

Praseodymium oxide coated anode for organic light-emitting diode

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Capping an indium–tin–oxide anode with a thin layer of praseodymium oxide (Pr_2O_3) has been found to enhance not only hole-injection, quantum, and power efficiencies but also the lifetime of organic light-emitting diode made using copper (II) phthalocyanine as the anode buffer layer, N, N'-diphenyl-N,N' bis(3-methylphenyl-1,1'-biphenyl-4,4'-diamine as the hole-transport layer and tris-8-hydroxyquinoline aluminum as the electron-transport/emission layer. The best results have been obtained on diodes with ~ 1 nm thick Pr_2O_3 . A possible mechanism behind the improvement is discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1476712]

The organic light-emitting diode (OLED)¹ is challenging liquid-crystal as an alternative flat-panel display technology because of its ease of manufacturing due to its all solid-state nature as well as its relative merits of having a faster switching speed and being self-emitting with a wider viewing angle.

The performance of an OLED is influenced not only by the properties of its constituent organic materials but also by those of the injecting electrodes and the interfaces they form with the organic carrier-transport layers. The electroluminescence (EL) efficiency of an OLED can be improved by enhancing either its internal quantum efficiency² or the injection efficiencies of electrons^{3,4} or holes.⁵ The latter typically results in a reduction of the OLED driving voltage.

For the injection of electrons, metals with low work functions³ are typically used as cathodes. Such metals tend to be highly reactive, hence unstable if they are not properly encapsulated. They are typically capped with more stable metals. Examples of stable composite cathodes are Ca/Al, Mg/Ag, Mg/MgAg, and Gd/Al^{6–9} etc. Alternatively, ultrathin insulating compounds containing low work-function metals have been used to generate interfacial dipoles¹⁰ that result in favorable alignment of the Fermi levels of the cathode and the lowest-unoccupied molecular orbital energy levels of the electron-transport layers. The barrier against electron emission is subsequently reduced. Examples of such electron injection promoters are lithium and cesium fluorides.^{11,12}

For the injection of holes, indium–tin–oxide (ITO) has been used mainly as a transparent anode. However, ITO needs to be properly treated for efficient hole injection. Such surface treatments include ultraviolet ozone (UV/O₃) cleaning,¹³ argon ion bombardment,¹⁴ or oxygen plasma exposure.¹⁵ In addition, organic anode buffer layers, such as copper (II) phthalocyanine (CuPc)¹⁶ with suitable highest-occupied molecular orbital (HOMO) energy levels or metals with high work functions¹⁷ can be used to enhance hole injection efficiencies.

While surface treatments of ITO increase not only hole injection efficiency but also quantum and power efficiencies,

improvement only in hole injection efficiency but not in power efficiency has been reported for high work-function metals deposited on ITO.¹⁷ Clearly, this implies reduced quantum efficiencies. Furthermore, such metals are only semitransparent, hence diminishing gains in efficiencies resulting from the high work functions.

In this letter, the use of praseodymium (Pr) oxide capped ITO as anodes to improve not only the hole-injection, quantum, and power efficiencies but also the operating lifetimes of OLEDs based on N, N'-diphenyl-N,N' bis(3-methylphenyl-1,1'-biphenyl-4,4'-diamine (TPD) as hole-transport layers and tris-8-hydroxyquinoline aluminum (Alq₃) as electron-transport/emission layers is described.

Glass coated with 70 nm ITO was used as the starting substrate. The sequence of precleaning prior to loading into the evaporation chamber consisted of an ultrasonic detergent soak for 30 min, de-ionized (DI) water spray for 10 min, ultrasonic DI water soak for 30 min, oven bake dry for 1–2 h, and UV/O₃ illumination for 9 min.¹⁸

The Pr oxide and the constituent organic layers for the OLEDs were deposited on ITO glass substrates by thermal vacuum evaporation of commercial grade Pr_2O_3 , CuPc, TPD, and Alq₃ powder sources loaded in resistively heated evaporation cells. The as-deposited Pr oxide was treated with UV/O₃ for 9 min prior to the deposition of the organic layers. It has been verified using x-ray photoelectron spectroscopy that the Pr oxide existed mainly in the form of Pr_2O_3 . The base pressure in the evaporator was $\sim 8 \mu\text{Torr}$. The deposition rates of the organic thin films were 0.2–0.4 nm/s. The deposition rate of Pr oxide was ~ 0.01 –0.03 nm/s. While the ITO or ITO coated with Pr oxide formed the anodes of the OLEDs, 0.1 nm lithium fluoride (LiF) topped with 150 nm aluminum (Al) composite layers were used as the cathodes. The deposition rates of LiF and Al were 0.02–0.05 nm/s and 1–1.5 nm/s, respectively. Film thickness was determined *in situ* using a crystal monitor.

