

Enhanced Hole Injections in Organic Light Emitting Diode using Rhodium Oxide Coated Anode

Soo Young Kim*, Ho Won Choi, Kwang Young Kim, Yoon-Heung Tak** and Jong-Lam Lee***

Abstract—We compare electrical and optical properties of organic light emitting diodes (OLEDs) using rhodium-oxide-coated indium-tin-oxide (*O₂-Rh/ITO*) to that using *O₂*-plasma-treated ITO (*ITO*) anodes. The turn-on voltage decreased from 7 V to 5 V and luminance value increased when the *O₂* plasma treated Rh layer was deposited on ITO. Synchrotron radiation photoelectron spectroscopy results showed the dipole energies of both *ITO* and *O₂-Rh/ITO* were same with each other, - 0.3 eV, meaning the formation of same amount of interface dipole. The secondary electron emission spectra revealed that the work function of *O₂-Rh/ITO* is higher by 0.2 eV than that of *ITO*, resulting in the decrease of the turn-on voltage *via* reduction of hole injection barrier.

Index Terms—organic light emitting diodes, hole injection layer, synchrotron radiation photoemission spectroscopy, interface dipole, *O₂* plasma treatment

I. INTRODUCTION

Ever since the high efficiency organic light emitting diode (OLED) was reported, numerous efforts have been made to improve the characteristics of OLEDs. The performance of an OLED is influenced by the properties of the injecting electrodes and the electrode-organic interfaces. At the interface of indium tin oxide (ITO)

anode with organic materials, enhanced hole injection was desired to increase internal quantum efficiency. According to the vacuum level alignment rule, hole injection barrier is defined by the difference between the ionization energy of the organic material and metal work function. To reduce hole injection barrier, many researchers gave an effort to elevate the work function of ITO anode, such as surface plasma treatment, insertion of metal oxides with high work function between ITO and organic material, and the formation of metal-doped indium tin oxide layer on ITO surface.[1-3] However, numerous photoelectron studies and Kelvin probe measurements have demonstrated that the actual situation is more complex, because an interface dipole (Δ) can appear at the metal-organic material interface and affect the charge injection barrier.[4] In thick metal-organic material system, a linear dependence of the Δ on the metal work function is observed.[5] Therefore, Δ as well as the work function of anode should be considered to reduce hole injection barrier.

In this paper, we report the enhancement of electrical and optical performance of OLEDs using an interfacial layer of rhodium oxide (RhO_x) between ITO anodes and the hole transport layer of 4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD). The RhO_x layer was prepared by exposing the thin Rh layer to *O₂* plasma. The change in the work function with the formation of RhO_x was examined using synchrotron radiation photoelectron spectroscopy (SRPES). SRPES was also employed to observe the change of the energy level with in situ deposition of α -NPD layer on RhO_x coated ITO anode. From this, the effects of RhO_x layers on the enhancement of both electrical and optical properties of OLEDs were discussed.

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II. EXPERIMENT

A glass coating with ITO (150 nm thick, $\sim 20 \Omega/\square$) was used as the starting substrate. The ITO surface was cleaned in sequence with acetone, iso-propyl alcohol and deionized water, and then dried with a high purity nitrogen gas. The ITO surface was treated with O_2 plasma for 1 min under 100 mTorr ("*ITO*"). The plasma power was 150 W. A thin layer of Rh with a thickness of 2 nm was deposited on the plasma-treated ITO by e-beam evaporator ("*Rh/ITO*"). The Rh film was also exposed to the O_2 plasma for 1 min to produce a RhO_x layer ("*O₂-Rh/ITO*"). The thickness of the thin layer was deduced from the period of the oscillations in x-ray reflection, measured at the 3C2 beam line of the Pohang Acceleration Laboratory (PAL). These three types of samples were loaded into a thermal evaporator and α -NPD with a thickness of 70 nm, tris(8-hydroxyquinoline) aluminum (Alq_3 , 60 nm), and aluminum (Al, 150 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 devices were measured. The surface treatment conditions for the three kinds of anodes are summarized in Table 1.

In order to investigate the chemical bonding states of *ITO* by inserting the interfacial layer of RhO_x , the three

samples were loaded into a vacuum chamber, equipped with an electron analyzer, at the 4B1 beam line in PAL. An incident photon energy of 650 eV was used to obtain Rh 3*d*, In 3*d*, Sn 3*d*, O 1*s* and C 1*s* core level spectra. Then, α -NPD was in situ deposited on the samples using thermal evaporator. The evaporation of α -NPD was performed in a separately connected preparation chamber and core level spectra were obtained in a main chamber. The α -NPD coverage at each step was determined by comparing the atomic ratio of C 1*s* over In 3*d*. At each step, the sample was characterized by measuring the valence band spectra, the core level spectra, and the secondary electron emission spectra. The onset of photoemission, corresponding to the vacuum level at the ITO surface was measured with a negative bias (-20 V) on the sample to avoid the work function of detector. The incident photon energy was calibrated with the core level spectrum of Au 4*f*.

