Quantitative evaluation of spatial scale of carrier trapping at grain boundary by GHz-microwave dielectric loss spectroscopy

W. Choi¹, Y. Tsutsui¹, T. Miyakai², T. Sakurai¹, S. Seki¹

¹ Kyoto University, Kyoto, Japan.
² Osaka University, Osaka, Japan.

E-mail: seki@moleng.kyoto-u.ac.jp

Abstract. Charge carrier mobility is an important primary parameter for the electronic conductive materials, and the intrinsic limit of the mobility has been hardly access by conventional direct-current evaluation methods. In the present study, intra-grain hole mobility of pentacene thin films was estimated quantitatively using microwave-based dielectric loss spectroscopy (time-resolved microwave conductivity measurement) in alternating current mode of charge carrier local motion. Metal-insulator-semiconductor devices were prepared with different insulating polymers or substrate temperature upon vacuum deposition of the pentacene layer, which afforded totally four different grain-size conditions of pentacene layers. Under the condition where the local motion was determined by interfacial traps at the pentacene grain boundaries (grain-grain interfaces), the observed hole mobilities were plotted against the grain sizes, giving an excellent correlation fit successfully by a parabolic function representative of the boarder length. Consequently, the intra-grain mobility and trap-release time of holes were estimated as 15 cm² V⁻¹ s⁻¹ and 9.4 ps.

1. Introduction

Organic field-effect transistors (OFETs) are of great interest in organic electronic devices due to their low-cost and light-weight characters attractive for practical applications [1–3]. Pentacene is a benchmark organic compound as a semiconducting layer in OFETs that has been studied over the last quarter century. The landscape of the overall charge transport in pentacene have been intensively investigated by field-induced electron spin resonance (FI-ESR) [4–6], electric field induced second harmonic generation (EFI-SHG) [7,8], and photoelectron spectroscopy [9–11], and successfully interpreted by the representative trap-release model of positive charge carriers. In contrast, the local scale carrier mobility as well as the interfacial trap density in pentacene were evaluated by field-induced time-resolved microwave conductivity (FI-TRMC) [12,13], leading to a characteristic upper limit of intra-grain in-plane hole mobility. It is known that the pentacene thin film shows diverse morphologies depending on the deposition condition and underlying material or substrate [14–17]. The grain size of pentacene has been revealed to show the positive correlation to their FET mobility, however few studies achieved the quantitative evaluation on the correlation between the morphology and charge carrier transport [18–20]. This is most likely due to the strong deterioration in the carrier mobility by the trap, since direct current method requires long-range translational motion of charge carriers detected as an electric current. In contrast to such direct current methods largely influenced by the carrier trapping, the charge transport property is spatially averaged in the FI-TRMC method,
regardless of the carrier state—free or trapped. Here we report that this distinct feature of FI-TRMC enables to estimate the spatial and temporal scale of the grain-boundary trapping, which is discussed based on the quantitative evaluation of the correlation between the grain size and the local scale mobility.

2. Experimental

2.1. Fabrication of Metal-Insulator-Semiconductor (MIS) Devices.
The MIS devices used in this study was fabricated as follows; (1) A quartz substrate (4.9 × 50 mm², 1 mm thick) was treated with UV–O₃ prior to use; (2) Ti (adhesion layer, 5 nm) and Au (gate electrode, 30 nm) layers were successively deposited on the quartz substrate by DC sputtering and thermal vacuum deposition, respectively; (3) As the first insulating layer, a 300-nm-thick SiO₂ was deposited by RF sputtering; (4) As the second insulating layer, a 250-nm-thick poly(methyl methacrylate) (PMMA; Sigma-Aldrich) or 250-nm-thick polystyrene (PS; Sigma-Aldrich) layer was spincoated from its 3 wt% PS solution in toluene; otherwise, a 250-nm-thick layer of Cytop® (AGC Chemicals) was spincoated; (5) Thermal annealing was carried out for 1 h to remove residual solvent at 100 °C for PMMA and PS or at 180 °C for Cytop®; (6) a 75 nm thick pentacene layer, was thermally evaporated at a rate of 0.03 nm s⁻¹ under 2 × 10⁻⁴ Pa, with controlling the temperature of the substrate (Tsub); (7) A 30-nm-thick top Au electrode was overcoated by vacuum deposition.

