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Field-Induced Electron Spin Resonance Spectroscopy for Density of Trap States in Organic Transistors

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1. Introduction

Organic field-effect transistors (FETs) have attracted considerable attentions for their applications to low-cost, large-area, and flexible electronic devices. A fundamental issue of organic FETs is to reveal the microscopic nature of charge dynamics and to establish the device physics that provides a clear basis for improving the device characteristics. Recently, we successfully detected motion of charge carriers by means of field-induced electron spin resonance (FESR) technique [1-3]. We observed gate-voltage-dependent and temperature-dependent single-Lorentzian FESR spectra in pentacene thin-film transistors (TFTs) and rubrene single-crystal FETs. The features are well understood in terms of motional narrowing due to the trap-and-release transport processes. The FESR linewidth allows us to estimate the autocorrelation time of spin precession frequency as a few ns that can be ascribed to the average residence time at respective trap sites. However, the effective temperature range of the motional narrowing remains unclear, although the trapping time becomes considerably long and carriers tend to be localized with decreasing temperature. Puzzling issue is that the FESR spectra still agree well with the first derivative of single Lorentz curves down to very low temperature, although the simple assumption of localized spins predicts the Gaussian-type features due to the inhomogeneous broadening.

Here we establish the limit of motional narrowing in the FESR spectra of pentacene TFTs. On the basis of continuous wave (cw) saturation experiments, we show that the motional narrowing is completely suppressed at temperature below 50 K. The result indicates that the spectra below 50 K originate from electron spins that semipermanently "freeze" at traps. Then we analyze the low-temperature FESR spectra by assuming sum of multiple Gaussians, which results in the distribution of discrete trap levels with different spatial extents.

2. Experiments

The methods to fabricate pentacene TFTs for the FESR measurements were reported before [1]. The measurements were conducted with using X-band microwave. The integrated intensity of the FESR spectra is proportional to the negative gate voltage V_G. In the cw saturation experiments, we measured the integrated intensity as a function of the microwave power P at $V_G = -200$ V.

We also carried out high-precision measurements of low-temperature FESR spectra for the analyses of trap density of states. In order to achieve large number of field-induced spins, we stacked six TFTs. The spectra were averaged by repeated scans for 20 hours.

3. Saturation Experiments of Field-Induced ESR

The FESR cw saturation measurements were carried out to examine the homogeneity of the spectra. We observed saturation of FESR intensity by increasing microwave power P at respective temperature (Figure 1(a)); the FESR intensity is proportional to $P^{1/2}$ at low P while it becomes constant at higher P values. Although the saturation starts at different P at different temperatures, all the results followed the typical saturation curve as

$$integrated\ intensity \propto \left(\frac{P}{P+P_S}\right)^{1/2}. \qquad (1)$$

Here, P_S is the microwave power at which the saturation starts to appear. P_S decreases with decreasing temperature as shown in the inset of Figure 1(a).

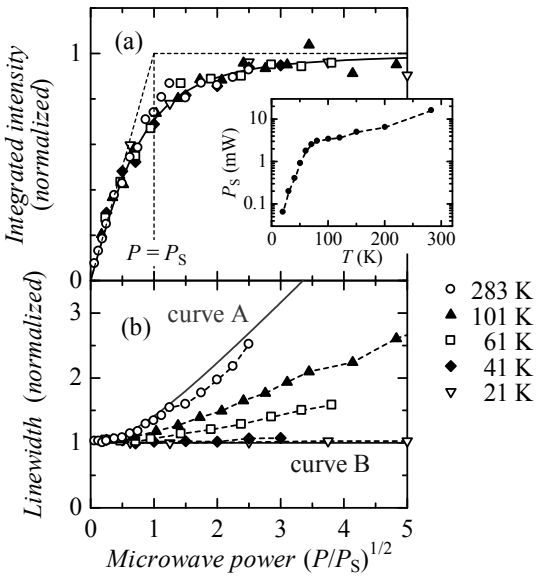

Fig. 1 Microwave-power-dependence of (a) FESR intensity and (b) linewidth. Microwave power P is normalized at the saturation microwave power P_S. The curves A and B show the ideal lines for the homogeneous and inhomogeneous cases. Inset shows the temperature-dependence of P_S.

Although the saturated features are similar with each other, the variation of linewidth under saturation differs by the temperature due to the change of spectral homogeneity, as shown in Figure 1(b). The broadening of linewidth under saturation is observed at temperature above 50 K, which implies that the spectrum is homogeneous because of the motional narrowing. By contrast, the linewidth does not show any broadening under saturation at temperature below 50 K, which clearly indicates that the FESR spectra are inhomogeneous. From these observations we conclude that the motional narrowing is completely suppressed at temperature below 50 K, where the FESR spectra derive from the frozen carriers at trap sites.

