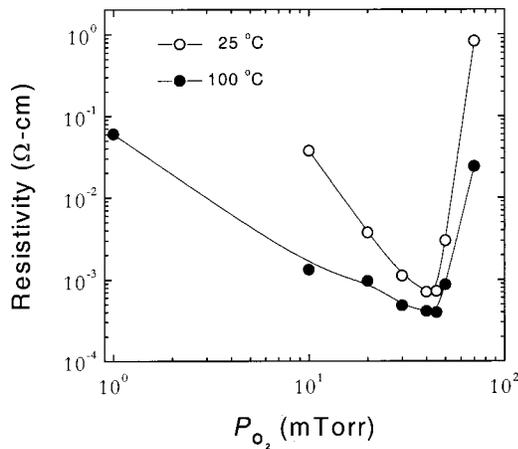


FIG. 1. Resistivity vs oxygen partial pressure during deposition for films deposited on PET substrates held at two different temperatures (25 and 100 °C). The film thickness is about ~200 nm.

be explained by the change in the number of oxygen vacancies in the deposited film. Decreasing the oxygen partial pressure increases the number of oxygen vacancies in the film leading to an increase in free electrons and a concomitant decrease in film resistivity. Resistivity values of $7 \times 10^{-4} \Omega \text{ cm}$ and $4.1 \times 10^{-4} \Omega \text{ cm}$ were reproducibly obtained for ITO films deposited at 25 and 100 °C, respectively.

A strong correlation is observed between the oxygen deposition pressure and the electrical and optical properties of ITO films. Figure 2 shows the variation of electrical resistivity and optical transmittance as a function of oxygen deposition pressure for ITO films deposited on PET at 100 °C. The resistivity decreases rapidly with increasing P_{O_2} to 40 mTorr and then rapidly increases with a further increase in P_{O_2} up to 70 mTorr. The optical transmittance increases rapidly as P_{O_2} increases up to 40 mTorr and then becomes less dependent on the P_{O_2} . This increase in resistivity with P_{O_2} might be related to the improvement of the film crystallinity with P_{O_2} .¹²

ITO films grown by PLD ($T_s=125^\circ\text{C}$ and $P_{O_2}=40\text{ mTorr}$) on PET substrates are observed to be crystalline

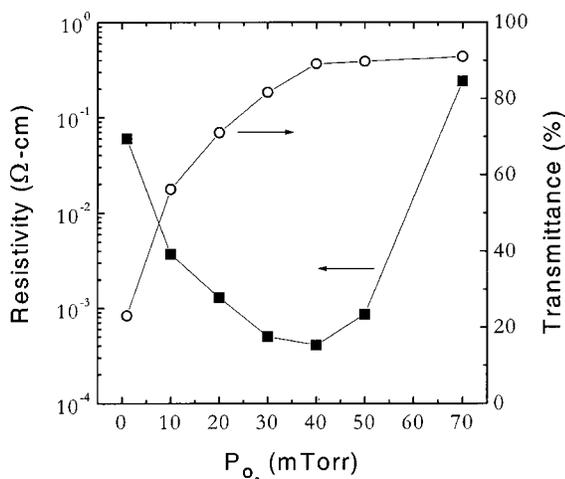


FIG. 2. Optical transmittance and electrical resistivity as a function of oxygen partial pressure during deposition for films deposited on PET substrate. During deposition the substrate temperature was kept at 100 °C. The film thickness is about ~200 nm.