III. RESULTS AND DISCUSSION

Table 2 shows the current density and luminance value as a function of applied voltage. The turn-on voltage decreased from 7 V to 5 V when the O_2 plasma treated Rh layer was deposited on ITO. Furthermore, the luminance value of *O₂-Rh/ITO* is higher than that of *ITO* at the same

Table 1. Anode preparation methods for OLEDs

OLEDs Anodes	
<i>ITO</i>	ITO + O_2 plasma treatment
<i>Rh/ITO</i>	ITO + O_2 plasma treatment + deposition of Rh
<i>O₂-Rh/ITO</i>	ITO + O_2 plasma treatment + deposition of Rh + O_2 plasma treatment

Table 2. Current density and luminance value as a function of applied voltage

Voltage (V)	<i>ITO</i>		<i>O₂-Rh/ITO</i>	
	Current density (mA/cm ²)	Luminance (Cd/m ²)	Current density (mA/cm ²)	Luminance (Cd/m ²)
8	5.57	280	6.5	300
10	14.96	730	19.81	740
12	37.82	1400	51.44	1600
14	66.59	1920	122.41	2100
16	131.01	2680	271.59	2800

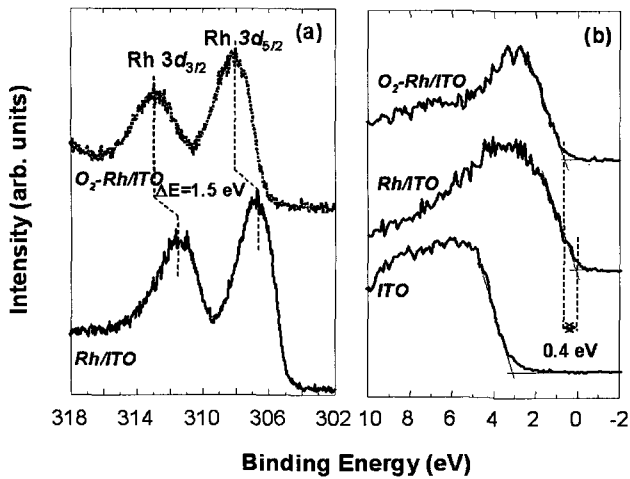


Fig. 1. (a) Rh 3d core level spectra and (b) relative change of valence band maximum for the samples

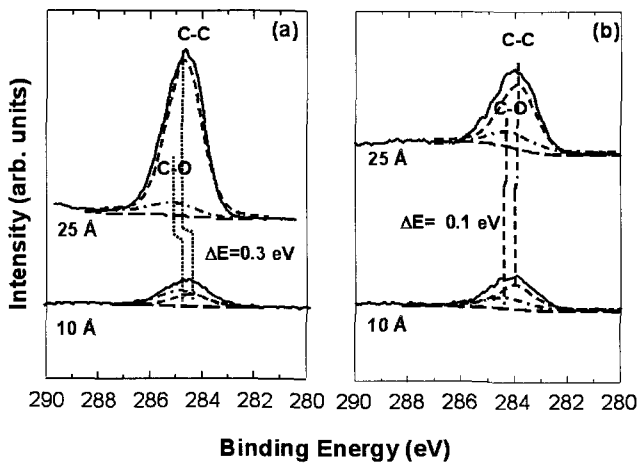


Fig. 2. C 1s core level spectra for (a) ITO and (b) O₂-Rh/ITO

applied voltage. The decrease in turn-on voltage is a reflection of improved hole injection efficiency. It is thought that holes were effectively injected from anode to organic layer, promoting internal quantum efficiency.

Figure 1(a) shows Rh 3d core level spectra of Rh/ITO and O₂-Rh/ITO. The Rh 3d_{5/2} and Rh 3d_{3/2} peaks shifted about 1.5 eV toward a higher binding energy after O₂ plasma treatment. It is reported that the binding energy of Rh-O bond is 1.4 ~ 1.6 eV higher than that of the Rh-Rh bond[6]. Thus, the shift of Rh 3d_{5/2} and Rh 3d_{3/2} peaks is due to the formation of RhO_x layers. Figure 1(b) shows the relative change in valence band maximum (VBM) with the formation of RhO_x layer. The VBM was calibrated with a clean Au surface. The VBM at the surface of ITO is located at 3.0 eV apart from the Fermi level. After the Rh layer deposition on ITO surface, the VBM of Rh/ITO

coincided with Fermi level, showing the metallic valence band. However, the VBM of O₂-Rh/ITO is located at 0.4 eV apart from the Fermi level. This means that the band gap was produced due to the formation of RhO_x.

