Direct investigations of the interface impedance of organic field-effect transistors with self-assembled-monolayer-modified electrodes

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ABSTRACT

It has been demonstrated that the modification of electrodes with self-assembled monolayers (SAMs) reduces the contact resistance and improves the device performances of organic field-effect transistors (OFETs). However, it has been difficult to judge if the contact resistance was reduced by the change in the electronic properties or by the change in the morphology of the metal−organic interface caused by the SAM modification because they have been difficult to be separately assessed. We have directly investigated the local impedance and the potential difference at the electrode−channel interfaces of the OFETs with and without modification of the electrodes by a pentafluorobenzenethiol SAM using frequency-modulation scanning impedance microscopy (FM-SIM). The potential profile measurement and the FM-SIM measurement at the interface showed that the improvement of the field-effect mobility in the SAM-modified OFET was caused by the reduction of the energy level mismatch, namely, the hole injection barrier at the source−channel interface, presumably with the reduction of the hole trap sites at the source−channel interface.

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1. Introduction

Organic field-effect transistors (OFETs) have currently been widely studied for their potential applications to light-weight and flexible electronic devices [1,2]. The performance of the OFETs, however, is still not sufficient for practical applications partly because they are limited by the electronic properties at the non-ideal metal−organic interfaces [3,4]. Such metal−organic interfaces not only exhibit high contact resistances, but also cause non-linearities in the current−voltage characteristics. The dependence of the field-effect mobility on the gate bias voltages is also caused by a non-ideal metal−organic interface, which makes it difficult to control the device performances. The influence of the metal−organic interfaces on the electronic properties becomes a major issue that limits the device performances of the OFETs, especially of those having a short channel length and those using organic molecules exhibiting a high carrier mobility [5,6].

Recent studies showed that modification of the electrodes with self-assembled monolayers (SAMs) reduces the contact resistances and thereby improves the device performances of the bottom-contact in the OFETs [7–11]. The contact resistances at the metal−organic interfaces correlate with the carrier injection barrier induced by an energy level mismatch between the Fermi energy (E_F) of the metal and the highest occupied molecular orbital (HOMO) energy (E_{HOMO}) of the organic film. Thus, the use of SAMs having negative electronic dipoles increases the work function of the electrodes, which results in the reduction of the carrier injection barrier at the metal−organic interfaces [8,9,12]. Another report, however, showed a greater reduction in the contact resistance of the OFETs with SAM-modified electrodes, despite the fact that the modified electrode showed almost the same work function as that of bare electrodes [10]. Usually SAMs not only modify the surface energy of the metal electrodes, but also affect the crystallinity and grain sizes of the organic thin films [11]. While the performance can be improved by changing the electronic properties or by a change in the morphology of the metal−organic interface caused by the SAM-modification, they have been difficult to be separately assessed by conventional measurements using large-area films and electrodes like the transition line method [13] or photoelectron spectroscopy [9].

We recently developed frequency-modulation scanning impedance microscopy (FM-SIM) that can sensitively measure not only the potential differences, but also the local impedances at the

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metal−organic interface [14]. In a previous paper [14], we investigated the impedance of a Pt electrode and a single pentacene grain by FM-SIM and revealed that the reduction of the contact resistance at the interface by the voltage application was caused by the reduction of the energy level mismatch. In the present study, the electrodes of OFETs having dinaphtho[2,3-b:2′3′-f]thieno[3,2-b]thiophene (DNTT) active layers are modified by pentafluorobenzenethiol (PFBT), which is a thiol-based SAM material widely used in small molecule OFETs [15,16]. We first characterized the electrical characteristics of the OFETs with SAM-modified and bare electrodes, and directly investigated the potential difference and the local impedance at the electrode−channel interfaces of the operating OFETs by the FM-SIM. We then discuss the mechanisms for improving the device performance in the SAM-modified OFET in terms of the change in the interface impedance as a function of the gate bias voltage.

2. Experimental

We fabricated bottom-contact OFET devices of DNTT with and without the electrodes modified by PFBT-SAM. The schematic of the DNTT-OFET with the PFBT-SAM-modified Au electrodes, and chemical structures of the DNTT and PFBT, are shown in Fig. 1(a). Twenty-nm-thick Au electrodes, whose channel width and channel length were approximately 1 μm and 500 nm, respectively, were fabricated by photolithography on a heavily doped n-type Si substrate with a 100-nm-thick thermally grown oxide layer. The PFBT-SAM was formed by immersing the Si substrate with Au electrodes in a 30 mM isopropanol solution of PFBT for 5 min followed by a rinse with isopropanol. A 100-nm-thick active layer of DNTT was deposited on the substrates with (PFBT-Au) and without SAM modification (bare-Au). The transfer characteristics of the DNTT-OFETs were obtained using the Keithley 4200 semiconductor characterization system.

