

방사광 가속기의 광전자 분광법을 이용한  
전면 발광 유기발광 다이오드에서의 열증착 산화구리와 유기물 사이의  
계면 **dipole** 에너지 및 정공 주입 효율에 대한 연구

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**초록**

We report the enhancement of hole injection using thermally evaporated  $\text{CuO}_x$  layer between Ag anode and 4,4'-Bis[N-(1-naphthyl)-N-phenylamino]biphenyl ( $\alpha$ -NPD) in top-emitting organic light-emitting diode (TEOLED). The operation voltage at the current density of  $1\text{mA}/\text{cm}^2$  of TEOLEDs decreased from 6.2 V to 5.0 V as the  $\text{CuO}_x$  layer inserted between Ag and  $\alpha$ -NPD.  $\alpha$ -NPD was deposited *in situ* on Ag/ $\text{CuO}_x$  and Ag anodes, and their interface dipole energies were quantitatively determined using synchrotron radiation photoemission spectroscopy. The dipole energy of Ag/ $\text{CuO}_x$  was lower by 0.05 eV even though Ag/ $\text{CuO}_x$  had a higher work function. The work function of Ag/ $\text{CuO}_x$  is higher by 0.53 eV than that of Ag, resulting in a decrease of the turn-on voltage via reduction of hole injection barrier.

**1. 서론**

Ag has been used for anode of TEOLEDs because of its high reflectivity (~94 %) and the low electrical resistivity of  $1.47\ \mu\Omega\ \text{cm}$ . However, Ag anode has poor hole-injection property due to its low work function (~4.3eV).[1] 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)[2].

Copper oxide ( $\text{CuO}_x$ ) is a transparent conducting oxide.[3] It was reported that  $\text{CuO}_x$  could be produced by an ultra violet ozone treatment of Cu, and its work function increased from 4.7 eV to 5.4 eV.[4] However, there was no result on the thermally evaporated  $\text{CuO}_x$  as the HILs in TEOLEDs. The work function of  $\text{CuO}_x$  is higher than that of Ag (~4.3 eV).[4] Thus, it is expected that a thin thermally evaporated  $\text{CuO}_x$  interfacial layer inserting between Ag anodes and organic materials could improve injection of holes via enhancement TEOLED electrical properties. However, the effect of  $\Delta$  on the reduction of hole injection barrier at the  $\text{CuO}_x$ /organic interface should be considered.

In this letter, we investigated the formation of  $\Delta$  between  $\text{CuO}_x$ -coated Ag anode and 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl ( $\alpha$ -NPD). Synchrotron radiation photoemission spectroscopy (SRPES) was employed to observe the change of the energy level with *in situ* deposition of  $\alpha$ -NPD layer on  $\text{CuO}_x$  coated Ag anode. From this, the effect of  $\text{CuO}_x$  layer on the formation of  $\Delta$  in TEOLED is discussed.

**2. 실험 방법**

As an anode, Ag (100 nm) layer was deposited on glass substrate. The substrate was then transferred into the treatment chamber, and then exposed for 10 min to the oxygen partial pressure of 700 mtorr ("Ag") under ultra violet. The treated

samples were transferred to a thermal evaporator and 20-Å-thick  $\text{CuO}_x$  was deposited on the treated Ag (“Ag/ $\text{CuO}_x$ ”). Both types of samples were simultaneously loaded into a thermal evaporator, and  $\alpha$ -NPD with a thickness of 70 nm, tris(8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ , 40 nm) doped with the fluorescent dye C545T (1%), undoped  $\text{Alq}_3$ (20 nm), LiF (1 nm), calcium (10 nm) and Ag (10 nm) layers were deposited in sequence. The current density-voltage and luminescence-voltage characteristics of the devices were measured in nitrogen ambient.

For the measurement of SRPES spectra, both Ag and Ag/ $\text{CuO}_x$  samples were loaded into a vacuum chamber, equipped with the electron analyzer, at 4B1 Beamline in Pohang Accelerator Laboratory.

### 3. 실험 결과

Figure 1(a) shows current density-voltage characteristics of the two types of devices. The operation voltage of Ag at a current density of  $1 \text{ mA/cm}^2$  was 6.2 V. It decreased to 5.0 V when a 20-Å-thick  $\text{CuO}_x$  layer was inserted. Luminescence-voltage curves are shown in Fig. 1(b). The operation voltage corresponding to  $5000 \text{ cd/m}^2$  was 14.6 V for Ag and 12.1 V for Ag/ $\text{CuO}_x$ . This is due to that holes were effectively injected from the anode to organic layer.

