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High Efficiency Blue Organic Electroluminescent Devices Having a Metal-Doped Electron Injection Layer

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Abstract

We report high efficiency blue organic electroluminescent (OEL) devices having a metal-doped electron injection layer at the cathode interface. The typical device structure is an indium-tin oxide (ITO) / arylamine derivative (α-NPD) / blue emitting distyrylarylene derivative / metal-doped organic electron injection layer / Al. The device efficiency is dependent on the work function of the dopant metals and the host organic materials composing the metal-doped layer. A device having Cs-doped bathophenanthroline (Bphen) layer as the cathode interface layer exhibited a high luminous efficiency of 9 lm/W and an external quantum efficiency of 6.5% at luminance of 300 cd/m^2, which are the highest values reported for blue organic EL devices.

Keywords: Organic semiconductors based on conjugated molecules, Electroluminescence, Organic/Inorganic Interfaces

1. Introduction

Organic electroluminescent (OEL) devices are a class of light-emitting devices similar to inorganic light-emitting diodes (LEDs). The efficiency and device stability have been substantially improved for the last decade, and small size organic EL displays have been commercialized and are expected to be the next generation flat-panel displays. One of the issues remained is the performance of blue devices. Since full color displays requires the three primary colors of red, green, and blue, the development of high performance blue OEL devices became particularly important.

It was reported that a blue-light-emitting device having an emitting layer composed of distyrylarylene derivatives (DSAs) doped with distyrylarylene derivatives having carbazolyl groups exhibits a high luminous efficiency of 1.5 lm/W and the external quantum efficiency of 2.4% [1]. Recently, higher luminous efficiency of 6 lm/W was obtained by the optimization of the device structure and materials [2]. Other materials such as silyl-substituted ter-(phenylene-vinylene) [3], dipyrazolopyridine derivatives [4], and metal complexes [5, 6] have been synthesized and used for blue-light-emitting devices.

In addition to the development of blue emitter materials, it is important to optimize device structure to balance the hole and electron injection, and to achieve high quantum efficiency. For electron injection, several cathode materials have been developed. Mg:Ag cathode was introduced by Tang and VanSlyke in 1987 [7]. Other cathode materials such as Al:Li alloy [8] and a bilayer cathode of Li/Ag [9] have been reported. Later, bilayer cathodes using thin inorganic layer such as Li_2O/ Al [10] and LiF/ Al [11] were also developed. Recently, Kido and Matsumoto demonstrated that the use of a metal-doped organic layer at the cathode interface is effective in reducing the drive voltage [12]. The organic molecules in the metal-doped layer form radical anions or charge transfer complexes [13], which facilitate electron injection from the cathode. More recently, alkaline metal complexes were reported to be effective as an electron injection layer due to self-doping effect [14].

In this paper, we report the fabrication of high efficiency blue OEL devices using the metal-doped electron-injection layer. The effect of alkaline metals as the dopant in the metal-doped layer was studied. Several electron-transporting organic materials were also studied as the host materials in the metal-doped layer to optimize the composition of a metal-doped layer.

2. Experimental

The typical structure of blue organic EL device is shown in Fig. 1. *N,N'*-Bis-(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (α-NPD) was used as a hole-transport layer. The molecular structures of blue emitting materials, distyrylarylene (DPVBi), and distyrylarylene amines (BCzVBi) are shown in Fig. 1. 4,7-Diphenyl-1,10-phenanthroline (Bphen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), tris(8-quinolinolato)aluminium (Alq_3), DPVBi were used as electron-transporting materials.

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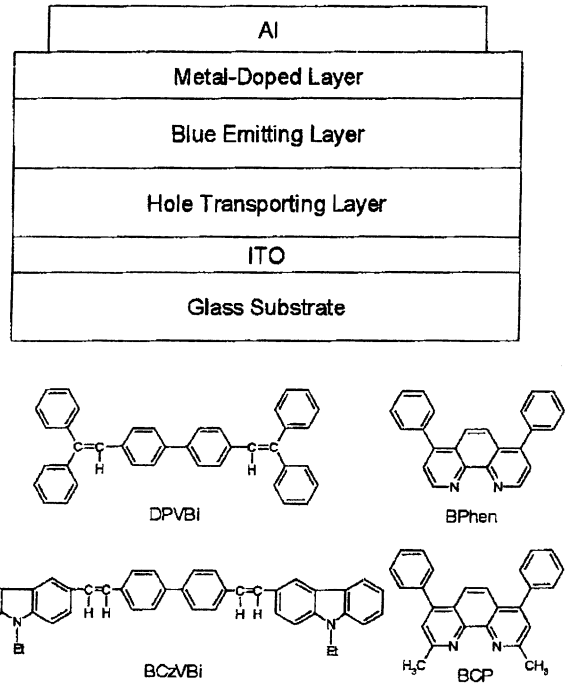

