Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp19-20

Probing of Transient Electric Field Distribution in ITO/PI/P3HT/Au Using Time-Resolved Second Harmonic Generation Measurement

Ryo Miyazawa, Dai Taguchi, Takaaki Manaka, and Mitsumasa Iwamoto*

Department of Physical Electronics, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo, 152-8552, Japan
Phone: +81-3-5734-2191 *Email: iwamoto@pe.titech.ac.jp

1. Introduction

The discovery of highly conducting organic materials, e.g., pentacene, polythiophene, etc. has resulted in studies of their possible application to organic electronics devices, such as organic electroluminescent devices (OLEDs), organic solar cells and organic field-effect transistors (OFETs).[1)] The study of the nature of organic materials with a low carrier density has already shown the importance of the injected carrier behavior.[1,2)] Recent studies have revealed that injected electrons regulate the operation of OFETs.[3)] Using optical second-harmonic generation measurements, we have shown the contribution of injected carriers to space charge field formation.[4)] On the other hand, in a metal-insulator-organic semiconductor structure (MIS) using an organic semiconductor layer, e.g., poly(3-hexylthiophene) (P3HT), it became clear that threshold voltage in *C-V* was shifted by photoillumination. This result obviously showed that electrons generated by photoillumination were trapped in the MIS structure [5)]. Using Electric-field-induced second harmonic generation (EFISHG) measurement, we have probed the carrier behaviors in organic material and the location of the trapped electrons in steady state. However, a detailed discussion about charging processes in transient state has not yet been carried out.

In this study, we studied the charging process of MIS with an active layer of P3HT using time-resolved second harmonic generation measurement.

2. Experimental Procedure

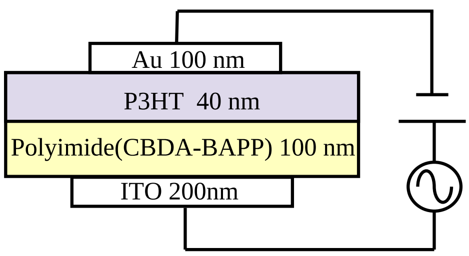

Fig.1 Schematic diagram of the MIS structure with an active layer of P3HT

We used P3HT as an active layer (semiconductor) of MIS diodes where Au and indium tin oxide (ITO) were electrodes (see Fig. 1). Thickness of Au electrode was 100 nm. The working electrode area was 7.5 mm^2. A polyimide insulator (100 ± 20 nm thickness) was prepared by using the thermally imidized polyamic acid derived from cyclobutane dianhydride and 2,2-bis(4-aminophenoxyphenyl) propane (CBDA-BAPP PI). The P3HT layer (40 nm in thickness) was deposited using a spin coating method. All measurements were carried out in a dry N_2 atmosphere at room temperature.

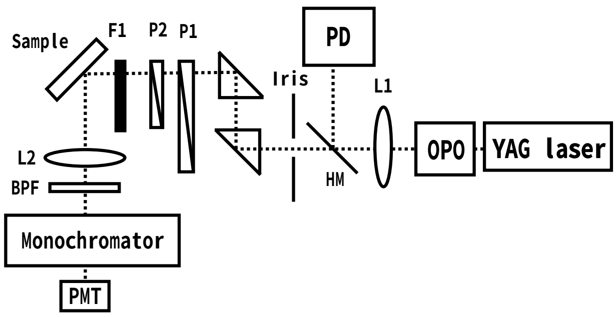

Fig.2 Experimental setup for the EFISHG measurement

Figure 2 portrays the experimental setup used for the EFISHG measurement. Light source was Nd:YAG laser coupled with optical parametric oscillator. Incident light (1060 nm) impinged on the sample from ITO side at an angle of 45 °, and reflected light through monochromator was detected using a photomultiplier tube (The wavelength of detected light was 530 nm). The voltage dependence of the SHG signal generated from P3HT showed the enhancement of EFISHG[6)]. Impedance measurements were also conducted using an LCR meter in the dark. The applied AC amplitude and frequency were 0.1 V and 1 kHz, respectively.

3. Results and discussion

Figure 3 shows the results of the *C-V* measurement in the region V_{DC} between -30 and 30 V. The measurement was done in a cycle as V_{DC} = 30 → -30 → 30 V. In the region -10 V > V_{DC}, the capacitance saturated with a value corresponding to the capacitance of PI layer, indicating that injected holes from the Au electrode accumulated at PI/P3HT interface. In the region -10 < V_{DC} < 0 V, the capacitance decrease with increase of V_{DC}, suggesting that injected holes distributed in the P3HT layer. In the region 10 V < V_{DC}, the capacitance again saturated, and the saturated value corresponded to the series capacitance of PI and P3HT layer. This result suggested that P3HT layer was free from holes and working as an insulator.

