

Transparent conducting Zr-doped In_2O_3 thin films for organic light-emitting diodes

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Zirconium-doped indium oxide (ZIO) thin films (~ 2000 Å thick) have been deposited by pulsed-laser deposition on glass substrates without a postdeposition anneal. The structural, 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 25 °C to 400 °C in O_2 partial pressures ranging from 0.1 to 50 mTorr. The films (~ 2000 Å thick) deposited at 200 °C in 25 mTorr of oxygen show electrical resistivities as low as 2.5×10^{-4} Ω cm, an average visible transmittance of 89%, and an optical band gap of 4.1 eV. The ZIO films were used as a transparent anode contact in organic light emitting diodes and the device performance was studied. The external quantum efficiency measured from these devices was about 0.9% at a current density of 100 A/m². © 2001 American Institute of Physics.

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Transparent conducting oxide (TCO) films have been widely utilized as an essential part of many optoelectronic devices, such as flat panel displays, thin film transistors, electroluminescent devices, and solar cells, because of their unique properties of high electrical conductivity and high optical transparency.^{1–5} A large number of TCO materials has been investigated over the years such as In_2O_3 , SnO_2 , and ZnO (doped and undoped). Of all these TCO films, Sn-doped In_2O_3 (ITO) films have been by far the most widely used anode materials for organic light-emitting diodes (OLEDs) due to their good transparency ($\sim 90\%$ at 550 nm), low resistivity ($\sim 2 \times 10^{-4}$ Ω cm), and relatively high work function (~ 4.8 eV).^{3–5} However, ITO is not always an ideal anode contact for OLEDs because of the high energy barrier for a hole injection at its interface with the hole transport layer (HTL). One approach for improving the performance of OLEDs is to develop anode material with high work function. Many efforts have focused on improving the device performance including reducing the drive voltage and increasing the electroluminescence quantum efficiency, using several different approaches.^{6–8} Recently, zirconium-doped indium oxide (ZIO) thin films have been proposed as an alternate material to ITO for OLEDs.⁹ However, there have neither been systematic studies on the electronic and optical properties of ZIO films as a function of film processing conditions nor any attempts to fabricate OLEDs using these materials as electrodes.

Recently, pulsed laser deposition (PLD) has been used to grow various TCO thin films.^{3,4,10–13} PLD¹⁴ provides several advantages compared to other deposition techniques in the growth of multicomponent oxide thin films. For a multicomponent target, the composition of films grown by PLD repro-

duces that of the target. PLD films crystallize at lower substrate temperatures relative to other physical vapor deposition techniques due to the high kinetic energies (>1 eV) of the ionized and ejected species in the laser-produced plasma.¹⁴ Also, the surface of the TCO films grown by PLD is very smooth.^{3,4} ITO films, grown by PLD, have already been used as the anode contact in OLEDs.^{3,4,15} In this letter, we report a study of the electrical and optical properties of ZIO films deposited by PLD on glass as a function of substrate deposition temperature and oxygen deposition pressure. Along with this, we report the performance of the first OLEDs with a ZIO anode.

ZIO thin films (1000–2000 Å thick) were deposited on glass substrates (Corning 7059) using a KrF excimer laser (Lambda Physics LPX 305, 248 nm, 30 ns full width at half maximum). 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 1 J/cm². The target-to-substrate distance was 7 cm. The ZIO targets were prepared from In_2O_3 (purity, 99.99%) and ZrO_2 (purity, 99.99%) powders (Alfa AESAR). The powders were mixed in a mechanical shaker for 1 h, pressed into a 1 in. diameter pellet at 15 000 lb., and then sintered at 1300 °C for 6 h in air. The substrates were carefully cleaned in ultrasonic cleaner for 10 min with acetone and then methanol. Films were deposited at substrate temperatures ranging from 25 °C to 400 °C in oxygen partial pressures ranging from 0.1 to 50 mTorr.

