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Micro-Cavity Effect of ZnO/Ag/ZnO Multilayers on Green Quantum Dot Light-Emitting Diodes

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ABSTRACT

ZnO/Ag/ZnO multilayers were fabricated and their optical properties were investigated in terms of the micro-cavity effect in electroluminescent devices based on colloidal quantum dots. The top and bottom ZnO layers were formed by a sol-gel method while the middle Ag layer was deposited by thermal evaporation. After the fabrication of the ZnO/Ag/ZnO structure, the transmittance increased to 74%. When the oxide/metal/oxide multilayers were applied to quantum dot light-emitting diodes, the color purity was enhanced due to the narrower full width at half maximum.

Key words : ZnO, Optical properties, Sol-gel process

1. Introduction

The micro-cavity effect is a key technology that will be deployed in next-generation displays due its enhancement of the color purity, as caused by a narrowing of the broad emission spectra of electroluminescent (EL) devices without complicated optics.[1,2] Generally, to attain an efficient micro-cavity effect in EL devices, a pair of reflective electrodes and a transparent electrode are required. Unlike the simple fabrication of a reflective electrode by metal deposition, many requirements must be satisfied to enable the use of transparent conducting oxides (TCOs) as a transparent electrode for application to flat-panel displays and touch screens.[3,4] Although indium tin oxide (ITO) thin films are the most commonly used TCO materials, the world's limited reserves of indium makes ITO more expensive.[5,6] ZnO has been investigated as a possible replacement for ITO electrodes as its deposition is relatively inexpensive and yet offers good optical/electrical properties. ZnO has good transparency in the visible range, with high electron mobility, and a wide bandgap of 3.37 eV.[7,8] Recently, oxide/metal/oxide (OMO) multilayers with very thin metal middle layer have exhibited enhanced electrical and optical properties resulting from the combination of the metal with a low refractive index and oxides with a high refractive index.[9,10]

In the present study, ZnO/Ag/ZnO multilayers were fabricated and applied to quantum dot light-emitting diodes (QLEDs), one of the most promising EL devices,[11,12] to verify the micro-cavity effect. Commonly, OMO multilayers are fabricated by the RF sputtering method, which is limited to large-area fabrication. In this case, however, OMO multilayers were fabricated using the convenient sol-gel method for the ZnO layers and thermal evaporation for the thin Ag layer. Their optical properties were systemically studied. When EL spectra from QLEDs with/without OMO multilayers were compared with each other, the narrowed full width at half maximum (FWHM) resulting from the micro-cavity effect of the OMO multilayers was observed.

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2. Experimental Procedure

2.1. Preparation of ZnO/Ag/ZnO multilayer

The top and bottom ZnO layers, each 100 nm thick, were formed using a sol-gel method. First, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was dissolved in 2-methoxyethanol. The solution was then stirred for 2 h at 75°C and then the temperature was increased up to 200°C and remained for about 5 min to get clear solution of ZnO. This clear solution was spin-coated onto the opposite side of an ITO patterned glass substrate at 5,000 rpm for 30 s and then placed on a hotplate at 50°C to evaporate the residual solvent. To form a dense, crystalized ZnO layer, the temperature of the hotplate was increased to 380°C, and maintained at that temperature for 1 h. The middle Ag layer (6 nm) was deposited by thermal evaporation at a pressure of 1.5×10^{-6} torr.

2.2. Fabrication of QLEDs

First, the ITO glass, patterned to form an anode, was cleaned by sonication using isopropyl alcohol and then deionized water. The cleaned ITO anode was dried, after which an oxygen plasma treatment was applied to the surface of the ITO patterned glass for 5 min. For the hole injection layer (HIL), poly(3,4-ethylenedioxythiophene) : poly (styrene sulfonate) (PEDOT : PSS) was spin-coated onto the ITO substrate at 3000 rpm for 35 s and then dried on a hotplate at 180°C for 30 min. For the hole transport layer

(HTL), poly[(9,9-dioctylfluorene-co-*N*-[4-(3-methylpropyl)]-diphenylamine] (TFB) was dissolved in chlorobenzene (8 mg/ml) and then spin-coated onto the PEDOT:PSS layer at 2,000 rpm for 35 s. It was then dried on a hotplate at 150°C for 30 min. Similarly, for the EML, green CdSe/ZnS QDs were dispersed in heptane (0.5 mg/ml) and then spin-coated onto the TFB layer at 2,000 rpm for 5 s. Likewise, for the ETL, ZnO NPs were synthesized using a protocol described in the literature.[13] The ZnO NPs were then re-dispersed in ethanol prior to spin-coating on the QD emission layer at 3,000 rpm for 60 s. After the completion of the solution process, the cathode (Al, about 120 nm) was deposited by thermal evaporation on the ZnO NP layer. Finally, the devices were encapsulated in glass using a UV sealant.

