Rapid Evaluation of Electron Mobilities at Semiconductor–Insulator Interfaces in an Ambient Atmosphere by a Contactless Microwave-Based Technique

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Supporting Information

ABSTRACT: Intrinsic mobility of electrons at the interfaces between crystalline organic semiconductors and insulating dielectric polymer films was rapidly evaluated in an ambient atmosphere by TRMC@Interfaces, a noncontact and nondestructive method based on dielectric loss spectroscopy of microwaves. By just preparing simple metal–insulator–semiconductor devices, local-scale motions of charge carriers injected into the interface by pulses of gate bias voltage were monitored through reflected microwave changes, resulting in the evaluation of local-scale charge carrier mobilities together with the value of trap density at the interface. The evaluated high electron mobilities of 12 cm² V⁻¹ s⁻¹ for N,N'-bis(cyclohexyl)naphthalene-1,4,5,8-bis(dicarboximide) (DCy-NDI) and 15 cm² V⁻¹ s⁻¹ for N,N'-dioctylperylen-1,4,5,8-bis(dicarboximide) (DC8-PDI) are the benchmarks for organic semiconducting materials that are comparable with the highest ones reported from the field-effect transistor devices. The present TRMC@Interfaces was found to serve as a rapid screening technique to examine the intrinsic performance of organic semiconducting materials as well as a useful tool enabling the precise discussion on the relationship among their local-scale charge carrier mobility, thin-film morphology, and packing structure.

INTRODUCTION

Versatile and convenient methods to access the charge carrier transport property of organic semiconductors are highly in demand along with the recent progress of organic electronics. Representative techniques commonly used so far include the Hall effect, field-effect transistors (FETs), time-of-flight, and space charge limited current, where the long-range translational motion of electrons in the device.23 However, FETs has several requisites to operate, such as proper injection of electrons from a source to the semiconductor layer, and then to drain. Thus, a tedious device optimization process is required before FET operation, resulting in the time-consuming issue to judge the potential of the target semiconducting materials. Microwave dielectric loss spectroscopy has provided an electrodeless platform for the measurement of local-scale motion of charge carriers injected by ionizing radiation,5,6 photocarrier injection into organic heterojunctions,7–9 and/or inorganic semiconductors,10,11 demonstrating the versatile and prompt diagnosis of mobility free from the device optimization processes. A planar microstrip microwave resonator was also designed, offering a wide flexibility of the measurement system for electron/hole-transferring semiconductor films.12 We have recently developed a microwave-based evaluation technique (time-resolved microwave conductivity: TRMC@Interfaces)13–17 that uses dielectric loss spectroscopy of field-induced charge carriers in simple metal–insulator–semiconductor (MIS) devices. In this method, hole or electron carriers are injected at the insulator–semiconductor interfaces of the MIS device by applying pulse gate bias (V_g) (Figure 1b). Simultaneously, the local-scale motions of the charge carriers are independently monitored by microwave-based dielectric loss spectroscopy toward the MIS device set in a resonant cavity. This fully experimental technique eventually provides local-scale, intrinsic hole/electron mobility as well as trap density particularly at the insulator–semiconductor interfaces. Using this technique, we have reported the mobility of pentacene and heteroacene derivatives, revealing high intrinsic hole mobilities (e.g., ~6 cm² V⁻¹ s⁻¹ for pentacene).13,14 In the present study, we focused on the rapid evaluation of the electron transport property even in an ambient atmosphere with the TRMC@Interfaces technique. Investigating n-type semiconducting character is a more challenging issue than that of holes due to the effect of impurities containing water and oxygen that severely inhibit the long-range translational motion of electrons in the device.
Thus, evaluation of electron transport property has mostly been addressed under high-vacuum conditions. Here, we tried to determine electron mobilities of relatively air-stable arylenediamides in an ambient atmosphere with a simple device structure. Because the characterized mobilities are dominantly based on the intragrain motion, the observed high-mobility values were discussed correlating with the crystalline order of semi-conducting molecules.

■ RESULTS AND DISCUSSION

$N,N$-bis(cyclohexyl)naphthalene-$1,4,5,8$-bis(dicarboximide) (DCy-NDI),$^{18}$ $N,N'$-dioctylperylen-$1,4,5,8$-bis(dicarboximide) (DC$\text{g}$-PDI),$^{19}$ and $N,N'$-bis(cyclohexyl)perylen-$1,4,5,8$-bis(dicarboximide) (DCy-PDI)$^{20}$ are chosen as semiconducting layer materials (Figure 1a) because these are well-known n-type materials applied in FETs and organic photovoltaic devices.$^{21,22}$

MIS devices were fabricated according to the previous reports.$^{13,14}$ (see the Experimental Section). The microwave circuit was constructed using a waveguide system with a homodyne setup (Figure 1b) and our previous report.$^{13}$ Other detailed experimental methods are described in the Experimental Section. As shown in Figure S1 (Supporting Information), the resonance of microwave was successfully obtained when a MIS device was loaded in the cavity. It should be noted that the change in the capacitance value upon applied gate bias was monitored by means of the displacement current measurement (DCM) of the MIS device, suggesting that charge carriers were certainly injected into the insulator–semi-conductor interface (Figure S2).