The film thickness was measured by a stylus profilometer (KLA-Tencor P-10 surface profiler). The sheet resistance (R_s) measurements were performed using a four-point probe. By assuming that the thickness of the films was uniform, the film resistivity (ρ) was determined using the simple relation $\rho = R_s(d)$, where d is the film thickness. The optical

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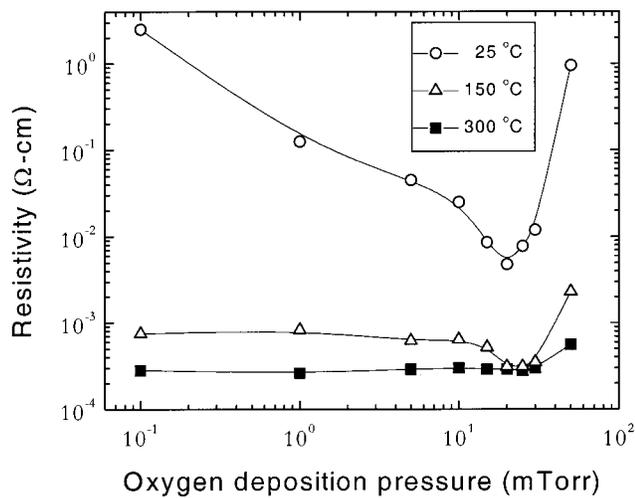


FIG. 1. Electrical resistivity of ZIO films, plotted as a function of oxygen deposition pressure at various growth temperatures: \circ (25 °C), \triangle (150 °C), and \blacksquare (300 °C). The film thickness was held constant (~ 2000 Å).

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 band gap (E_g) was determined by extrapolations of the straight regions of the plots of square of the absorption coefficient α^2 versus photon energy ($h\nu$).¹⁶ The absorption coefficient α was determined by the equation, $\alpha = (1/d)\ln[(1-R)/T]$, where T is the optical transmittance, R is the reflectance, and d is the film thickness.

We have studied the electrical properties of the ZIO films as a function of a target composition with Zr content (0 to 10 at. %) and found that the target with 2.5 at. % of Zr was the optimum concentration for maximum film conductivity. Hence, the 2.5 at. % Zr-doped In_2O_3 target was the composition used in this work. Rutherford backscattering spectrometry measurements indicated that the Zr/In ratio ($\sim 0.057 \pm 0.006$) of ZIO films is similar to that ($\sim 0.065 \pm 0.006$) of the target. Figure 1 shows a plot of electrical resistivity (ρ) as a function of oxygen deposition pressures for films deposited at three different substrate temperatures (T_s). For the ZIO films deposited at $T_s = 25$ °C, the resistivity is very sensitive to the oxygen deposition pressure. Low resistivity ZIO films can be obtained only between 15 and 30 mTorr of oxygen. The decrease in the resistivity with a decrease in oxygen deposition pressure from 50 to 20 mTorr, can be explained by the number of oxygen vacancies in the film. Decreasing the oxygen deposition pressure increases the number of oxygen vacancies in the deposited film leading to an increase in carrier concentration and a concomitant decrease in film resistivity.^{3,4} A resistivity of $\sim 5.3 \times 10^{-3}$ Ωcm was obtained for the ZIO film deposited at 25 °C in 20 mTorr of oxygen. However, as the T_s increases, the resistivity of ZIO films is less dependent on the oxygen deposition pressure. The lowest resistivity observed for the ZIO film deposited at 300 °C in 25 mTorr of oxygen was about 2.5×10^{-4} Ωcm , and is similar to that previously obtained (2×10^{-4} Ωcm) for ITO films.³

Figure 2 shows the variation of electrical resistivity (ρ) as a function of T_s for ZIO films deposited in two different