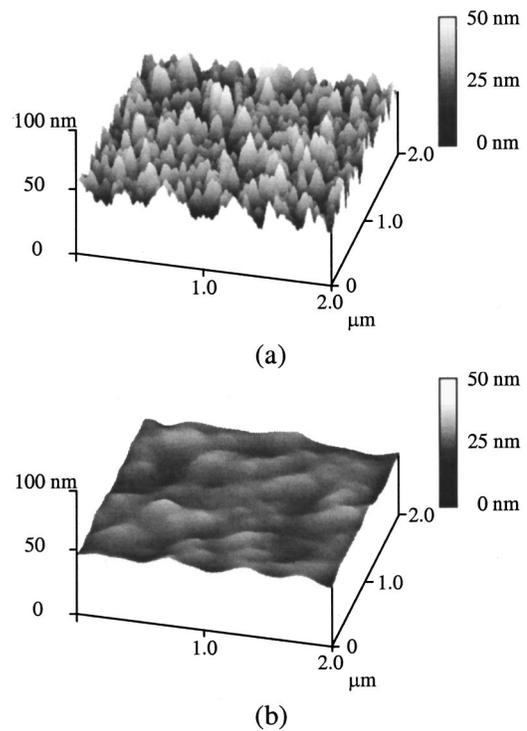


FIG. 3. AFM images ($2 \mu\text{m} \times 2 \mu\text{m}$) of (a) the bare PET substrate and (b) ITO film surface grown by PLD on the same PET substrate, shown in (a). ITO film was deposited at $T_s=100^\circ\text{C}$ and $P_{O_2}=40\text{ mTorr}$. Note that the scale in the z direction (50 nm/div.) is greatly expanded with respect to the scales in the x and y directions (1 $\mu\text{m}/\text{div.}$) and therefore, in fact, the crystallites are flat and broad in the lateral direction.

by x-ray diffraction (XRD). The lattice parameter, calculated from the XRD patterns of ITO films grown on PET, is $10.163 \pm 0.056 \text{ \AA}$, which is larger than the Joint Committee on Powder Diffraction Standard's (JCPDS) value of 10.118 \AA ¹⁶ for the In_2O_3 powder. The increase in the lattice parameter of the ITO films can be explained by the substitutional incorporation of Sn^{4+} ions into In^{3+} sites and/or the incorporation of Sn ions in the interstitial positions. This increase in the lattice parameters may be also related to oxygen deficiencies^{17,18} and strain due to thermal expansion coefficient mismatch between the ITO film ($8.5 \times 10^{-6}/^\circ\text{C}$)¹⁹ and the PET substrate ($12 \times 10^{-6}/^\circ\text{C}$).

Figure 3 shows two atomic force microscopy (AFM) images ($2 \mu\text{m} \times 2 \mu\text{m}$) of the bare PET substrate and the ITO film grown by PLD on the same PET substrate. The ITO film was deposited at $T_s=100^\circ\text{C}$ and $P_{O_2}=40\text{ mTorr}$. Prior to AFM measurements, both samples were ultrasonically cleaned with methanol and then blown dry with nitrogen gas. The rms surface roughness of the bare PET substrate is ~9 nm while that of the ITO film coated on the same PET substrate is ~2.5 nm. Films deposited by PLD on PET show a reduced rms surface roughness compared to their bare substrates indicating planarization of the underlying substrate. This planarization effect was also observed for films grown by PLD on glass substrates.¹¹⁻¹³ The grain size of the film shown in Fig. 3(b) is observed to be 100–150 nm.

We have used the above PLD grown ITO films as an anode contact to fabricate OLEDs and measured the device performance. Figure 4 shows comparison of the characteristics of current density (J)–voltage (V) and current density

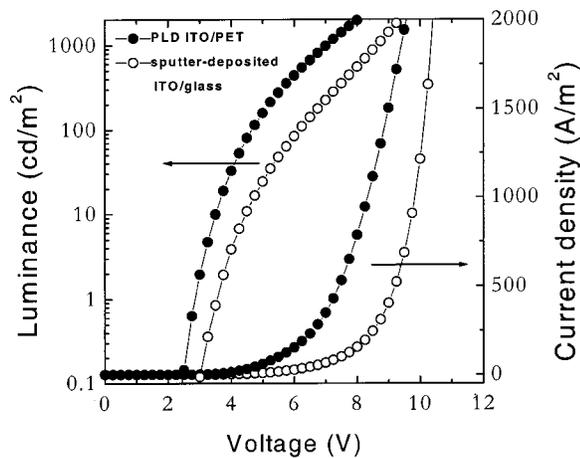


FIG. 4. (a) Current density (J) vs applied voltage (V) and (b) luminance (L) vs applied voltage (V) characteristics for devices based on PLD ITO/PET and sputter-deposited (commercial) ITO/glass.

(J)–luminance (L) output for OLEDs made using both PLD grown ITO on PET and sputter-deposited ITO (supplied by Applied Films) on glass. The thickness of both ITO films was ~ 100 nm. The sheet resistance of the ITO on PET was $\sim 70 \Omega/\text{sq}$, while that of the sputter-deposited ITO on glass was $\sim 20 \Omega/\text{sq}$. The J – V curves for both devices show typical diode behavior, with current and luminance power output observed only in the forward bias. For the device based on the PLD ITO/PET, a current density of 100 A/m^2 can be obtained only at an applied voltage of ~ 5.5 V while the same current density was observed at a voltage of ~ 7.5 V for the control device based on the commercial ITO/glass. As seen in Fig. 4, a luminance level of 1000 cd/m^2 is obtained at only 7 V in the device on ITO/PET, while the same value of luminance is observed at 8.5 V for a control device using ITO/glass. These J – V – L results indicate that the device performance is not affected by the electrical properties of the ITO films used in OLEDs. A luminous power efficiency of 1.6 lm/W measured at 100 A/m^2 for the device fabricated on ITO/PET is slightly higher than that ($\sim 1.5 \text{ lm/W}$) measured for a control device made on the commercial ITO/glass under the same conditions. Similar results have been previously obtained for the same device configuration using sputter-deposited ITO on both glass and PET substrates; at 100 A/m^2 , a luminous power efficiency of 1.2 lm/W was achieved for a device using sputter-deposited ITO on glass in comparison with that of 1.5 lm/W for a device using sputter-deposited ITO on glass.⁶

