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Direct Observation of Field-Induced Carrier Dynamics in Pentacene Thin-Film Transistors by ESR Spectroscopy

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1. Introduction

Electron spin resonance (ESR) is a useful method for investigating the microscopic nature of charge carriers in conducting materials. In particular, π-conjugated organic materials, such as conducting polymers [1] or molecular conductors [2], have been probed to investigate the movements of charge carriers and their interactions with their environments. Recently, Marumoto and his co-workers successfully detected ESR signals for field-induced charges accumulated at the interfaces of metal-insulator-semiconductor (MIS) device structures composed of organic semiconductor layers [3,4]. They discussed the origin of the ESR linewidth only in terms of the static viewpoint for field-induced charges, although the dynamics attract considerable attentions in physics as well as in applications associated with the recent striking advances in organic thin film transistors (OTFTs).

In this report, we present our recent studies for direct observation of field-induced carrier dynamics in pentacene thin-film transistors by ESR spectroscopy [5]. For this purpose, we fabricated the devices that show high mobility and are composed of nonmagnetic substrates and gate insulators. We observe Lorentzian ESR signals, whose linewidth depend on both gate voltage and temperature. We discuss the variation of ESR linewidth in terms of the motional narrowing associated with the field-induced charge dynamics in the OTFTs.

2. Experimental

We fabricated OTFTs with large-area pentacene channel layers for high-sensitivity ESR measurements; total area of pentacene film was 2.5×20 mm^2 on top of parylene C gate capacitance layer (4.5 nF/cm^2). Channel length and width were 1 mm and 20 mm, respectively. The device exhibits typical p-type transfer characteristics with the mobility of 0.6 cm^2/Vs in linear region and on/off ratio of more than 10^4. ESR measurements were carried out by X-band ESR spectrometer (JEOL, JES-FA200). Static magnetic field was parallel to the pentacene film. During the ESR measurements, gate voltage was kept applied as to the source electrode, while drain electrode is shorted with source electrode.

3. Results and Discussion

Application of negative gate voltage V_G allows one to clearly observe ESR signal whose intensity is proportional to the amplitude of V_G. No background ESR signal is detected in the device at zero gate voltage. The estimated number of 1/2 spins for field-induced ESR signals presents good agreement with the carrier number estimated from the gate capacitance.

Figure 1 (a) shows ESR spectra at various gate voltages at room temperature. ESR linewidth becomes narrower as the gate voltage increases. The *peak-to-peak* linewidth is as small as 35 μT at the highest gate voltage of −200 V. This unique gate-voltage dependence could be ascribed to the motional narrowing effect; motion of field-induced carriers average the inhomogeneous local magnetic field at each molecular sites. We can also find a clear evidence for the motional narrowing effect in the temperature dependence of ESR linewidth that is shown in Figure 1 (b) and Figure 2 (a). ESR linewidth becomes broader as temperature decreases in the range of 150 K ~ 50 K. It demonstrate that thermal carrier motion is suppressed at lower temperature and then the narrowing effect reduces. We note that the temperature dependence of the integrated ESR intensity clearly follows Curie law, while the peak height tends to decrease with lowering of temperature due to the broadening of the linewidth.

Here we give a brief discussion on the dynamics of hole carriers based on the variation of ESR linewidth with gate voltage and temperature. According to the motional narrowing theory, the linewidth is given as [6];

$$\Delta B_{1/2} = \gamma \left(\Delta B_{\mathrm{inhomo}}\right)^2 \tau_{\mathrm{C}} \qquad (1)$$

Here, $\Delta B_{1/2}$ is observed half width at half maximum, γ is gyromagnetic ratio of electron, $\Delta B_{\mathrm{inhomo}}$ is amplitude of

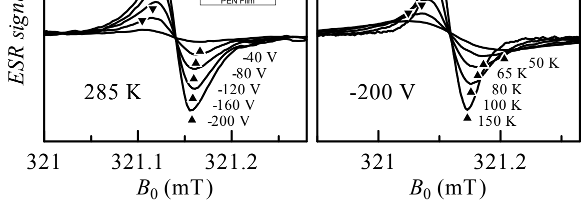

Fig. 1 (a) Field-induced electron spin resonance (ESR) spectra at various gate voltages at room temperature. (b) Field-induced ESR spectra at various temperatures at −200 V.

