



Research paper

Energy level alignment and hole injection property of poly(9-vinylcarbazole)/indium tin oxide interface

Junkyeong Jeong^a, Jiyeon Lee^b, Hyunchan Lee^b, Gyeongho Hyun^a, Soohyung Park^a, Yeonjin Yi^a, Sang Wan Cho^c, Hyunbok Lee^{b,*}

^a Institute of Physics and Applied Physics, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

^b Department of Physics, Kangwon National University, 1 Gangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea

^c Department of Physics, Yonsei University, 1 Yonseidaegil, Wonju-si, Gangwon-do 26493, Republic of Korea

ARTICLE INFO

Article history:

Received 2 April 2018

In final form 8 June 2018

Available online 15 June 2018

Keywords:

UPS

PVK

ITO

UV-ozone treatment

Energy level alignment

ABSTRACT

The energy level alignment at the interface between an organic layer and an electrode plays a critical role in the performance of organic electronic devices. To improve the charge injection efficiency, the energy barrier between the charge transport level of an organic layer and the Fermi level of an electrode should be reduced. Especially, poly(9-vinylcarbazole) (PVK) is a polymeric semiconductor that is widely used as a hole transport and electron blocking layer in various optoelectronic devices. Thus, an understanding of the energy level alignment between PVK and an electrode is of great importance. In this study, the energy level alignment of PVK and indium tin oxide (ITO) was determined with X-ray and ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy measurements. The effect of UV-ozone (UVO) treatment on the formation of a hole injection barrier (Φ_h) in ITO was also investigated. In both cases of bare ITO and UVO ITO, only small interface dipole and band bending were observed, which indicates charge transfer between PVK and ITO is miniscule. The UVO treatment significantly increases the work function of ITO from 4.05 eV to 4.40 eV, which results in the reduction of Φ_h from 1.70 eV to 1.50 eV. This reduced Φ_h value dramatically improves the current density-voltage characteristics of PVK-based hole-only devices.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconductors have been considered to be a next-generation semiconductor owing to their unique advantages of simple fabrication methods, low cost, light weight, and mechanical flexibility [1]. Since intrinsic carriers are deficient in organic semiconductors, charge carriers should be injected from the electrode to the organic layer during device operation. Thus, charge injection efficiency is one of the most important factors in organic electronic devices. For this reason, organic electronic devices are generally composed of a multilayer structure, including functional interlayers to improve the charge injection property. To understand the charge injection property in organic electronic devices, the energy level alignment at the interface between an organic layer and an electrode must be determined [2–5]. In particular, indium tin oxide (ITO) is the most popular transparent conducting oxide (TCO) used as a bottom anode in optoelectronic devices, and thus its interfacial energetics with various p-type organic semiconductors has been

widely investigated [6–10]. Since ITO itself does not have a high enough work function (Ψ) to match the highest occupied molecular orbital (HOMO) level in p-type organic semiconductors, surface modification of ITO is required to reduce the hole injection barrier (Φ_h). Among various methods for surface modification, UV-ozone (UVO) treatment is commonly performed since it significantly increases Ψ of ITO. UVO treatment eliminates hydrocarbon contamination on the ITO surface. The hydrocarbon generates an interface dipole, which decreases Ψ [11–13]. The UVO treatment can be also efficiently used to increase Ψ in other TCOs, including indium zinc oxide and aluminum zinc oxide [14,15].

The adjacent layer with an ITO anode in organic light-emitting diodes (OLEDs) plays a role as a hole transport layer (HTL) and electron blocking layer (EBL), which enhance hole injection and the balance of holes and electrons. From the perspective of energy level alignment, for an efficient HTL/EBL, the HOMO level of the organic layer should be well-aligned with the Fermi level (E_F) of an electrode and the electron affinity (EA) should also be low in order to block electrons. Among various organic materials, poly(9-vinylcarbazole) (PVK) is a widely used polymer in OLEDs as the HTL/EBL due to its solution-processability and wide band gap

* Corresponding author.

