

Efficient Top-Emitting Organic Light Emitting Diode with Surface Modified Silver Anode

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Abstract: The enhancement of quantum efficiency using a surface modified Ag anode in top-emitting organic light emitting diodes (TEOLEDs) is reported. The operation voltage at the current density of 1 mA/cm² of TEOLEDs decreased from 9.3 V to 4.3 V as the surface of anode coated with CuO_x layer. The work function of these structures were quantitatively determined using synchrotron radiation photoemission spectroscopy. Secondary electron emission spectra revealed that the work function of the Ag/CuO_x structure is higher by 0.6 eV than that of Ag. Thus, the CuO_x structure acts as a role in reducing the hole injection barrier by about 0.6 eV, resulting in a decrease of the turn-on voltage of top-emitting light emitting diodes.

Keywords: Top-emitting organic light emitting diodes, Hole injection layer, Copper oxide, Thermal evaporation, Synchrotron radiation photoemission spectroscopy

1. INTRODUCTION

Achieving improved electroluminescent property of top-emitting organic light-emitting diodes (TEOLEDs) requires optimization of charge injection and transport at the interface of electrode with organic layer. According to the vacuum level alignment rule, the hole injection barrier is defined as the difference between the ionization energy of organic material and metal work function. Therefore metal/organic interfaces play important roles in the electroluminescence efficiency and stability in TEOLED [1]. Large numbers of experimental results have demonstrated that the performance of OLEDs is directly related to the energy barrier and interface stability at the anode. [2,3].

Silver (Ag) has been used for anode of TEOLEDs because of its high reflectivity (~94%) at the

wavelength of 520 nm and the low electrical resistivity of 1.47 μΩ cm at 298 K [4]. However, Ag anode has poor hole-injection property due to its low work function (~4.3 eV) [5,6]. A number of attempts have been conducted to enhance the hole-injection property of anode, such as inserting a high work function metal oxide buffer layer between anode and organics as the hole-injection layers (HILs) [7-9]. Copper oxide (CuO_x) is a transparent conducting oxide [10]. A thin CuO_x layer could be produced on the surface when a Cu film was exposed to an ultra violet. This treatment caused the work function to increase about 0.8 eV [11]. No works has been, however, conducted on the formation of CuO_x by thermal evaporation. Here, we first show the possibility of CuO_x as a HIL, produced by thermal evaporation. We report the enhancement of the TEOLEDs using a thermally evaporated CuO_x-coated Ag anode. The change of work function was examined using a synchrotron

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radiation photoelectron spectroscopy (SRPES). From this, the effects of the CuO_x -coated Ag on the enhancement of the electroluminescence properties of OLEDs are discussed.

2. EXPERIMENTS

The glass was used as the starting substrate. The surface of glass was cleaned in sequence with the acetone, iso-propyl alcohol, and de-ionized water, and then dried with high purity nitrogen gas. The cleaned glass substrate was loaded into the electron-beam evaporator, followed by the deposition of Ag (100 nm) layer. The substrate was then transferred into the treatment chamber, and then exposed for 10 min to oxygen ambient with a partial pressure of 700 mtorr ("Ag") under ultra violet. The treated samples were transferred to a thermal evaporator and 20-Å-thick CuO_x was deposited on the treated Ag ("Ag/ CuO_x "). Both types of samples were simultaneously loaded into a thermal evaporator, and then α -NPD with a thickness of 70 nm, tris(8-hydroxyquinoline) aluminum (Alq_3 , 60 nm), LiF (1 nm), calcium (10 nm) and Ag (10 nm) layers were deposited in sequence. During the deposition, the base pressure of the chamber was maintained as low as 10^{-6} Torr. The active area of the device was $3 \times 3 \text{ mm}^2$. The current density-voltage and luminescence-voltage characteristics of the TEOLEDs were measured in nitrogen ambient. [Fig. 1].

