Study of injected carrier energetics in organic-field-effect-transistor by charge modulation spectroscopy

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1. Introduction

Organic materials have found a variety of applications in electronics and electrical engineering [1]. The discovery of high conducting organic materials [2], e.g., pentacene, polythiophene, etc. has motivated us to study organic electronics devices, e.g., organic electroluminescent devices (OLED) or, organic field effect transistors (OFETs). Much effort has been made to the development of organic devices, however, understanding of organic device physics is not yet satisfactory. The inherent nature of organic materials with low-carrier density showed the importance of injected carrier behaviors [3,4]. Recent studies have revealed that the operation of OFETs is regulated by injected carriers [5]. Using optical second harmonic generation measurement, we could show the contribution of injected carriers [6]. Further, we could show that analyzing OFETs as a system of Maxwell-Wagner effect element has well accounted for the transfer characteristics of pentacene OFET [7,8]. However these are still not sufficient, owing to a lack of information concerning energetics of injected carriers. Understanding of injected carriers from viewpoints of energetics is needed to give a clear picture of carrier motion in organic devices.

With taking into account these, we have been studying injected carrier behaviors using charge modulation spectroscopy (CMS) [9]. In this paper, using CMS method, we studied Poly-3-hexylthiophene (P3HT) in MIS diode. Results showed that polaron states of P3HT made a significant contribution for injected carrier behaviors in P3HT films. Furthermore, by coupling the CMS results with our experiments based on impedance spectroscopy, C-V, I-V and SHG measurements, we could also model the behaviors of charges accumulated and trapped at the P3HT and insulator interface.

2. Experiment

[Diagram: Schematic diagram of apparatus set up for CMS]

We used P3HT as an active layer of the MIS diode, where Au and Indium Tin oxide (ITO) was used as electrodes. The thickness of Au layer was around 8 nm, transparent to incident light coming through the monochromator. The working area of Au electrode was about 3.8 mm². Polyimide (CBDA-BAPP) (PI) was used as an insulator (160 nm thick). P3HT layer (about 40 nm in thickness) was deposited by spin coating method.

CMS measurement was carried out in N₂ atmosphere at room temperature after heating at 150 °C for more than 1h in the N₂ atmosphere without illumination. For CMS experiment the Xenon lamp as a light source was used and light through the monochromator was irradiated to the sample perpendicular to the sample surface. Applied AC signal amplitude and frequency were 1 V and 2 kHz, respectively. Transmitted light was measured by using the photodiode. The signal of the fundamental frequency was measured by lock-in amplifier. Impedance measurement and other measurement were carried out in N₂ atmosphere at room temperature after heating at 150 °C for more than 1h in the N₂ atmosphere in dark. Applied AC amplitude was 0.1 V with a frequency of 2 kHz (same as in the CMS measurement). The measurement also carried out under illumination, when it was needed.

3. Results and Discussion

Figure 3 shows the C-V characteristics of the MIS diode with the DC bias voltage sweep, \( V_{DC} = 20 \text{ V} \rightarrow -20 \text{ V} \rightarrow 20 \text{ V} \). The result shows a typical behavior with a hysteresis. Charge accumulation and depletion at the P3HT and PI interface was suggested from the change of capacitance with applied DC voltages.

The maximum capacitance corresponded to the capacitance, given by

\[
C_{ins} = \frac{\varepsilon_{ins} \varepsilon_0 A}{d_{ins}} \tag{1}
\]

Here \( \varepsilon_{ins} \) is relative dielectric constant of the insulator, \( \varepsilon_0 \) is the permittivity of vacuum, \( d_{ins} \) is the thickness of insulator, and \( A \) is the area of the device. Assuming \( \varepsilon_{ins} \) is 3.3, the maximum capacitance is calculated as 700 pF. The capacitance of 800 pF at \( V_{DC} = 0 \) well corresponds to that calculated one. This result shows that injection holes come together and go away at the P3HT-PI interface. When P3HT are free from injected carriers, the capacitance
becomes minimum with a series capacitance of P3HT as a dielectric material and PI insulator. Assuming that a relative permittivity of P3HT layer is 3.0, the minimum capacitance is calculated as 550 pF. This calculated value is in accordance with the measured value (500 pF at $V_{DC} = 20$ V). This correspondence shows that P3HT layer was free from injected carriers at $V_{DC} = 20$ V. On the other hand, when applying bias is in the region from 0 V to 15 V, the P3HT layer acquires injected carriers and it is charged. Dependent on the amount of charges acquired by P3HT, the capacitance of the MIS diode changed in this bias region. The hysteresis observed in the C-V characteristics suggested that there was the presence of trapped holes in the P3HT.

Figure 3 shows the CMS spectra of MIS diode. The inset shows the absorption spectrum of the P3HT and PI single layer. In the region $\Delta > 2$ eV, the CMS at $V_{DC} < 0$ corresponds well with the absorption spectrum of P3HT single layer, indicating that the $\pi - \pi^*$ transition decreased due to hole injection, or sweeping of electrons in bonding orbital [9]. In the region $\Delta < 2$ eV, it is considered that the absorption ascribed to polaron states was observed. On the other hand, when the P3HT layer is free form injection holes, $V_{DC} = 20$ V, CMS spectrum intensity decreased significantly. Finally, when the P3HT layer is partially charged, DC bias is 15V, CMS intensity is small, but not zero. This result indicates that the P3HT films were partially charged with holes.

Finally, on the basis of our experimental data on C-V and CMS, we proposed a simple model of the organic P3HT MIS diode, assuming the presence of carrier traps at the interface as well as polaron states in the P3HT film. The details will be presented at the conference.

4. Conclusion
We measured the CMS spectra and C-V characteristics of the P3HT MIS diodes. From impedance measurement, we know whether injected holes are accumulated or free and from CMS measurement, polaron state in P3HT layer are occupied by the injected holes. Considering the CMS measurement and impedance measurement, it is obvious that injected holes are accumulated at the semiconductor/insulator interface in P3HT layer. Futhermore, we observed the threshold voltage shift due to photo-illumination and we concluded that the threshold voltage shift resulted from the accumulation of electrons generated by illumination at the P3HT and insulator interface. Results show the presence of interfacial states at the P3HT and PI interface, as well as polaron states in the P3HT. Taking into account these, a simple model was proposed that accounted for the MIS diode characteristics.

Reference