High-Efficiency Phosphorescent OLEDs using Chemically Doped Layers

Soichi Watanabe*, Yuya Agata**, Daisaku Tanaka**, and Junji Kido* **

*Graduate school of Science and Engineering, Yamagata University
Yonezawa, Yamagata 992-8510, Japan.
**Optoelectronic Industry and Technology Development Association,
Bunkyo-ku, Tokyo, 112-0014, Japan.

Organic light-emitting devices (LEDs) were fabricated using wide-energy-gap (over 3.30 eV) materials and fac-tris(2-phenylpyridine) iridium complex (Ir(ppy)_3) as the carrier transporting materials and the emitting material, respectively. The organic layers at the electrode interfaces were chemically doped to reduce operating voltage. The p-type and n-type doped layers have specific resistance of 10^5~10^6 Ω·cm. The device exhibited green emission peaking at approximately 510 nm, and the external quantum efficiency of 19.7% (69 cd/A). A high power efficiency of 68 lm/W was observed at 100 cd/m² at voltage of 3.22 V.

Keyword: chemical doping, EL, phosphorescence, iridium complex, OLED

1. Introduction
Organic LEDs have been expected to be the next generation flat panel displays and illumination light sources because of their high efficiency. In these days, extremely high efficiencies have been observed by using so called phosphorescent metal complexes as emitting centers [1, 2, 3]. This is due to the fact that both singlet and triplet excited states are involved in the luminescence process at room temperature. Thus, internal quantum efficiencies could reach 100% [4, 5, 6].

Phosphorescent metal complexes require properly chosen wide-energy-gap host materials and carrier transporting materials so that the high triplet excited energy at the metal complex can be confined to the emitting center.

To achieve high power efficiencies, reducing drive voltages is effective. Because organic LEDs consist of organic layers (~100nm) that are essentially insulating materials, having no intrinsic carriers, the operating mechanisms involve injection of holes and electrons to the organic layers from electrodes. Therefore, it is important to reduce barrier heights for the carrier injection at the organic/electrode interface to realize low operating voltage. The insertion of chemically doped organic layer at the electrode interfaces is quite effective in reducing the driving voltage [7, 8, 9].

In this paper, we report on the fabrication of high efficiency organic LEDs using the chemical doping method and phosphorescent fac-tris(2-phenylpyridine) iridium complex (Ir(ppy)_3) as the emitting center.

2. Experimental
2.1. Materials
Fig. 1 shows organic materials used in this study. 2,2'-(5-Phenyl)-di-p,p'-diphenyl(di-p,p'-dipheny)-di-carbazole (3DTPBP) [10] was used as hole transporting materials. 4,4'-Carbazole)biphenyl (CBP) and 4,4',4'-tris(N-carbazolyl)-triphenylamine (TCTA) [5] were used as host materials for Ir(ppy)_3. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline was used as an electron transporting material.
Fig. 1. Molecular structures of materials used in this study, the energy diagram and the configuration of Device: ITO / PC1020 (50nm) / 3DTAPBP (10nm) / Ir(ppy)$_3$ 8wt.% doped TCTA (5nm) / Ir(ppy)$_3$ 8wt.% doped CBP (5nm) / BCP (32.5nm) / BCP:Cs (20nm) / Al (80nm).

2.2. Fabrication of OLEDs

Firstly, a p-doped layer, consisting of a p-doped arylamine polymer (MCC-PC 1020) was formed by spin-coating on the pre-cleaned Indium-Tin Oxide (ITO) substrate with a sheet resistance of 13 $\Omega$/sq. MCC-PC 1020, provided by Mitsubishi Chemical Group Science and Technology Research Center, INC, exhibits a specific resistance of $5.66 \times 10^6$ $\Omega$-cm. On the top of the p-doped layer, organic materials were vacuum deposited at a base pressure of $2.0 \times 10^{-5}$ Pa without breaking the vacuum. After n-doped layer is formed by co-evaporation of BCP and Cs from a Cs dispenser source at a molar ratio 1:1 (specific resistance of $2.59 \times 10^5$ $\Omega$-cm), the Al top electrode was vacuum deposited using a metal shadow mask to define an emitting area 4mm$^2$. After the cathode formation, the devices were encapsulated using an UV-epoxy resin and a glass lid with desiccant under a dry nitrogen atmosphere (<1 ppm H$_2$O/O$_2$) [11].