For comparison, three types of 4 mm diam OLEDs were fabricated using a set of shadow masks. These are:

- 1) type C: ITO (75 nm)/CuPc (20 nm)/TPD (40 nm)/Alq₃ (50 nm)/LiF (1 nm)/Al (150 nm);
- 2) type P: ITO/ Pr_2O_3 (1 nm)/TPD/Alq₃/LiF/Al; and
- 3) type PC: ITO/ Pr_2O_3 (1 nm)/CuPc/TPD/Alq₃/LiF/Al.

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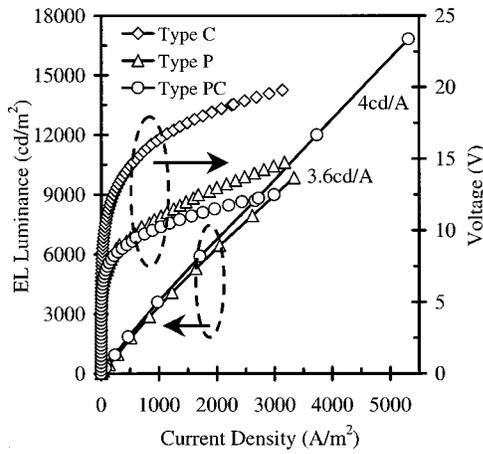


FIG. 1. The EL luminance (L)–current density (J)–voltage (V) characteristics of device types C, P, and PC. The diode turn-on voltage and current efficiency are the best for device type PC.

The type C device is the conventional OLED for which optimized structure and performance have been obtained.¹⁸ Against the performance of this control device, that of types P and PC devices were compared. In the type P device, only Pr_2O_3 but not CuPc was used. In the type PC device, both Pr_2O_3 and CuPc were used. Where not specified, the thickness of the layers in device types P and PC are the same as those of the corresponding layers in device type C.

The EL luminance (L)–current density (J)–voltage (V) characteristics of the three types of devices are shown in Fig. 1. From the J – V characteristics, it can be seen that the diode turn-on voltage is decreased significantly when CuPc is replaced by Pr_2O_3 in device type P, with further reduction observed when CuPc and Pr_2O_3 are used in combination in device type PC. The decrease in turn-on voltage is a reflection of improved hole injection efficiency. A similar trend is observed in the L – J characteristics. A more significant increase in current efficiency, defined as the slope of an L – J characteristic, is observed when CuPc and Pr_2O_3 are used in combination rather than when CuPc is simply replaced by Pr_2O_3 . The current efficiency is a reflection of the effective quantum efficiency of a diode. Both the significant reduction in diode turn-on voltage and the increase in current efficiency lead to obvious improvement in power efficiency.

Shown in Fig. 2 are the lifetimes of unencapsulated diodes stressed in room ambient at respective J values neces-

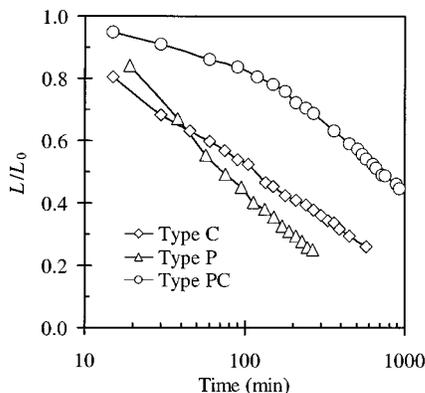


FIG. 2. Comparison of the stability of device types C, P, and PC under constant current stress.

