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Reduction of Threshold Voltage in Organic Thin-Film Transistors by Treating ITO Gate Electrode with Phosphoric Acid Solution

Jaehoon Park¹, Kangmin Kim², Jong Won Lee², Dong Wook Kim², Youngmin Kim², Yeonghan Chun²
and Jong Sun Choi²

¹Univ. of Hanyang, Research Institute of Information Display
17, Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea
Phone: +82-2-2220-0343 E-mail: jaypark0420@gmail.com

²Univ. of Hongik, Dept. of Electrical, Information & Control Eng.
72-1, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea

1. Introduction

Organic thin-film transistors (OTFTs) have enormous market potential in a wide range of applications for driving elements of flexible displays, radio-frequency identification (RFID) tags and large-area sensors [1-3]. Recently, pioneering works in OTFTs have established an encouraging electrical performance. Nevertheless, there is still room for characteristic improvement to meet the needs of such emerging markets. In particular, OTFTs often require large operating voltages to achieve the high mobility and on/off current ratio, which can make themselves impractical or restrict their applications within low-end devices.

In this work, we have investigated the influence of phosphoric acid treatment of indium tin oxide (ITO) gate electrode on the threshold voltage (V_{TH}) of OTFTs. The treatment is shown to increase the work function of ITO electrode by about 0.9 eV and induce negatively charged states at the organic semiconductor-insulator interface. These results contribute to reduce V_{TH} from -10.2 V for OTFT with the untreated ITO gate to -4.0 V for the device with the treated ITO gate.

2. Experimental Details

The 100-nm-thick ITO-coated glass substrates were supplied by LG Display and an ITO gate electrode was patterned by the conventional photolithography processes. And the gate-patterned substrates were cleaned with acetone, iso-propyl alcohol, and distilled water in ultra sonic bath, successively. Immediately after cleaning, they were treated by dipping in 1 wt.% phosphoric acid solution for 5 min, followed by drying in a vacuum dry oven at 175 °C. Poly(4-vinylphenol) with cross-linking agent was spin-coated on the gate-patterned substrates and baked consecutively at 180 °C for 1 h in a vacuum dry oven. A 480-nm-thick layer of cross-linked poly(4-vinylphenol) (cPVP) was used as a gate insulator, here. Pentacene (TCI, without purification) was thermally evaporated through a shadow mask onto the insulator-coated substrates at a rate of 0.05 nm/s, up to 60 nm. Top-contact OTFTs were constructed by forming 40-nm-thick Au source/drain electrodes using a shadow mask. The channel length and width of our TFTs are 100 and 200 μm , respectively. And, in order to measure the work function of ITO electrodes, ultraviolet photoemission spectroscopy (UPS) characterization

was done by introducing the samples into an UHV chamber equipped with helium (He) discharge lamp at $h\nu = 21.2$ eV. An incident photon energy of 650 eV was used to obtain a secondary electron emission spectrum.

3. Results and Discussion

The work functions of ITO electrodes were evaluated by an elastic secondary electron cutoff of UPS energy distribution curve. The UV light, generated by He discharge, excites the electrons below the Fermi level of ITO. And the excited electrons emit into vacuum, arbitrarily chosen as vacuum level which is usually the cutoff energy of the UPS spectrum. From these data, the ITO work function can be determined by subtracting the cutoff energy of the UPS spectrum from the He excitation energy of 21.2 eV. Figure 1 shows the change in the ITO work function according to the phosphoric acid treatment. The phosphoric acid-treated ITO exhibits an increased value of 5.7 eV, compared to that of untreated ITO (4.8 eV). Nüesch *et al.* reported that the absorption of acids induces substantial increase in the ITO work function by the order of 1 eV [4]. Accordingly, it is believed that the ITO work function increase in our experiment was attributed to the ionic layers initiated by the chemical absorption of protons, forming a surface dipole.

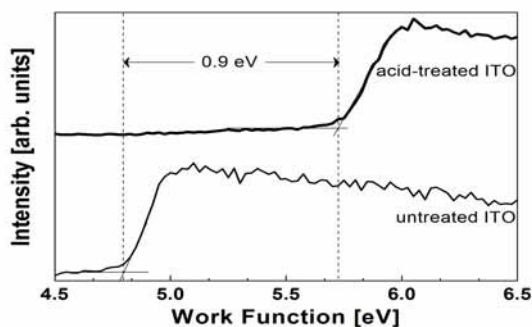


Fig. 1 Work function change according to the phosphoric acid treatment of ITO electrode.