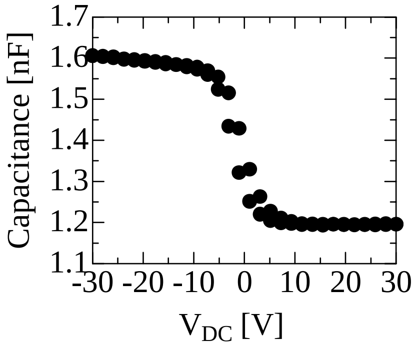

Fig.3 C-V characteristics of the MIS diode.

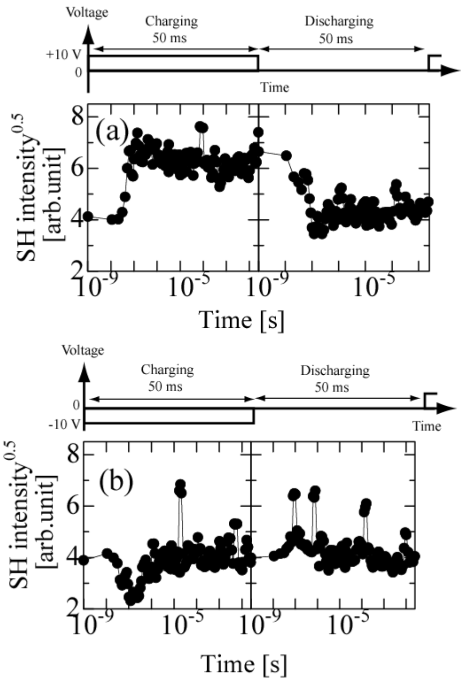

Fig.4 Transient EFISHG intensity. (a) applied 0 to 10 V、(b) applied 0 to -10 V.

Figure 4(a) shows the transient EFISHG enhanced from the P3HT layer by applying 10 V to the MIS diode. Note that the square root of SHG signal is proportional to internal electric field formed in P3HT layer. Therefore, the change of SH intensity indicated the variation of electric field in P3HT. The SHG intensity increased rapidly with a response time of 100 ns, corresponding to the time constant R_s C*. Here, R_s is the resistance originated from Au, ITO electrode and the lead wire of circuit. C* is the series capacitance of PI and P3HT layer. After that, the enhanced SHG intensity saturated. On the other hand, when we removed the applied voltage, the SHG decayed reversely with a response time of 100 ns. These results suggested that P3HT was working as an insulator, and charging and discharging was induced on electrodes.

Figure 4(b) shows the result obtained by applying -10 V. The SHG signal decreased rapidly with a response time of 100 ns in a manner as seen in Fig.4(a), but it decayed to initial value at a time around 1 μs. This results indicated that holes were injected from Au electrode into the MIS diode and accumulated at the interface to reduce the electric field in the P3HT layer. The response time of 1μs was around relaxation time $\tau = \varepsilon/\sigma$ of P3HT. Here σ is the conductivity by injected carriers. On the other hand, after removing the applied voltage, we could see increase and decrease of SH signals in series. The increase by around 100 ns was due to the extinction of charges on the electrodes, while the decrease after 100 ns for 1 μs was caused by decaying of accumulated charges at the interface.

As mentioned above, we could directly probe the electric field change, caused by injected carriers in MIS diodes. Details of the transient-EFISHG generated from MIS diodes will be discussed at the conference.

4. Conclusions

We studied the transient carrier behavior in P3HT layer of MIS diodes using time-resolved second harmonic generation measurement, and we can have observed the SHG signal changes due to the formation of internal electric field in P3HT. Results evidently showed that the EFISHG measurement is very effective for probing carrier dynamics in terms of charging and discharging of the diodes.

References

1) *Organic Electronics* , ed. G. meller and T. Grasser (springer, Berlin, 2009)
2) M. A. Lampert: *Current Injection in Solids* (Academic, New York, 1970).
3) *Conjugated Polymer and Molecular Interfaces; Science and Technology for Photonic and Optoelectronic Applications,* ed. W. R. Salaneck, K. Seki, A. Kahn, and J. J. Pireaux (Marcel Decker, New York, 2001) .
4) T. Manaka, R. Tamura, E. Lim, and M. Iwamoto: Nat. Photonics **1** (2007) 581.
5) R. Miyazawa, D. Taguchi, M. Weis, T. Manaka, and M. Iwamoto : Jpn. J. Appl. Phys. (in press)
6) Y. Shibata, Motoharu Nakao, Takaaki Manaka, Eunju Lim, and Mitsumasa Iwamoto: Jpn. J. Appl. Phys **48** (2009) 021504