Non-Contact Measurement of Charge Carrier Mobility in Inorganic and Organic Semiconductor Materials

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1. Introduction

Recent successful reports on the variety of organic and/or organic-inorganic compounds with conjugated electronic systems based on covalent/non-covalent chemical bondings have extended rapidly the feasibility of the compounds as practical electronic devices. One of the most important properties of the materials is the mobility of charge carriers because the value is concerning and dominating all the device performance including switching rate, energy efficiency, reliability, etc. The optimization of the mobility value in a variety of the organic materials is the key issue to give the materials a chance to challenge the conventional inorganic semiconductor industries and substitute them in part by the organics.

One of the target values of the mobility in organic materials has been set at 1 - 5 $cm^2V^{-1}s^{-1}$ where the mechanisms of the charge carrier transport have been in face of drastic paradigm shift from thermally activated hopping processes (below) to the (ballistic) band conduction model (almost equivalent to the values in amorphous silicon). The higher values of mobility than the target have been reported in several conjugated organic crystals, however the other organic architectures have not reached in the range. The values of mobility in Si as a covalent crystal are ~ 1500 cm2V-1s-1 (electron) and ~500 $cm^2V^{-1}s^{-1}$ (hole), respectively which are the second target values for the organics. The "covalent" nature of c-Si with relatively small overlap integral of Si sp3 atomic orbitals predicts that the higher values of mobility are expected intrinsically in the other π- and/ or σ-conjugated systems of the macromolecules and supramolecular architectures. To date, the methodologies of time-of-flight (TOF), field-effect-transistor (FET), space-charge-limited-current (SCLC) are often the choices for the determination of the values of mobility in the organic materials. Recently we have developed time-resolved microwave conductivity (TRMC) measurement for the determination of the mobility in the materials. Unlikely to the DC techniques of TOF and FET where the translational motion of charge carriers induced by the external electric field, an alternating-current (AC) method of TRMC is probing the motion of charge carriers on conjugated molecules and their assemblies without contacts (electrode-less)[1-6]. This has been applied to elucidate the intrinsic value of mobility free from the above mentioned "disturbing" processes, because the translational motion of charge carriers on the molecular materials is limited within the nm-scaled spatial area. The size of the area is depending on the frequency of the AC electric field and the mobility of charge carriers, and the "tuning" of the size by the frequency can deduce not only the value of mobility but also its dependence on the "shape" of the molecules and the conjugated molecular orbitals[3-11]. In the present paper, the independent three methodologies: TRMC, FET, and TOF have been applied to determine the value of mobility in the conjugated macromolecular systems, and we discuss comprehensively the mechanisms of charge carrier transports in the materials in view of what the determinant processes of the charge carrier transport in the respective three measurement systems.

2. Mehods

In-situ time-resolved microwave conductivity (TRMC) and transient absorption spectroscopy (TAS) measurements of a variety of materials were carried out using mainly a X-band microwave as a probe. A microwave cavity in TE102 resonance mode was designed and set in the circuit, loaded with materials at the point of maximum amplitude of the standing microwave. The power of the microwave incident into the cavity was set at 1~5 mW which does not disturb the charge motion and geminate ion recombination. The details of the measurement system will be reported elsewhere. The SHG(532 nm), THG (355 nm), and FHG(266 nm) from Nd:YAG laser (Spectra Physics, IN-DY-HG, FWHM 1-8 ns) and ArF excimer laser (193 nm, Lambda Physik, Optex, FWHM 15-20 ns) were used as an excitation source. The spot size of the laser was adjusted at 5 mm diameter, and its power was set sufficiently lower than 5 $mJcm^{-2}$ not to cause the sample damages. Continuum white light from Xe lamp was used as a probe light and guided into the microwave cavity. The probing light for TAS measurement was led to a grating unit (Hamamatsu, C5094) and scanned by a wide-dynamic-range streak camera (Hamamatsu, C7700). The streak image was collected via a CCD camera (Hamamatsu, C4742-95). The experiments were carried out at room temperature.

3. Discussions

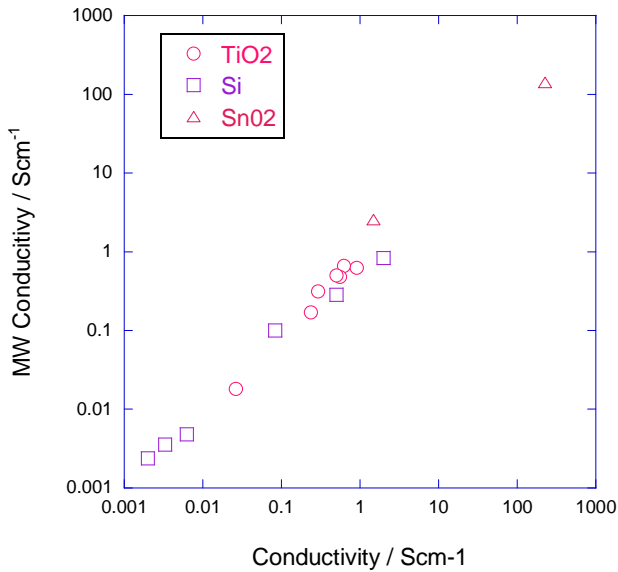The TRMC measurement with a resonant cavity is

