# Injected Carrier Behavior in Single Crystalline Grains of TIPS Pentacene studied by Time-Resolved Optical Microscopic Second Harmonic Generation

Takaaki Manaka, Kentaro Abe, Kohei Matsubara, Dai Taguchi and Mitsumasa Iwamoto

Tokyo Tech. 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan Phone: +81-3-5734-2673 E-mail: manaka@ome.pe.titech.ac.jp

## Abstract

Injected carrier behavior such as transport and trapping in single crystalline grain of TIPS pentacene was studied by using time-resolved microscopic second harmonic generation (TRM-SHG) measurement. TRM-SHG imaging successfully visualized anisotropic carrier transport in the ab-plane of TIPS pentacene single crystal. Carrier trap at the edge of grain was also visualized.

## 1. Introduction

With the development of high-performance organic semiconductor materials, organic electronic devices, such as field effect transistors (FETs) have attracted considerable research interests. The important applications of organic FETs (OFETs) are as driving transistors in organic electroluminescence (EL) display and printed organic radio frequency (RF) identification tags. Current researches on organic field-effect transistors (OFETs) have mostly focused on the techniques and technology that are available for increasing the carrier mobility [1]. One of the most effective ways is to utilize a single crystalline organic semiconductors [2,3]. Depending on the crystal structure, organic crystal possibly shows large anisotropic carrier transport characteristics, i.e., mobility anisotropy. Further, in the practical application such as EL display and RF identification tags, OFETs are operated under a transient state, rather than in a simple steady state. However, understanding of the carrier behavior of OFET in the transient state is not satisfactory.

Nevertheless, anisotropic carrier behavior is also important in the microcrystalline films, which consists of a mixed phase of small crystalline grains, because a large anisotropic nature of each crystalline grain sometimes causes a lowering of mobility. This is because the grain boundaries become more serious compared with the case of crystalline grains with a low anisotropy. The I-V measurement is simple, but cannot discriminate the effect of the grain boundary and the transport inside the grains. On the other hand, the time-resolved microwave conduction (TRMC) measurement is one of the powerful techniques to study the mobility anisotropy [4]. However, the TRMC measurement cannot directly obtain the field effect mobility. In this study, anisotropic carrier behavior in TIPS (6,13-Bis(triisopropylsilylethynyl)) pentacene FETs is studied by using the TRM-SHG measurement [5]. We also applied this technique to visualize the trapped carrier at

grain boundary.

## 2. Experiments

Samples used in the experiments were top-contact TIPS pentacene FETs. Heavily doped Si wafers covered with a 500 nm thick oxide (SiO<sub>2</sub>) layer were used as the substrate. TIPS pentacene was deposited on the SiO<sub>2</sub> layer by dip-coating method. After the deposition of pentacene, top-Au source and drain electrodes with a thickness of 100 nm were deposited.

Figure 1 shows the optical setup for the TRM-SHG measurement. The light source was an optical parametric amplifier (OPA) excited by Ti:Sapphire regenerative amplifier (OPerA solo and Libra, Coherent Inc.). The external trigger signal of a regenerative amplifier was also supplied from a function generator to synchronize the voltage pulse applied to OFET with the laser pulse. Fundamental light was focused onto the channel region of the OFET with normal incidence angle using a long working distance objective lens (Mitutovo: M Plan Apo SL20x, numerical aperture=0.28, working distance = 30.5 mm). The fundamental light was uniformly irradiated over the channel region using a beam expander and the SHG image was acquired from the FET channel. The fundamental wavelength was fixed at 1100 nm, and SHG signal from the TIPS pentacene was selectively probed. The SH light generated from the FET was filtered using a fundamental-cut and an interference filters with which fundamental and other unnecessary light were removed. Finally, the generated SH light from the pentacene was detected using a cooled charge-coupled device (CCD) camera. The I-V and TRM-SHG measurements were performed in laboratory ambient atmosphere.



Fig. 1 Optical setup for the TRM-SHG measurement.

