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Energetic distribution of interface states extracted from photo-conductance of organic thin film transistors

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ABSTRACT

In this paper, a new method is introduced to obtain the energetic distribution of the interface states (density of states; DOS) extracted from the photo-conductance of organic thin film transistors (OTFTs) which exhibit varied transfer characteristics under illumination with different photon energies. The method was applied to pentacene OTFTs, and the results were compared with existing data. The major findings were not only the existence of the well-known peaks of DOS at 1.82 eV (free exciton of pentacene), and at 1.49 eV (extrinsic exciton due to dihydropentacene) but also new peaks were found at 1.25 eV, 1.29 eV, 1.31 eV, and 1.35 eV in the mid-gap. The new peaks were strongly enhanced under exposure to oxygen, and thus seem to be related to the defects associated with the presence of oxygen.

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1. Introduction

Organic thin film transistors (OTFTs) have attracted much attention due to their potential applications in flexible and large area electronics [1–5]. Recently, the performance has been sufficiently improved for the application to be realized in flexible displays [1,2], RFIDs [3], sensors [4], and memories [5]. However, their performance instability in air and under bias stress is still an important issue that needs to be resolved [6].

The instability mostly originates from the interface states. It has been reported that the interface states are generated for various reasons, such as molecular displacement affected by the electric dipoles of the gate dielectric [7,8], the presence of impurities [9], and the structural defects at the gate surface [10]. They also have been created as a result of environmental effects, such the presence of oxygen and moisture [11–15] and bias stress [6,10]. However, it is difficult to obtain the energetic distribution of the interface states (the density of states; DOS) in the band gap energy region, even though such measurements provide important elemental experimental data to analyze the properties of interface states. Several articles reported on the DOS of the interface states within the shallow energy region (<0.5 eV) near the valence band by using the activation energy of the temperature dependent transfer curves of OTFTs [15,16]. However, the deep states above 0.5 eV cannot be obtained by the same method because it is difficult to produce high activation energy with high enough temperature to change the Fermi energy level. The DOS for the deep states was also reported by analyzing the variation of the threshold voltage under illumination [17]. However, there is an ambiguity in determining the threshold voltage, resulting in a deviation of the DOS value depending on how the threshold voltage is defined. In particular, the OTFTs with large interface states density produce super-linearity in the square root of the drain current (which is fitted to the measured data to extract the threshold voltage) so that the ambiguity becomes large, and thus the large deviation is generated in the DOS extraction by this method.

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In this paper, a method is reported to obtain the energetic distribution of DOS for the interface states in OTFTs by investigating the variation of the photo-conductance under illumination with various wavelengths. This method can eliminate the ambiguity associated with the determination of the threshold voltage because the photo-conductance is used instead of the threshold voltage to extract the DOS of the interface states. In particular, this method is adequate for organic semiconductors with large interface states and, thus, whose threshold voltage is not clear by exhibiting super-linearity in the square-root of the drain current. In addition, the method produces the DOS along a large energy range in band gap.

2. Theory for extraction of interface states density

First of all, we need to describe the definition of 'interface' used in this study because it may be a region including the organic–organic boundary in organic devices because they consist of molecular layers. The method proposed in this study is associated with photo-ionization of carriers at the traps existed in the channel region of OTFTs because it is measured in the accumulation mode. Thus, the interface states extracted by this method are related to the traps distributed within the channel. Since the carriers in channel is mostly concentrated in the first monolayer of semiconductor near the gate insulator [18], the extracted interface states can be assumed to reflect the trap states in the first monolayer with the thickness of a few nm. Therefore, the definition of interface is the channel region (1–10 nm, depending on V_{GS}) including the interface at the gate insulator–semiconductor.

Next, let's discuss about the validity of usage of the conventional energy band theory for the organic semiconductors. What is the difference of organic semiconductors from the inorganic counterparts is that they consist of molecules with the weak van der Waals interaction, which is compared to the inorganic semiconductors consisting of the atoms with strong covalent bonds. In energy band, the difference is reflected by a small bandwidth of 0.1–0.5 eV for the organic semiconductors, resulting in small mobility of a few tenth $cm^2/V\,s$ [19]. Considering the small bandwidth, the energy band theory has been frequently applied to analyze the organic devices [20,21]. Therefore, the energy band theory is also adopted to describe the model of the interface states in this study.

By the way, we must be careful to apply the energy band to the organic–organic interfaces. Frequently, the vacuum level (VL) shift is taken place at the metal–organic and organic–organic interfaces due to chemical interaction and charge transfer, and thus the VL shift affects the charge transport across the interface, and modifies the electrical characteristics from expectation by Schottky–Mott model. However, in OTFTs the organic–organic interface between gate insulator and semiconductor may not produce a significant VL shift due to the following reason. Since generally the materials with a large gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) or the amorphous polymers are used for the gate insulators, the weak overlap of wave functions between two materials is expected due to the misalignment of the LUMO and HOMO level of the gate insulator having a large gap with those of the semiconductor having a small gap or the amorphous nature for the gate polymers. Therefore, only a weak van der Waals interaction exists and thus results in the ignorable VL shift. Such an expectation is supported by the results of several articles which show 'zero' VL at the organic–organic interfaces [22–26].

Even though there existed VL shift at the organic–organic interfaces due to the unknown reasons, it dose not affect the drain current of OTFTs because the drain current flows parallel along the interface instead of crossing it. Particularly, the method proposed in this study is associated with the photo-ionized charges from the interface traps to LUMO or HOMO in the semiconductor layer so that the VL shift is not involved in the variation of photoconductance. Therefore, the energy alignment of the organic–organic interface formed at the gate insulator and semiconductor can be estimated by Schottky–Mott model without considering VL shift.

The theory of this study is based on the variation of the charge state at the interface states when illuminated by various photon energies and the reflection on the conductance of OTFTs. When light with photon energy smaller than the band-gap energy of semiconductor illuminates the interface states through the OTFTs semiconductor, two processes are possibly taking place, as shown in Fig. 1. The electrons in the energy levels below HOMO (VB: valence band) are excited to the trap states above the Fermi energy levels (E_F) which are empty and neutral initially, and are then captured by the trap states to form the negative charge on the states as shown in Fig. 1(a). The traps are named acceptor-like interface states since they are neutral before trapping electrons and become negatively charged after trapping them. The negatively-charged traps attract holes in the VB and thus increase the conductance of the p-type organic semiconductors as shown in Fig. 1(c) [27]. The other process is generated by the donor-like traps. The electrons trapped at the interface states below E_F are excited to the energy levels above LUMO (CB: conduction band) or to the tail states near LUMO and leave the positively-charged states behind at the interface states, as shown in Fig. 1(b). The positive charges repel holes in the VB, resulting in a decrease in the conductance, as shown in Fig. 1(c) [27]. In general, the electrons of the p-type organic semiconductors cannot contribute to conductance because they are mostly trapped by the electronic traps [28,29]. With respect to the energy level E in the band gap, the interface trap density $D_{it}(E)$ can be extracted from the varied conductance of the transfer curves which are measured under illumination with the various photon energies. In addition, the type of the interface trap states at E is also identified by the increment or decrement of conductance under illumination.

The energetic distribution of the density of interface states $D_{it}(E)$ can be determined from the variation of conductance under illumination. For the acceptor-like traps, as shown in Fig. 1(a), the electrons in the VB are excited into the empty trap states above E_F because the states below E_F are occupied by electrons. The excited-electrons