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High-efficiency Organic Light-emitting Diodes(OLEDs) with optimized multi-layer transparent electrodes

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Abstract

High-efficiency organic light-emitting diodes (OLEDs) based on multilayer transparent electrodes (MTEs) are reported. The dielectric/metal/dielectric (DMD) multilayer electrode based on a thin silver layer achieved high sheet conductance as small as 6 Ω/sq and a tuning capability in the optical and electrical properties by engineering the inner and outer dielectric layers. In the conventional normal bottom-emitting structure, a DMD-based OLED can be fabricated with 90% higher forward luminous efficiency and 30% higher external quantum efficiency (EQE) compared to ITO-based devices. Special attention was paid to the optimization method of such MTE structure considering both the injection and optical structures.

Keywords: organic light-emitting diode, transparent electrode, thin-film optics

1. Introduction

The transparent electrode (TE) is one of the key components of organic light-emitting diodes (OLEDs). Since the development of OLEDs several decades ago, indium tin oxide (ITO) films have become a popular choice for TEs due to their transparent and conductive nature. The price hike of indium, however, and the demand for an alternative electrode with higher conductivity or a better injection property have fueled a search for new types of TEs [1]. Among the many alternatives to ITO films, the dielectric/metal/dielectric (DMD) multilayer system is a potential candidate as its high sheet conductance and transparency are comparable to those of the conventional ITO films [2]. Recently, it was demonstrated that ZnS/Ag/WO$_3$ (ZAW) electrodes can lead to high-performance flexible OLEDs with a mechanical flexibility that is far superior to that of ITO-based flexible devices [3]. Further, an efficient inverted OLED with a ZAW electrode as a damage-free transparent anode on top of the organic layer has been reported [4]. Especially, DMD electrodes have attracted much interest due to their electrical and optical tuning capabilities with the selection of dielectric layers, and due to their thickness.

Although several improvements have been proposed, no systematic approach to the optimization of DMD structures considering their optical structure and injection behavior has been investigated. In this study, how the luminous efficiency of OLEDs varies depending on the structure of DMD electrodes in consideration of both their optical and electrical properties was investigated. Then the optimization method was proposed, by which the luminous and power efficiencies can be maximized.

2. Experiment

The DMD multilayer electrode consists of an outer dielectric layer, a thin metal layer, and an inner dielectric layer. In this study, two types of DMD electrodes, ZnS/Ag/ZnS (ZAZ) and ZnS/Ag/WO$_3$ (ZAW), were prepared on a glass substrate planarized with an additional polymeric coated layer (SU-8, Kayaku Microchem) via thermal evaporation. In both cases, ZnS was used for the outer dielectric layer to enhance the optical transparency and to reduce the surface roughness of the planarized substrate. For the inner dielectric layer, ZnS and WO$_3$ were used so that both the hole-injection difference and the organic semiconductor could be seen. Especially with the ZAW electrodes, the thicknesses of the inner and outer dielectric layers were varied to confirm the influences of op-

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tical transparency on the device performance.

The OLEDs that were used in this study were based on a normal bottom-emission geometry with N,N'-Bis (naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) as a hole-transporting layer, Tris(8-hydroxy-quinolinato) aluminium (Alq_3) as an emitting and electron-transporting layer, and LiF/Al as a cathode. The thicknesses of NPB and Alq_3 were fixed at 50 nm, respectively. OLEDs based on a conventional ITO glass were also fabricated in the same batch, for comparison purposes.

All the devices were measured in a nitrogen-filled glove box. EL spectra were obtained using a fiber-optic spectrometer (EPP2000, StellarNet). The current-voltage (*J-V*) and luminance-voltage (*L-V*) characteristics were recorded using a source-measure unit (Keithley 2400) and a calibrated photodiode (FDS100, Thorlab). To analyze the angular dependency, all the measurements were performed while varying the incident angles between a device and a detector.

In the optimization method, some of the optical constants that were used in the simulation were measured via spectral ellipsometry, and the others were borrowed from the commercial software (The Essential Macleod, Thin-Film Center, Inc.) for thin-film optics. The program was also used to analyze the overall optical properties of the OLEDs under study.