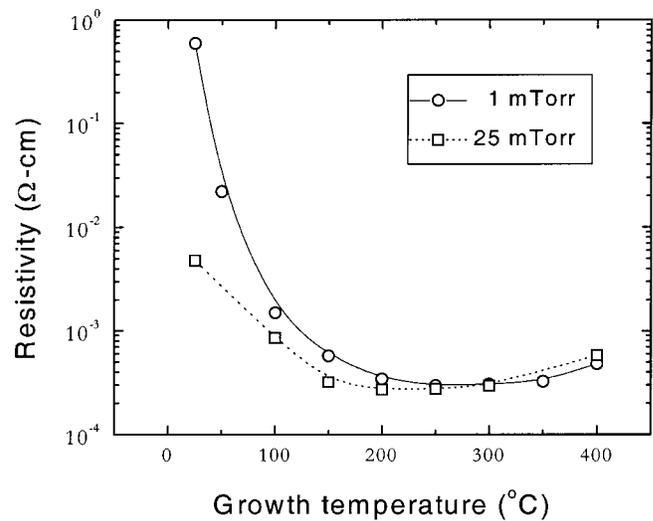


FIG. 2. Electrical resistivity of the ZIO films, plotted as a function of film growth temperature at various oxygen deposition pressures: \circ (1 mTorr) and \square (25 mTorr).

oxygen pressures. For films grown in 1 mTorr of oxygen, the resistivity decreases from 5×10^{-1} to 5.2×10^{-4} Ωcm as the T_s is increased from 25 °C to 200 °C and then remains constant up to 350 °C. For films grown in 25 mTorr of oxygen, the resistivity decreases from 5×10^{-3} to 2.7×10^{-4} Ωcm with an increase in T_s from 25 °C to 150 °C, and then remains almost constant up to 300 °C. The decrease in resistivity with increase in T_s is due to an improved crystallinity. X-ray diffraction (XRD) analysis indicated that films grown at 25 °C were amorphous, while films grown at higher temperature (>100 °C) showed a polycrystalline structure. As the substrate temperature increases from 100 °C to 300 °C, the calculated grain size from XRD¹⁷ increases from ~ 10 to ~ 28 nm. An increase in grain size with increasing the T_s leads to a reduction in grain boundary scattering and a decrease in electrical resistivity.

The oxygen deposition pressure also affects the optical properties of the films. Figure 3 shows the optical transmittance spectra for ZIO films deposited at various oxygen pressures. The average transmittance in visible range (400–700

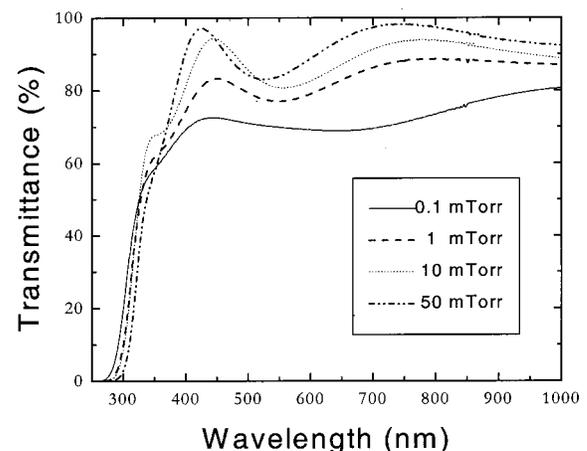


FIG. 3. Transmittance spectra of ZIO films deposited at various oxygen pressures. The film thickness was about 2000 Å for all films. All films were deposited at 300 °C.