2.2. TRMC@Interfaces Measurements.
The microwave circuit was constructed using a waveguide system with homodyne setup, as described in our previous report [12,13]. The TRMC@Interfaces measurements were carried out with a microwave at 9 GHz from a signal generator (Rohde & Schwarz, SMF 100A). After the MIS device was loaded in the microwave cavity, a pulse gate bias voltage \( V_g(t) \) at an interval of 50 ms was applied based on a multifunction generator (NF Corporation, WF 1973). The current injected into the semiconductor–insulator interface (\( I(t) \)) was monitored using a digital phosphor oscilloscope (Tektronix, MDO 3022). Simultaneously, the reflected microwave (\( P_r(t) \)) is first amplified with a high gain FET amplifier (Gain 30 dB, 8 to 12 GHz, Ciao CA812-304), then evolved by a Schottky diode, and monitored by the oscilloscope. All experiments were conducted under ambient atmosphere at room temperature.

2.3. Characterization of Semiconducting Layers.
A 10-nm thick pentacene was thermally deposited on PMMA, PS, and Cytop® with the same condition to the device fabrication. The morphology of pentacene was characterized by a tapping-mode atomic force microscope (AFM: SII NanoTechnology, SPI-4000, Nanonavi II) using silicon cantilevers with a frequency of 150 kHz and spring constant of 9 N/m (OMCL-AC200TS-R3, OLYMPUS). The average grain radius is estimated from the topographic image in AFM (Figure 2).

3. Results and discussion
The schematic illustration of the measurement setup is shown in Figure 1. Electric field-induced hole carriers were injected at the pentacene–insulator interface in the MIS device with applied pulse gate biases, where these holes were oscillated by 9 GHz microwave.
As summarized in Table 1, the averaged grain radius and its distribution was 102.49 ± 0.26, 225.46 ± 0.09, 121.78 ± 0.35, and 76.86 ± 0.18 nm for PMMA, PMMA ($T_{\text{sub}} = 80 \, ^{\circ}\text{C}$), PS, and Cytop®, respectively. It was obvious that grain sizes were different among the four devices, which was caused by the different surface energy of the insulators.

With FI-TRMC, a dielectric loss is induced by the charge carriers injected into the pentacene–insulator interface of the MIS device in the microwave cavity [21–24]. The change in reflected microwave power ($\Delta P_r$) is associated with the change of pseudo conductivity ($\Delta N\mu$) as follows:

$$\Delta P_r = K\Delta N\mu, \quad (1)$$

where K, N and $\mu$ is the experimentally determined sensitivity factor which was previously calibrated to be $2.4 \times 10^{-21}$ W V s cm$^{-2}$ [12], the number of charge carriers, and the charge carrier mobility, respectively. In this study, the values of $\Delta N\mu$ for various $V_g$ are determined from the observed $\Delta P_r$. On the other hand, the number of injected charge carriers ($N_{\text{inj}}$) is estimated independently from the integration of $I(t)$ measured with the external circuit:

$$N_{\text{inj}} = \frac{1}{e} \int I(t) dt, \quad (2)$$
where \( e \) denotes the elementary charge. \( N_{\text{inj}} - \Delta N\mu \) plots for different second insulating layer are shown in Figure 3. The slope and intercept of the plot in high \( V_g \) region signify the charge carrier mobility and the number of trap sites, respectively [13, 24].

![Figure 3](image.png)

**Figure 3.** Correlation between the number of injected charge carriers \( (N_{\text{inj}}) \) and pseudo electrical conductivity \( \Delta N\mu \) for various insulators.

| Insulator          | Grain radius / nm | Hole mobility / cm² V⁻¹ s⁻¹ | Trap density / 10¹² cm⁻² |
|--------------------|-------------------|-----------------------------|--------------------------|
| PMMA               | 102.49 ± 0.26     | 11                          | 0.94                     |
| PMMA \( (T_{\text{sub}} = 80 ^\circ \text{C}) \) | 225.46 ± 0.09     | 13                          | 1.0                      |
| Polystyrene        | 121.78 ± 0.35     | 11                          | 1.0                      |
| Cytop®             | 76.86 ± 0.18      | 6.9                         | 0.89                     |

Table 1. Summary of grain sizes, hole mobility, and trap density.