4. Analyses of Low-Temperature Spectra

It is known that the inhomogeneous broadening should give Gaussian lineshape in the ESR spectra. It is discussed for pentacene TFTs that the inhomogeneous linewidth should be proportional to $N^{-1/2}$ due to the averaging of hyperfine interactions with protons, where N is the effective number of molecules which each field-induced carrier covers [4]. However, the observed lineshape itself does not show a simple Gaussian lineshape [1-2]. It means that the spectra are composed of multiple Gaussian components with different spatial extents N. The different N should correspond to the different trap depths. Accordingly, the FESR spectrum $S(B)$ as a function of magnetic field B should be given as the sum of the multiple Gaussians with different linewidths:

$$S(B) = \int_1^{+\infty} D(N) G(B,N) dN , \qquad (2)$$

$$G(B,N) = \left(\frac{N}{2\pi\sigma_0^2} \right)^{1/2} \exp\left[-\frac{N(B-B_0)^2}{2\sigma_0^2} \right]. \qquad (3)$$

Here, $D(N)$ is the distribution function of N, $G(B,N)$ the normalized Gauss function with the linewidth $\sigma_0 N^{-1/2}$, σ_0 the linewidth when $N = 1$, and B_0 the resonance magnetic field.

We used stochastic optimization method to determine the unknown $D(N)$ from the observed $S(B)$ as shown in Figure 2 [5]. In the method, initial distribution function $D_0(N)$ are randomly generated, and then optimized by the iterative procedures. Notice that we do not assume any specific function forms for $D(N)$, so that any kinds of function can, in principle, be reproduced as a result of the analyses. The final optimized distribution function $D(N)$ is shown in Figure 3. The $D(N)$ is found to show three discrete peaks at $N = 1.5$ (density: 2.0×10^{12} cm^{-2}), $N = 7.1$ (2.5×10^{12} cm^{-2}), and $N = 19$ (1.1×10^{12} cm^{-2}). We conclude that there are three kinds of trap levels in pentacene TFTs whose localized wavefunctions span 1.5, 7.1, and 19 molecules, respectively.

5. Summary

In summary, we revealed the density of localized trap levels in pentacene TFTs by the high-precision low-temperature FESR spectroscopy. We first demonstrated that the motional narrowing is completely suppressed at temperature below 50 K on the basis of the cw saturation experiments, indicating that the low-temperature FESR spectra derive from the frozen carriers at trap sites. We analyzed the high-precision FESR spectra at 20 K by the stochastic optimization method, and found that there are three characteristic trap levels with the localized wavefunctions spanning 1.5, 7.1, and 19 molecules, respectively. We believe that the FESR spectroscopy should be quite useful to reveal the microscopic nature of charge dynamics and to establish the device physics in organic transistors.

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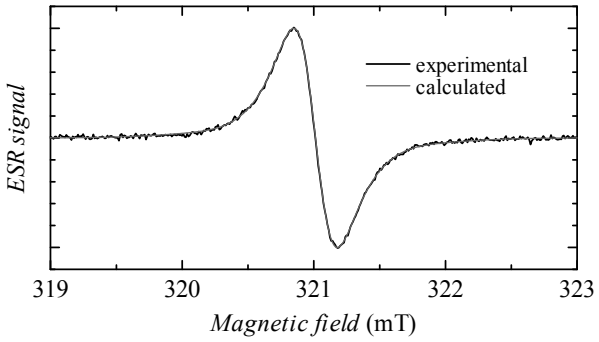

Fig. 2 Experimental FESR spectrum at 20 K at –200 V, and the calculation by eq. (2) and (3). Magnetic field is perpendicular to the substrate.

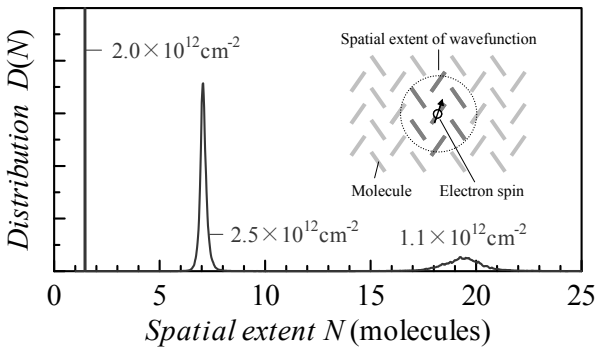

Fig. 3 Distribution of spatial extent N obtained by the stochastic optimization method. Inset shows the rough image of the localized electron spin with spatial extent $N = 7$.