Direct probing of carrier motion and interfacial phenomena in organic films and devices by optical second harmonic generation and Maxwell-displacement-current

M Iwamoto

Department of Physical Electronics, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

E-mail: iwamoto@pe.titech.ac.jp

Abstract. Probing and modelling of dynamical motions of carriers in organic materials is a fundamental research subject in science and electronics. According to the Maxwell’s electromagnetic field theory, electrons and dipoles are source of electric fields. As a result organic materials surrounding electrons and dipoles are polarized. By probing the dielectric polarization, we can visualize carrier motion in organic materials. An optical method based on electric-field-induced optical second harmonic generation (EFISHG) is available for directly probing the dynamical electron (and hole) transport as the migration of electric field. On the other hand, an electrical method based on the Maxwell-Displacement current generation can probe rotational dipolar motion in organic films. In this proceeding, basic concept for probing carrier motions, e.g. translational motion of electrons and rotational motion of dipoles, by paying attention to dielectric polarization phenomena is discussed. Finally, it is concluded that experiments and analyses based on dielectrics physics is a very effective way for analyzing carrier behaviours in organic films and devices.

1. Introduction

Probing and modelling of polarization phenomena originating from dipoles and electrons is a fundamental research subject in electronics and materials science. According to the Maxwell’s electromagnetic field theory, the total current flowing across organic materials is the sum of the conduction current and Maxwell’s displacement current (MDC). The conduction current is generated when electrons and holes are conveyed under the external electric field produced by applying potentials to electrodes. In contrast, the MDC is generated when electric flux originating from electrons, holes and dipoles changes with time. By probing the change of electric flux with time as MDC, we could study the transient-state carrier motions that include rotational dipolar motion in organic materials [1,2].

In the MDC experiment, organic materials are sandwiched between two electrodes that are connected each other through an electrometer. On applying an external stimulus (for example, light, pressure, heat or external electric field) to organic materials, a current pulse is generated and it is recorded as the trace of change of induced charge on the electrodes with time. Note that we do not need to contact the two electrodes to organic materials for probing rotational motion of dipoles in the MDC measurement, where an air-gap between the electrode and organic materials works as a good

1 To whom any correspondence should be addressed.
electrical insulator and eliminates leakage currents. Accordingly we can probe dipolar motions in organic materials as the MDC. Further, by coupling the MDC experimental system with Brewster-Angle microscope (BAM), we could visualize surface dielectric polarization phenomena in monolayers on the water surface [3].

On the other hand, a long-range carrier-(electron and hole) transit through organic materials is fundamental, and time-of-flight (TOF) measurement has been used for the probing. On applying a laser pulse to organic materials, induced charge on electrodes is monitored along with carrier-transit by using an electrometer. Consequently TOF is basically the MDC measurement, but we need to install a system of organic materials that contact with electrodes. For the MDC experiment used for probing dipolar motion in monolayer at the air-water interface, the location of dipoles is known a-priori. It is of course on the water surface. On the other hand, we have no idea on the location of moving carriers in organic materials, a-priori. Hence for the TOF measurement, an elegant mathematical approach for analyzing the current pulse is needed. However, the method leads to a puzzling situation in which there are many possible solutions that can reproduce an observed current pulse. This means it is difficult to probe actual carrier motion in organic materials by the TOF method. The only way to overcome this situation is to directly probe moving carriers in organic materials. Although it is a difficult task to probe carriers themselves by using microscope, nanoscope and others, the Gauss’s law in the Maxwell’s electromagnetic field theory suggests us an insightful principle for probing the carrier motion in organic materials. That is by probing the propagation of the electric field diverging from moving electrons and holes, the carrier motion could be visualized if the organic material surrounding the moving electrons and holes is polarized by the electric field arising from the moving carriers. Time-resolved microscopic optical second harmonic generation (TRM-SHG) measurement is a technique that enables us to probe the propagation of the polarization induced from moving electrons and holes [4]. Further, the use of CCD camera visualises the motion [5].

2. Probing of dipolar motion by MDC measurement

On account of symmetry breaking, monolayers are spontaneously polarized at the interface, where orientational ordering of the constituent dipoles makes a main contribution. The orientational distribution of rod-like molecules is expressed using a set of order parameters defined as $S_n (\equiv \langle P_n(\cos \theta) \rangle)$ (n=1, 2, 3, …), where $P_n(\cos \theta)$ is the Legendre polynomial of the n-th rank, $\theta$ is a tilt angle from the normal direction to the surface, and $\langle \rangle$ represents thermodynamic average. $S_1$ and $S_3$ express the non-symmetric property of monolayers. Spontaneous and nonlinear polarizations of monolayers are thus described using these parameters. On the other hand, $S_2$ specifies the symmetric property, and linear polarization is expressed using this parameter. The liquid crystalline property of bulk nematic LCs is generally characterized using the parameter $S_2$. Interestingly, a set of order parameters $S_1$, $S_2$ and $S_3$ are non-zero for monolayers on the water surface. In other words, non-zero $S_1$ and $S_3$ have relation with the presence of spontaneous polarization. This means that electrostatic energy stored in domains on a water surface governs domain shapes. Experimentally, by coupling the MDC experimental system with Brewster Angle Microscope (BAM), spontaneous polarization is probed with the order parameter $S_1$. At the same time, the BAM image visualizes domain shapes on the water surface.

