



Dynamics of carrier injection in picene thin-film field-effect transistors with an ionic liquid sheet and ionic liquid gel

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ABSTRACT

We fabricated picene thin-film field-effect transistors (FETs) with an ionic liquid gel and ionic liquid sheet as the gate electrolyte, and then used electron spin resonance (ESR) to investigate the carrier injection process in the organic electric double layer (EDL) FET. The ESR spectra strongly depended on the morphology of gate electrolytes. Three types of carrier injection processes in the EDL-FET were observed by examining the applied-bias time, organic-layer thickness, and gate-voltage dependencies of the electric-field-induced ESR spectrum: (1) interface injection due to electrostatic EDL formation, (2) bulk injection due to penetration of ions (electrochemical bulk doping), and (3) electrochemical reaction. These findings are significant for designing novel materials using the EDL-FET technique because three different carrier injection processes may lead to different physical properties, even in the same organic material.

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1. Introduction

An electric double layer field-effect transistor (EDL-FET) is a powerful tool for investigating high-density carrier accumulation in various materials wherein only carriers are accumulated without any chemical doping of ions [1–13]. Any additional factors, such as structural changes and the formation of scattering centers, may be ruled out in electrostatic carrier accumulation in an EDL capacitor. This allows us to selectively extract the intrinsic physical phenomena that are induced by carrier accumulation into materials. Recently, this technique has been effectively used with semiconductors [1–4] and superconductors [5], revealing interesting physical properties. One of the first successful applications of an EDL-FET in solid state physics was the emergence of superconductivity in SrTiO₃ [1]. The superconducting transition in SrTiO₃ was successfully

achieved in an EDL-FET without doping any chemicals such as Nb. This is called field-induced superconductivity. Subsequently, superconductivity was produced by the EDL-FET technique in two-dimensional layered materials such as ZrNCl [2], KTaO₃ [3], and MoS₂ [4].

These examples illustrate that the EDL-FET technique is a powerful way to realize novel physical properties in inorganic materials. However, no emergence of novel physical properties has yet been achieved in any organic materials. Although the EDL-FET technique has been applied to many organic materials, superconductivity was only observed in C₆₀ [7]. In this case, electrochemical doping with electrolyte ions was required. This is intrinsically different from electrostatic carrier doping in which the material is not doped with any ion. We stress that electrostatic doping of carriers often coexists with electrochemical doping [8]. In particular, the interface of thin films and single crystals of organic materials is so soft and flexible that electrolyte ions in electrolytes and ions in ionic liquids, used as EDL capacitors, can easily penetrate from the interface into

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bulk. Some studies have described electrochemical doping in EDL-FETs with organic materials [9,10] and polymers [8,11]. In such cases, electrochemical doping means reversible ion penetration into the bulk region of the active layer. We previously reported electrochemical carrier doping on organic thin films in an EDL-FET [12]. In this case, the EDL-FET with [7] phenacene thin films was fully investigated with an ionic liquid gel (ILG) for an EDL capacitor; this required an extremely long duration (more than 10^3 s) for saturation of the drain current, I_d , measured at the fixed gate voltage, V_g , and drain-source voltage, V_{ds} . The enhancement of I_d with thickness of the [7] phenacene thin film verifies electrochemical carrier doping (or penetration of ions into the thin film). Thus, electrochemical doping is more significant in organic materials than in inorganic materials with hard interfaces, although it was recently found that electrochemical bulk doping occurs even in inorganic materials [13]. Thus, a detailed investigation of the processes of electrostatic interface carrier doping and electrochemical bulk doping in organic materials is essential to determine how the carriers are accumulated and to be able to distinguish purely electrostatic interface doping. If carrier injection processes, such as electrostatic and electrochemical doping, can be precisely controlled using the EDL-FET technique, we may be able to exploit diverse functionalities in target materials.

In this study, we have fully investigated the process of gate-induced carrier accumulation in an organic thin film using electron spin resonance (ESR). The target organic material was picene, which consists of five benzene rings and is W-shaped (phenacene-type structure). ESR studies for organic FETs with solid gate insulators [14–16] and with ILGs using rubrene [17] and poly(3-hexylthiophene) [18] have been reported. These studies mainly consider trap states in organic thin films and single-crystal FETs, whereas the present study addresses the process of carrier accumulation in an organic thin-film FET with an ionic liquid capacitor. The alkali-metal intercalated picene has shown superconducting transitions at 7 and 18 K [19], i.e., a high-density electron accumulation can produce superconductivity. We may obtain a strategy for field-induced superconductivity in picene by fully investigating the processes of electrostatic (interface) and electrochemical (bulk) carrier accumulation. Here, we used two types of EDL capacitors, i.e., an ILG and ionic liquid sheet (ILS) because two EDL capacitors may produce a clear difference in the process of carrier accumulation.

