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Raman imaging of carrier distribution in the channel of an ionic liquid-gated transistor fabricated with regioregular poly(3-hexylthiophene)

Y. Wada [a], I. Enokida [a], J. Yamamoto [b], Y. Furukawa [a,b,*]

[a] Department of Advanced Science and Engineering, Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
[b] Department of Chemistry and Biochemistry, Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

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ABSTRACT

Raman images of carriers (positive polarons) at the channel of an ionic liquid-gated transistor (ILGT) fabricated with regioregular poly(3-hexylthiophene) (P3HT) have been measured with excitation at 785 nm. The observed spectra indicate that carriers generated are positive polarons. The intensities of the 1415 cm^{-1} band attributed to polarons in the P3HT channel were plotted as Raman images; they showed the carrier density distribution. When the source–drain voltage V_D is lower than the source–gate voltage V_G (linear region), the carrier density was uniform. When V_D is nearly equal to V_G (saturation region), a negative carrier density gradient from the source electrode towards the drain electrode was observed. This carrier density distribution is associated with the observed current–voltage characteristics, which is not consistent with the "pinch-off" theory of inorganic semiconductor transistors.

1. Introduction

Raman spectroscopy imaging has emerged as a powerful tool for the characterization of materials and spatial distribution of chemical species in various research fields such as biology, medicine, pharmacy, materials science. with the space resolution of about 1 μm. There are few papers dealing with organic electronic devices. A Raman imaging study of pentacene thin films has shown the two-dimensional solid-phase structure and structural disorders existing in the pentacene films [1,2]. McCreery and colleagues [3] conducted Raman imaging studies of electrochemical memories fabricated with regioregular poly(3-hexylthiophene) (P3HT, Fig. 1a) and viologen, and observed carriers (positive polarons) in the oxidized states of the memories. Raman imaging can be used for elucidating carriers in organic transistors as well as memories.

A thin-film transistor is composed of (a) a thin semiconductor layer, (b) an insulator layer, and (c) three electrodes: source; drain; gate [4]. Thin films of conjugated polymers are used as the active semiconductor of the transistor. It is called the organic field-effect transistor (OFET) or the organic thin-film transistor (OTFT). The source and the drain electrodes are in contact with the semiconductor film at a short distance from each other. The gate is separated from the semiconductor layer with the insulator layer. The OFET operates like a capacitor. When a voltage V_G is applied between the source and the gate electrodes, a charge is injected from the source electrode into the semiconductor film. Then, the injected charge is accumulated at the insulator–semiconductor interface. This charge forms a conducting channel between the source and the drain electrodes. Accordingly, a current I_D flows between the source and the drain electrodes through the conducting channel when a drain voltage V_D is applied between these electrodes.

An ionic liquid can function as an ultra-high capacitance gate dielectric in OTFTs [5]. The benefits of high capacitance are a low operating gate voltage and a high output current. These favorable features originate from the high charge density induced by the high capacitance in the transistor channel. The charges may be induced by the electrostatic effect and/or electrochemical oxidation. A transistor fabricated with P3HT and an ionic liquid is called the ionic-liquid gated transistor (ILGT). In an ILGT, a negative bias on the gate electrode can lead to the positive carrier generation in the P3HT film between the source and drain electrodes. The characteristics of the transistor depend on the density, the distribution, and the mobility of carriers. However, the behavior of carriers associated strongly with the performance of transistors has not been fully elucidated yet.

Conjugated polymers are used as the active semiconductors of the OFET. Carriers in conjugated polymers are charged quasi-particles with structural changes extending over several repeating units [6–10]. A conjugated polymer having a nondegenerate ground state such as polythiophene and its derivatives can support charged quasi-particles such as polarons or bipolarons. A polaron has charge $+e$ (or $-e$) and spin 1/2, whereas a bipolaron has charge $+2e$ ($-2e$) and no spin. It

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[*] Corresponding author.
E-mail address: furukawa@waseda.jp (Y. Furukawa).

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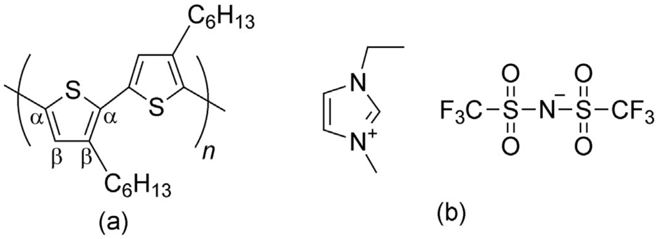

Fig. 1. Chemical structures: (a) P3HT; (b) [EMIM][TFSI].

has been demonstrated that Raman spectroscopy can identify positive polarons and bipolarons in P3HT [11], because the structural changes associated with the formation of a polaron are different from those of a bipolaron. In particular, in situ Raman measurements are very useful for studying carriers generated in the polymer films used in organic transistors [12,13].

The performance of a transistor can be evaluated by current–voltage characteristics [14]. For each V_G, I_D is plotted against V_D, which is called the output characteristics. At low V_D region, I_D is approximately proportional to V_D, which is called the linear region. On the other hand, beyond the “pinch-off” voltage, I_D shows saturation in high V_D range, which is called the saturation region. This feature can be explained by the pinch-off theory. The pinch-off means the depletion in carrier density at the channel near the drain electrode by the application of large V_D. It is important to make clear carrier densities at the channel for studying the current–voltage characteristics of a transistor. The electric field in the channel has been studied by electric-field induced optical second harmonic generation method [15,16].