The phosphorescence spectra of the thin films of the wide gap materials were obtained using a streak camera (C4334 from Hamamatsu Photonics) at T<8K. Photoexcitation of the samples was carried out at a wavelength of 337 nm by N$_2$ laser with 500-ps pulses at 10Hz. The triplet energy level was determined from the highest energy of the phosphorescence spectra. Luminance measurements were carried out using a Topcon BM-8 luminance meter and electroluminescence (EL) spectra were taken on a Hamamatsu photonics PMA-10 optical multichannel analyzer at room temperature. The observed power efficiency and the external quantum efficiencies were corrected by measuring angular distributions of light emission from the devices [12].

Fig. 2. The phosphorescence spectra and the triplet energy of materials at T<8K.

3. Results and Discussion

The phosphorescence spectra of 3DTAPBP, BCP, TCTA and BCP are shown in Fig. 2 together with the room-temperature PL spectrum of Ir(ppy)$_3$ in the Ir(ppy)$_3$ (8wt.%) doped TCTA film. These results indicate that these materials exhibit high triplet excited energy levels, ensuring the confinement of the excited energy of Ir(ppy)$_3$.

Organic LEDs using the chemical doping method
and phosphorescent fac-tris(2-phenylpyridine) iridium complex (Ir(ppy)$_3$) as the emitting center. We optimized the carrier balance in the emitting layer and the optical interference effect by considering the thickness of BCP/BCP:Cs layers. Fig. 3 shows luminance-voltage (a), current density-voltage (a), external quantum efficiency-luminance (b), and power efficiency-luminance (b) characteristics of the device. The optimized device exhibited green emission peaking at approximately 510 nm and the CIE color coordinates of $x = 0.298$, $y = 0.629$. The operating voltages are low, exhibiting 100 cd/m$^2$ at 3.22 V, and the maximum luminance of 114000 cd/m$^2$ at 9.75 V. At 100 cd/m$^2$, the external quantum efficiency of 19.7% (69 cd/A) and a high power efficiency of 68 lm/W were observed. Assuming the light out-coupling efficiency of 20%, the internal quantum efficiency is approximately 100%. These results demonstrate that the wide energy gap materials are useful in confining triplet excited energy to the emitting center, Ir(ppy)$_3$.

To realize low drive voltages and high power efficiencies, the chemically doped layers at the electrode interfaces play critical roles. Specific resistance of PC1020 and BCP:Cs were determined by measuring current density (J) –voltage (V) characteristics. The device configuration was ITO / chemically doped organic layer (80 nm) / Al. In these devices, only holes or electrons are injected to the organic layer. The calculated specific resistance from the J-V curves of PC1020 and BCP:Cs were $5.66 \times 10^6$ $\Omega$·cm and $2.59 \times 10^5$ $\Omega$·cm, respectively. In general, specific resistance of undoped organic materials is over $10^6$ $\Omega$·cm [8]. These results indicate the significant increase in the conductivity of the doped organic layers, which results in the low operation voltages for the organic LEDs.

4. Conclusion
In conclusion, we demonstrated a high power efficiency organic LEDs with wide gap materials using chemical doping method. The device exhibited green emission peaking at approximately 510 nm, and the external efficiency organic LEDs with wide gap materials using chemical doping method. The device exhibited green emission peaking at approximately 510 nm, and the external quantum efficiency of 19.7% (69 cd/A). A high power efficiency of 68 lm/W was observed at 100 cd/m$^2$ at voltage of 3.22 V.

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References
11. GDO/CA/R18 × 10 × 0.4, *Saes Advanced Technologies, Avezzano, Italy.*