For the measurement of SRPES spectra, both "Ag" and "Ag/ CuO_x " samples were loaded into a vacuum chamber, equipped with the electron analyzer, at 4B1 Beamline in Pohang Accelerator Laboratory. Then, core-level spectra, valence band spectra, and secondary electron emission spectra were obtained in a main chamber using an incident photon energy of 650 eV. The onset of photoemission was measured with a negative bias (-5 V) on the sample to avoid the work function of the detector. The incident photon energy was calibrated with the core-level spectrum of Au 4f.

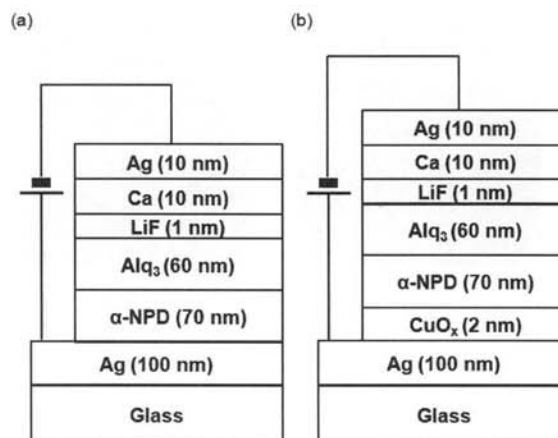


Fig. 1. Device structure of (a) "Ag" and (b) "Ag/ CuO_x ".

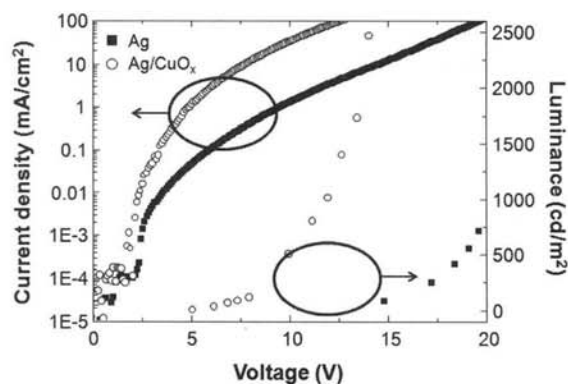


Fig. 2. Current density-voltage (log plot) and luminance-voltage (linear plot) characteristics of TEOLEDs with "Ag" and "Ag/ CuO_x " anodes.

3. RESULTS AND DISCUSSION

Figure 2 shows current density-voltage and luminance-voltage characteristics of TEOLEDs with different HIL layers. The operation voltage of device with the Ag HIL at a current density of 1 mA/cm^2 was 9.3 V. It decreased to 4.3 V when a 20-Å-thick CuO_x layer was inserted. The decrease in operation voltage is a reflection of improved hole injection efficiency. The operation voltage corresponding to 1000 cd/m^2 was 20 V for "Ag" and 11.9 V for "Ag/ CuO_x ". This is due to that holes were effectively injected from the anode to organic layer.

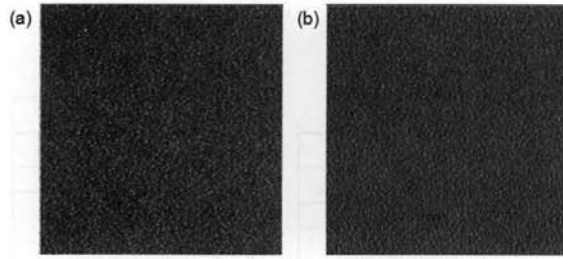


Fig. 3. Atomic force microscopy images of (a) "Ag" and (b) "Ag/CuO_x".

Table 1. Secondary electron emission (SE) for "Ag" and "Ag/CuO_x".

Sample	Kinetic energy
Ag	5.3 eV
Ag/CuO _x	5.9 eV
ΔSE	0.6 eV

Figure 3 shows the atomic force microscopy images of 100 nm-thick Ag and 2 nm-coated Ag. The image shows that both Ag and CuO_x films are continuously and uniformly formed.