Evaluation of Electron Mobility for DCy-NDI in an Ambient Atmosphere and at Controlled Temperature. Figure 2 shows typical microwave and current transients for a DCy-NDI-based MIS device. After the MIS device was set in the cavity, a 50 ms pulse gate bias ($V_g(t)$) was applied to inject electrons at the DCy-NDI–poly(methyl methacrylate) (PMMA) interface. Accordingly, electric current ($I(t)$) was monitored, which can be converted to the charge amount ($q(t)$) profile by integrating $I(t)$ with time (Figure 2a). In parallel with the current-flow monitoring, the changes in reflected microwave power ($\Delta P_r(t)$) were confirmed to respond to the gate bias voltages (Figure 2b). Although the relatively slow decay of $\Delta P_r$ at 50–80 ms in Figure 2b suggested the presence of some barrier for the discharging process of electrons, the shape of the $\Delta P_r(t)$ curves was basically similar to that of the $q(t)$ traces, proving that the
resulted dielectric loss phenomenon was contributed by the injected electrons. In the TRMC@Interfaces measurement, the transient dielectric loss ($\Delta(1/Q)$) in the cavity is proportional to the conductivity changes ($\Delta\sigma$)

$$\Delta P \propto Q^{-1} \Delta \sigma = \frac{1}{\omega \varepsilon} e \Delta n \mu$$

(1)

where $e$, $\varepsilon$, $\omega$, and $n$ are the elementary charge, dielectric constant, angular frequency of microwave, and change in the charge carrier density, respectively. The linearity between $\Delta P$ and $\Delta(1/Q)$ was preserved in the present range of $\Delta P$, and hence, the pseudoconductivity ($\Delta N \mu$) was calculated from the saturated value of $\Delta P$, for each $V_g$ using the reported calibration equation below.

$$\Delta P = 2.4 \times 10^{-23} (\Delta N \mu)$$

(2)

On the other hand, the numbers of injected charge carriers ($N_{inj}$) were easily calculated from the saturated value of $q(t)$ (at 50 ms). From the sets of pseudoconductivity $\Delta N \mu$ and injected carriers $N_{inj}$, the $N_{inj} - \Delta N \mu$ plot was obtained (Figure 2c), where the first derivative represents electron mobility. It comprises four regions: (i) the silent region of $N_{inj} < 0.5 \times 10^{11}$, (ii) high-mobility region, (iii) slightly lower mobility region, and (iv) saturation region. The first silent region corresponds to carrier trapping at the interface ($n_{trap} \sim 5 \times 10^{11}$ cm$^{-2}$). After filling up the traps, the second region appears where a higher mobility is estimated than that of region (iii). We consider that this second region reflects intrabulk mobility. With a weak gate bias, charge carriers are injected not only at the interface but also into the bulk region because of thermal diffusion. As the interface is affected by the random potential of insulators, it can be expected that the bulk mobility is higher than that near the interface. For this reason, we ascribed the mobility estimated from region (ii) to the interfacial mobility. Application of further higher gate voltages results in the saturation of the mobility (iv). The explanation of high-injection region is debatable, but there is a clue to elucidate this phenomenon: the saturation of microwave signal in the high-injection regime completely disappears under vacuum conditions (Figure S3). This contrast was observed in different devices with reproducibility. We, at present, have no absolute evidence but suppose that oxygen or water molecules could deteriorate the conduction of electron in the high concentration of anionic species. It should be noted that the estimated mobility (slope) was comparable between ambient atmosphere and vacuum conditions for each DCy-NDI device.

The XRD analysis of the DCy-NDI MIS device revealed an ordered layer structure ($d_{100} = 18.1$ Å) of NDI cores (Figure 2d), where the layer distance agrees with the reported single crystal structure. A smooth surface of polycrystalline semiconducting layer with a small root-mean-square roughness of 4.0 nm was visualized by atomic force microscopy (AFM) (Figure 2e and Table S1). The transport mechanism of the...
local-scale motions of these highly mobile charge carriers is another important subject. The prototype of low-temperature TRMC@Interfaces systems has been developed to approach the temperature dependence of carrier mobility. As a trial using the DCy-NDI-based MIS device, the obtained $N_{inj}-\Delta N\mu$ plot from 210 to 300 K indicated a slightly positive correlation between temperature and electron mobility with a small activation energy of $\sim 60$ meV (Figure S4). This observation implies that the local-scale electron conduction at the DCy-NDI/PMMA interface relies principally on a hopping-like mechanism, though there is a large electron mobility of $\sim 10$ cm$^2$ V$^{-1}$ s$^{-1}$.26