3. Results and Discussion

The previous studies on the DMD multilayer structure as an alternative TE focused on its high sheet conductance and optical transparency [2]. Due to its high conductivity and low light absorption property, silver (Ag) has been regarded as the best material for a thin metal layer. The 15-nm-thick Ag film was shown to provide a sheet conductance as small as 6 Ω/sq. In the DMD structure, the optical transparency increased with the help of both the inner and outer dielectric layers with the proper refractive index (n) and thickness. Normally, it is known that a dielectric layer with a high refractive index n, like zinc sulfide (ZnS, n=2.35 at λ=550 nm), is preferable as it can achieve high transmission [3]. As can be seen in Fig. 1(a), with the help of a 40-nm-thick ZnS film as the inner and outer dielectric layers, the 84% air-to-air transparency transmittance was measured at a 550 nm wavelength, which was comparable to the conventional ITO glass (Fig. 1(b)). Fig. 1(d) shows the device characteristics of the OLEDs with various transparent anodes. The OLED with the ZnS/Ag/ZnS (ZAZ) anode, however, showed a very high turn-on voltage (10.8 V) and poor efficiency (0.5 cd/A at 100 cd/m^2) due to the hole-injection barrier of the ZnS inner dielectric layer. To improve the hole-injection property, instead of ZnS, tungsten oxide (WO_3) was used as the inner dielectric material [5]. The OLED based on the ZnS/Ag/WO_3 (ZAW) electrode showed a device performance that was almost similar to that of the ITO-based device, even though its optical property is much worse than that of the ZAZ electrode (Fig. 1(c)).

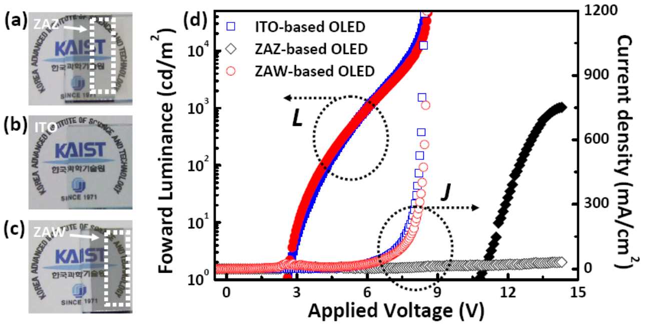

Fig. 1. Images of ZAZ glass (a), conventional ITO glass (b), and ZAW glass (c). Graph (d) shows the forward-luminance-vs.-applied-voltage and current-density-vs.-applied-voltage curves of the OLED with various transparent anodes. ZAZ and ZAW correspond to glass/ZnS(40nm)/Ag(15nm)/ZnS(40nm) and glass/ZnS (40nm)/Ag(15nm)/ WO_3 (5nm), respectively.

Unlike the ITO-based device, the OLEDs with ZAW anodes can form a microcavity structure between the highly reflective cathode (Al) and the ZAW anode depending on the transmission of the ZAW electrodes. To interpret such good device performance, not only the optical transparency but also the microcavity effect has to be considered. Fig. 2 shows the device structure of the ZAW-based OLED and

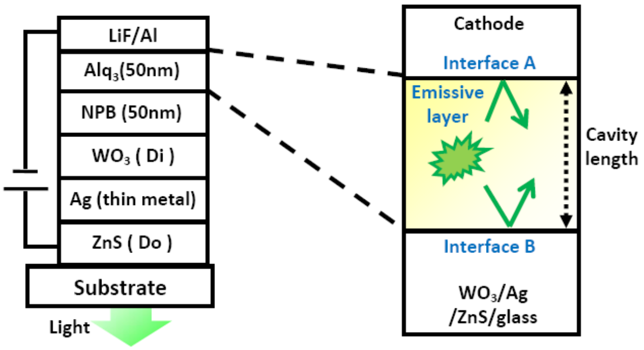

Fig. 2. Schematic device structure of OLEDs based on the ZnS/Ag/WO_3 anode, and its simplified microcavity structure.

the equivalent microcavity structure of the OLED under study.

Generally, the intensity of the light emitted from the resonator can be described by the following equation, assuming that the organic layers can be regarded as a single layer [6],

$$I(\lambda,\theta) = f_{FP} \cdot f_{TI} \cdot I_O(\lambda,\theta) \tag{1}$$

Where

$$f_{FP} = \frac{T_{ZAW}}{\left(1-\sqrt{R_{Al}R_{ZAW}}\right)^2 + 4\sqrt{R_{Al}R_{ZAW}}\,sin^2\left(\frac{\Delta\phi}{2}\right)} \tag{2}$$

$$f_{TI} = 1 + R_{Al} + 2\sqrt{R_{Al}}\,cos\left(-\phi_{Al} + \frac{4\pi n_{org} z_o\, cos\left(\theta_{org,EML}\right)}{\lambda}\right) \tag{3}$$

and

$$\Delta\phi = -\phi_{\mathrm{Al}} - \phi_{\mathrm{ZAW}} + \sum_i \frac{4\pi n_i d_i\, cos\left(\theta_{org,i}\right)}{\lambda} \tag{4}$$

In the above equations, f_{FP}, f_{TI}, and $I_0(\lambda,\theta)$ correspond to the Fabry-Perot multiple-beam interference factor, a two-beam interference factor, and to an electroluminescence spectrum of the emissive layer at wavelength λ and emission angle θ, respectively. $\theta_{\mathrm{org,i.}}$ is the internal angle within an organic layer indexed with i corresponding to θ. As can be seen in equations (2) and (3), the f_{FP} and f_{TI} terms can be affected by the transmittance and reflectance of the ZAW electrode. To determine the influence of such parameters of the ZAW electrode on the device performance, an OLED device was fabricated, varying the thicknesses of both the ZnS and WO_3 layers.