E-mail address: hyunbok@kangwon.ac.kr (H. Lee).

[16–18]. Solution-processing is regarded as a substitute for thermal evaporation, which has low materials use efficiency and shadow mask problems [19,20]. This implies that material candidates for OLED can be expanded to polymers. The PVK layer has also been used successfully in quantum dot light-emitting diodes and organic-inorganic hybrid perovskite solar cells [21,22]. Thus, the electronic structure of a polymer such as PVK and its energy level alignment with an electrode are highly important and should be well understood when designing an efficient anode system in a wide range of device applications.

In this study, the electronic structure of the interface between PVK and ITO was investigated with X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) measurements. Various thicknesses of PVK films were deposited onto ITO, and the electronic structure was measured in each sample. The transport gap of PVK was determined via combined UPS and inverse photoelectron spectroscopy (IPES) measurements. UVO treatment was conducted on ITO to understand its effect on the formation of Φ_h . The energy level alignment between PVK and ITO with or without UVO treatment were determined, and their Φ_h values were compared. Hole-only devices were fabricated, and their current density–voltage (J - V) characteristics were measured to determine the hole injection improvement due to UVO treatment.

2. Experimental details

ITO-coated glass substrates were cleaned with ultrasonication in deionized (DI) water, detergent, ethanol, acetone, and DI water for 10 min each. To investigate the effect of UVO treatment on the hole injection property from ITO to PVK, a series of ITO substrates was treated with UVO for 15 min at 100 °C (UVO ITO hereafter). PVK was purchased from Luminescence Technology Corp (Mw > 20,000). PVK was dissolved in chlorobenzene with different concentrations (0.5–4.0 mg mL⁻¹) to vary the film thickness, and the films were fabricated by spin coating onto bare ITO or UVO ITO at a spin rate of 2000 rpm for 60 s in ambient atmosphere.

XPS measurements were conducted with a K Alpha + XPS system (Thermo Fisher Scientific Co.) using an Al K α X-ray source (1486.6 eV) to obtain core level spectra. UPS measurements were performed with a PHOIBOS 150 spectrometer (SPECS GmbH) using a He I discharge lamp (21.22 eV) to see the density of states in the valence region. To obtain the secondary electron cutoff (SEC), a sample bias of -5 V was applied. IPES measurements were used to determine the lowest unoccupied molecular orbital (LUMO) level with an IPES system (PSP Vacuum Technology Ltd.) consisting of a low-energy electron gun with a BaO cathode and a band pass filter of 9.5 eV in the isochromat mode. The samples were transferred to the analysis system as soon as prepared (in a few min).

Hole-only devices were fabricated by forming an Al (100 nm)/MoO₃ (10 nm)/PVK (100 nm)/ITO structure. A concentrated PVK solution was spin-coated onto bare ITO or UVO ITO, and the sample was loaded into the vacuum chamber with a base pressure below 10⁻⁶ Torr. The MoO₃ hole injection layer and Al anode were sequentially deposited onto the sample with thermal evaporation at the rate of 0.01 nm s⁻¹ and 0.1 nm s⁻¹, respectively. The device area was 0.04 cm². The J - V characteristics were measured with a Keithley 2400 source measure unit (Tektronix Inc.).

3. Results and discussion

Fig. 1 shows the In 3d and N 1s XPS core level spectra of PVK on bare ITO. In the In 3d XPS spectra, the thickness of a PVK layer can be evaluated using the equation

