Recombination zone in organic light emitting diodes with emitting layer of diphenylanthracene-derivative host

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Abstract

White organic light emitting diode devices based on blue-green emitter DSA-ph (1,4-di-[4-(N,N-di-phenyl)amino]styryl-benzene) has been studied by co-doping orange emitter. The recombination zone is confirmed to be a region near the interface of hole transport and emitting layers. Although the emission color changes with increasing applied voltage in the co-doped device, white light with high luminance of 16800 cd/m\textsuperscript{2} was obtained at low voltage of 3.8 V. The maximum luminance efficiency of 14 cd/A was obtained in non-co-doped device.

Keywords: Electronluminescence; White OLEDs; Complementary color; Recombination zone; DSA-ph

1. Introduction

White organic light-emitting diodes (OLEDs) have gained interest for the applications to flat panel displays and lighting sources. Three primary color emitting chromophores are doped in a common conductive host to achieve the white-light emission [1,2], or two complementary color emitting chromophores are used [3,4]. In the mass production of the devices, the OLEDs using the complementary color emitting dopants and a common host material are preferable to the OLEDs using the primary color dopants and three different host materials because the fabrication cost is reduced.

Wide electron-hole recombination zone gives a longer OLED operational lifetime compared with narrow recombination zone [5]. This is reasonable because the recombination of high-density carriers confined in a narrow zone induces heating of the device. It is known that the recombination zone resides mostly at the interface of hole transport layer (HTL) and emitting layer (EML). The zone extends into inside the EML [6]. It is interesting to know how much the zone extends in the EML and how much the excitons diffuse from the recombination site.

Here we fabricate white OLEDs with two complementary color (blue and yellow) emitting dopants in a common host and investigate the OLED characteristics and recombination zone.

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2. Experimental Procedures

Before fabrication of white OLED, we firstly fabricated a blue OLED which gives a complimentary color to yellow color. This OLED is called Device A with the following layer structure:

Device A : ITO/2-TNATA(75nm)/NPB(20nm)/ADN:3%DSA-ph(30nm)/Alq3(20nm)/LiF(0.5nm)/Al

The layer thickness of each layer is indicated. The ITO has a thickness of 220 nm.

DSA-ph (1-4-di-[4-(N,N-di-phenyl)amino] styryl-benzene) was used as the blue dopant in EML, and ADN (diphenylanthracene derivatives 9,10-di(2-naphthyl)anthracene) was used as the host. The 2-TNATA (4,4',4’”-tris(2-Raphpthylphenylamino)triphenylamine), NPB (N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine), and Alq3 (tris(8-quinolinololato) aluminum) were selected as materials for hole injection layer (HIL), HTL, and electron transport layer (ETL), respectively. The layer structure of Device A is shown in Fig. 1, together with the HOMO and LUMO energy levels of each layer. The OLED device was fabricated by thermal evaporation method. The base pressure was lower than $7 \times 10^{-4}$ Pa during the evaporation of organic materials and Al cathode. The deposition rate was lower than 0.3 nm/s. All the device processes were performed without breaking the vacuum.

To obtain white electroluminescence (EL), another OLED (called Device B) was fabricated. Device B is the same as Device A except the following point. A yellow-light emitting fused aromatic ring material RD-001 [7] was co-doped in the EML in the blue emitting Device A. The co-doped layer thickness is 5 nm. The concentration of RD-001 is 0.5 wt %. The RD-001 co-doped layer was inserted at one of three positions in the 30 nm thick EML, i.e., (1) immediately adjacent to the interface of HTL and EML, (2) at the middle of ADN layer, or (3) adjacent to the interface of EML and ETL, which are called Devices B-HTL, B-center, or B-ETL, respectively (see Fig. 2).

3. Results

Figure 3 shows the EL spectra of Device A measured at 10 V. Intense peak at 470 nm accompanied by vibronic sidebands at 504, about 540, and about 594 nm. The peak height ratio of the 470 nm band to the 504 nm band to the 540 nm band is 1.00:0.67:0.37. This blue-green emission is due to DSA-ph dopant. Emission from ADN host, which is at 452-455 nm, is not observed, indicating efficient energy transfer from ADN host to the dopant. A very weak emission is observed at about 422 nm, which is attributable to NPB of the HTL.