Fig. 3 shows the *L-J* and *J-V* (inset, Fig. 1) characteristics of the OLEDs with ZAW electrodes, for different thicknesses of the WO_3 layers, compared to those with the conventional ITO electrodes (here, *L* was measured at θ=0). In the case of luminous efficiency, which can be measured from the slopes of the *L-J* curves in Fig. 3, the ZAW-based OLEDs clearly outperformed the ITO-based OLEDs in the normal direction to the substrates. It was noted that the thinner WO_3 layer showed higher device efficiency even though the ZAW electrodes with thicker WO_3 layers were more transparent. As f_{TI} is common to all the devices, it is considered that the higher efficiency is due to the better match between the peaks of the f_{FP} and the Alq_3 EL spectrum. As the thickness of WO_3 increases, the phase term upon reflection at the ZAW electrodes will vary to accommodate the increased thicknesses of the WO_3 layers, resulting in the net red shift of the resonance wavelength in microcavity terms.

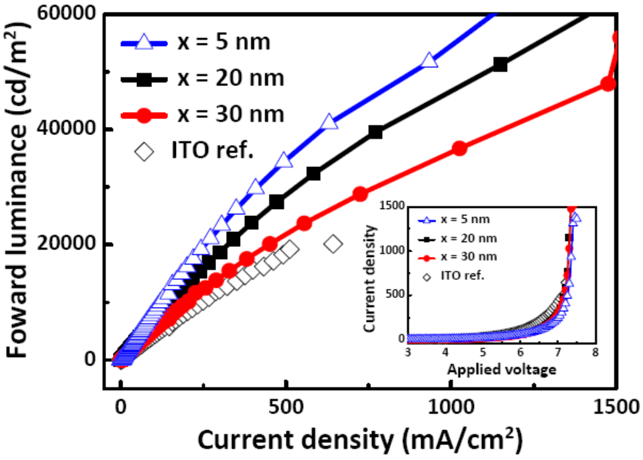

Fig. 3. OLED characteristics with the structure of glass/X/NPB(50nm)/Alq_3(50nm)/LiF:Al. X=ITO or ZnS(40nm)/Ag(20nm)/WO_3(5,20,30nm): forward-luminance-vs.-current-density and current-density-vs.-applied-voltage curves (inset).

Fig. 4 presents the *L-J* and *J-V* (inset, Fig. 4) characteristics of the OLEDs with different ZnS layer thicknesses. In this case, the OLED with a 60-nm-thick ZnS layer showed the best performance, although the relative difference was smaller than in the previous case. It was noted that the ZAW electrode with a 60-nm-thick ZnS layer was the least transparent among the three samples that were compared. Considering that the major interface of the reflection within the ZAW electrode was the Ag/WO_3 interface, the variation in ZnS thickness would not affect the cavity length much. Special attention must still be paid to this, however, because it influences the overall transmittance and reflectance of the ZAW electrodes, which affect the Fabry-Perot factor.

With the ZAW electrode having a 60-nm-thick ZnS layer and a 5-nm-thick WO_3 layer, the ZAW-based OLEDs showed the best device performance. The luminous ef-

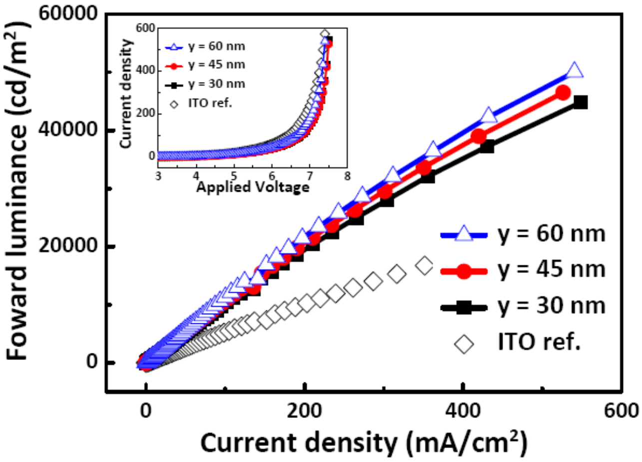

Fig. 4. OLED characteristics with the structure of glass/Y/NPB (50nm)/Alq_3(50nm)/LiF:Al. Y=ITO or ZnS(30,45,60nm)/Ag(20nm)/WO_3(5nm): forward-luminance-vs.-current-density and current-density-vs.-applied-voltage curves (inset).