2.3. Characterization

A PerkinElmer Lambda 19 spectrometer was used to measure the transmittance of the films over a wavelength range of 300 - 750 nm. The electroluminescence (EL) spectra were measured by using a spectroradiometer (Minolta CS 2000) with a Keithley 2400 source meter under ambient conditions.

3. Results and Discussion

The transmittance spectra for a wavelength range of 350 - 750 nm for ZnO/Ag/ZnO multilayers with Ag middle layers of different thicknesses are shown in Fig. 1. The OMO multilayers were fabricated using the convenient sol-gel method for the top and bottom ZnO layer and thermal evaporation for the middle Ag layer. It is well known that bare crystallized ZnO film has a visible spectrum transmittance of more than 80%.[14] Once the OMO multilayers have been formed, a degree of waviness can be observed over the entire visible region. In the OMO multilayers, the Ag layer acts as a mirror for the incident light, while the ZnO layers act as an anti-reflective coating. The light reflected by the front and rear surfaces of each ZnO layer are of opposite phase and of nearly equal amplitude, which results in a decrease in the amount of light that is reflected. The region around 500 nm exhibits a relatively low value due to the excitation of the localized surface plasmons in the thin Ag layer.[15] This is caused by the micro-cavities formed in the OMO layers. Upon increasing the thickness of the middle Ag layer (from 6 to 10 nm), the transmittance of the OMO multilayers decreases across most of the visible light spectrum. Interestingly, the transmittance of the OMO multilayers increases to 74% in the long wavelength region. It is assumed that a 6-nm Ag film is too thin to form a perfect layer, with some Ag atoms still existing as aggregated Ag islands, prior to forming a continuous layer. Therefore, longer-wavelength light (red and near-IR) can pass through it easily.

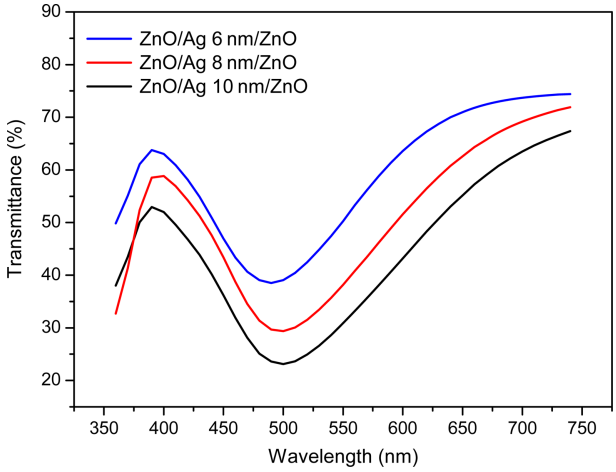


Fig. 1. Transmittance spectra of ZnO/Ag/ZnO multilayers.

To investigate the spectral response after light passes through the OMO multilayers, QLEDs were fabricated and positioned 15 mm from the fabricated OMO multilayers. Fig. 2 is a schematic of the structure of a QLED device on an OMO multilayer. The QLEDs have the standard structure with ITO/PEDOT : PSS/TFB/green QDs/ZnO NPs/Al. The QLEDs were carefully designed to achieve efficient carrier injection and balance in the QD emission layer. In this device structure, PEDOT : PSS was used as the HIL on the ITO anode to increase the anode work function and compensate for the surface roughness, thus producing a stable interface. TFB was used as the HTL to reduce the energy barrier between the work function of the PEDOT : PSS and the valence-band edge of the green QDs. Due to the chemical stability of the TFB thin films to nonpolar solvents, QDs can be simply spin-coated over the TFB layer. ZnO NPs have become well known as inorganic materials for application to ETL in recent QLEDs due to their robustness and efficient electron injection.[13,16]

Figure 3 shows the current efficiency as a function of the luminance for the fabricated QLEDs. The luminance increases with the voltage, attaining a maximum of 5,700 cd/m^2 under an applied voltage of 8 V. A maximum current efficiency of 3.6 cd/A was achieved at 200 cd/m^2. Since the OMO multilayers separate from the QLEDs, they have no effect on the performance of the QLEDs.