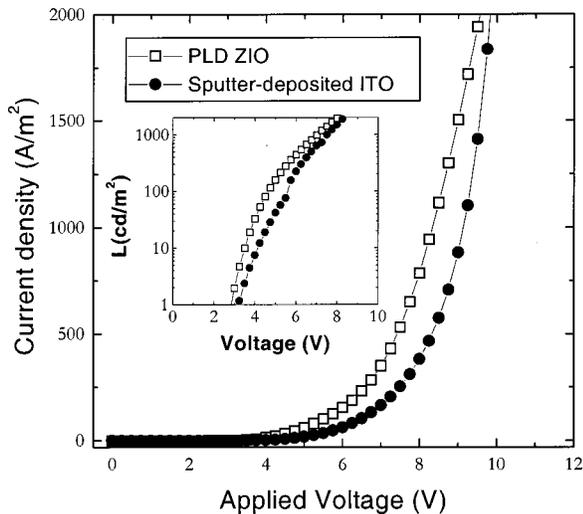


FIG. 4. Current density (J) versus applied voltage (V) and luminance (L) versus applied voltage (V) (inset) characteristics of OLEDs fabricated with a ZIO anode and a commercial ITO (~ 1000 Å) anode. ZIO film (~ 900 Å), grown by PLD at 200°C and 5 mTorr of oxygen, was used as an anode contact in this device.

nm) increases from 70% to 90% with an increase in the oxygen deposition pressure from 0.1 to 50 mTorr. This increase in transmittance is related to an increase in grain size of the films from 10 to 56 nm as indicated by a decrease in the width of the (222) XRD peak (data not shown) with increasing oxygen deposition pressure. The optical band gap, determined from the transmittance and reflectance measurements, is about 4.1 eV, which is close to those previously obtained (3.9–4.2 eV) for ITO films.^{3,4}

Figure 4 shows current density (J) or luminance (L) versus applied voltage (V) characteristics of OLEDs using a PLD ZIO anode and a sputter deposited ITO anode (supplied by Applied Films, USA). The ZIO anode (~ 900 Å) was deposited at 200°C and 25 mTorr of oxygen. The thickness of the commercial ITO was ~ 1000 Å. The device structure is made of a HTL (thickness ~ 500 Å) of N, N'-diphenyl-N, N-bis (3-methylphenyl)1,1'-diphenyl-4,4'-diamine (TPD), and an electron transport/emitting layer (ETL/EML, thickness ~ 700 Å) of tris (8-hydroxyquinolinolato) aluminum (III) (Alq_3). The cathode contact deposited on top of the ETL is an alloy of Mg:Ag (ratio=12:1 by weight and a thickness of 2000 Å). Details of fabrication are described elsewhere.¹⁸ The active emissive area is $\sim 2 \times 2$ mm². The current density–voltage–luminance (J – V – L) measurements were made in a dry N_2 atmosphere using a Keithley Model 236 current/voltage source and a luminance meter (Minolta LS-110). The JVL characteristics of both devices showed a typical diode behavior with current and power output observed only in the forward bias. For devices with the sputter deposited ITO, a current density of 100 A/m² is observed at 6.5 V while for devices with the PLD ZIO the same

current density can be obtained at a lower applied voltage of 5.5 V. This slight reduction in the driving voltage for the devices with the PLD ZIO anode may be due to an increase in hole injection efficiency from the ZIO layer into the TPD layer. As seen in the inset of Fig. 4, a luminance of 1000 cd/m² is obtained at only 7 V in the ZIO device while the same value of luminance is observed at a higher voltage of 7.5 V in case of the ITO device. An external quantum efficiency measured at a current density of 100 A/m² was 0.9%. The reduction in the driving voltage and the high external quantum efficiency achieved for OLEDs based on a ZIO anode are quite promising for use of ZIO as an attractive, transparent electrode.

In conclusion, highly transparent and conducting ZIO films have been deposited on glass substrates by PLD. The electrical and optical properties of the ZIO films have been investigated as a function of substrate deposition temperature and oxygen deposition pressure. For 200 nm thick ZIO films deposited at $T_s = 200^\circ\text{C}$ and 25 mTorr of oxygen, an electrical resistivity of 2.5×10^{-4} Ω cm with an average transmittance in the visible range of 89%, and an optical band gap of 4.1 eV was measured. ZIO films have been used as transparent anode contacts in OLEDs with reduced driving voltage and high electroluminescence quantum efficiency.

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