## 3. Results and discussion

Figure 2 shows the TRM-SHG images from TIPS pentacene single crystalline grain covered with a round-shaped electrode at various delay times. Since the round-shaped electrode can inject carriers every direction, the angular dependence of the carrier velocity (carrier mobility) is directly visualized at once. Positive voltage pulses (V<sub>pulse</sub> = 100 V) were applied to the electrode with respect to the gate electrode for hole injection. At a delay time of 0 ns, the SHG signals are found near the edge of the electrode, indicating that carrier injection is just started. As the increase of the delay time, the SHG distribution gradually spread from the edge of the round-shaped electrode. Interestingly, the shape of the SHG distribution for the TIPS pentacene device (Fig. 2(c)) is not a perfect circle, indicating that the carrier velocity strongly depends on the flowing direction. In other words, the ellipse directly represents the anisotropic carrier transport property of the film. Noteworthy that the velocity anisotropy was not observed for the vacuum evaporated pentacene device (not shown here), indicating the in-plane isotropipc carrier transport.

Carrier velocity along the major axis of the ellipse is maximum, and that along the minor axis is minimum. Hence, maximum and minimum direction of the mobility can be uniquely determined. It should be noted that mobility anisotropy evaluated from the TRM-SHG measurement is smaller than that evaluated from the I-V measurement. The difference is ascribed to the presence of the grain boundary formed in the channels of the device in which the dipping direction is perpendicular to the source-drain direction. Averaged property of the whole



Figure 2 TRM-SHG images from TIPS pentacene single crystalline grain with the round-shaped electrode at delay times of (a) 0 ns, (b) 15 ns and (c) 30 ns. Polarized microscope image is shown in the inset of (a).

channel is only obtained from the simple I-V characteristics, whereas local information can be obtained by using the SHG microscopy.

Even in the single crystalline grains carrier transport is sometimes governed by the defects and invisible grain boundaries. As mentioned, a simple I-V measurement cannot directly discriminate the effect of the grain boundary and the transport inside the grains. On the other hand, the TRM-SHG measurement enables us to directly visualize the intra-grain and inter-grain carrier behavior. As shown in Figure 2(a), bright lines were observed at the edge of grains (see inside a white circle). It should be noted that this image was taken at the delay time of 0 ns. Generation of strong SHG signal implies that strong electric field is formed at that point. Therefore, some carriers have already accumulated at the edge of grains before carrier injection. After the carrier injection such bright lines disappear as shown in Fig. 2(c). We successfully visualize the carrier trap at the edge of crystals, and such trapped carrier may cause the hysteresis in the I-V characteristics. Further, we could observe the transport barrier inside the grains. Accordingly, the effect of the grain boundary on the carrier transport is directly visualized by the TRM-SHG measurement. In the presentation, temperature dependence of the anisotropic carrier transport will be also exhibited to discuss the mechanism of carrier transport in TIPS pentacene single crystalline grain.

# 3. Conclusions

We successfully visualized the injected carrier behavior in single crystalline grain of TIPS pentacene by the time-resolved microscopic second harmonic generation (TRM-SHG) imaging. It was found that the transient carrier motion strongly depends on the transport direction in *ab*-plane of TIPS pentacene single crystal owing to the mobility anisotropy. Trapped carrier at the edge of grains was also directly visualized.

#### Acknowledgements

Supports from the Grant-in-Aid for Scientific Research, Nos. 22226007 and 24360118 from Japan Society for the Promotion of Science (JSPS) are greatly acknowledged.

# References

[1] H. E. Katz, Chem. Mater. 16, 4748 (2004).

[2] R. W. I. de Boer, T. M. Klapwijk, and A. F. Morpurgo, Appl. Phys. Lett., 83, 4345 (2003).

[3] J. Takeya, M. Yamagishi, Y. Tominari, R. Hirahara, Y. Nakazawa, T. Nishikawa, T. Kawase, T. Shimoda, S. Ogawa, Appl. Phys. Lett., 90, 102120 (2007).

[4] G. Dicker, M. P. de Haas, L. D. A. Siebbeles, J. D. Warman, Phys. Rev. B, 70, 045203 (2004).

[5] T. Manaka, E. Lim, R. Tamura, M. Iwamoto, Nature Photon. 1, 581(2007).