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$_2$O$_3$) has been found to enhance not only hole-injection, quantum, and power efficiencies but also the lifetime of OLEDs made using copper (II) phthalocyanine as the anode buffer layer, 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$_2$O$_3$. A possible mechanism behind the improvement is discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1476712]

The organic light-emitting diode (OLED) 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 efficiency or the injection efficiencies of electrons or holes. The latter typically results in a reduction of the OLED driving voltage.

For the injection of electrons, metals with low work functions 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. Alternatively, ultrathin insulating compounds containing low work-function metals have been used to generate interfacial dipoles 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.

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/O$_3$) cleaning, argon ion bombardment, or oxygen plasma exposure. In addition, organic anode buffer layers, such as copper (II) phthalocyanine (CuPc) with suitable highest-occupied molecular orbital (HOMO) energy levels or metals with high work functions 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. 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 lifetime of OLEDs based on N,N’-bis(3-methylphenyl-1,1’-biphenyl-4,4’)-diamine (TPD) and tris-8-hydroxyquinoline aluminum (Alq$_3$) 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/O$_3$ illumination for 9 min. 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$_2$O$_3$, CuPc, TPD, and Alq$_3$ powder sources loaded in resistively heated evaporation chambers. The as-deposited Pr oxide was treated with UV/O$_3$ 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$_2$O$_3$. The base pressure in the evaporator was ~8 μTorr. 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 nm diam OLEDs were fabricated using a set of shadow masks. These are:

1. type C: ITO (75 nm)/CuPc (20 nm)/TPD (40 nm)/Alq$_3$ (50 nm)/LiF (1 nm)/Al (150 nm);
2. type P: ITO/Pr$_2$O$_3$ (1 nm)/TPD/Alq$_3$/LiF/Al; and
3. type PC: ITO/Pr$_2$O$_3$ (1 nm)/CuPc/TPD/Alq$_3$/LiF/Al.

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The type C device is the conventional OLED for which optimized structure and performance have been obtained. Against the performance of this control device, that of types P and PC devices were compared. In the type P device, only Pr$_2$O$_3$ but not CuPc was used. In the type PC device, both Pr$_2$O$_3$ 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$_2$O$_3$ in device type P, with further reduction observed when CuPc and Pr$_2$O$_3$ 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$_2$O$_3$ are used in combination rather than when CuPc is simply replaced by Pr$_2$O$_3$. 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 necessary to give initial luminance $L_0$ values of 300 cd/m$^2$. With CuPc replaced by Pr$_2$O$_3$, a slight reduction in lifetime is observed. When Pr$_2$O$_3$ 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$_2$O$_3$ not covered by CuPc is not sufficiently stable.

Enhancement of hole-injection efficiency in the presence of Pr$_2$O$_3$ can be explained in terms of a reduction of the effective barrier against hole emission from ITO to the organic layer. Without the Pr$_2$O$_3$ layer, hole emission is represented by the arrow against an energy barrier $E_{bi}$ in Figure 3(a). A positive voltage drop across Pr$_2$O$_3$ 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)]

Consequently, the emission of holes would require overcoming a smaller energy barrier $E_{bi}$, followed by tunneling through the thin insulating Pr$_2$O$_3$ layer across Pr$_2$O$_3$ could be induced by a spontaneous electric dipole layer associated with the thin Pr$_2$O$_3$ layer, a portion of the applied bias dropping across the insulating Pr$_2$O$_3$ layer, or a combination of both.

In principle, any insulator could be used in place of Pr$_2$O$_3$. 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$_2$O$_3$ 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 different Pr$_2$O$_3$ thickness.
different thickness of Pr$_2$O$_3$ divided by the highest power efficiency of the type C diode. The initial increase in hole injection and power efficiencies with Pr$_2$O$_3$ thickness could be explained by increasing Pr$_2$O$_3$ coverage. The highest hole injection and power efficiencies were obtained with a Pr$_2$O$_3$ thickness of ∼1 nm. Subsequent decrease in efficiencies beyond ∼1 nm could be explained by rapidly decreasing tunneling probability across thicker Pr$_2$O$_3$.

In summary, capping ITO anodes with thin layers of Pr$_2$O$_3$ has been found to enhance not only hole-injection, quantum and power efficiencies but also the lifetimes of OLEDs consisting of CuPc/TPD/Alq$_3$. The optimal thickness of Pr$_2$O$_3$ is ∼1 nm, resulting in a ∼250% improvement in power efficiency.

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