P-64: A Comparative Study of Metal Oxide Coated Indium-tin Oxide Anodes for Organic Light-emitting Diodes

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Abstract

Indium-tin oxide anodes capped with certain oxides of metals enhance while other oxides degrade the hole-injection and quantum efficiencies of organic light-emitting diodes (OLEDs). The oxides of tin, zinc, praseodymium, yttrium, gallium, terbium and titanium have been investigated. The power efficiency of an OLED with a 1nm thick praseodymium oxide cap is improved by 2.5 times over that of a conventional OLED without an oxide capped anode.

1. Introduction

Organic light-emitting diode (OLED) is challenging liquid-crystal as an alternative flat-panel display technology because of its ease of manufacturing, all solid-state nature, faster switching speed and being self-emitting with a wider viewing angle [1].

The performance of an OLED is strongly affected not only by the properties of its constituent organic layers [2] but also by the electrodes [3] and the interfaces they form with the carrier-transport layers. Efforts have been focused on improving various performance measures, such as driving voltage [4], emission efficiency [5], electron- or hole-injection efficiency [6,7] and durability.

For the injection of electrons, it is commonly accepted that the lower the work function of the cathode metal, the higher the efficiency of the injection. Though low work function metals enhance injection, they are generally chemically active, hence unstable. Therefore it is sometimes necessary to replace low work function metals, such as magnesium (Mg) or calcium, with more stable ones, such as aluminum (Al) or silver (Ag) [8]. Alternatively, a low work function metal can be alloyed with a stable metal, such as Mg with Ag, or inserted between the organic electron-transport layer (ETL) and a stable metal. Yet another approach is to insert an ultra-thin layer of lithium or cesium fluoride between the ETL and the cathode [9].

For the injection of holes, indium-tin oxide (ITO) has been widely used as an anode because of its high transparency, conductivity and injection efficiency. ITO with surface-adsorbed hydrocarbon is found to have reduced injection efficiency [10]. Many treatments have been reported to remove adsorbed hydrocarbon [7,10,11]. These include ultra-violet (UV) ozone cleaning, argon ion bombardment or oxygen plasma exposure [10]. In addition, organic anode buffer layers (ABLs), such as copper (II) phthalocyanine (CuPc) [12], with suitable highest-occupied molecular orbital energy levels or metals with high work functions, such as gold, nickel and platinum [13] can be used to enhance injection efficiencies.

While UV ozone or oxygen plasma treatment of ITO not only enhances the hole-injection, but also the quantum and power efficiencies of OLEDs, only hole-injection but not power efficiency has been reported for high work function metallic ABLs [13, 14]. This clearly implies an undesirable reduction in quantum efficiency. Furthermore, metals are only semi-transparent, hence diminishing potential gains in efficiencies resulting from their high work function values.

Recently, variety of transparent inorganic ABLs have been studied[14,15,16]. In this work, the performance of OLEDs with ITO anodes capped with thin (~1nm) layers of metal oxides is presently reported. The candidates studied included praseodymium oxide (Pr_2O_3), yttrium oxide (Y_2O_3), terbium oxide (Tb_4O_7), titanium oxide (TiO_2), zinc oxide (ZnO), gallium oxide (Ga_2O_3) and tin oxide (SnO_2). Tris-8-hydroxyquinoline aluminum (Alq_3) was used as the ETL and principle emission layer. N, N'-diphenyl-N,N' bis(3-methyl-phenyl-1,1'-biphenyl-4,4'-diamine (TPD) was used as the hole-transport layer and CuPc as an organic ABL. Certain species of metal oxide caps were found to enhance not only the hole-injection but also the quantum and power efficiencies. The power efficiency of an OLED with 1nm Pr_2O_3 cap can be improved by 2.5 times over a similar device without a metal oxide cap.

2. OLED fabrication

The starting substrates were commercial glass coated with 70nm ITO and a sheet resistance of 30Ω. The sequence of pre-cleaning prior to loading into the evaporation chamber consisted of ultra-sonic detergent soak for 30mins, de-ionized (DI) water spray for 10mins, ultra-sonic DI water soak for 30mins, oven bake-dry for 1-2hrs and UV ozone illumination for 9mins [17].

The ultra-thin metal oxide (MO) cap layers were evaporated using 99.99% pure powder loaded in resistively heated evaporation cells. The range of the deposition rates of the various oxides was 0.01-0.03nm/s. After the evaporation, the samples were subjected again to DI water rinse and UV ozone exposure.