Figures 2(a) and 2(b) show the drain current-drain voltage curves (I_D - V_D) of the OTFTs operating at different negative gate voltages (V_G), according to the phosphoric acid treatment of ITO gate electrode. Both types of devices

exhibited excellent saturation behaviors. Slight increase in the saturation current is observed, where -3.2 and $-2.6 \mu\text{A}$ at V_G of -40 V for the OTFTs with the acid-treated ITO gate and without treatment, respectively. Important device parameters can be obtained from the transfer characteristics [Fig. 2(c)]. In the saturation regime, the field-effect mobilities for both devices were almost identical to be about $0.32 \text{ cm}^2/\text{Vs}$. The on/off current ratios for the OTFTs with and without the gate electrode treatment were 1.9×10^5 and 1.3×10^5 , respectively. Nevertheless, the change in V_{TH} is quite apparent. We found that the phosphoric acid treatment of ITO gate electrode reduced V_{TH} from -10.2 to -4.0 V. This result is of interest because the gate metal has no direct contact with the organic semiconductor.

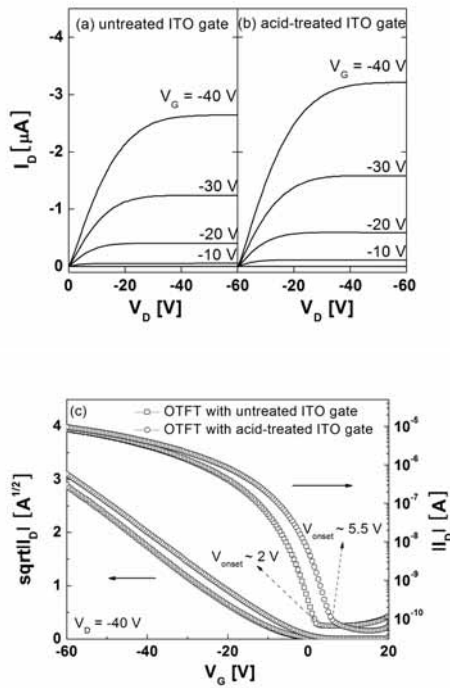


Fig. 2 Typical output [(a) and (b)] and transfer (c) characteristics of OTFTs according to the phosphoric acid treatment of ITO gate.

The flat band voltage (V_{FB}) can be the important parameter to account for the prominent V_{TH} shift because V_{TH} is the gate bias beyond flat band just starting to form a conducting channel. V_{FB} is correlated with fixed oxide charges Q_f and the work function difference Φ_{MS} between the gate metal and the semiconductor as in eq. (1) [5].

$$V_{FB} = \Phi_{MS} - Q_f/C_{ins} \quad (1)$$

V_{FB} corresponds to the voltage which when applied to the gate electrode yields a flat energy band in the semiconductor and can be approximated to the onset voltage (V_{onset}) of the device [6]. From Fig. 2(c), the phosphoric acid treatment of the ITO gate electrode led to a positive shift (~ 3.5 V) in V_{FB} . It is noteworthy that the shift of V_{FB} is more critical than the ITO work function change of 0.9 eV. This

discrepancy indicates that the phosphoric acid treatment does not merely change the ITO work function but also induces charged states at the organic semiconductor-insulator interface. From Eq. (1) considering the V_{FB} shift and the ITO work function change, it is confirmed that the phosphoric acid treatment of ITO induced negatively charged states at the interface between the pentacene layer and the cPVP layer and its density is calculated to be about $1.39 \times 10^{11} \text{ cm}^{-2}$. The negatively charged states can trap holes at the organic semiconductor-insulator interface. The density of trapped holes is estimated by using $C_{ins}(\Delta V_{TH} - \Delta V_{FB})/q$ because V_{TH} above V_{onset} is an estimate of the trap density in the channel [7] and found to be about $1.45 \times 10^{11} \text{ cm}^{-2}$. The value is good agreement with the density of negatively charged states, which indicates that the negatively charged states accumulate holes even at zero V_G . Therefore, it can be explained that the pronounced reduction of V_{TH} is attributed to the positive shift of V_{FB} and the accumulated holes.

3. Conclusion

Metal-semiconductor work function difference and interface states are decisive factors for the threshold voltage and flat band voltage of OTFTs. Phosphoric acid treatment of an ITO electrode increased its work function by about 0.9 eV and induced negatively charged states at the semiconductor-insulator interface, causing a positive shift in V_{FB} . Consequently, OTFT with the treated ITO gate showed a reduced V_{TH} of -4.0 V compared to that (-10.2 V) for the device without treatment. It should be emphasized that our approach is quite simple as dipping the gate-patterned substrates in aqueous solutions, and compatible with any other organic semiconductors because the treatment is done with a gate electrode, prior to the deposition of organic materials. Hence, the result of this study can be applied to the general practice of controlling the performance of OTFTs.

Acknowledgement

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