2. Experimental

We fabricated a picene thin film on a gold substrate by physical vapor deposition under vacuum. The typical dimensions of the device used in ESR experiments were $2 \text{ (mm)} \times 15 \text{ (mm)} \times d \text{ (}\mu\text{m)}$, where the thickness was either $d = 0.5 \mu\text{m}$ or $1 \mu\text{m}$. X-ray diffraction (XRD) patterns were measured with Smart Lab-Pro (RIGAKU) to investigate sample morphology and alignment of picene molecules. Sample morphology was also checked by atomic force microscopy experiments (SPA 400-DFM, SII Nano Technologies). The thin-film sample on the gold substrate and a Pt

electrode were placed together in a quartz glass tube, which was filled with an ILG of [bmim]PF₆ as the gate electrolyte (see Fig. 1(a)). We also measured ESR with an ILS as the gate electrolyte. The ILS was made by mixing a polymer (p[VDF-HFP], Sigma Aldrich, CO. Ltd.) and the ionic liquid. The sandwiched device with the Pt/ILS/picene/Au structure was placed in a quartz glass tube (see Fig. 3(a)). We carefully checked the quality factor of the cavity to ensure that it was not reduced by insertion of the ILG and device. We measured frequency-dependent dielectric properties for the ILG and ILS at room temperature and obtained EDL capacitances for the ILG and ILS of $\sim 7 \mu\text{F}/\text{cm}^2$ and $\sim 1.2 \mu\text{F}/\text{cm}^2$, respectively. For both the ILS and ILG gate electrolytes, spin carriers can be injected by applying a negative voltage to the Pt electrode, implying that holes are injected into picene molecules. The number of spins, N_s , can be estimated from the integrated intensity of ESR signals. Time-dependent ESR spectra were measured with an X-band ESR spectrometer (Bruker, ESP-300e). All ESR spectra in this study were recorded at room temperature.

3. Results and discussion

The device used for ESR measurements with the ILG is shown in Fig. 1(a), and photos of the picene thin film before and after the experiments are shown in Fig. 1(b). The device consisted of two electrodes: the gate electrode (Pt wire) applying V_g and counter electrode (Au substrate) grounded. The picene thin film on the Au substrate was always grounded, and both electrodes were immersed in the ILG (bmim[PF₆]), i.e., all the picene thin film was in the ILG.

First, we present the ESR results using the ILG capacitor. Fig. 1(c) shows the gate-induced ESR spectrum for a picene thin film of thickness $d = 0.5 \mu\text{m}$ to which a V_g of -3 V was applied. No ESR signals were observed at $V_g = 0 \text{ V}$. The ESR spectrum (Fig. 1(c)) observed at $V_g = -3 \text{ V}$ definitely decomposed into two components: one peak has a narrow line width ($\sim 0.5 \text{ Oe}$; blue¹ line), whereas the other has a broad line width ($\sim 5 \text{ Oe}$; red line). Note that $V_g = -3 \text{ V}$ is slightly out of the electrochemical potential window for bmim[PF₆] at room temperature [20]. When we applied a V_g within the electrochemical potential window, only a sharp ESR signal was observed.

Fig. 1(d) shows the angle dependence of the g -factor for the sharp ESR signal at $V_g = -3 \text{ V}$. The error in the g -factor was ± 0.00005 . The value $\Theta = 0^\circ$ corresponds to the magnetic field, B , perpendicular to the substrate. The g -factor for the sharp ESR signal clearly depends on the B -direction and shows a large value when B is nearly perpendicular to the substrate. The XRD measurement for the picene thin film grown on the Au substrate indicates that the long molecular axis was inclined by $20\text{--}30^\circ$ to the normal axis of the substrate [21]. Anisotropy of the g -factor for picene molecules has not been previously reported. The principal value of the g -factor along the long axis was the largest among the three principal values in rubrene [17],

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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