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Direct imaging of carrier motion in organic transistors by optical second-harmonic generation

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Interest in dynamic behaviour of carriers in organic materials is motivated by possible applications that include organic thin film transistors, organic electro-luminescent (EL) devices, and organic photo-conductors. It can also provide insight into modelling of carrier transport and trapping in organic semiconductors and insulators. Here, we employ advanced SHG technique to probe and visualize real carrier motion in organic materials. This is a time-resolved microscopic optical SHG (TRM-SHG) technique that allows direct and selective probing of dynamic carrier motion in organic materials. TRM-SHG experiments using pentacene field effect transistors (FET) revealed dynamic changes of SHG intensity profiles arising from pentacene. Carrier velocity in organic solids is thus determined from the visualized carrier motion. We anticipate that this direct visualization technique will find wide application in the illustration of space charge field formation in organic and inorganic materials, including biomaterials and polymers.

Understanding of carrier motion in materials is the most fundamental and important subject in physics, materials science, electronics and electrical engineering^{1,2}. Maxwell's displacement current, generated in accordance with dynamic-carrier motion, is thus explored using a variety of electrical techniques^{3,4}. The underlying concept of these techniques is indirect probing of carrier motion and its related electrical phenomena, using electrical instruments such as the electrometer. Among these, the time of flight (TOF) technique is widely used for evaluating the drift mobility of materials, including inorganic amorphous solids and organic materials^{3,5}, where a Maxwell's displacement current flowing through the external circuit is monitored to indirectly probe the long-range carrier motion in the material. A thin carrier sheet generated by light pulse irradiation in the region close to one electrode travels toward the counter electrode. It crosses the sandwiched materials of thickness d by an applied electric field E . In this process, charge Q induced at the counter electrode changes in accordance with the drift of the carrier sheet. Thus the drifting carrier sheet is monitored as transient current through the change in induced charge Q , and the drift mobility $\mu = d/\tau_r E$ is estimated after determining its transit time τ_r . Other information, such as carrier traps, is also obtained by analyzing the transient-current trace. These advantages allow us to use the TOF measurement for organic devices such as organic FET (OFET)⁶. Because this method is an indirect one, an elaborate mathematical approach is required for analyzing the current pulse. Therefore, this method leads to a puzzling situation in which there are many possible solutions to reproduce an observed current pulse, particularly in the cases with multiple carrier traps and with applying external electric pulse to generate a carrier sheet. Furthermore, contact resistance causes another problem because of the difficulty in distinguishing carrier-injection and carrier-transport processes. A similar situation arises when using other electrical techniques, such as pressure-wave propagation^{7,8}, pulsed electro-acoustic⁹, and laser pulse¹⁰ for analyzing space-charge profiles in dielectrics. In other words, the above-mentioned problem

remains as long as we use electrical methods that indirectly probe carrier motion. The only solution is to develop a method of directly probing carrier motion. What we demonstrate here is the direct observation of carrier motion in an organic thin film using an optical method, which relies on time-resolved microscopic optical second-harmonic generation (TRM-SHG). The time-resolved SHG image from organic thin film was directly visualized using high sensitivity cooled-CCD. This approach is based on nondestructive probing of a local electric field induced in materials because of the two-photon process, and can be employed in device applications such as OFET and organic EL device. The results obtained by TRM-SHG are useful in modelling carrier motion in organic insulators and semiconductors.

We developed a procedure for evaluating the “static” electric field in organic devices by electric field induced SHG (EFISHG)¹¹⁻¹⁴, which efficiently uses SHG signals generated in proportion to the local electric field. Microscopic SHG measurements for pentacene FETs revealed electric field distribution in the OFET channel during on and off states of the OFET^{13,14}. Electric field distribution probed by EFISHG during the off state obeys the Laplacian field. Here, Laplacian field is the electric field in an insulator caused by the electrodes in the absence of any charge between the electrodes, and that is formed when the pentacene shows the intrinsic nature of the materials, i.e., low carrier density and high resistivity. On the other hand, electric field distribution during the on state deviates from this Laplacian field formed during the off state, because excessive carriers injected from the source electrode dominate the carrier transport across the FET channel. Furthermore, EFISHG revealed that SH signals were selective, and were generated only from pentacene and not from the SiO₂ gate insulator, by selecting an appropriate wavelength. Similarly, EFISHG from polydiacetylene FETs revealed that, trapped carriers in polydiacetylene activate SHG signals because of the presence of a local electric field originating from excess charges in polydiacetylene FET, and could be the origin of the EFISHG¹⁵. Although

these findings are confined to EFISHG related to the electrostatic phenomena in steady state, they encourage us to directly probe carrier motion in organic materials—to study dynamic carrier behaviour in organic materials. According to Gauss's law, in Maxwell's electromagnetic theory, the electric flux density diverges from charge carriers. This simple principle allows real-time detection of carrier motion in organic materials using TRM-SHG. However the concept of transient measurement differs completely from that used for static observation by EFISHG.

