Direct Evidence of Hole Injection Enhanced by \( \text{O}_2 \) Plasma Treatment on Indium Tin Oxide

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We have investigated interface dipole energies and the energy alignment between 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (\( \alpha \)-NPD) and bare indium tin oxide (ITO)/O\(_2\)-plasma-treated ITO (O\(_2\)-ITO) anodes using synchrotron radiation photoemission spectroscopy (SRPES). SRPES spectra showed that the work function of O\(_2\)-ITO is 0.6 eV higher than that of ITO. After deposition of \( \alpha \)-NPD, the dipole energy and amount of band bending were calculated to be - 0.1 and - 0.5 eV for ITO and - 0.3 and - 0.3 for O\(_2\)-ITO, respectively. It is thereupon concluded that the work function of O\(_2\)-ITO is still 0.6 eV higher than that of ITO, resulting in a decrease of the turn-on voltage via reduction of the hole injection barrier.

Keywords: organic light emitting diodes, hole injection barrier, x-ray photoemission spectroscopy, O\(_2\) plasma treatment, indium tin oxide

1. INTRODUCTION

Organic light emitting diodes (OLEDs) have received considerable attention in recent years because of their scientific and commercial significance. One of the most important factors determining device function and performance is charge carrier injection from electrodes into the organic material. According to the vacuum level alignment rule, hole injection barriers are defined by the difference between the ionization energy of the organic material and the metal work function. In OLEDs, indium tin oxide (ITO) is widely used as a hole-injection electrode due to its high work function (~ 4.7 eV)\(^{[1]} \). In order to increase the work function of ITO, several kinds of surface treatment have been extensively studied in recent years\(^{[2,3]} \). A number of surface treatment methods were applied to the surface of ITO, such as mechanical polishing, plasma, and UV-ozone treatment. However, numerous photoelectron studies and Kelvin probe measurements have demonstrated that interface dipoles (\( \Delta \)) can appear at the interface of metal with organic materials and affect the charge injection barrier\(^{[4]} \). It was reported that \( \Delta \) originates from the charge transfer across the interface, redistribution of electron cloud, interfacial chemical reaction, or other types of electronic charge rearrangement\(^{[5]} \). Therefore, it is essential to understand the formation of the interface dipole between ITO and organic materials.

In this letter, we investigated the formation of an interface dipole between oxygen plasma-treated ITO (O\(_2\)-ITO) anode and 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (\( \alpha \)-NPD). Synchrotron radiation photoemission spectroscopy (SRPES) was employed to observe the change of the energy level with \textit{in situ} deposition of a \( \alpha \)-NPD layer on an O\(_2\)-ITO anode. Based on these observations, the formation of an interface dipole between O\(_2\)-ITO and \( \alpha \)-NPD in OLED is discussed.

2. EXPERIMENTAL PROCEDURE

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 high purity nitrogen gas. The ITO surface was treated with O\(_2\) plasma for 1 min with a power of 150 W. For reference, ITO without plasma treatment (ITO) was also prepared. Two samples were loaded into a thermal evaporator and \( \alpha \)-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 3×3 mm\(^2\). The current density-voltage characteristics of the devices were measured.

For the measurement of SRPES spectra, O\(_2\)-ITO and ITO...
samples were loaded into a vacuum chamber equipped with an electron analyzer at the Pohang Accelerator Laboratory 2B1 beam line. α-NPD was then deposited in situ on the samples using a thermal evaporator. The evaporation of α-NPD was performed in a separately connected preparation chamber and core level spectra were obtained in the main chamber using an incident photon energy of 600 eV. In order to exclude the photovoltaic effect, samples were kept in darkness during photoemission measurements. The α-NPD coverage at each step was determined by comparing the atomic ratio of C 1s over In 3d. At each step, the sample was characterized by measuring the valence band spectra, the core level spectra, and the secondary electron emission spectra. The changes in core level binding energy indicate band bending and secondary electron emission spectra give the change in work function. Here, following the convention in surface science, the change of work function is considered as positive when the vacuum level is raised by deposition. Therefore, the dipole energies are calculated by the sum of band bending and change of work function. The onset of photoemission was measured with a negative bias (-20 V) on the sample so as to avoid the work function of the detector. The incident photon energy was calibrated with the core level spectrum of Au 4f.

3. RESULTS AND DISCUSSION

Figure 1 shows the current density-voltage characteristics of the two devices. The operation voltage at the current density of 100 mA/cm² of OLEDs using O₂-ITO decreased from 34 V to 14 V. The decrease in operation voltage is a reflection of improved hole injection efficiency. Luminance-voltage curves are shown in Fig. 1(b). The operation voltage corresponding to 500 cd/m² was 13 V for O₂-ITO and 35 V for ITO, respectively. The optical image at a luminance of 500 cd/m² is shown in the inset of Fig. 1(b). It is thought that holes were effectively injected from the anode to the organic layer, promoting internal quantum efficiency.

Figure 2 shows the change of C 1s SRPES spectra according to the deposition steps of α-NPD on (a) ITO and (b) O₂-ITO. The molecular structure of α-NPD is shown in the inset of Fig. 2(a). In order to separate the chemical bonding states included in the spectra, the spectral line shape was simulated using an asymmetric Gaussian-Lorentzian sum function. We used an 80% Gaussian function and a 20% Lorentzian function to fit the sum of the separation peaks to the original peaks. Shirley background subtraction was used to minimize the background effects of C 1s spectra. The C 1s peak was separated into two components. The bulk component of C-O and the surface component of C-C were considered. The binding energy of the C-O bond was higher than that of the C-C binding energy, which agrees well with a previously reported value. In the as-deposited state, C 1s peaks are wholly composed of C-O bonds. According to the deposition of α-NPD on both samples, the peak corresponding to the C-C bond shifted about 0.5 eV in ITO and 0.3 eV in O₂-ITO toward high binding energy and the peak intensity increased due to the composition of α-NPD. These results demonstrate that the amount of downward band bending in