The constituent organic layers for the OLEDs were next deposited on the substrates using thermal vacuum evaporation of commercial grade CuPc, TPD and Alq_3 powder sources. The base pressure in the evaporator was ~8μTorr. The deposition rates of the organic thin films were 0.2-0.4nm/s. While ITO with or without capped layers formed the anodes, 0.1nm lithium fluoride (LiF) topped with 150nm Al composite layers were used as the

cathodes. The deposition rates of LiF and Al were 0.02-0.05nm/s and 1-1.5nm/s, respectively. Film thickness was determined *in situ* using a crystal monitor. The fabrication process of the OLEDs is summarized in Figure 1.

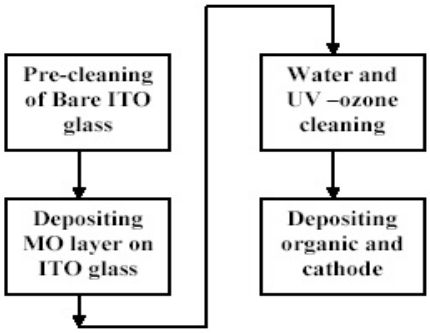

Figure 1. Summary of the fabrication process.

Two types of 4mm-diameter OLEDs (Fig. 2) were fabricated using a set of shadow masks:

Type C: ITO(75nm)/CuPc(20nm)/TPD(40nm)/Alq_3(50nm)/LiF (1nm)/Al(150nm),

Type MO: ITO/MO(1nm)/CuPc/TPD/Alq_3/LiF/Al, where MO can be any one member of the list of Pr_2O_3, Y_2O_3, Tb_4O_7, TiO_2, ZnO, SnO_2 or Ga_2O_3.

Against the performance of the control device Type C, that of device Types MO was compared.

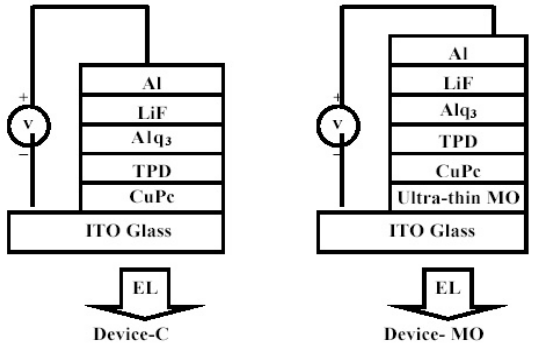

Figure 2. OLED structures with and without metal oxide cap.

3. Results

The luminance-voltage (*LV*) characteristics of Types MO and C devices are shown in Figure 3. Compared to those of the Type C reference device, it can be seen that the turn-on voltage (V_{on}) is decreased and *L* at a given voltage is increased for Type MO devices with Pr_2O_3, Y_2O_3, ZnO or Tb_4O_7 capped ITO anodes. The lowest turn-on voltage is obtained on an OLED with a Pr_2O_3 cap. However, V_{on} is increased and *L* at a given voltage is decreased for Type MO devices with ITO capped with SnO_2, TiO_2 or Ga_2O_3.

Similar trends were observed from the typical current-voltage (*IV*) characteristics of Types MO and C devices shown in Figure 4. Compared to those of the Type C reference device, it can be seen that V_{on} is decreased for Type MO devices with Pr_2O_3, Y_2O_3, ZnO or Tb_4O_7 capped ITO anodes, reflecting higher hole-injection efficiencies. However, V_{on} is increased for Type MO devices with ITO capped with SnO_2, TiO_2 or Ga_2O_3, reflecting lower hole-injection efficiencies.

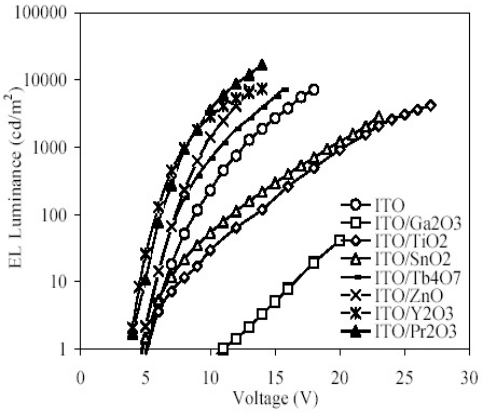

Figure 3. Typical *LV* characteristics.

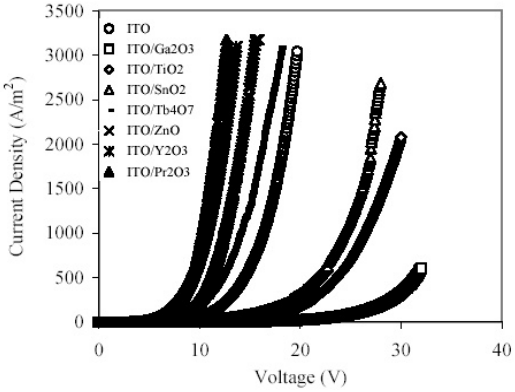

Figure 4. Typical *IV* characteristics.

