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Analysis of interfacial energy states in Au/pentacene/polyimide/indium-zinc-oxide diodes by electroluminescence spectroscopy and electric-field-induced optical second-harmonic generation measurement

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Abstract

By using electroluminescence (EL) spectroscopy and electric-field-induced optical second-harmonic generation (EFISHG) measurement, we analyzed interfacial energy states in Au/pentacene/polyimide/indium-zinc-oxide (IZO) diodes, to characterize the pentacene/polyimide interface. Under positive voltage application to the Au electrode with reference to the IZO electrode, the EFISHG showed that holes are injected from Au electrode, and accumulate at the pentacene/polyimide interface with the surface charge density of \( Q_s = 3.8 \times 10^{-7} \text{ C/cm}^2 \). The EL spectra suggested that the accumulated holes are not merely located in the pentacene but they are transferred to the interface states of polyimide. These accumulated holes distribute with the interface state density
greater than $10^{12}$ cm$^2$eV$^{-1}$ in the range $E = 1.5–1.8$ eV and $E = 1.7–2.4$ eV in pentacene and in polyimide, respectively, under assumption that accumulated holes govern recombination radiation. The EL–EFISHG measurement is helpful to characterize organic-organic layer interfaces in organic devices and provides a way to analyze interface energy states.
1. Introduction

Organic field-effect transistors (OFETs) are attracting much attention in R&D studies for new applications in electronics. Among them are flexible OFETs, organic ambipolar transistors, organic memory transistors, and other devices [1-3]. In these devices, holes and electrons are injected from Source and Drain electrodes and they are then accumulated at the interface between organic active layer and gate insulating layer. Accordingly, detection and analysis of interface carriers is a key to optimize device structures and to design synthetic materials. The conventional $C-V$ measurement of metal-insulator-semiconductor-type (MIS) diodes provides one way to investigate interface carrier behaviors on the basis of RC equivalent circuit model [4]. For example, interface states of MIS capacitors incorporating polyimide and regioregular poly(3-hexylthiophene) layers were analyzed by using the $C-V$ measurement [5]. The $C-V$ measurement is useful, but a choice of appropriate equivalent circuit model is not an easy task owing to the dielectric property of organic materials used in them. Furthermore, ambiguous carrier injection process at metal-organic contacts [6], complex carrier transfer process at organic-organic layer interface [7], possible double-injection process into organic layers [8], and other unknown factors lead to a puzzling situation in the analysis. In contrast, the electric-field-induced optical
second-harmonic generation (EFISHG) measurement which we have been developing is capable of directly probing carrier behavior, without aid of the equivalent circuit model [9-11]. By using an optical probe of pulsed laser beam, EFISHG is activated at molecules in response to dynamical motion of carriers that are injecting, accumulating, and transporting in OFET-type devices [12, 13] and in organic metal-insulator-metal (MIM) structure devices [14, 15]. These activated EFISHGs allow motion of carriers in organic devices to be probed directly and selectively. However, these are no longer sufficient. We need to energetically characterize contacts between adjacent two layers, which govern carrier trapping, rectification, and others. In the field of electrical insulation engineering, electroluminescence (EL) spectroscopy has been employed to analyze energy states of polymer insulators [16-19]. Polymers used for electrical insulation is a non-EL material, but once electrons and holes are injected into the polymer nearby electrode under high ac voltage ($> 10^4$ V/cm), very weak EL is generated. The optical spectrum of this EL well reflects energy states, which are created and distributed in the band gap of polymers. In OFETs, holes and electrons are allowed to be injected under high dc voltage ($> 10^5$ V/cm). Accordingly, EL spectroscopy of OFETs gives an opportunity to determine interfacial energy states. In the present paper, we employed EL spectroscopy and EFISHG measurement to study
the status of carriers in MIS diodes with a structure of Au/pentacene/polyimide/indium-zinc-oxide (IZO). Under positive dc voltage application to the Au electrode with reference to IZO, holes are injected and accumulated at the pentacene/polyimide interface and EL is emitted from the diodes accordingly. The EL spectra indicated that accumulated holes are located around the pentacene/polyimide interface, but simultaneously at the pentacene and at the polyimide. The EL-EFISHG measurement is helpful for characterizing contacts between adjacent two layers in organic devices.

2. Experimental methods

In Fig. 1, the Au/pentacene/polyimide/IZO MIS diode used here is portrayed. It was prepared on glass substrates with patterned IZO electrodes as follows: Firstly, the substrate was cleaned in an UV/ozone cleaning apparatus. Then, polyimide precursor of cyclobutanedianhydride-2,2-bis(4-aminophenoxyphenyl)propane (CBDA-BAPP) was spin-coated on IZO electrodes. After that, the substrate was baked in an oven kept at 260 °C for 2 h, to thermally imidize the deposited polyimide precursor film. The resulting polyimide film on the substrate was 100 nm in thickness, onto which pentacene layer (thickness: 100 nm) and Au electrode were deposited successively, by
using the thermal evaporation process in vacuum. As a reference device for EL spectrum measurement, we prepared single-layer devices with structures of Au/pentacene/IZO and Au/polyimide/IZO in the way similar to the MIS diode. Note that these devices were covered with a glass plate with UV cure resin to eliminate further photo-degradation, oxidation, etc.

