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Influence of *p*-isopropenylcalixarenestyrene copolymer buffer layer over Alq₃ based OLEDs

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Abstract: The characteristics of organic light-emitting devices based on aluminum tris-(8-hydroxyquinoline) (Alq₃), N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) with novel p-Isopropenylcalix[8]arenestyrene copolymer buffer layer and Al cathode were investigated. The devices with TPD/Alq₃/Al were also fabricated in the same way for comparison. The p-Isopropenylcalix[8]arenestyrene copolymer used as buffer layer greatly improved the performance of the device and increased the device efficiency and stability.

1. Introduction

Since efficient green electroluminescence from an organic light emitting device (OLED) was first reported [1], there has been considerable interest in utilizing OLEDs for full color flat panel display applications. Early investigations indicated that OLEDs have a limited lifetime, characterized by a decrease in EL efficiency and an increase in drive voltage. To enhance the efficiency, to prolong the durability and to lower the driving voltage of OLEDs continue to be the key challenges to meet the requirements of practical application in flat panel display technology. The performance of OLED is affected not only by the properties of its constituent organic layers but also by the electrodes and their interfaces with charge-transporting layers. One of practical approach to improve interfacial properties especially electrode/organic contact behaviors is to insert a thin buffer layer between the electrodes and the organic transporting layers. The quality of a buffer layer in OLED is a crucial factor for driving voltage, power efficiency and stability of a device.

A variety of inorganic insulators like transparent metal oxides as SiO₂, Al₂O₃, CuO_x Pr₂O₃, Y₂O₃, Tb₄O₇, ZnO [2], NiO [3], WO₃ [4], $MoO_x[4]$, V_2O_5 [5], silicon nitride Si_3N_4 [2], carbon nitride a-C:N [6], organic compounds such phthalocyanine copper [7], poly(3,4as. ethylenedioxythiophene) [8], Langmuir-Blodjett of poly(methylmethacrylate) [9], films polytetrafluoroethylene [10], fluoropolymers [11], fluorene-based poly(iminoarylene)s [12], α-Septithiophene [13], etc. have been tested as the buffer layers.

In this paper, we offer for the first time *p*-Isopropenylcalix[8]arenestyrene copolymer (iPrCS) as a novel buffer layer for the fabrication of OLED

with improved efficiency and life time. Until now the calix[4]arene compounds were used only for design of electroluminescent complexes - for ex. a calix[4]arene [Al I]³⁺ complex [14], lanthanide complexes with calix[4]arene derivatives [15].

2. Experimental

Two types of devices were investigated: ITO/iPrCS/TPD/Alq₃/Al, and ITO/TPD/Alq₃/Al as a reference structure.

Materials: The *p*-Isopropenylcalix[8]arenestyrene copolymer employed for this study (Fig.1) was obtained according to described procedure [16]. Alq₃, TPD, and polyethylene terephtalate (PET) substrates coated with ITO (40 Ω /sq) were purchased from Aldrich and used as received.

Device fabrication: Devices with area 1 cm² were prepared on commercial ITO (40 Ω /sq) as the anode material. A 5 mm wide ITO strip line was formed on PET substrates by selective etching in hydrochloric acid (HCl) and nitric acid (HNO₃) with a volume ratio HCl:HNO₃:H₂O = 1:1:2 for 1 min at room temperature. Then the patterned ITO substrate was cleaned in acetone, isopropanole and rinsed in deionized water.

The buffer layer ($\delta = 10 - 16$ nm) of iPrCS was deposited onto PET/ITO substrates by spin-coating from 0.1 - 0.3% solution in THF (filtered through a 0.8 μ PA filter) at 2000 rpm.

The hole transporting TPD layer (HTL) (δ =30 nm), the emissive layer (EL) of Alq₃ (δ = 50, 75 nm) and the Al cathode (δ = 120 nm) were obtained by thermal evaporation in a vacuum better than 10⁻⁴ Pa at rates of 2-5A/s.

Measurements: TGA measurement was carried out from Perkin Elmer TGA at a linear heating rate of 10°C min⁻¹ under highly pure nitrogen gas. Temperature was ranged from ambient to 750°C. The weight of sample was 18 mg. The morphologies of the deposited buffer layer, HTL and EL were studied with a scanning electron microscopy (SEM) (Philips 515).

The current-voltage (I/V) and luminescencevoltage (L/V) curves were automatically measured with an "Organic LED Monitor 1000" system produced by "Advanced Technologies Ltd." in continuous DC mode, where the light output was detected using a calibrated silicon photodiode Hamamatsu S 2281.

The luminous efficiency (η_L) in candelas per amp [cd/A], calculated by Eq. 1, was used for quantifying the properties of the OLEDs [17].

 $\eta_L = L/I$

(1)

The devices were characterized in room ambient and temperature without encapsulation.

3. Results and discussion

3.1. Effect of morphology

SEM micrographs of the studied layers were presented on figure 2. The surface of iPrCS thin film deposited on ITO (Fig.2a) is amorphous and very smooth. TPD thin film sample, deposited upon iPrCS layer (Fig.2c) has a more ordered surface texture. The vacuum deposited TPD layer on a bare ITO (Fig.2d) shows a granular structure with bubbles, which is a prerequisite for recrystallization and oxidation. A dense and smooth surface image of Alq₃ thin film was found, with no defects observed in OLED with buffer layer (Fig.2e). Not so smooth is the surface of Alq₃ thin film in the structure without buffer layer (Fig.2f).

The used by us iPrCS has high thermal stability and good film formability. The TGA obtained shows that the copolymer undergoes a small 9.906% weight loss transition at 193°C, and thermal degradation beginning at 397.48 °C with mass loss of 52.20%.