Table 1 shows the secondary electron emission of "Ag" and "Ag/CuO_x". The onset of the secondary electron emission was determined by extrapolating two solid lines from the background and straight onset in the valence band spectra [14]. The onset of secondary electron emission of Ag/CuO_x is 0.6 eV higher than that of Ag. It means that the workfunction of "Ag/CuO_x" is 0.6 eV higher than that of "Ag".

Based on these experimental observations, the reduction in the operation voltage and the increase of quantum efficiency is explained below. When the CuO_x layer coated on Ag, the current density and luminance value increased, indicating an increase of hole current density. This increase is explained by the energy level diagram, as shown in Fig. 4. The energy levels for Ag, α-NPD, Alq₃, and LiF/Ca/Ag refer to the isolated materials and were taken from the literature. The injection barrier for the hole from the anodes to the organic materials corresponds

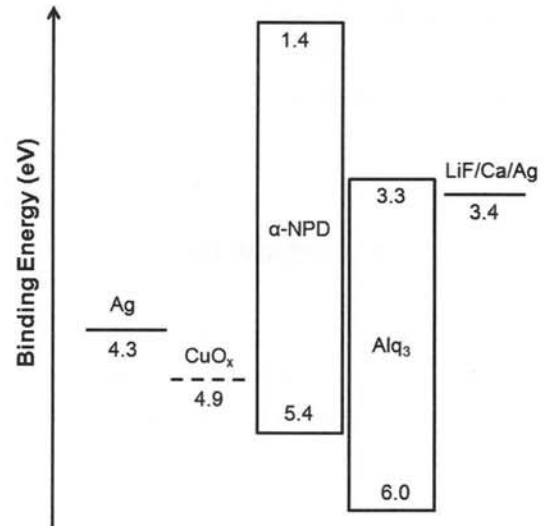


Fig. 4. Energy level diagrams of the individual device components. The change of work function of the Ag and CuO_x were determined using a synchrotron radiation photoemission spectroscopy. The energy levels for other components are taken from the literature.

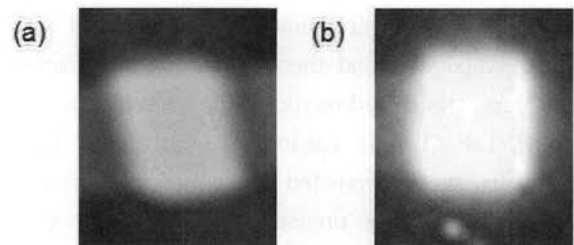


Fig. 5. Luminance of devices at 15 V: (a) "Ag" and (b) "Ag/CuO_x".

the energy difference between the Fermi level of the anode and the lowest unoccupied molecular orbital of the organic materials. The work function of the Ag/CuO_x was higher by 0.6 eV than that of Ag, as shown in Table 1. Thus, the hole injection barrier between Ag and α-NPD(Φ) decreased to Φ - 0.6 eV, enhancing the recombination probability via increasing the hole injection. Therefore, the operation voltage of TEOLEDs at 1 mA/cm² using CuO_x decreased from 9.3 to 4.3 V, and the luminance of device with Ag/CuO_x anode at 15 V is higher than that of device with Ag [Fig. 4].

4. CONCLUSIONS

We have successfully grown 20-Å-thick CuO_x on Ag anode by thermal evaporation and investigated the formation of the interface dipole between the CuO_x and α-NPD. The operation voltage at the current density of 1 mA/cm² of TEOLEDs decreased from 9.3 V to 4.3 V as the CuO_x layer inserted between Ag and α-NPD. SRPES spectra showed that the work function of "Ag/CuO_x" is higher by 0.6 eV than that of "Ag". Thus, the CuO_x layer lowered the potential barrier for hole injection from Ag to α-NPD, reducing the turn-on voltage of TEOLEDs.

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