A photoelectron spectroscopy study of tunable charge injection barrier between metal/organic interface

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Photoelectron spectroscopy has been used to investigate a tunable charge injection barrier at the metal/organic interface. Results in this study show that the morphology of the Al electrode in the indium tin oxide (ITO)/LiF/Al/pentacene structure plays a critical role. When the sample is biased across ITO and Al electrodes, shifts in the binding energies of certain core-level electrons are observed on the surface of the discontinuous thin Al electrode. In contrast, no such shifts are observed on the thick Al electrode. Further studies indicate that applying a voltage bias changes the energy alignment between the discontinuous thin Al electrode and the pentacene layer deposited on it. © 2008 American Institute of Physics. [DOI: 10.1063/1.2957979]

In the past two decades, strong attention has been devoted to organic electronic devices such as high performance organic/polymer light emitting diodes,1,2 organic field effect transistors [OFETs (Refs. 3 and 4)], and memory devices.5–7 One of the important issues for efficient device operation is the charge injection from the electrode to the organic layer. The injection process is determined by the energy barrier between the Fermi level of the metal and the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) of the organic material. A number of interface modification schemes have been developed to adjust the charge injection barrier and to improve the device performance.8–10 On the other hand, fundamental research on metal/organic interface properties also attracts intensive interest because of its value in both device engineering and solid state theory.11–13

Recently, we reported an OFET with a vertically stacked structure consisting of a capacitor cell and an active cell connected by a thin source electrode.14 The device achieved promising performances in terms of its low working voltage (less than 5 V), high current output (up to 10 mA or 4 A/cm²), and high on/off ratio (4 × 10⁶). It was proposed that the bias applied over the capacitor can adjust the injection barrier between the source electrode and the active layer and thus modulate the transistor’s output current. This hypothesis was supported by the current-voltage (I-V) characteristics of the device and the behavior of the vertical light emitting transistor using similar structure.15 However, direct evidence showing the adjustment of the barrier is still necessary. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) offer effective methods to study the electronic structures at the surfaces and interfaces of electronic organic devices.11–13,16–18 In this letter, these methods were chosen to investigate samples with similar capacitor structures as the bottom half of our vertical OFETs (VOFETs). The results provide a plausible explanation of the relationship between the injection barrier adjustment and the capacitor bias.

The samples were fabricated on patterned indium tin oxide (ITO) glass substrates. A 300 nm LiF layer and an Al top electrode were deposited in a thermoevaporator with pressure below 5 × 10⁻⁹ mbar (Fig. 1). In order to understand the thickness dependence, samples with different top electrode thicknesses (10, 16, and 80 nm) were fabricated. After the deposition, the samples were immediately transferred into an Omicron XPS/UPS system containing two separate chambers. In the preparation chamber a thin pentacene layer (10 nm) was deposited on certain samples. During the deposition, the pressure of the chamber was maintained at less than 5 × 10⁻⁹ mbar. The XPS/UPS measurements were performed inside the analysis chamber, where the base pressure is better than 10⁻⁹ mbar. Al Kα (1486.6 eV) and He I excitations (21.2 eV) were used for XPS and UPS measurements, respectively. During the XPS/UPS measurements, the top aluminum electrode of the sample was grounded while the bottom ITO electrode was biased under various voltages using a Keithley 2400 Source meter.

Figure 2(a) shows the Al 2p region of the XPS spectra obtained from the surface of the 10 nm Al electrode. Two peaks are observed in this region: (1) the metallic Al peak appearing at a binding energy of 72.7 eV for all biases and (2) the oxidic Al peak at 75.6 eV (at 0 V bias) shifting with different applied biases on the bottom electrode. Similar

FIG. 1. The structure and connection of the samples for the XPS/UPS test. During the XPS measurement, the bottom electrode was biased with various voltages while the top electrode was kept grounded.

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shifts can also be observed in O 1s and F 1s peaks showed in Figs. 2(a) and 2(c). The strong fluoride peak observed from the surface of the sample indicates that the Al electrode is not a flat and uniform metal film. This result is consistent with the cross-sectional transmission electron microscope images of similar structures, which show that the thin Al electrodes are composed of metal Al mixed with aluminum oxide and LiF. Due to its large number of free electrons, the grounded metallic Al film shields all of the electric field. The bias applied on the bottom electrode cannot affect the XPS spectra obtained from the surface of the grounded top metal layer. Therefore, the metal aluminum 2p peak is fixed at 72.7 eV. However, as we mentioned above, the Al electrode is very rough and mixed with aluminum oxide and LiF islands. This structure allows the electric field generated by the bias to penetrate through the sites not covered by the metallic Al, subsequently induces charges in the aluminum oxide and LiF at the sample surface. Positive charges at the sample surface cause the corresponding peaks in the XPS spectra to move to a higher binding energy whereas negative charges shift these peaks towards a lower binding energy.

It is also interesting to note that the shift of the peaks increases with bias time. This phenomenon can be attributed to the drift of the ions under high electric field (~2.7×10⁷ V/m). When the sample is biased, a very small amount of lithium cations and fluoride anions in the LiF film move along the electric field and accumulate at the electrode/LiF interface. This process increases the charge density at the sample surface and thus induces further peak shifts. Similar results in a capacitor with the structure of metal/LiF/metal were reported previously. Due to the movement of the ions, the device reported in Ref. showed a much higher capacity than the value calculated using the dielectric constant of LiF. In other researches, polymer electrolyte films containing mobile ions were used as gate dielectrics in OFETs to achieve low working voltages. However, the device mentioned in Ref. was tested in high humidity conditions. The moisture dissolved part of LiF and made the ions more mobile. As a result, the device exhibited a relatively fast response; the capacitance reached a stable value in 10 seconds. In our experiments, the moisture level in the ultrahigh vacuum chamber is extremely low. Without the help of the moisture, the drift of the ions is much more difficult and slower. It was observed that the peaks continued shifting slowly even after 30 min of bias, due to this slow ion movement.

The peak shifting discussed above was only observed in samples with thin Al electrodes. As the thickness of the electrode increases, the metal Al eventually covers the entire sample surface and this effect disappears. The Al 2p peaks of the sample with a 16 nm aluminum electrode (Fig. 3) illustrates only a slight shift of the oxidic Al peak (less than 0.1 eV) at much higher bias voltage (~16 V) and same bias period. In the sample with 80 nm Al electrode, the fluoride peak cannot be observed and all the other peaks are fixed at the same positions regardless of the bias condition.

To further investigate how the gate electrode affects the injection barrier between the Al electrode and the top organic layer, we deposited 10 nm of pentacene onto the 10 nm aluminum electrode. Figure 4(a) shows the shift of the C 1s peak of pentacene. The peak shifts in the same direction as the O, F peaks shown in Fig. 2, which indicates that the bias conditions slightly affect the injection barrier.
applied on the capacitor cell changes the energy alignment between the top electrode and the organic material deposited on it. More direct evidence come from the UPS spectra [Fig. 4(b)], which shows the shift of the pentacene HOMO structure. When the bottom electrode is negatively biased, the HOMO of pentacene shifts to a lower binding energy, which corresponds to a lower hole injection barrier. In contrast, biasing the bottom electrode positively causes the HOMO to shift to a higher binding energy and reduces the electron injection barrier. These changes are consistent with the switching behaviors of our vertical organic transistors.

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