Figure 2 (a) shows the change of work function with deposition of  $\alpha$ -NPD on Ag. The onset of the secondary electron peak shifted toward lower work function by 0.96 eV after deposition of  $\alpha$ -NPD. After deposition of  $\alpha$ -NPD, the VBM was located at 1.66 eV, meaning that the HOMO level of  $\alpha$ -NPD was located at 1.66 eV apart from  $E_F$ . [Fig. 2(b)]

Figure 3(a) shows the change of work function with deposition of  $\alpha$ -NPD on Ag/ $\text{CuO}_x$ . The onset of the secondary electron peak shifted toward lower kinetic energy about 1.04 eV after deposition of  $\alpha$ -NPD. After deposition of  $\alpha$ -NPD, the VBM was located at 1.12 eV, meaning that the HOMO level of  $\alpha$ -NPD was located at 1.12 eV apart from  $E_F$ . [Fig. 3(b)]

As the thickness of  $\alpha$ -NPD on Ag increases, the core-level peak shifts to the higher binding energy about 0.03 eV. The onset of secondary emission in Ag shifted to lower kinetic energy about 0.96 eV with deposition of  $\alpha$ -NPD [Fig. 2(a)]. Considering the band bending of 0.03 eV toward the  $\alpha$ -NPD,  $\Delta$  is determined to be -0.93 eV. Figure 4(b) shows the schematic band diagram in the deposition of  $\alpha$ -NPD on Ag/ $\text{CuO}_x$ . The work function of Ag/ $\text{CuO}_x$  is higher by 0.53 eV than that of Ag. The amount of band bending and the change of work function with deposition of  $\alpha$ -NPD are 0.16 eV and 1.04 eV, respectively. Thus, the value of  $\Delta$  produced at the interface of Ag/ $\text{CuO}_x$  with  $\alpha$ -NPD corresponds to -0.88 eV.

### 4. 결론

we investigated the formation of the interface dipole between the  $\text{CuO}_x$  deposited on Ag by thermal evaporation and  $\alpha$ -NPD. The operation voltage at the current density of  $1 \text{ mA/cm}^2$  of TEOLEDs using Ag/ $\text{CuO}_x$  decreased from 6.2 V to 5.0 V as the  $\text{CuO}_x$  layer inserted between Ag and  $\alpha$ -NPD. SRPES spectra showed that the work function of  $\alpha$ -NPD on Ag/ $\text{CuO}_x$  is higher by 0.45 eV than that of Ag. The interface dipole energies of Ag/ $\text{CuO}_x$  and Ag are -0.88 eV and -0.93 eV, respectively. Thus, the  $\text{CuO}_x$  layer lowered the potential barrier for hole injection from Ag to  $\alpha$ -NPD, reducing the turn-on voltage of TEOLEDs.

### 참고문헌

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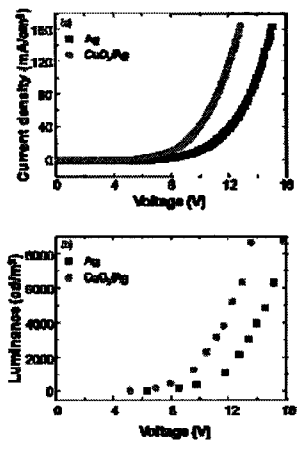


Fig. 1. (a) Current density-voltage and (b) luminance-voltage characteristics of TEOLEDs with different anodes.

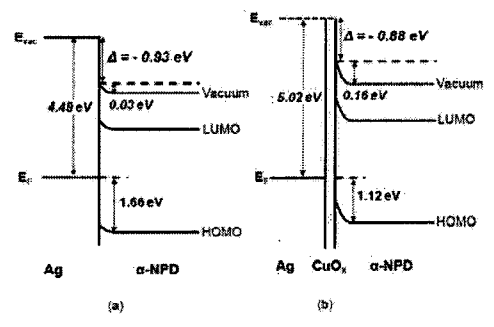


Fig. 4. Schematic band diagram: (a) Ag and (b) Ag/CuO<sub>x</sub>

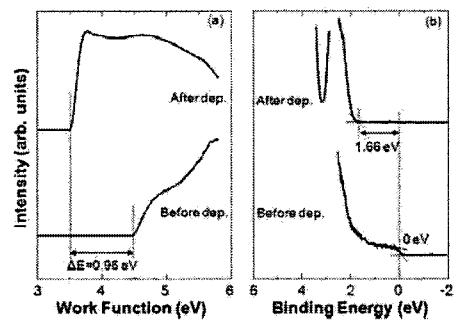


Fig. 2. (a) Secondary electron emission spectra and (b) valence-band spectra for Ag.

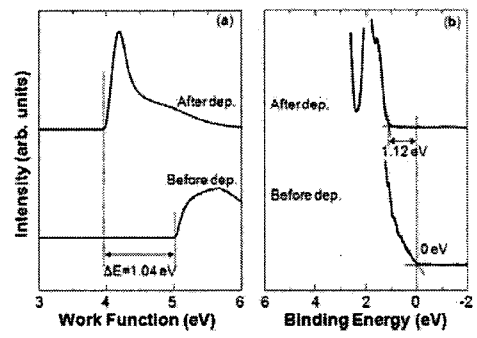


Fig. 3. (a) Secondary electron emission spectra and (b) valence-band spectra for Ag/CuO<sub>x</sub>