ficiency in the forward direction was 10.7 cd/A, 90% higher than that of the ITO-based devices. To calculate the external quantum efficiency (EQE) of the current ZAW-based OLEDs, the luminance was measured at various oblique angles, from 0 to 60° (0° corresponds to the normal direction of devices). Fig. 5(a) is the intensity variation of OLEDs with a ZnS(60nm)/Ag(15nm)/WO_3(5nm) electrode as a function of emission angle θ. Normally, the light output of ITO-based OLEDs is Lambertian, where the intensity decreases following $\cos\theta$ as θ increases (see the dotted line in Fig. 5(a)). In ZAW-based OLEDs, however, the intensity drops slightly more quickly than does the ideal Lambertian curve. This directional anisotropy of emissive light happens because the resonance wavelength becomes shorter, and thus, the resonance mismatch with respect to the emission spectrum grows as θ increases. This behavior is confirmed in Fig. 5(b), which shows the slight blue shift of the EL spectrum peak at an oblique angle. In Fig. 5(b), the numbers within the brackets correspond to the CIE x, y color coordinates. As the emission angle increases, the y value decreases much while the x value hardly changes. Using equation (1), the spectrum and the intensity of the light output was also simulated at four different emission angles (0, 20, 40, and 60°), which were shown to match well with the experiment results. Based on the interpolation data of the experiment results, the EQE was estimated to be around 1.7 and 30% higher than that of the conventional ITO devices (see the solid line in Fig. 5(a)).

As verified above, the optical property of the DMD multilayer electrode is strongly governed by the microcavity effect. Of course, there will be a concern about the color variation of emissive light as the oblique angle increases in OLEDs based on the DMD TEs. It is expected, however, that it can also be tuned by modulating the dielectric materials and the thickness. Further studies on this will be conducted in the future.

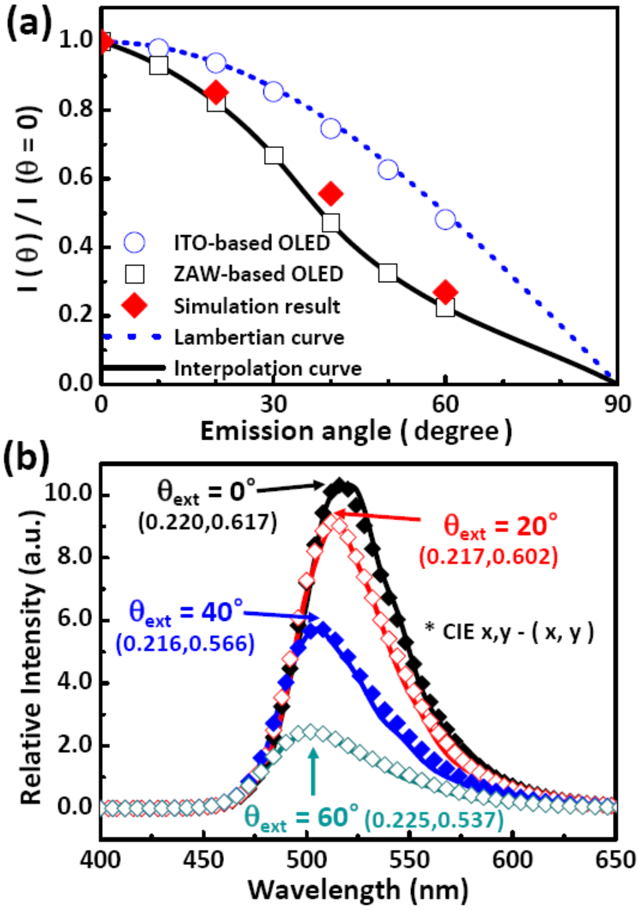

Fig. 5. (a) Intensity distribution vs. emission angle θ angles: In the y-axis, the intensities are normalized by the intensity of the forward direction (θ=0). (b) Electroluminance spectrum of OLEDs based on glass/ZnS(60nm)/Ag(15nm)/WO_3(5nm)/NPB(50nm)/Alq_3(50nm)/LiF:Al. The scattered points and solid lines correspond to the experiment results obtained by the spectrometer and the simulation results obtained by using equation (1), respectively. The numbers within the brackets are the coordinates in the CIE x, y chromaticity diagram.

4. Conclusion

OLED devices using a ZnS/Ag/WO_3 (ZAW) multilayer transparent electrode (MTE) exhibit a luminous and power efficiency far superior to those based on any other alternative to ITO films, and to those with ITO films themselves. These MTEs can be easily prepared via thermal evaporation, which has been widely adopted in the OLED industry and is mild enough to be used in top-emitting geometry without any concern regarding plasma-induced damage.

In this work, the overall optical structure of the ZAW electrode in full microcavity geometry was investigated, which will lay the foundation for the optimization of OLEDs with MTEs in general.

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