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Hybrid color-conversion layers for white emission from fluorescent blue organic light-emitting diodes

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ABSTRACT

Hybrid color-conversion layers (CCLs) were developed to convert a blue emission from fluorescent organic light-emitting diodes (OLEDs) to obtain a white emission with a high color rendering index (CRI). The hybrid CCLs were composed of an inorganic phosphor, organic dye, and silicon dioxide (SiO_2) scattering nanoparticles. The inorganic phosphors convert a part of blue emission from OLEDs to a green-yellow emission effectively. A part of the green-yellow emission was consecutively converted to a red emission with the organic dye. Using the hybrid CCLs, we obtained a balanced white emission with the highest CRI of 93 and the color temperature of 3500 K. The high CRI white OLED showed the power efficiency of 11 lm/W which was enhanced by 1.9 times from that of the blue fluorescent OLED. We showed that the utilization of the SiO_2 nanoparticles did not only enhance the power efficiency but also significantly reduce the white color variation to the viewing angle.

1. Introduction

White organic light-emitting diodes (OLEDs) have already been commercialized as a general solid-state lighting. Unlike inorganic light-emitting diodes, OLEDs possess high spectrum-tailoring flexibility because there is a wide variety of organic emitters ranging from red to violet. White OLEDs can be easily achieved by stacking two or more different color emitters in a large area. However, the white OLEDs require complicated device engineering in order to accurately tune their chromaticity. Due to their complicated structures, they also require careful fabrication processes in order to maintain a high production yield. Another way to achieve white OLEDs is to utilize down-conversion of simple blue-emitting OLEDs. The down-conversion from blue to white can be accomplished by inorganic phosphors [1,2], organic emitters [3–7], quantum dots [8], or combined emitters [9]. Even though the down-conversion method to achieve white OLEDs are simple in view of device and process, it requires high-efficiency and stable blue OLEDs with a proper emission spectrum for the color conversion. To date, stable fluorescent blue materials have a limited power efficiency (PE), while highly efficient blue phosphorescent materials have a short lifetime and high longer-wavelength portion in the emission. In this study, we fabricated a fluorescent blue OLED and converted the blue emission to white by utilizing a combined hybrid structure of an inorganic phosphor, organic emitter, and scattering nanoparticle. Due to the low PE of fluorescent blue OLEDs, the down-converted white OLEDs show lower PE than that of the state-of-the-art stacked phosphorescent white OLEDs. However, many research groups are actively developing highly efficient phosphorescent and thermally-activated-delayed-fluorescent blue materials. If the efficient blue-emission materials are available, the down-converted white OLEDs could be an importance method especially for large-area OLED applications because the mass production of OLEDs with simpler structures could potentially have a higher production yield.

In order to achieve an efficient color conversion, the blue-emission spectrum should be well matched with the absorption spectrum of the color converters. At the same time, the amount of inorganic phosphor and organic emitter should be well controlled to convert a proper portion of the blue emission. In this regards, we carefully selected an inorganic phosphor of which the absorption

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spectrum overlapped the blue emission spectrum. To control the amount of the color-conversion materials, we piled up a monolayer of inorganic phosphor particles with an adhesive resin containing an organic emitter. In this study, we aim to develop an optimized structure of color-conversion layer (CCL) and achieve the down-converted white emission with a high color rendering index (CRI) from a blue OLED. We also report the utilization of the scattering silicon dioxide (SiO_2) particles to further enhance the white OLED efficiency and reduce the angular dependence of white emission.

2. Experimental

Indium-tin-oxide (ITO)-coated glass substrates of 50 mm × 50 mm size were utilized as the transparent-electrode substrate for the fabrication of OLEDs. The ITO was pre-patterned to form the emission area of 20 mm × 20 mm. The patterned ITO substrates were ultrasonically cleaned in acetone, methanol, and isopropyl alcohol baths for 10 min each. After the substrates were treated in an ultraviolet (UV)-ozone environment for 20 min, they were loaded in a vacuum evaporator for the OLED deposition. We fabricated blue-emitting fluorescent OLEDs, of which the emission spectrum has the peak wavelength at 460 nm. Organic materials and cathode metal were evaporated under 8×10^{-7} torr. 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) and *N*,*N*′-bis-(1-naphyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) were utilized as the hole injection layer (HIL) and hole transport layer (HTL), respectively. 4,4′,4″-Tri(*N*-carbazolyl)triphenylamine (TCTA) was utilized as the electron blocking layer (EBL). For blue fluorescent emission, 2-methyl-9,10-di(2-naphthyl) anthracene (MADN) and 1,6-bis(*N*-phenyl-p-CN-phenylamino)-pyrenes (Pyrene-CN) were utilized as the host and dopant materials, respectively. To complete blue OLED devices, electron transporting LG201 (LG Chem. Ltd) doped with lithium quinolate (Liq), electron injecting Liq, and aluminum (Al) cathode were successively deposited. The blue-emitting OLED structure was HAT-CN (35 nm)/NPB (80 nm)/TCTA (20 nm)/MADN:Pyrene-CN (5%, 20 nm)/LG201:Liq (50%, 40 nm)/Liq (1.5 nm)/Al (100 nm). The fabricated OLEDs were encapsulated with a glass for the device-performance measurement. The OLED performance was measured using a spectro-radiometer (CS-2000, Konika Minolta) and source meter (Keithley 2400).