Figure 2 shows the change of C 1s SRPES spectra according to the deposition steps of α-NPD on (a) ITO and (b) O₂-Rh/ITO. In order to separate the chemical bonding states including those in the spectra, the spectral line shape was simulated using a suitable combination of Gaussian and Lorentzian functions. The C 1s peak separated into two components. Bulk component of C-O and surface component of C-C were considered. The binding energy of the C-O bond was higher than that of the C-C one, which agrees well with a previously reported value[6]. At as-deposited state, C 1s peak is wholly composed of C-O bond. According to deposition of α-NPD on both samples, the peak intensity increased due to the composition of α-NPD. In ITO sample, the peak corresponding to the C-C bond shifted about 0.3 eV toward higher binding energy, meaning the downward band bending. However, in O₂-Rh/ITO sample, the C-C bond peak shifted about 0.1 eV toward lower binding energy, indicating the upward band bending.

In order to clarify the change of work function with deposition of α-NPD on ITO, the SRPES spectra of secondary electron were measured, as shown in Fig. 3(a). The onset of secondary electrons was determined by extrapolating two solid lines from the background and straight onset in the spectra[7]. The onset of secondary electron peak shifted toward lower kinetic energy by 0.6 eV after deposition of α-NPD, meaning the decrease of

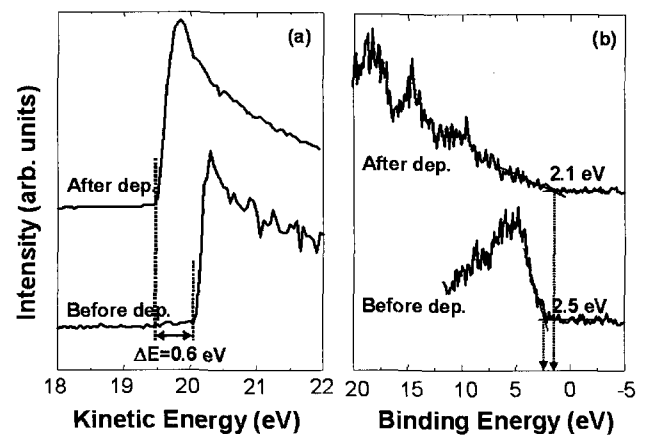


Fig. 3. (a) Secondary electron emission spectra and (b) valence band spectra for ITO

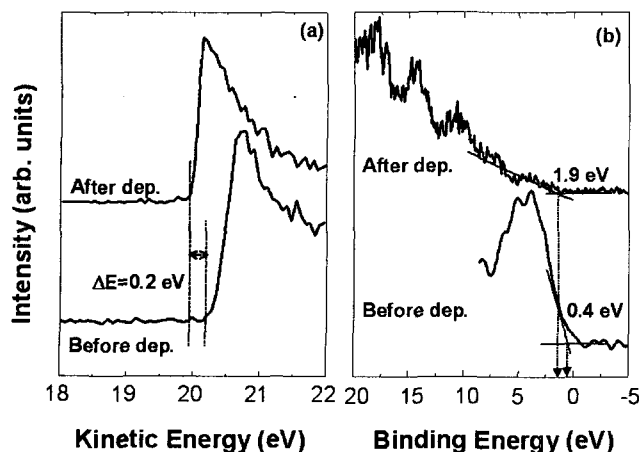


Fig. 4. (a) Secondary electron-emission spectra and (b) valence band spectra for O_2 -Rh/ITO

work function. Figure 3(b) shows the change of valence band spectra with deposition of α -NPD. Before deposition of α -NPD, VBM was located at 2.5 eV, showing that the energy difference between VBM of ITO and Fermi level (E_F) is 2.5 eV. After deposition of α -NPD, VBM was located at 2.1 eV, meaning that the energy difference between highest occupied molecular orbital (HOMO) and E_F of α -NPD on ITO is 2.1 eV. This result showed that hole injection barrier from ITO to α -NPD is 2.1 eV.