Besides ITO is known to form an excellent electrode, its morphology can gradually affect the organic layers evaporated on ITO substrate, where the small spikes in the ITO surface can lead to local crystallization of HTL and EL causing a bright white-spot that may increase the leakage and instability of the device. The amorphous and very smooth surface of spin-coated thin film of iPrCS creates more suitable conditions for vacuum deposition of TPD thin films compared to the bare ITO and improves substantially the thermal stability of TPD during the operation of the devices. The results obtained show that the buffer layer of iPrCS copolymer modifies successfully the film morphology thus preventing the recrystallization of hole transporting layer (TPD) and emissive layer $(Alq_3).$

3.2. OLEDs performance

The characteristics of OLEDs were studied in dependence on the thickness of iPrCS buffer layers.

Figure 3 presents typical nonlinear current/voltage (I-V) (Fig.3a), luminance/voltage (L-V) (Fig.3b) and efficiency characteristics (Fig.3c) of ITO/iPrCS (10-16 nm)/TPD (30 nm)/Alq₃ (50 nm)/Al, and ITO/TPD (30nm)/Alq₃ (50nm)/Al as a reference structure. It was shown that the luminance and efficiency of the devices depends substantially on the thickness of the buffer layers. The most suitable thickness of the buffer layer is 13 nm. The efficiency of the device with 13 nm iPrCS is nearly 80 % higher than that of the reference structure.

Later, we studied the effect of the thickness of Alq₃ on the performance of the devices with iPrCS films. The current/voltage (I-V), luminance/voltage (L-V) and efficiency characteristics of the ITO/iPrCS (13 nm)/TPD (30 nm)/Alq₃ (50, 75 nm)/Al, and ITO/TPD/Alq₃ (50, 75 nm)/Al as the reference structures were presented on figure 4. It was established that the luminance (fig.4b) and efficiency (fig.4c) of the devices with iPrCS are much higher compared to the similar reference structures. The devices with 13 nm buffer layer and emissive layer of 75 nm Alq₃ have best characteristics.

The results obtained in this paper showed that the buffer layer of iPrCS greatly improves the performance of OLEDs - decreases the turn-on and the driving voltage, increases the brightness and the efficiency and prolong the life time. Besides that the turn-on and the driving voltage especially for the reference structure are still relatively high, the current efficiencies of the studied devices are close to the results of the other authors. The efficiency of our reference structure with 75 nm EL of Alq₃ at luminance 100 cd/m² is 1.89 cd/A at current density of 5.3 mA/cm² while the efficiency of the OLED with buffer layer of iPrCS at luminance 100 cd/m² increases more than 1.5x - up to 3.11 cd/A at current density of 3.2 mA/cm^2 . The maximum efficiency of the devices with iPrCS is 3.54 cd/A, similar to those of Okamoto - 3.4 cd/A at current density of 20 mA/cm² for structure ITO/CF_x/NPB (60 nm)/Alq₃ (60nm)/LiF/Al [18]. An efficiency of 4.46 cd/A at a current density of 200 mA/cm² was with achieved ITO/PFA(10nm)/Alq₃(60nm)/ Mg:Ag/Ag device by H.Wang et al. [11]. The luminescence of OLED with buffer layer increases 3x, the operational stability -4x, while the driving voltage decreases about 30% compared to the reference structure. It was established that the iPrCS buffer layer substantially modify the morphology of the next hole transporting and emissive layer thus creating the conditions for obtaining of very reproducible and bright OLED with very good performance and better life time. It could be supposed that besides the iPrCS is an insulator, it seems to enhance the hole injection thus improving a hole-electron balance in OLED. The calixarenes are a class of bowl-shaped cyclooligomeres obtained via phenol-formaldehyde condensation with a defined upper and lower rim, and a cavity. This speciality enable them to act as host molecules due to their cavities, and allow utilized them as chemical sensors, extractants for radioactive waste processing, materials for nonlinear optics, bio-active compounds. The molecular structure of used by us for the first time novel buffer layer of calixarenes makes the tunneling injection in OLED very probable.

4. Conclusion

For the first time the *p*-Isopropenylcalix[8]arenestyrene copolymer is proposed as a buffer layer for the obtaining of OLED. It was established that the buffer layer lowers the turn-on and the driving voltage, increases the luminance and efficiency and improves the life time of OLED compared to the devices without buffer layer.

The characteristics of OLED with different thickness of buffer layer and emissive layer have been investigated. It was found that the best characteristics have OLEDs with 13 nm p-Isopropenylcalix[8]arenestyrene copolymer buffer layer and emissive layer of 75 nm Alq₃. Even though more detailed investigations on the mechanisms due to the incorporation of p-Isopropenylcalix[8]arenestyrene copolymer buffer layer still remain to be carried out the results obtained are very promising for further improvement of OLED performance.

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Figure 1. Chemical structure of the *p*-Isopropenylcalix[8]arenestyrene copolymer used in device fabrication as buffer layer.



e) PET/ITO/iPrCS/TPD/Alq₃ PET/ITO/TPD/Alq₃

Figure 2. SEM images



Figure 3. The current/voltage (3a), luminance/voltage (3b) and efficiency (3c) characteristics of ITO/iPrCS (10-16 nm)/TPD (30 nm)/Alq₃ (50 nm)/Al, and ITO/TPD (30 nm)/Alq₃ (50 nm)/Al.

Figure 4. The current/voltage (4a), luminance/voltage (4b) and efficiency (4c) characteristics of the ITO/iPrCS (13 nm)/TPD (30 nm)/Alq₃ (50, 75 nm)/Al, and ITO/TPD (30 nm)/Alq₃ (50, 75 nm)/Al.