The changes in the EL spectrum of the QLEDs with ZnO/Ag/ZnO multilayers are shown in Fig. 4(a). For the bare

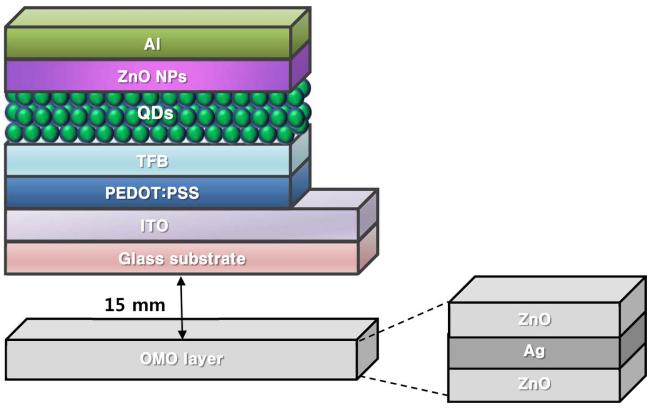


Fig. 2. Schematic of QLEDs on OMO multilayers.

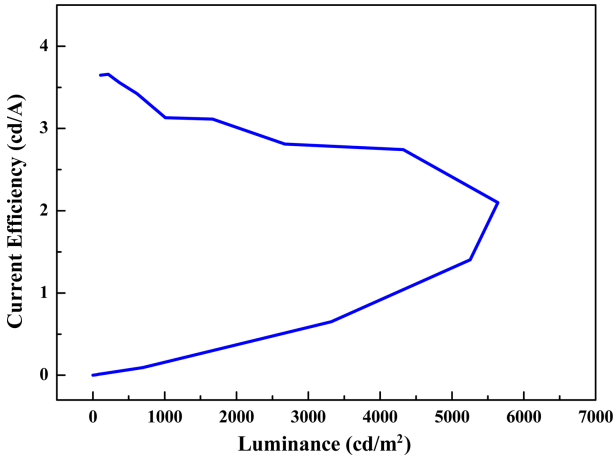
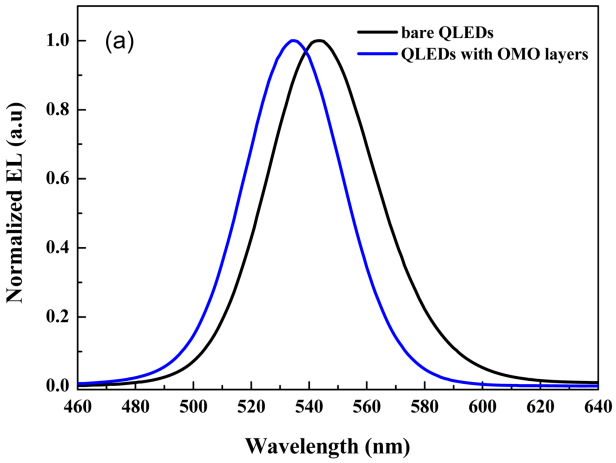


Fig. 3. Current efficiency as function of luminance of QLEDs on OMO multilayers.



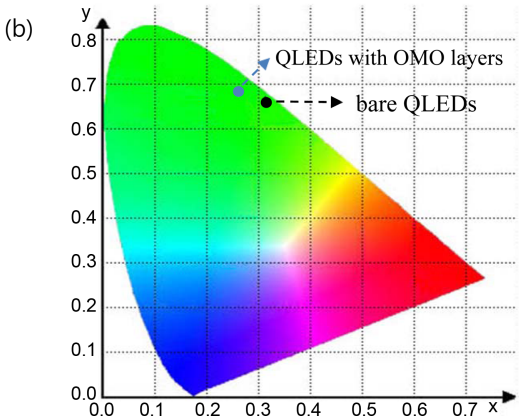


Fig. 4. (a) Change in EL spectrum and (b) CIE 1931 color diagram showing color coordinates of green QLEDs with OMO multilayers.

QLEDs, a narrow peak with a FWHM value of 45 nm is observed at 540 nm without any notable parasitic emission from the charge-transport layers. When the OMO multilayers are applied to the QLEDs, the normalized EL spectrum is blue-shifted by 9 nm and the FWHM becomes narrower, being only 40 nm. As shown in Fig. 1, the green spectral emission (near 500 nm) is limited by the low transmittance due to the micro-cavity effect. Relative to a device without any OMO multilayers, the FWHM decreased by 5 nm. The change in the green color is visualized by plotting the color coordinates on a CIE 1931 standard color diagram, as shown in Fig. 4(b). Generally, the color purity is sensitive to the FWHM of the emission peak and the plotted dots at the edge of the diagram represent the pure color.[17] By optimizing the OMO multilayers, a relatively narrow EL spectrum is obtained from the QLEDs. This enhances the color purity.

4. Conclusions

We investigated the optical properties of ZnO/Ag/ZnO multilayers. ZnO layers were formed using the convenient sol-gel method while the mid-metal layers were formed using thermal evaporation. After the fabrication of the OMO structure, the transmittance increased to 74%. When the OMO multilayers were applied to QLEDs, the normalized EL peak was narrowed due to the micro-cavity effect. These results show that OMO multilayers can be used to enhance the color purity of future display applications.

Acknowledgments

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