In more detail, an experimental arrangement of the MDC with a BAM observation system has been constructed, where a suspended electrode is used to probe electric field generated from monolayer on water surface. Induced charge $Q_S$ on this suspended electrode is proportion to the spontaneous polarization of the monolayer $P_0$. Here $P_0$ is thus proportion to $\mu S_1$, where $\mu$ is permanent dipole moment of the constituent molecule of monolayer, and $S_1$ is the orientational order parameter. Monolayer compression causes the change of $Q_S$, and MDC current pulse is thus generated. This means that MDC probes the orientational change of molecules on the water surface, and the $S_1$ is evaluated. Along with the monolayer compression, the electrostatic energy is stored in monolayers. Hence domain shape of monolayer at the air-water interface should be dependent on the electrostatic energy of monolayers. Minimizing the free energy of monolayers, the shape equation describing
domain shapes is derived [6], where the Maxwell-stress term (2nd and 3rd terms) has relation with the
electrostatic energy:

\[ \Delta P - \lambda \kappa(s) - P_{0n}E_{0n}(r(s)) = 0, \quad (1) \]

where \( \Delta P \) is pressure difference between inner and outer domain, \( \lambda \) is line tension, \( E_{0n}(r(s)) \) and 
\( E_{0L}(r(s)) \) are the normal and in-plane components of electric field (spontaneous polarization), respectively, at the domain boundary \( (r(s)) \) with curvature \( \kappa(s) \). To solve Eq.(1) is a hard task, but employing the Taylor’s expansion approach we could obtain the solution in simpler cases, such as circle and \( m \)-sided quasipolygon. MDC experiment with the BAM observation for phospholipid monolayers on the water surface have evidently showed the generation of MDC along with such predicted domain shapes by monolayer compression. As mentioned earlier, using MDC measurement coupled with BAM observation method could probe surface polarization phenomena originating from dipoles and its related surface phenomena.

3. Probing of carrier motion in organic materials as dielectric polarization phenomena

Since the discovery of conducting materials, organic material electronics has commanded increasing attention, and development of techniques that can probe carrier motion is highly motivated by scientists and electronics engineers. As mentioned in section I, it is very instructive once to trace back to the Faraday’s idea. Using an EFISHG technique, we can directly probe carrier motion in organic materials [4]. The concept is to probe the propagation of polarization induced by moving carriers in organic materials. Nonlinear polarization \( P \) is induced by laser irradiation, owing to the quantum coupling between electromagnetic fields and electrons in organic materials. As electron clouds of molecules would be distorted by D.C. field, this kind of nonlinear polarization \( P \) can be induced in centro-symmetric molecular system, such as pentacene and phthalocyanine. That is, induced polarization is given as

\[ P(2\omega) = \chi^{(3)} E(0)E_i(\omega)E_j(\omega), \quad (2) \]

where \( \omega \) and 0 represents the angular wave frequency of incident electromagnetic wave, \( E_i \) and \( E_j \) represent the electric field of light, and \( E(0) \) is the static electric field induced from carriers. The induced polarization \( P(2\omega) \) is a source of second harmonic signal, and the enhanced SH is in proportion to \( P(2\omega) \) as

\[ I(2\omega) \propto \left| \chi^{(3)} E(0)E_i(\omega)E_j(\omega) \right|^2 \propto \left| P(2\omega) \right|^2, \quad (3) \]

where \( I(2\omega) \) describes the SH intensity. From eqs.(2) and (3), it is clear that SH is capable of probing carrier transfer.

Fig. 1 shows the TRM-SHG image from the channel of top-contact pentacene FET with Au-source and drain electrodes [5]. The SHG image was obtained at various times after a pulse voltage of \( V_{\text{pulse}} = \text{Vds} = \text{Vgs} = -100 \text{ V} \) were applied to the gate and drain electrodes. At \( t = 0 \text{ ns} \), the laser pulse coincides with the rising edge of the voltage pulse, and SHG signals were found near the edge of source electrode, indicating that carrier injection just started, and a very high Laplace field was formed only around source electrode. Interestingly, as clearly shown in the image, the emission band of SHG signal gradually moved in the channel from source to drain electrode with elapsed times of 100, 200 and 400 nsec. Propagation of the emission band from source electrode, not from drain, evidently shows the hole-injection followed by hole-propagation from Au-source electrode. That is, pentacene FET shows a p-type behaviour.
As mentioned above, it is clear that we can probe a long-range carrier motion in organic materials by monitoring the propagation of the electric field diverging from the moving carrier. In our recent study, we could show that the peak and shoulder of SHG signals migrate along the channel in a way of square-root of time. Further the technique can apply to probing carrier motion in Organic solar cells, Organic Electroluminescence devices and so forth.

Figure 1. Experimental configurations and results of the TRM-SHG measurement.

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