Figure 4(a) shows the change of work function with deposition of α -NPD on O_2 -Rh/ITO. It is shown that the onset of secondary electron for O_2 -Rh/ITO shifted to the higher kinetic energy by 0.2 eV with respect to the onset for ITO. This result means that the work function of RhO_x -coated ITO is higher by 0.2 eV than that of O_2 plasma treated ITO. The onset of the secondary electron peak shifted toward lower kinetic energy about 0.2 eV after deposition of α -NPD, meaning the decrease of work function. The change of VBM with deposition of α -NPD was shown in Fig. 4(b). Before deposition of α -NPD on O_2 -Rh/ITO, VBM was located at 0.4 eV due to the band gap of RhO_x . After deposition of α -NPD, VBM was located at 1.9 eV, meaning that the HOMO level of α -NPD was located at 1.9 eV apart from E_F . This result indicated that hole injection barrier from O_2 -Rh/ITO to α -NPD is 1.9 eV.

Based on these experimental observations, the reduction in operation voltage could be explained as below. As the thickness of α -NPD on ITO increases, the core level peaks shift to the higher binding energy about 0.3 eV [Fig. 2(a)], indicating the downward band bending

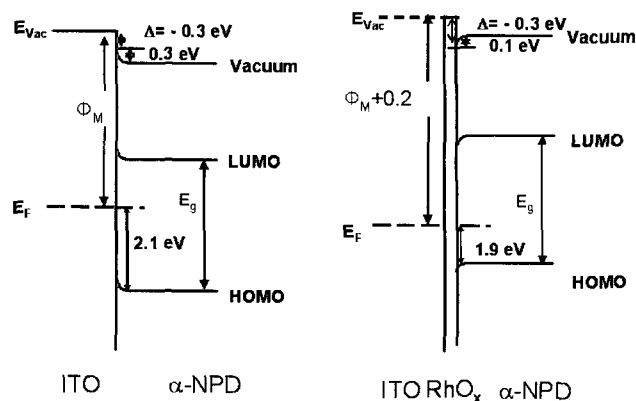


Fig. 5. Schematic band diagram: (a) ITO and (b) O_2 -Rh/ITO

in α -NPD along from the interface to the surface. The onset of secondary emission in ITO shifted to lower kinetic energy about 0.6 eV with deposition of α -NPD [Fig. 3(a)], indicating the decrease of the work function on the surface of α -NPD. Considering the band bending of 0.3 eV toward the α -NPD, Δ is determined to be -0.3 eV, as shown in Fig. 5(a). Figure 5(b) shows the schematic band diagram in deposition of α -NPD on O_2 -Rh/ITO anode. When the Rh layer changed to a transparent RhO_x layer by O_2 plasma treatment, the work function increased. The work function of O_2 -Rh/ITO is higher by 0.2 eV than that of ITO. The amount of band bending and the change of work function with deposition of α -NPD are 0.1 eV [Fig. 2(b)] and 0.2 eV [Fig. 4(a)], respectively. Thus, the value of Δ produced at the interface of O_2 -Rh/ITO with α -NPD corresponds to -0.3 eV, as shown in Fig. 5(b).

It was previously reported that the higher work function of metal substrate is, the higher Δ exists due to the more sensitive electron density tail[8]. However, the value of Δ is same in our case even though the work function of O_2 -Rh/ITO is higher than that of ITO, as shown in Figs. 7(a) and 7(b). In the metal-organic system, the metal work function could be changed with surface-dipole which originates from the tail of free electrons[9]. The contribution of surface-dipole could be modified by the presence of an adsorbate. The 2-nm-thick RhO_x has much fewer free electrons than the metals[10], resulting in the reduced contribution of surface electron tail. As a result, Δ in O_2 -Rh/ITO coincides with the Δ in ITO. Consequently, RhO_x layer plays a role in increasing the work-function of electrode, leading to the decrease of the hole injection barrier from 2.1 to 1.9 eV. Therefore, the turn-on voltage of OLEDs using O_2 -Rh/ITO decreased from 7 V to 5 V.

IV. CONCLUSIONS

We have reported the advantage of interfacial RhO_x layers between anodes of ITOs and hole transport layers of α -NPD on the electrical properties of OLEDs. The turn-on voltage of OLEDs decreased from 7 V to 5 V and luminance value increased as the RhO_x layer exists between ITO and α -NPD. SRPES spectra showed that the dipole energies of both ITO and O₂-Rh/ITO were same with each other, - 0.3 eV. The work function of α -NPD on O₂-Rh/ITO is higher by 0.2 eV than that on ITO. Thus, the RhO_x layer lowered the potential barrier for hole injection from ITO to α -NPD, reducing the turn-on voltage of OLEDs and increasing quantum efficiency.

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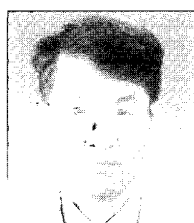
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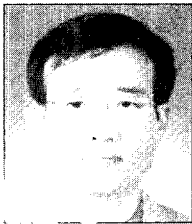


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