$$I = I_0 \exp\left(-\frac{d}{\lambda \sin \phi}\right)$$

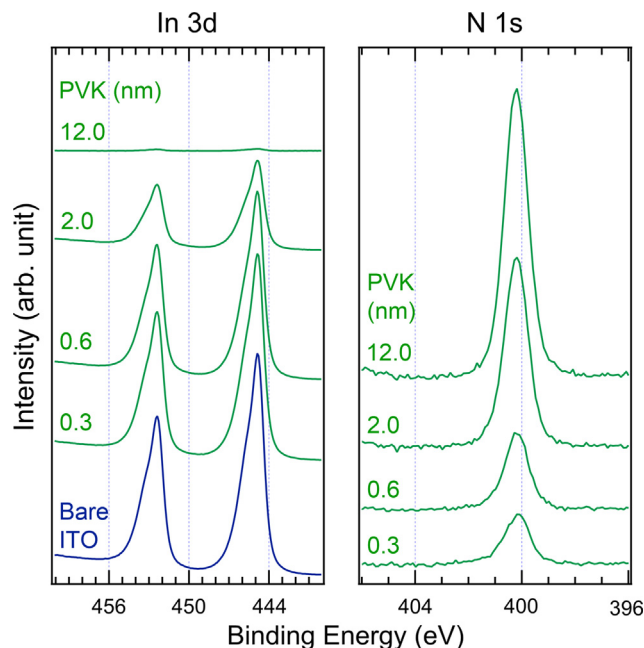


Fig. 1. In 3d and N 1s XPS core level spectra of PVK (0.3, 0.6, 2.0, and 12.0 nm) on bare ITO. The film thickness was controlled by varying the solution concentration.

where I is the In 3d intensity of PVK/ITO, I_0 is the In 3d intensity of ITO, d is the film thickness, λ is the inelastic mean free path, and ϕ is the XPS take-off angle (90° in our measurements). We assumed that λ is 3 nm in PVK based on a rough average of the λ values of polymers [23]. Thus, we could determine the thickness of a PVK layer at each concentration as: 0.5 mg mL⁻¹ = 0.3 nm, 1.0 mg mL⁻¹ = 0.6 nm, 2.0 mg mL⁻¹ = 2.0 nm, and 4.0 mg mL⁻¹ = 12.0 nm. As the PVK layer was thickened, the In 3d intensity gradually decreased. The energetic positions of the In 3d_{5/2} and 3d_{3/2} peaks were observed at 444.9 eV and 452.4 eV, and they did not shift as the thickness of a PVK layer increased. In the N 1s XPS spectra, a single peak originating from the carbazole N atom was observed at 400.2 eV. As the PVK layer was thickened, the intensity became higher, but no energetic shift was observed. This indicates that charge transfer between bare ITO and PVK would be minimal.

Fig. 2 shows the UPS spectra of PVK (0.3, 0.6, 2.0, and 12.0 nm) on bare ITO. The SEC region of the spectra were normalized, and the Shirley-type background was removed from the measured HOMO region spectra to accurately determine the onset. The SEC region spectra are shown with the kinetic energy scale so that the SEC directly displays its Ψ value. Ψ in bare ITO was measured to be 4.05 eV. As the PVK layer was thickened, the Ψ value gradually increased by 0.15 eV. In the HOMO region, the broad valence band features of ITO, which mainly originate from O 2p contribution, were observed in the 3–10 eV range [24] and its valence band maximum (VBM) was measured at 3.30 eV. As the PVK layer was deposited, the HOMO peak was seen around 2.4 eV. We determined the first reliable HOMO onset at 0.6 nm thickness since it would be close to monolayer thickness. The HOMO onset slightly shifted toward a lower binding energy by 0.10 eV as the PVK layer was thickened by 12.0 nm. The reason why this subtle energy level shift was not observed in the XPS spectra would be the shallower probing depth and higher energy resolution of UPS than XPS.

Fig. 3 shows the In 3d and N 1s XPS core level spectra of PVK on UVO ITO. In the In 3d spectra, the thickness of a PVK layer was evaluated from the attenuation of the In 3d peak intensity, and

Download English Version:

<https://daneshyari.com/en/article/7837625>

Download Persian Version:

<https://daneshyari.com/article/7837625>

[Daneshyari.com](https://daneshyari.com)