The trap sites can be mainly categorized into 3 causes: (1) chemical impurities in the pentacene layer [25], (2) physical defects in the pentacene layer (mainly accumulated at the grain boundary [26], but structural imperfection and surface roughness [27] are also included), and (3) random potential from the dielectric layer [28]. Herein, (1) is considered in the same level for all samples. Since the charge carriers are only locally perturbed in FI-TRMC measurement, the measured mobility is insensitive to (3) the surface roughness itself and the random potential from the dielectric layer. As shown in Table 1, the density of interfacial trap sites is almost constant despite of the change of interface, indicating that this deep trap sites originate rather from the pentacene such as pentacenequinone chemical impurities [25] than the boundary structure of gate dielectrics [8]. Microwave-perturbation silent characteristics imply the deep-enough stabilization of the charge carriers at trap sites where the thermal activation energy cannot cause even trap-release processes, and thus no equilibrium can be postulated to lead certain amount of free (mobile) charge carriers. Consequently, both the relaxation time of the momentum and the effective mass of the charge carriers in intra-grain region of pentacene is independent to the organic insulating layer, suggesting that the observed difference in the charge carrier mobility resulted from (2), the difference in grain sizes.

On the assumption of the “sallow” traps accumulated at the grain boundary, we built a simple geometrical model with two concentric circles to assess quantitatively the reduced mobility of holes via thermally activated trap-release processes with an equilibria. Here, the outer circle represents a single grain while the inner one indicates an area with intra-grain hole mobility. In the area between
the two circles, holes were trapped at the grain boundary. This theoretical model relies on the fact that spatial information of mobility is uniformly averaged in FI-TRMC measurement. Based on this model, the evaluated mobility can be expressed as following equation:

$$\mu = \frac{\mu_{\text{intra}} (r - L)^2}{\mu^2},$$

where $\mu_{\text{intra}}$, $r$ and $L$ denote the intra-grain mobility, average radius of the grain, and spatial length dominated by the grain boundary (microwave-silent region), respectively. Here, the charge carrier mobility in grain boundary is assumed as 0 because it is much lower than the intra-grain mobility [26,29]. As shown in Figure 4, $r$ dependence of $\mu r^2$ is clearly fitted with the parabolic function.

![Figure 4](image)

**Figure 4. $r$ dependence of $\mu r^2$.** Parabolic dependence is shown as a solid line.

From the parabolic fit, $\mu_{\text{intra}}$ and $L$ are derived as 15 cm$^2$ V$^{-1}$s$^{-1}$ and 19 nm, respectively. The turn-over period of the electric field of the 9 GHz microwave is much longer than the time scale of the charge carrier scattering. Consequently, the obtained characteristics from FI-TRMC reflect the equilibrium state of the charge carriers. Since the equilibrium between the free carriers and the traps of the grain boundary is established, the average time of the carrier trapping is same with the average time of the trap-release. That implies that the diffusion length for the trap-release time is the spatial length of the carrier-trapping region. The trap-release time ($\tau$) in the grain boundary could be evaluated from the following diffusion equation:

$$L = \left(\frac{\mu_{\text{intra}} kT}{e \tau}\right)^{1/2},$$

where $k$ and $T$ denote the Boltzmann constant and temperature, respectively. From this equation, $\tau$ is derived as 9.4 ps. In relation to this analysis, there has been little work to quantify the attempt-to-escape frequency of the trapped carriers in organic semiconductors. Several studies to evaluate the attempt-to-escape frequency show very wide-range values ($10^8$–$10^{14}$ Hz) [30–33]. The estimated trap-release time indicates that the attempt-to-escape frequency in the grain boundary of pentacene ($1.0 \times 10^{11}$ Hz) is comparable to that of the inorganic semiconductors ($10^{11}$–$10^{13}$ Hz). The other detailed energetic information on the trap sites such as trap depth and energetic distributions will be revealed precise analysis of frequency dependent microwave conductivity based on the perturbation model [34].
with the disclosed value of $\tau$ in the present study, which will interpret the total landscape of the hole transport mechanism in pentacene.

4. Conclusions
Dielectric loss spectroscopy using 9 GHz microwave was demonstrated for pentacene-based metal-insulator-semiconductor (MIS) devices with field-induced hole carriers. Four MIS devices with different crystalline grain sizes of pentacene were prepared by controlling the substrate temperature at r.t. or 80 °C and choosing different insulating polymers including poly(methylmethacrylate), polystyrene, and Cytop®. Considering that interfacial traps originate from the pentacene grain boundaries, the correlation between grain sizes and observed hole mobilities were plotted and successfully fit by a parabolic function. Consequently, the intra-grain hole mobility and trap-release time of the trapped carriers were estimated as 15 cm² V⁻¹ s⁻¹ and 9.4 ps. The present work provided a general possibility that the microwave-based technique enables to estimate the intra-grain intrinsic mobility and trap-release time of charge carriers in semiconductors from the simple theoretical model, which is important for further development of organic electronics.

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