The performance of the various types of OLEDs is summarized in Table I.

Table I. Summary of the characteristics of OLEDs with ITO anodes capped with various metal oxides. Characteristics of the reference device without metal cap is given in the first data column.

Metallic Oxide	ITO	Ga_2O_3	TiO_2	SnO_2	Tb_4O_7	ZnO	Y_2O_3	Pr_2O_3
Injection (8 V, A/m^2)	20	0.3	4.2	10.5	50.7	69.9	285	238
Power Efficiency (20A/m2, lm/w)	1	0.5	0.7	0.76	1.34	1.34	1.7	1.87
Max. Power Efficiency (lm/w)	1.1	0.5	1.3	0.96	1.34	1.34	2.0	2.5
Current Efficiency (20A/m^2,cd/m^2)	2.5	2.7	3	2.1	3.0	3.0	3.1	3.6
Max. Current Efficiency (cd/A)	3.5	2.7	3.5	2.9	3.6	3.6	3.7	4.0

Compared with the reference device with uncapped ITO (1st column of data), more than 20 times increase in current injection is observed in the devices with Y_2O_3 or Pr_2O_3 capped ITO, all biased at 8V. On the other hand, Ga_2O_3 capping resulted in a significant reduction in the amount of current injection.

The relationship between the current efficiency (h_I) and L of Types MO and C devices are shown in Figure 5. h_I of all devices initially increase with L until reaching their maximum values, then decrease with further increase in L. Clearly, h_I has been improved by capped ITO with rare earth metal oxide layers, such as Pr_2O_3, Y_2O_3, ZnO and Tb_4O_7 and decays only slowly with increasing L after reaching their maximum values. OLEDs with ITO anodes capped with Pr_2O_3 exhibited the highest h_I at a current density of 20A/m^2, improving to 3.6cd/A from a value of 2.5cd/A for a reference device (Table I).

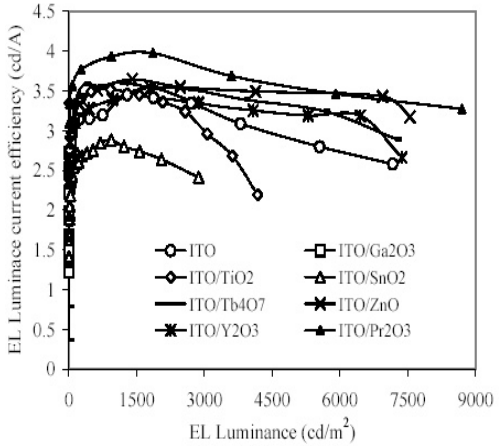

Figure 5. Typical h_I –L characteristics.

The relationship between the power efficiency (h_P) and L of Types MO and C devices are shown in Figure 6. h_P is improved for devices with ITO capped with Pr_2O_3, Y_2O_3 ZnO and Tb_4O_7. The largest values of h_P were measured on OLED with Pr_2O_3 or Y_2O_3 cap layers. They are respectively 2.5 and 2 times (Table I) better than that of the reference device.

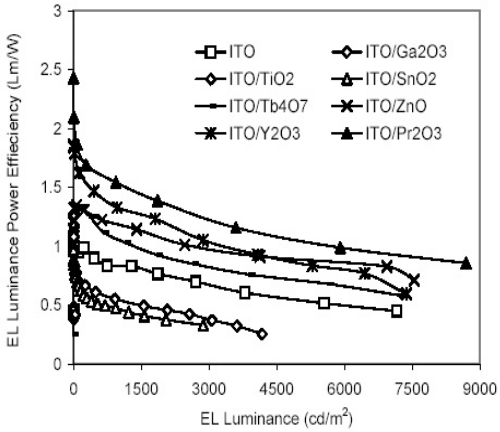

Figure 6. Typical h_P –L characteristics.

4. Conclusion

OLEDs with ITO anodes capped with various kinds of ultra-thin layers of metal oxides have been investigated. It is found that rare earth metal oxides such as Pr_2O_3, Y_2O_3, ZnO and Tb_4O_7 resulted in enhanced hole-injection, current and power efficiencies. A 20 times increase in injection current and more than 2 times increase in power efficiency have been observed in the cases of Pr_2O_3 and Y_2O_3.

5. Acknowledgement

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