Evaluation of Electron Mobility for DCy-PDI and DC$_8$PDI in an Ambient Atmosphere. To screen a series of n-type materials for TRMC@Interfaces, DCy-PDI MIS devices were investigated under an identical vapor-deposition condition to that of DCy-NDI. The proposed core-size effect,27 where a larger $\pi$-system is favorable for intermolecular charge transport in view of Marcus theory, was another important interesting subject by studying extended $\pi$-conjugated materials with the present TRMC technique probing local-scale charge carrier motions. However, the microwave response was very small for the DCy-PDI MIS device (Figure 3a), and it is difficult to distinguish with noise signals. In fact, mobility evaluation is not possible from the $N_{inj}-\Delta N\mu$ plot (Figure 3c). The observation of film morphology and measurement of packing structure indicated that the DCy-PDI film formed a different packing structure from the reported crystalline phase.28 One of the striking features in the observed XRD pattern was the lamellar...
The periodicity of \( d'_{001} = 28.9 \, \text{Å} \) was far larger than the reported axes (Figure 3e). It is probably because PDI cores have a strong intermolecular \( \pi-\pi \) interaction and thus are trapped to form a kinetically stabilized structure at the PMMA surface at room temperature (r.t.). With this hypothesis, a new MIS device was fabricated by controlling the substrate temperature \( T_{\text{sub}} \) at 80 °C during the vapor deposition. Then, a set of sharp diffraction peaks was observed (Figure 3f), where the spacing of \( d_{001} = 18.4 \, \text{Å} \) corresponds to one of the reported lattices. Moreover, AFM images disclosed that the crystalline grains of the DCy-PDI surface (Figure 3h) were highly developed with \( T_{\text{sub}} = 80 \, \text{°C} \) rather than the case with \( T_{\text{sub}} = \text{r.t.} \). As a consequence, a small but significant increase in the microwave response was observed (Figure 3b). The estimated electron mobility by TRMC@interfaces is \( \mu_e = 0.2 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \) (Figure 3d).

Another PDI derivative, DC8-PDI, was examined in a similar way by preparing two types of MIS devices with \( T_{\text{sub}} = \text{r.t.} \) and 80 °C. As the \( \pi-\pi \) stacking tendency was more obvious for this system, drastic difference in TRMC@interfaces measurements was confirmed. However, in this case, we concluded that the difference originated from the uniformity of the films that determine the sufficient/insufficient injection of electrons at the PMMA–DC8-PDI interface. In the case of \( T_{\text{sub}} = \text{r.t.} \), an estimated electron mobility of \( \mu_e = 0.9 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1} \) was recorded (Figure 4a). Although the obtained weak diffraction peaks in XRD were likely assigned to a reported crystalline packing (Figure 4c), AFM observation revealed that the semiconductor layer was composed of nonuniform aggregates (Figure 4e) probably due to the very strong \( \pi-\pi \) interactions.

Spatial Size of Mobile Charge Carriers and Structure–Mobility Correlations. On the basis of Kubo’s equation derived from the Einstein–Smoluchowski relation\(^{31}\)

\[
\Delta x = (\mu k_B T f e^{-1})^{1/2}
\]

the spatial size \( \Delta x \) of statistical local motion of charge carriers was estimated during the turn-over period of the electric field of the 9 GHz microwave (see the Supporting Information in detail). As summarized in Table 1, the \( \Delta x \) values range from 5 to 66 nm, all of which appear much smaller than the crystalline grain size, judging from the corresponding AFM images (Table S1). Therefore, the evaluated mobility dominantly reflects the
intragrain charge carrier motions at semiconductor—insulator interfaces.

The relationship between local-scale structure and property can be discussed on the basis of the XRD patterns and charge carrier mobility evaluated by TRMC@interfaces. It is considered that the observed difference between the local-scale electron mobilities of DCy-PDI and DC8-PDI is dominantly due to the dimensionality of the electron transport pathways. DC8-PDIs adopt a herringbone structure25,30 that enables two-dimensional conductive routes parallel to the direction of the electric field of the microscope, whereas electron transport pathways of DCy-PDIs align linearly25 parallel to the electric field. Even in the local area probed by the present TRMC@interfaces method, thermal fluctuations at r.t. may disturb the one-dimensional conductive pathways of charge carriers, whereas the two-dimensional conductive network is less affected.