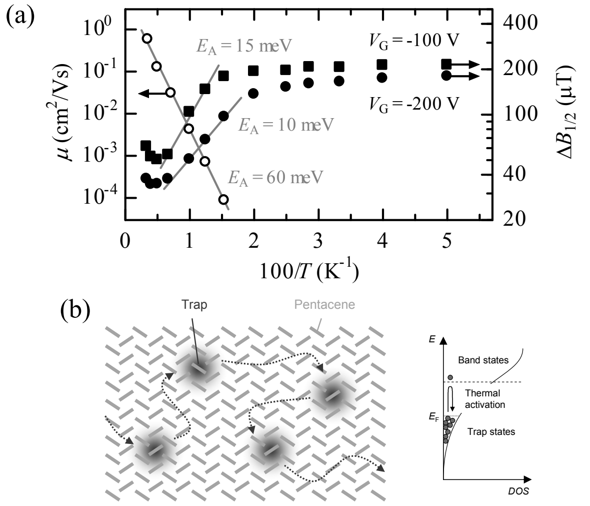

Fig. 2 (a) Arrhenius plot for temperature dependence of field-induced ESR linewidth and field-effect mobility. Activation energy for the plots are estimated (solid lines). (b) Schematic picture for multiple trap and release (MTR) processes in pentacene thin-film transistors.

inhomogeneous local field, and τ_C is autocorrelation time of the Larmor frequency. In the present case, the ΔB_{inhomo} should be attributed to the hyperfine interaction with protons, which are the only element to have nuclear spins in pentacene molecule. Dipole-dipole interaction between the carrier spins should be negligible in such a low density of carriers, 0.03 per molecule at the maximum, because linewidth decreases as carrier density increase. By using the estimated hyperfine coupling constant of pentacene cation in solution [7], τ_C is calculated as about 1 ns at room temperature at $V_G = -200$ V.

By the definition, the estimated τ_C should be associated with the residence time of carriers at respective molecular sites. However, it is found to be considerably longer than the expected value of about $10^{-12} \sim 10^{-14}$ s for the band transport ($\Delta t \sim \hbar / \Delta E$; ΔE is band width). It indicates that almost all carriers are trapped, and sometimes move to another trap site with thermal activation [8,9], as schematically shown in Figure 2 (b). It is concluded that the observation of motional narrowing in the field-induced ESR directly prove the presence of trap-dominated conductions along the semiconductor-insulator interfaces. The variation of $\Delta B_{1/2}$ with the gate voltage, shown in Figure 1 (a), can be understood in terms of the variation of distribution at deep and shallow traps. From the activation energy of $\Delta B_{1/2}$ shown in Figure 2 (a), we can also estimate the shallow trap energy as 10 ~ 15 meV. We found that the value is roughly consistent with the results estimated by atomic force microscope potentiometry [10]. In contrast, activation energy of field-effect mobility is much larger, estimated as about 60 meV at −200 V. We consider that the ESR measurements should probe the intragrain transport, while mobility is affected both by the grain boundaries as well as by the channel-electrode interfaces [11].

4. Conclusions

We successfully observed motional narrowing of ESR spectra for field-induced carriers in high-mobility pentacene thin-film transistors. The obtained single-Lorentzian ESR spectra become narrower with increasing gate voltage and temperature. The estimated long autocorrelation time, of the order of 1 ns, should correspond to average residence time at trap sites, proving the trap-dominated conduction along the semiconductor-insulator interfaces.

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