In this article, we present a Raman imaging study of carrier density distribution at the P3HT channel in an ILGT. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([EMIM][TFSI]) (Fig. 1b) was used as the electrolyte (gate dielectric) in the transistor.

2. Experimental

2.1. Raman Measurements

Raman images were measured using the backscattering configuration of a Renishaw InVia Raman microscope with a Leica N PLAN L 50× objective lens (numerical aperture, 0.50; working distance, 8.2 mm) by the line-scan method. The excitation wavelength was 785 nm. The spectral resolution was 2.8 cm^{-1}. In the Raman image measurements, Raman spectra were obtained from 2800 positions in a 84 μm × 48 μm area with the interval of 1.2 μm. The theoretical spatial resolution was 0.96 μm. The power of the 785-nm light was approximately 330 μW. The size of irradiated area was 50 μm × 3.8 μm. Accumulation time was 10 s/point spectrum. The total measurement time was ~1500 s/image. Raman images were generated using WiRE 4.3 software. From the measured Raman spectra, noises were removed using the principal component analysis. After broad background emissions were subtracted, the peak position and intensity of each band were obtained.

2.2. Devices and IV Measurements

A schematic illustration of an ILGT [12] is shown in Fig. 2. The 5 nm adhesion layer of Ni was deposited followed by 45 nm of Au on a glass substrate as the source and the drain electrodes by vacuum evaporation using a shadow mask. P3HT was purchased from Sigma–Aldrich and used as received. A thin film of P3HT was prepared from its chloroform solution (24 mg/mL) by spin-coating (1500 rpm, 60 s). The thickness of the P3HT layer was 2.0×10^2 nm. The width and the length of the channel of the transistor was 1 mm and 50 μm, respectively. [EMIM][TFSI] (Kanto Chemical) was used as ionic liquid gate dielectric. An indium-tin-oxide (ITO) coated glass substrate with the sheet resistivity of 30 Ω sq^{-1} was purchased from GEOMATEC. The surface of the ITO-coated electrode was cleaned with UV-ozone plasma treatment. An ITO-coated glass substrate was used as the gate electrode. The thickness of the [EMIM][TFSI] layer was set to 2.0×10^2 μm using a Naflon spacer. This device was passivated by an epoxy polymer under nitrogen atmosphere.

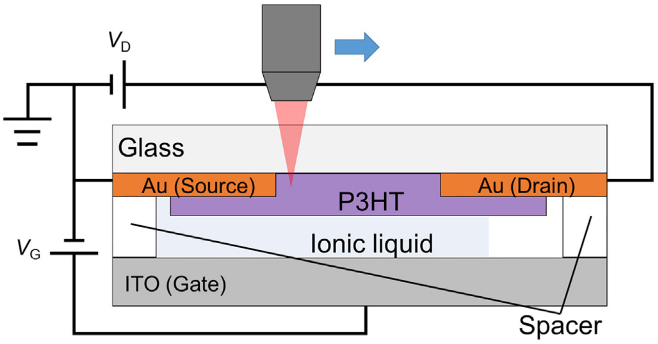

Fig. 2. Schematic illustration of an ILGT.

A metal–insulator–semiconductor (MIS) diode [12] based on P3HT and [EMIM][TFSI] was also fabricated as follows. A 2.0×10^2 nm thick film of P3HT was prepared on an ITO-coated glass substrate from its chloroform solution (24 mg/mL) by spin-coating (1500 rpm, 60 s); it was used as the working electrode. Another ITO-coated electrode was used as the counter electrode. [EMIM][TFSI] liquid was sandwiched between the working and the counter electrodes. These two electrodes were separated with a spacer of 2.0×10^2 μm. A voltage between the two electrode is described as V_G.

The current–voltage relations were measured on a home-made system based on two KEITHLEY 6487 DC picoammeters and ADVANTEST TR6163 and R6243 DC voltage source/current monitors controlled by a home-made LabVIEW program. The I_D values were measured as a function of V_G at a V_D value.

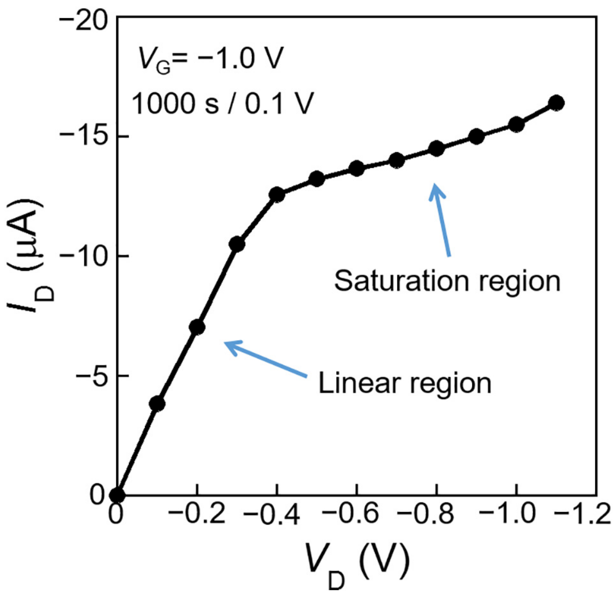

Fig. 3. I_D–V_D characteristics at $V_G = -1.0$ V.

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