Fig. 1(c) shows the TRM-SHG image from the channel of pentacene FET with Au-source and drain electrodes at various delay times between the laser pulse and the rising edge of the positive voltage pulse. Positive voltage pulses ($V_{\text{pulse}} = 70 \text{ V}$) were applied to the source electrode with the gate and drain electrodes shorted and grounded (see Fig. 1(a)). At a delay time of 0 ns, the laser pulse coincides with the rising edge of the voltage pulse, and SHG signals are found near the edge of source electrode, indicating that carrier injection is just started. Interestingly, as clearly shown in the image, the emission band of SHG signal gradually moves in the channel from source to drain electrode with an increase in delay time. Motion of the emission band from source electrode, not from drain, is the direct evidence for hole injection from Au-source electrode with a low-injection barrier. That is, pentacene FET shows p-type behaviour, and it is in the on state when a positive voltage is applied. Note that general TOF method cannot determine carrier species only from the trace of transient current. In more detail, motion of electrons from drain to source generates the same trace of transient current as that of holes moving from source to drain. However, our TRM-SHG image clearly distinguishes the injection carrier species as holes. This is an advantage of the direct observation by TRM-SHG.

Why the emission band of SHG moves with an increase in delay time?
Immediately after carrier injection from source electrode begins, a quasi two-

dimensional carrier sheet extends its area rapidly into the OFET channel, and finally it covers the entire channel area, because carriers are supplied continuously from source electrode during the application of the positive pulse. Since the SHG can detect the in-plane component of an electric field, electric field distribution can be detected along the channel. Figure 2 shows the simulated results of in-plane electric field distribution in pentacene and the SHG intensity profile. The electric field distribution was estimated by solving a Poisson's equation, taking the charge distribution into consideration. As shown in the figure, strong in-plane electric field is formed at the edge of carrier sheet in the channel. Thus, the emission band observed in Fig. 1(c) just represents the position of the wave front of the carrier sheet travelling in the channel. Figure 1(d) shows SHG profile at various delay times when a negative pulse ($V_{\text{pulse}} = -70$ V) is applied. Under the negative bias, carrier injection from the electrode into pentacene is prohibited because the injection barrier for electron at pentacene/Au interface is quite high. Thus the strong electric field around the edge of electrode is maintained during bias application and the position of the SHG peak never moves; the SHG signals are concentrated around the edge of source electrode as shown in Fig. 1(d).

Figure 3 replots the relationship between the wave front position of travelling carrier sheet and the delay time. The slope of the plots indicates the carrier velocity, v_0 , in the channel, and the carrier mobility, μ , can be estimated, assuming μ is expressed as $\mu = v_0 L / V_{ds}$. Here, L and V_{ds} represent the channel length and voltage applied between source and drain electrodes, respectively. Electric field distribution along the FET channel is not constant, however, the average electric field along the channel is given by L / V_{ds} . The deviation of the plots from the dashed line possibly reflects the electric field distribution along the channel, but we do not need to go into the details for the following discussion. A simple calculation using the slope of the dashed line derives the mobility as $0.25 \text{ cm}^2/\text{Vs}$. The determination of mobility here is direct, in that the carrier velocity is determined from the direct image of the carrier motion illustrated in Fig. 1(c).

It is instructive to evaluate the field-effect mobility from the FET characteristics using an equation expressing drain current, I_{ds} , based on gradual channel approximation, although the evaluation is indirect. From the $\sqrt{I_{ds}}-V_{gs}$ characteristics in the saturated region¹⁶, a field-effect mobility of 0.11 cm²/Vs was obtained, where V_{gs} represents the applied voltage to gate electrode. This underestimates the field-effect mobility, compared with the estimate from the EFISHG, possibly because of factors such as contact resistance. As a result of the repetitive measurements using different samples, it is found that the slope in Fig. 3 depended on a preparation condition of devices, such as deposition speed and substrate temperature. This clearly indicates that carrier velocity strongly depends on the sample condition. Here, we would like to stress that the long-range motion of the emission band during hole injection was always observed, and correlation between delay time and the position of emission band was well reproduced between sample by sample.

It is noteworthy that the mobility determined by TRM-SHG is fundamentally different from the TOF mobility determined using a typical sandwiched type configuration. The TOF measurement provides bulk mobility, whereas the field-effect mobility represents surface mobility—the channel carrier is confined to a region within several nanometres from SiO₂ surface^{17, 18}. The TRM-SHG measurement proposed here directly evaluates surface mobility, because the SHG signal is activated by the channel carrier at the interface, and mobility evaluated by the TRM-SHG can be compared with the mobility obtained from the transfer characteristics of the FET. Thus, the present combination of microscopic SHG, with pulse driving of the OFET, is very effective for evaluating carrier mobility in organic materials. Moreover, when carriers are supplied from the dissociation of electron-hole pairs generated by photo excitation, the recombination of photo carriers is sometimes a drawback for typical TOF measurement. On the other hand, carriers are injected ones for TRM-SHG measurement. As shown in the SHG images, the shape of the emission band gradually loses its sharpness during

carrier travel in the channel. This indicates the diffusion of the edge of carrier sheet, presumably accompanying carrier trapping. In this sense, TRM-SHG measurement can be also used for investigating trapping phenomena, and the short-range carrier motion in materials.