The FM-SIM measurements were performed on both OFETs. Fig. 2 shows the schematic diagram of the FM-SIM measurement setup. The cantilever was oscillated at its resonance frequency and the constant tip−sample distance was performed by keeping the frequency shift of the cantilever (Δf) constant, that is, frequency-modulation atomic force microscopy (FM-AFM). The local potential V_{lo}^{dc} was measured by nullifying the f_t component in the Δf signal induced by an ac bias voltage applied to the cantilever (frequency: $f_t = 1$ kHz, amplitude: $V_t^{ac} = 2$ V$_{p-p}$), that is, Kelvin-probe force microscopy (KFM) [17]. At the same time, another ac bias voltage was applied to the source electrode (frequency: $f_s = 100$ Hz, amplitude: $V_s^{ac} = 1$ V$_{p-p}$). We now describe the variation in the surface potential under the tip induced by V_s^{ac} as
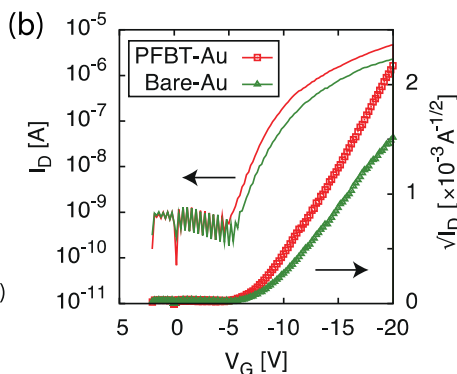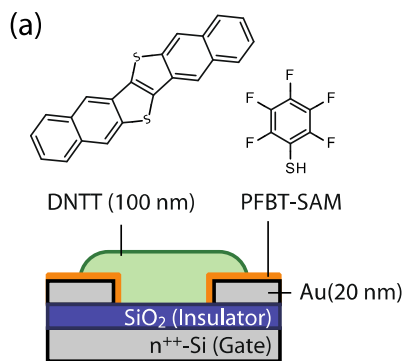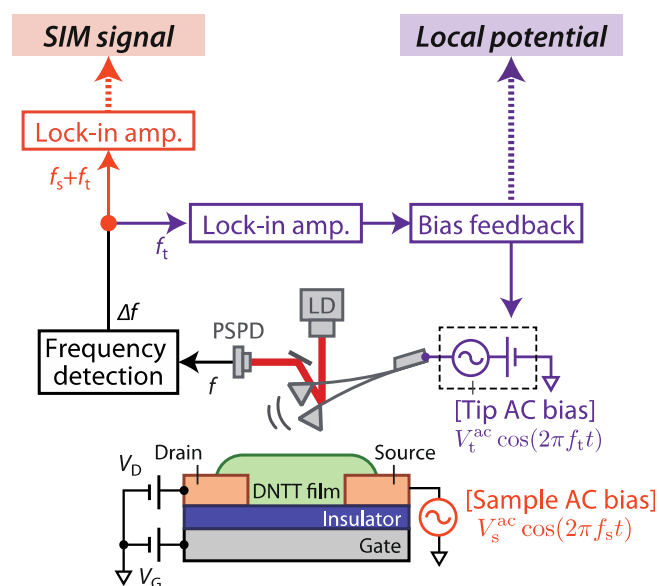

Fig. 2. Schematic diagram of FM-SIM measurement setup. The conductive cantilever is oscillated at its resonance frequency, and the topography is obtained by keeping the tip−sample distance constant (FM-AFM). Two ac bias voltages are applied to the cantilever ($V_t^{ac} \cos(2\pi f_t t)$) and the source electrode ($V_s^{ac} \cos(2\pi f_s t)$). The f_t component in the resonance frequency shift (Δf) signal is detected and then nullified to measure the local surface potential, while the $f_s + f_t$ component in the Δf signal is detected as the "FM-SIM signal", corresponding to the local ac voltage on the sample.

$V_{lo}^{ac} \cos(2\pi f_s t + \phi_{lo})$. Since the electrostatic force exerted on the cantilever tip is proportional to the square of the local voltage, the frequency component at $f_s + f_t$ in the Δf signal, called the "FM-SIM signal", is given by

$$\Delta f_{s+t} = \alpha V_{lo}^{ac} \cos[2\pi(f_s + f_t)t + \phi_{lo}] \tag{1}$$

where α is a proportional factor, which is constant while the tip−sample distance is kept constant. By measuring the amplitude and phase of the Δf_{s+t} component, we can calculate V_{lo}^{ac}, from which we can evaluate the interface impedance using the appropriate circuit model. Thus, we can visualize the variation in the interface impedance [14].

We performed the FM-SIM measurements using a commercially available AFM apparatus (JEOL: JSPM-4200) with a lab-built AFM controller and a Pt-coated conductive cantilever (Olympus: OMCL-AC240TM-R3), whose nominal spring constant and resonance frequency were 2 N/m and 70 kHz, respectively. The Δf signal was

Fig. 1. (a) Chemical structures of DNTT and PFBT, and schematic of DNTT-OFET with PFBT-SAM-modified Au electrodes. (b) Transfer characteristics of DNTT-OFETs with PFBT-SAM-modified and bare Au electrodes.