Figure 4 shows the EL spectra of Device B-HTL at various current densities. Emission band due to RD-001 is observed at 575 nm in addition to the emission bands due to DSA-ph and a very weak emission band due to NPB at about 420 nm as shown in inset of Fig. 8. The peak height of the 470 nm DSA-ph emission is lower at low current densities below 0.1 A/cm² than that of the 575 nm RD-001 emission, but it is reversed at high current densities above 0.1 A/cm² as shown in Fig. 5.
The Commission Internationale d’Eclairage (CIE) chromaticity coordinates of Device B-HTL is shown in Fig. 6. The coordinate approaches the equienergy white point (0.33, 0.33) with increasing applied voltage from 2.6 V to 4.0 V. A CIE coordinate (0.324, 0.402), which is close to the white point, is obtained at 3.8 V (91.46 mA/cm²), where the peak height ratio of the 470 nm emission to the 504 nm emission to the 570 nm emission is 1.00:0.65:0.77 and the luminance is 16800 cd/m² (Fig. 7). With increasing the voltage from 5 V, the color changes to blue-green since the intensity of orange emission from RD-001 decreases. Lower driving voltage operation was possible for Device B-HTL than for the other devices as seen in Fig. 7.

The change of relative peak height between the 470 and 575 nm emissions with increasing the current density is understood as follows.

RD-001 has a lower LUMO by 0.2 eV compared to DSA-ph (2.9 eV). The injected electrons are therefore easily trapped by the RD-001 besides DSA-ph. Moreover the energy transfer from DSA-ph to RD-001 is possible due to the overlap of the absorption spectrum of RD-001 with emission spectrum of DSA-ph. As a result the RD-001 emission intensity becomes much higher than the DSA-ph emission intensity as observed at low current densities. The concentration of RD-001 (0.5 wt %) is much lower than that of DSA-ph (3 wt %). Therefore, as the injected electrons increases with increasing current density, the excitation into RD-001 saturates more easily than the excitation into DSA-ph, leading to decrease of the RD-001 emission intensity relative to the DSA-ph emission intensity at high current densities. The color variation is therefore attributed to saturation of the emission sites at
RD-001 due to relatively low concentration as in the case of a white OLED [8] with EML of blue emitting TBPe (3 wt %) and yellow-orange emitting rubrene (0.2 wt %) doped in BAlq host.

It is found from Figs. 4 and 5 that the 420 nm NPB emission appears although it is very weak. This is suggested as follows. The hole mobility of NPB is high (10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} [9]), while the electron mobility is (6–9)\times 10^{-4} \text{ cm}^2/\text{Vs} [10] which is not so smaller than the hole mobility. Therefore the electrons injected from ETL to EML can move in the hole-transporting NPB layer, giving rise to emission of NPB.

The EL spectra of Device B-center were the same as those of Device A. The emission from RD-001 is not observed even at any current density. Same result was obtained for Device B-ETL. This indicates that the electron-hole recombination occurs at neither the middle site of EML nor the ETL site. This means that the recombination mostly concentrates near the HTL/EML interface and the excitons never diffuse to the middle of EML.

The same blue-green emission is obtained from Devices A and B-center. The maximum luminous efficiency is 11.5 cd/A in Device A, which is lower than 14 cd/A in Device B-center (Fig. 8), while the maximum power efficiency is 7.6 lm/W in Device A, which is close to the efficiency in Device B-center. The electron mobility of ADN is one order of magnitude higher than its hole mobility [11], leading to charge unbalance in ADN layer. Doping of a small amount of RD-001 impurities in the middle site of EML decreases the mobility of electrons in EML, which move from ETL to HTL, since RD-001 works as electron trap. Therefore, a charge balance in the recombination zone near the HTL/EML interface is achieved in Device B-center, resulting in a higher luminous efficiency for Device B-center than for Device A.

In conclusion, the recombination zone is confirmed to be a region near the HTL/EML interface. Although the emission color changes with increasing applied voltage in Device B-HTL, white-like light with high luminance of 16800 cd/m^2 was obtained at low voltage of 3.8 V. The maximum luminance efficiency of 14 cd/A for blue-green light was obtained in Device B-center, which is higher than that in Device A.

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