Figure. Correlation between the values of electric conductivity estimated by non-contact microwave conductivity measurement and four-contacts measurement techniques in inorganic electric semi-conducting and conducting materials of Si(crystalline and amorphous), TiO_2, and SnO_2 with a variety of dopant concentrations.

based on a microwave property that the change of reflected microwave power (ΔP_r) is proportional to the change of conductivity ($<\Delta \sigma>$) induced by laser or radiation.

$$<\Delta \sigma> = \frac{1}{A}\frac{\Delta P_r}{P_r} \qquad (1),$$

where A is a sensitivity factor of a resonant cavity and is determined by a Q value, a dielectric constant, a resonant frequency, and a ratio of incident microwave power to reflected microwave power. In the case of flash photolysis (FP)-TRMC, the following equation is obtained using Lambert-Beer's law,

$$\phi \sum \mu = \frac{1}{e \cdot A \cdot I_0 \cdot F} \cdot \frac{\Delta P_r}{P_r} \qquad (2),$$

where ϕ, $\Sigma\mu$, e, I_0, and F are the quantum yield of charge carrier generation, the sum of charge carrier mobilities, the charge of an electron, incident photon density, and a filling factor in the cavity (overlap ratio of special distribution of charge carriers and microwave electric field strength in the cavity), respectively. The TRMC signals ($\Delta P_r/P_r$) are converted directly to $\phi\Sigma\mu$ by this equation. The filling factor is calculated based on the optical absorption profiles of the sample reflecting the charge carrier distribution within the sample dimension.

Non-contact MC measurement technique gives directly the value of electric conductivity mounted in the microwave cavity via eq. (2). The charge carriers, however, show no translational motion in the media, thus the direct electric current is not observed in the present system. To confirm the origin of electric conductivity measured with the MC technique, the values of conductivity measured in a series of inorganic semi-conducting and conducting materials

with different dopants and charge carrier concentrations are compared relatively in terms of the conductivity measurement techniques. Figure plots the value of conductivity estimated by the MC technique vs. those estimated by the conventional techniques including four point measurements and/or Hall effect measurements. The values coincide with each other in the extremely wide range of 6 orders of magnitudes, suggesting the consistent origin of conductivity in these techniques. The plots contain the conductivity values of both electrons and holes as respective major carriers, hence the values observed in p and n type semiconductors. However good correlation between the conductivities determined by MC and other techniques, indicating the MC technique being independent on the major charge carrier species.

The conductivity values estimated bay Hall effect measurement leads the estimates of mobility of the major charge carriers, and the values of mobility in the present materials distribute in the range of $1 \sim 2000$ $cm^2V^{-1}s^{-1}$. It should be noted that the good correlation in figure also suggest the enough reliable estimates of mobility by MC technique in the range of charge carrier transport mechanism dominated by a band conduction scheme.

Conjugated polymers, molecules, and supra-molecular systems have been considered to organize a developed conjugated electronic system within the short (relatively short to the inorganic materials) range of order. A typical segment length in a rigid, rod-like backbone of conjugated polymer chains is a few nm, which is in the same range of order in the molecular aggregates. This short range "pseudo band-like view" of conjugated molecular orbitals provides the best systems evaluated by the present MC technique. We have successfully applied the present MC technique for these materials where the charge carriers have been injected by the direct photo-induced electron transfer reactions.[3-11] We also discusses the results on the value of mobility within isolated conjugated polymer backbones in a variety of configurations, and within organic conjugated materials in a variety of molecular aggregation, leading to the design of the materials optimized for the charge carrier transport in the present paper.

References
[1] J. Warman et al., *J. Am. Chem. Soc.*, **127** (2005) 14257.
[2] R.J.O.M. Hoffman et al., *Nature*, **392** (1998) 54.
[3] S. Seki, et al., *Adv. Mater.*, **14** (2002) 228.
[4] S. Seki, et al., *J. Am. Chem. Soc.*, **126** (2004) 3521.
[5] A. Acharya, et al., *J. Phys. Chem. B*, **109** (2005) 10015.
[6] A. Saeki, et al., *Adv. Mater.*, **20** (2008) 920.
[7] R. Yamagami, et al., *J. Am. Chem. Soc.*, **128** (2006) 2213.
[8] Y. Koizumi, et al., *J. Am. Chem Soc.*, **128** (2006) 9036.
[9] Y. Yamamoto, et al., *Science*, **314** (2006) 1761.
[10] S. Seki, *Polymer J.*, **39** (2007) 277.
[11] T. Amaya, et al., *J. Am. Chem Soc.*, **131** (2009) 408.