Fluorescent blue OLEDs were first fabricated on ITO/glass substrates. On the face of the glass substrate, a poly-acrylic acid (PAA) layer was formed using a bar coater and the layer was cured at 60 °C for 3 min. The PAA layer was utilized as an optically clear adhesive (OCA). A green-yellow $Sr_2SiO_4:Eu^{2+}$ phosphor was evenly spread on the adherent PAA surface. Non-bonded phosphor particles to the PAA surface were removed by nitrogen blowing. In this way, a monolayer of the phosphors was formed on the PAA surface. In order to put another phosphor layer, the same processes were repeated to coat another PAA layer and $Sr_2SiO_4:Eu^{2+}$ phosphor layer. The SiO_2 nanoparticle layer was coated using the same process for the phosphor layer. For the inclusion of an organic dye into our CCL structures, a red organic dye (ATTO 590, Sigma Aldrich) was dispersed with the poly-acrylic acid (PAA) at the concentration of 0.1 wt.%. The hybrid CCL structures were fabricated with the same processes using ATTO 590-dispersed PAA instead of the pure PAA.

3. Results and discussion

We prepared 6 different CCL structures using $Sr_2SiO_4:Eu^{2+}$ phosphor, ATTO 590 organic dye, and SiO_2 scattering nanoparticles as shown in Fig. 1. The CCL 1 and 2 structures have one and two monolayers of the phosphor particles, respectively. The phosphor particles were directly bonded with an OCA as a monolayer. The OCA was a PAA layer. As shown in Fig. 2, the size of the phosphor particles ranges from 5 to 10 μm and the OCA thickness is around 20 μm. We controlled the amount of the phosphors in CCLs by increasing the number of monolayer. The CCL 3 structure has an additional monolayer of SiO_2 nanoparticles on the CCL 2 surface in order to find out the scattering effect of the SiO_2 nanoparticles. The structures CCL 4–6 are the same as CCL 1–3 except the inclusion of ATTO 590 organic dye in each OCA layer. Therefore, we could control the amount of the organic dye by increasing the number of OCA layer. Fig. 2 shows the actual cross-sectional scanning-electron-microscopy (SEM) images of all the CCL structures fabricated in this study. The CCL thickness was as high as 60 μm for the three story CCL 3 and 6 structures. In the insets of CCL 3 and 6 structures, we showed the enlarged SEM images of the SiO_2 scattering nanoparticles of which the diameter was 300 nm.

Fig. 3 shows the emission or absorption spectra of the blue-emission OLED, $Sr_2SiO_4:Eu^{2+}$ phosphor, and ATTO 590 organic dye. The blue electroluminescence (EL) spectrum has a peak wavelength at 460 nm wavelength with a small shoulder peak at 480 nm wavelength. The full-width-half-maximum of the spectrum was 60 nm. As shown in the figure, the EL spectrum overlaps well the absorption spectrum of the $Sr_2SiO_4:Eu^{2+}$ phosphor in the range from 425 to 530 nm. We expect the efficient absorption of blue emission from the OLED by the $Sr_2SiO_4:Eu^{2+}$ phosphors. The green-yellow emission centered at 570 nm from the excited $Sr_2SiO_4:Eu^{2+}$ phosphors can be effectively absorbed by the ATTO 590 organic dye in the wavelength region of overlap between the emission and absorption spectra of the $Sr_2SiO_4:Eu^{2+}$ phosphor and ATTO 590 dye, respectively. The excited ATTO 590 dye can then generate a red emission centered at 624 nm wavelength. The ATTO 590 belongs to the class of rhodamine dye. It shows strong absorption and high fluorescence at 593 nm and 622 nm wavelengths with a quantum yield of 80%. The organic dye is effective to achieve white emission from blue OLEDs since it does not absorb the light in blue-wavelength region but selectively absorb the light in yellow-orange wavelength region unlike common inorganic red phosphors.

Because the 6 different CCL structures are attached to the face of the blue OLEDs with a same structure, the current-voltage curves are identical for all the devices as shown in Fig. 4(a). The luminance of the CCL-attached white OLEDs was always higher than that of the bare blue OLED. It is due to the difference in the emission spectra caused by the different color conversion. The highest luminance was obtained with the CCL 2 and 3. In Table 1, we listed the performance of the bare blue OLED and down-converted white OLEDs. Luminous efficacy of radiation (LER) measures the fraction of electromagnetic power which is useful for lighting. It is obtained by dividing the luminous flux by the radiant flux. Light with wavelengths outside the visible spectrum reduces LER because it contributes to the radiant flux while the luminous flux of such light is zero. The response of a typical human eye to light is the strongest at a wavelength of 555 nm and diminishes gradually to the longer and shorter wavelengths. As shown in Fig. 4(c)-(d), and Table 1, the emission spectra obtained with the CCL 2 and 3 resemble the most to the photopic response function among all the measured spectra and thus show the highest LER values. The luminance and power efficiency (PE) of down-converted white OLEDs with CCLs showed the same order as the LER values listed in Table 1. The external quantum efficiency (EQE) shows a little different behavior since it is related with the color conversion efficiency of $Sr_2SiO_4:Eu^{2+}$ phosphor and ATTO 590 organic dye. The highest EQE was obtained with the CCL 1 and 4 which were the simplest CCL structure in all the CCLs. More complex CCLs attached to the bare blue OLED result in more loss in EQE. The performance of the bare blue OLED and down-converted white OLEDs was summarized in Table 1. The bare fluorescent blue OLED has the LER of 200 and PE of 5.85 lm/W at