In summary, ITO thin films have been deposited by PLD on flexible PET substrates. The electrical, optical, and structural properties of these films were investigated as a function of substrate temperature and oxygen partial pressure during film deposition. ITO films (200 nm thick), deposited on PET at $T_s = 25^\circ \text{C}$ and $P_{\text{O}_2} = 45$ mTorr of oxygen, exhibit a low electrical resistivity $\sim 7 \times 10^{-4} \Omega \text{ cm}$ and high optical transmittance ($\sim 87\%$) in the visible range (400–700 nm). For films grown at $T_s = 100^\circ \text{C}$ and $P_{\text{O}_2} = 45$ mTorr, an electrical resistivity as low as $\sim 4 \times 10^{-4} \Omega \text{ cm}$ was obtained with an average transmittance of 90%. We have also used PLD grown ITO on PET substrate as the anode contact in OLEDs and the device showed enhanced luminous power efficiency in comparison with that of a control device using a sputter deposited ITO on glass substrate. The reduction in the drive voltage and enhanced luminous power efficiency make the PLD ITO on PET very promising for future OLED development.

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- ¹H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, *Semiconducting Transparent Thin Films* (Institute of Physics, Philadelphia, 1995).
- ²N. D. Young, R. M. Bunn, R. W. Wilks, D. J. McCulloch, S. C. Deane, M. J. Edwards, G. Harkin, and A. D. Pearson, *J. Soc. Inf. Disp.* **5/3**, 275 (1997).
- ³G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature (London)* **357**, 477 (1992); *Synth. Met.* **57**, 4123 (1993).
- ⁴G. Gu, P. E. Burrows, and S. R. Forrest, *Opt. Lett.* **22**, 172 (1997).
- ⁵G. M. Daly, H. Murata, C. M. Merritt, Z. H. Kafafi, H. Inada, and Y. Shirota, *Mater. Res. Soc. Symp. Proc.* **488**, 33 (1998).
- ⁶Y. He and J. Kanicki, *Appl. Phys. Lett.* **76**, 661 (2000).
- ⁷T. Minami, H. Sonohara, T. Kakumu, and S. Takata, *Thin Solid Films* **270**, 37 (1995).
- ⁸J. Ma, S. Li, J. Zhao, and H. Ma, *Thin Solid Films* **307**, 200 (1997).
- ⁹A. K. Kulkarni, T. Lim, M. Khan, and K. H. Schulz, *J. Vac. Sci. Technol. A* **16**, 1636 (1998).
- ¹⁰D. B. Chrisey and G. K. Hubler, *Pulsed Laser Deposition of Thin Films* (Wiley, New York, 1994).
- ¹¹H. Kim, A. Piqué, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, and D. B. Chrisey, *Appl. Phys. Lett.* **74**, 3444 (1999).
- ¹²H. Kim, C. M. Gilmore, A. Piqué, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, and D. B. Chrisey, *J. Appl. Phys.* **86**, 6451 (1999).
- ¹³H. Kim, J. S. Horwitz, A. Piqué, C. M. Gilmore, and D. B. Chrisey, *Appl. Phys. A: Mater. Sci. Process.* **69**, S447 (1999).
- ¹⁴H. Murata, C. D. Merritt, and Z. H. Kafafi, *IEEE J. Sel. Top. Quantum Electron.* **4**, 119 (1998).
- ¹⁵H. Murata, C. D. Merritt, H. Mattoussi, and Z. H. Kafafi, *Proc. SPIE* **3476**, 88 (1998).
- ¹⁶JCPDS Card No. 06-0416.
- ¹⁷S. Shin, *Mater. Res. Bull.* **16**, 299 (1981).
- ¹⁸J. Ye and K. Nakamura, *Phys. Rev. B* **48**, 7554 (1993).
- ¹⁹W.-F. Wu and B.-S. Chiou, *Thin Solid Films* **293**, 244 (1997).