An appropriate wavelength for the SH measurement enables us to detect carrier motion in selective organic materials; this invites us to study carrier motion in complex systems such as multi-layered systems in organic EL and organic photo-conductors. Furthermore, the direct imaging of carrier motion demonstrated here can be effective in proving the appropriateness of proposed models for carrier motion in organics, such as that of Scher and Montroll¹⁹⁻²¹. The data presented here are typical ones, and we did not deal with them on the basis of the device physics, because what we should do here is to demonstrate a novel technique in this paper. We are very confident that the deeply knowledge about the device physics of organic elements can be obtained using this method. More specifically, it can demonstrate the appropriateness of an analytical model for OFETs, such as a Maxwell-Wagner effect element²², and the effect of space charge²³ on OFET characteristics. Thus, the findings obtained by TRM-SHG will also prove useful for further development of a new electron-transport theory for organic materials, also for inorganic materials, including biomaterials and polymers. Note that, recently, OFET operation has been successfully probed by sum-frequency generation (SFG)²⁴ and infrared (IR) spectroscopy²⁵. Here the conformational change of the molecular structure and the creation of polarons, due to doping of the molecules by carrier injection from electrodes were probed by SFG and IR spectroscopy. We anticipate that the use of these optical methods coupled with our developed TRM-SHG technique will be of great help for the understanding of carrier transport of organic materials at a molecular level.

Methods

The light source was an optical parametric oscillator (OPO: Continuum Surelite OPO), pumped by the third-harmonic light of a Q-switched Nd-YAG laser (Continuum: SureliteII-10). The wavelength was fixed at 1120 nm, where the EFISHG peak is located²⁶. Fundamental light from the OPO passed through a prism polarizer and a long-pass filter, and was focused onto the channel region of the OFET with normal incidence, using a long working distance (W.D.) objective lens (Mitsutoyo: M Plan Apo SL20 \times , NA = 0.28 and W.D. = 30.5 mm). SH light generated from the sample was filtered by a fundamental-cut filter and an interference filter to remove fundamental and other unnecessary light. Finally, SH image was visualized by a high-sensitivity cooled CCD (Andor DU420-BV). Acquiring time for taking SH image was 90 s. In this configuration, polarization direction of the fundamental light was chosen in the direction corresponding to the channel direction (source-drain direction). All measurements were performed in laboratory ambient atmosphere.

Pulse voltage that drove the OFET was applied to the devices using a function generator (NF Corp.: WF1945) and a high-speed bipolar amplifier (NF Corp.: HSA4101, Slew rate = 5000V/ μ s). A rise-up time of the voltage pulse to the OFET is 20 ns. The external Q-switch trigger of the YAG laser was supplied simultaneously from a function generator. The time delay between the pulse voltage applied to the FET and the Q-switch trigger was precisely controlled by a function generator, to perform a time-resolved measurement. The pulse width and repetition rate applied to the FET were 50 μ s and 10 Hz, respectively.

Samples used in the experiments were top-contact pentacene FETs. Before deposition of pentacene, highly-doped Si substrates, covered with a 500-nm thick silicon dioxide (SiO₂) insulating layer, were immersed in 0.03 wt% toluene solution of octadecyltrichlorosilane (OTS) to improve the on/off ratio of the FET. A pentacene

layer, approximately 100 nm thick, was deposited on a SiO₂ surface. The process pressure during deposition of pentacene was kept at less than 1×10^{-4} Pa, and the deposition rate was controlled at approximately 3 nm/min. After deposition of pentacene, top Au electrodes (source and drain electrodes) with a thickness of 100 nm were deposited on the pentacene surface. The channel length (L) and width (W) were 40 μ m and 3 mm, respectively. For the FET structure, a highly-doped Si substrate was used as a gate electrode.

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Competing financial interests:

The authors declare no competing financial interests.

Figure captions:

Figure 1 Experimental configurations and results of the TRM-SHG measurement. **a**, Schematic image of the OFET device and electrical connection. Using microscopic objectives, fundamental light is focused on the device. Corresponding laser spot is represented as red circle in **c** and **d**. **b**, Timing chart of the laser pulse and applied voltage to the FET. A parameter τ represents the delay time. **c**, SHG image from the FET channel for different delay times with applying positive pulse to the source electrode. **d**, SHG image from the FET channel with applying positive pulse.

Figure 2 Calculated in-plane electric field distribution and the SH profile assuming the distribution of carrier density in channel. From top to bottom, device configuration, electric field distribution (blue line) and SHG intensity distribution (red line) are respectively displayed. Immediately after carrier injection from source electrode begins, a quasi two-dimensional carrier sheet extends its area rapidly into the OFET channel. In the calculation, the head of carrier sheet reaches the center of the channel. Strong electric field in the x -direction is formed in the pentacene layer around the head of carrier sheet.

Figure 3 Relationship between the position of the head of carrier in OFET channel and the delay time. Open squares represent the position of the head of carrier sheet evaluated from Fig. 1 **c**. Here, we define the center of SH emission band as the head of carrier sheet. Dashed line represents average carrier velocity evaluated as approximately 4400 cm/s.