CONCLUSIONS

As exemplified by the simple MIS devices containing a series of arylenediimide derivatives, we demonstrated the evaluation of local-scale, intrinsic electron mobility at insulator—semiconductor interfaces even in an ambient atmosphere. The estimated mobility values reflect nanometer-scale motion of the injected charge carriers at the interface. In fact, the mobility values are mostly larger than those reported for FET devices and comparable with the highest ones reported so far, suggesting the benchmark charge carrier mobilities of target semiconducting materials. We believed that the present TRMC@interfaces method serves as a rapid screening technique as well as a useful tool to discuss the relationship among the local-scale charge carrier mobility, thin-film morphology, and packing structure of organic semiconductors.

EXPERIMENTAL SECTION

Fabrication of MIS Devices. The MIS devices used in this study were fabricated as follows: (1) A quartz substrate (4.9 × 50 mm², 1 mm thick) was treated with UV−O₃ before use; (2) Ti (adhesion layer, 5 nm) and Au (gate electrode, 30 nm) layers were successively deposited on the quartz substrate by direct-current sputtering and thermal vacuum deposition, respectively; (3) As insulating layers, a 300 nm-thick SiO₂ layer was deposited by radio-frequency sputtering, and a 250 nm-thick PMMA (Alrich) layer was deposited by spin-coating from a 3 wt % PMMA solution in toluene; (4) Thermal annealing was carried out at 100 °C for 1 h to remove residual solvent; (5) DCy-NDI, DC₈-PDI, or DCy-PDI (Figure 1a), of 30–50 nm thickness, was thermally evaporated at a rate of 0.03 nm s⁻¹ under 2 × 10⁻⁴ Pa; (6) A 30 nm-thick top Au electrode was deposited by vacuum deposition.

TRMC@Interfaces Measurements. The microwave circuit was constructed using a waveguide system with a homodyne setup, as described in Figure 1b and our previous report.13 The TRMC@Interfaces measurements were carried out using a microwave at 9 GHz from a signal generator (SMF 100A; Rohde & Schwarz). After the MIS device was loaded in the microwave cavity, a pulse gate bias voltage V₆(t) at an interval of 50 ms was applied based on a multifunction generator (WF 1973; NF Corporation). The current injected into the semiconductor—insulator interface I(t) was monitored using a digital phosphor oscilloscope (MDO 3022; Tektronix). Simultaneously, the reflected microwave P(t) is first amplified with a high gain FET amplifier (Gain 30 dB, 8–12 GHz; Ciao CA812-304), then picked up by a Schottky diode, and monitored by the oscilloscope. All experiments were conducted under ambient atmosphere at r.t.

Characterization of Semiconducting Layers. The morphology of semiconducting layers was characterized by a tapping-mode atomic force microscope (SPI-4000, Nanonavi II; SII NanoTechnology) using silicon cantilevers with a frequency of 150 kHz and spring constant of 9 N/m (OMCL-AC200TS-R3; OLYMPUS). The molecular packing of semiconducting layers was analyzed by XRD measurements using an X-ray diffractometer (λ = 1.54 Å, MiniFlex600; Rigaku) with a semiconductor detector (D/teX Ultra; Rigaku). DCMs. Triangle voltage was applied to the MIS devices by a function generator (WF 1973; NF Corporation) equipped with a voltage amplifier. Transient current I₆(t) was picked up by a 30 kΩ terminal resistor serially connected to the MIS device and monitored by a digital oscilloscope (MDO 3022; Tektronix). On the basis of the following equation, the capacitance values were calculated.

$$I_{6(t)} = C \frac{dV}{dt}$$ (4)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00428.

Reflective microwave power spectrum, DCM results, N₉₀−ΔN₇₀ plot under vacuum, temperature dependence of electron mobility, summary of averaged grain size and root-mean-square roughness, discussion on the charge carrier injection in MIS devices, discussion on the relationship between crystalline sizes and diffusion length of carriers (PDF)

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Notes

The authors declare no competing financial interest.

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Table 1. Summary of the Parameters Studied by TRMC@Interfaces

| Tsub | μₑ (cm² V⁻¹ s⁻¹) | nexp (cm⁻³) | Δx (nm) |
|------|-----------------|-------------|---------|
| DCy-NDI | r.t. | 12 | 5 × 10¹¹ | 59 |
| DCy-PDI | r.t. | b | e | 5 |
| 80 °C | 0.2 | c | 8 |
| DC₈-PDI | r.t. | b | c |
| 80 °C | 15 | 2 × 10¹¹ | 66 |

“Substrate temperature during vacuum deposition of semiconductors (Tsub), evaluated electron mobilities (μₑ), trap density at the interface, and diffusion length of the charge carriers using the 9 GHz microwave. b:Not applicable for estimation of mobilities. c:Not applicable for estimation of trap density.

50 nm thickness, was thermally evaporated at a rate of 0.03 kΩ. On the basis of the following equation, the capacitance values were calculated.

$$I_{6(t)} = C \frac{dV}{dt}$$ (4)
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