Fig. 1. Configuration of EL device and chemical structures of the materials used.

doped with alkaline metals. EL devices were fabricated by vacuum deposition process. Organic layers were successively deposited onto precleaned ITO-coated glass substrate under 1×10^{-3} Pa. Metal-doped organic layers were formed by co-eposition of alkaline metal and organic material from separate sources at a molar ratio of 1:1. Alkaline metal dispensers from Saes Getters were used to deposit alkaline metals. The Al top electrode was finally deposited at 1×10^{-3} Pa using a metal shadow mask to define an emitting area of 5×5 mm^2. EL spectra were measured with an optical multichannel analyzer PMA 10 (Hamamatsu Photonics K. K.). Luminance measurements were carried out with a Topcon BM-8 luminance meter at room temperature. External quantum efficiencies were estimated from luminance, EL spectra, current densities assuming the Lambertian emission pattern.

3. Results and Discussion

First, we investigated alkaline metals, such as Cs, Rb, K, and Li, as the dopant in the metal-doped layer. The device structure was a glass substrate/ITO/α-NPD (40 nm)/DPVBi (50 nm)/Alq_3-doped with alkaline metal (20 nm)/Al. Figs. 2 (a) and (b) show the luminance-voltage characteristics and the current density- voltage characteristics, respectively. The device with Li doped Alq_3 layer exhibited the luminance of 1550 cd/m^2 at 10 V (Fig. 2(a), open circles). At that drive voltage, the current density was 46 mA/cm^2 (Fig. 2(b), open circles). In

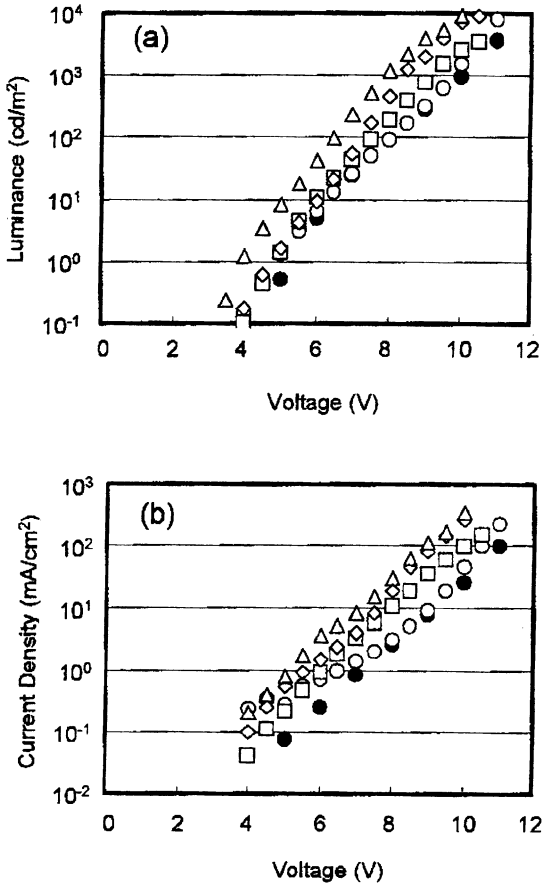

Fig. 2. (a) Luminance- voltage and (b) Current density- voltage characteristics for ITO/α-NPD (40 nm)/ DPVBi (50 nm)/ metal-doped Alq_3 (20 nm)/ Al, and (closed circles) ITO/ α-NPD (40 nm)/ DPVBi (50 nm)/ Alq_3 (20 nm)/ LiF (0.5 nm)/ Al. Dopant metals are (open triangles) Cs, (open diamonds) Rb, (open squares) K, and (open circles) Li.

contrast, LiF/Al bilayer cathode device showed the luminance of only 960 cd/m^2 (Fig. 2(a), closed circles) and the current density of 26 mA/cm^2 (Fig. 2(b), closed circles) at the same voltage (10 V). Thus, by introducing Li-doped layer at the cathode interface, the barrier height for electron injection from the cathode is reduced due to the formation of radical anions of Alq_3 at the interface [12]. Among several alkaline metals, the device having Cs-doped Alq_3 layer exhibited the highest luminance of 9200 cd/m^2 and the current density of 350 mA/cm^2 at 10 V. The work functions of Li, K, Rb, and Cs are 2.90, 2.30, 2.16, and 2.14 eV, respectively. And the current densities at 10 V were 46, 103, 270, and 350 mA/cm^2 for Li, K, Rb, and Cs-doped devices, respectively. These results suggest that the work function of metals reflects reactivity of the metals and the effect of metal doping in reducing the barrier height for electron injection from cathode.

We also studied the effect of the host electron-transporting materials in the metal doped layer on device performance. The device structure was a glass substrate/