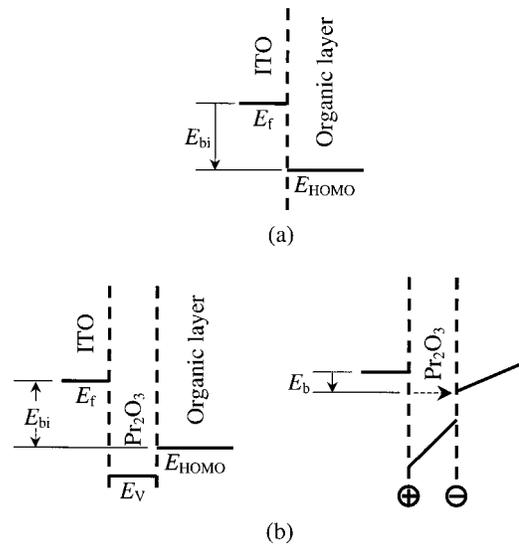


FIG. 3. Energy band diagrams showing how the barrier against hole emission is reduced in the presence of a thin insulating interfacial layer, such as Pr_2O_3 . (a) Energy level diagram of a diode without Pr_2O_3 . E_{bi} is the energy barrier against emission. (b) Energy level diagrams of a diode with Pr_2O_3 . E_v is the valence band level of Pr_2O_3 . Shown on the left is the flatband condition. Shown on the right is the bending of the Pr_2O_3 E_v level, induced either by a spontaneous dipole layer or a portion of applied bias. The bending leads to a reduced energy barrier E_b , but tunneling across Pr_2O_3 is required.

sary to give initial luminance L_0 values of 300 cd/m^2 . With CuPc replaced by Pr_2O_3 , a slight reduction in lifetime is observed. When Pr_2O_3 and CuPc are used in combination, significant improvement in lifetime is observed. Although the power efficiencies of device types P and PC are both better than that of device type C, it can be determined from the reduced lifetimes of type P devices that Pr_2O_3 not covered by CuPc is not sufficiently stable.

Enhancement of hole-injection efficiency in the presence of Pr_2O_3 can be explained in terms of a reduction of the effective barrier against hole emission from ITO to the organic layer. Without the Pr_2O_3 layer, hole emission is represented by the arrow against an energy barrier E_{bi} in Figure 3(a). A positive voltage drop across Pr_2O_3 from ITO to the adjacent organic layer could lead to a favorable relative displacement of the Fermi level E_f of ITO toward the HOMO level E_{HOMO} of the organic layer [Fig. 3(b)].¹⁹ Consequently, the emission of holes would require overcoming a smaller energy barrier E_b , followed by tunneling^{11,19} [dashed arrow in Fig. 3(b)] across the thin insulating Pr_2O_3 layer.²⁰ The voltage drop across Pr_2O_3 could be induced by a spontaneous electric dipole layer¹⁰ associated with the thin Pr_2O_3 layer, a portion of the applied bias dropping across the insulating Pr_2O_3 layer, or a combination of both.

In principle, any insulator could be used in place of Pr_2O_3 . A given material would be more effective if it possessed properly aligned spontaneous dipole moment or if it were a better insulator.

The dependence of diode performance on Pr_2O_3 thickness is shown in Fig. 4. The relative hole injection efficiency is defined as the ratio of the current density of a given type PC diode to that of a type C diode, all forward biased at 8 V. The relative power efficiency is defined as the ratio of the highest power efficiency of a given type PC diode with dif-

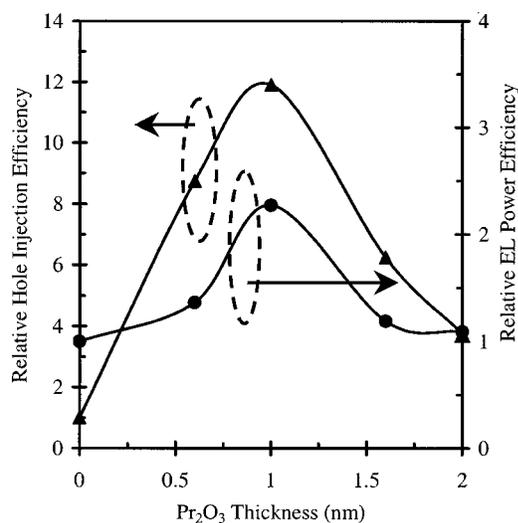


FIG. 4. Dependence on Pr₂O₃ thickness of the hole-injection and power efficiencies of device type PC to those of device type C.

ferent thickness of Pr₂O₃ divided by the highest power efficiency of the type C diode. The initial increase in hole injection and power efficiencies with Pr₂O₃ thickness could be explained by increasing Pr₂O₃ coverage. The highest hole injection and power efficiencies were obtained with a Pr₂O₃ thickness of ~1 nm. Subsequent decrease in efficiencies beyond ~1 nm could be explained by rapidly decreasing tunneling probability across thicker Pr₂O₃.

In summary, capping ITO anodes with thin layers of Pr₂O₃ has been found to enhance not only hole-injection, quantum and power efficiencies but also the lifetimes of OLEDs consisting of CuPc/TPD/Alq₃. The optimal thickness of Pr₂O₃ is ~1 nm, resulting in a ~250% improvement in power efficiency.

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