The EL spectrum and EFISHG measurements were carried out using the optical arrangement illustrated in Figs. 1 and Fig. 2(a), respectively. In these measurements, dc voltage was applied to the Au electrode in reference to the grounded IZO electrode. The dc voltage was increased with a step of 0.5 V, on applying it for a period of 30 s. The EL emitted from the diode was collected into the spectrometer by using an optical fiber probe positioned in front of the IZO of the diode. On the other hand, for the EFISHG measurement, p-polarized pulsed laser beam (duration: 4 ns, average power: 1 mW/cm², and repetition rate: 10 Hz) generated from an optical parametric oscillator, which is pumped by the third-harmonic light of neodymium-doped yttrium-aluminum-garnet laser, was used as an optical probe. It was incident on the diode from the glass substrate surface at an angle of 45°. The laser beam wavelength was set at 860 nm to selectively probe the electric field in the pentacene layer of the Au/pentacene/polyimide/IZO diode [20, 21]. Noteworthy that the laser irradiation at 860 nm does not assist nonlinear
optical process in polyimide layer. Consequently, we can selectively probe the electric field formed in the pentacene layer. In more detail, the EFISHG intensity $I_{2\omega}$ is produced in proportion to the square of the electrostatic field $E_1$ formed in the pentacene layer, in a manner as

$$I_{2\omega} \propto |P_{2\omega}|^2, \text{ with } P_{2\omega} = \epsilon_0 \chi^{(3)} : E_1 E_{\omega} E_{\omega},$$

(1)

where $P_{2\omega}$ is the second-harmonic polarization induced in the pentacene, $\epsilon_0$ is the dielectric permittivity of vacuum, $\chi^{(3)}$ is the third-order nonlinear susceptibility tensor, and $E_{\omega}$ is the electric field of the probing laser beam. The electrostatic field $E_1 (= E_m + E_s)$ is mainly formed by the external field $E_m$ caused by an applied voltage $V$ and the space charge field $E_s$ due to carriers $Q_s$ accumulated at the organic-organic layer interface. These electrostatic fields are given as

$$E_m = \frac{1}{d_1 C_1 + C_2} V, \quad E_s = \frac{Q_s}{d_1 C_1 + C_2},$$

(2)

where $d_1$ is the pentacene layer thickness, $C_1$ and $C_2$ are capacitance of pentacene and polyimide layers, respectively. Here, the positive direction of electrostatic field is defined as that it points in the direction from the Au electrode to the grounded IZO electrode. The EFISHG measurement was carried out under pulse and dc voltage application to probe the electrostatic field without carrier accumulation in device ($Q_s = 0$) $E'_1 = E_m$ and the electrostatic field with interface carrier accumulation ($Q_s \neq 0$)
$E''_1 = E_m + E_s$ formed in the pentacene layer. Using $E'_1$ and $E''_1$ with Eqs. (1) and (2), we obtained interface carrier density $Q_s$ in the way same as in our previous study [22, 23].

3. Results and discussion

Figure 1 shows the $I–V–EL$ characteristics of the Au/pentacene/polyimide/IZO diodes, and Fig. 2 shows the result of EFISHG measurement. The $I–V$ characteristics shows a rectifying property. That is, for $V > 0$ (forward), holes are smoothly injected from the Au electrode to the pentacene, and transported to the pentacene/polyimide interface. The $EL–V$ characteristics shows that the EL emission initiated at $V = 15$ V, suggesting that electrons are injected from the IZO electrode to the pentacene/polyimide interface in the region $V > 15$ V and they are then recombined with holes around the pentacene/polyimide interface. However, these are merely speculation.

Figure 2(a) plots the EFISHG intensity data we got by applying pulse and dc voltages. The solid curve represents the $I_{2\omega} \propto |E'|^2 \propto |V|^2$ characteristics, which is fitted to the data of EFISHG intensity under pulse voltage ($Q_s = 0$) [see Eqs. (1) and (2)]. Results show that a main contributor is the electrostatic field formed in the pentacene layer due to pulse voltages [24, 25]. On the other hand, the plots under dc
voltage application deviates from the $l_{2\omega} \propto |E'|^2 \propto |V|^2$ curve, indicating that the electric field in the pentacene layer is relaxed due to the presence of holes ($Q_s > 0$) accumulated at the pentacene/polyimide interface. In Fig. 2(b), we plotted the interface carrier density $Q_s$, calculated using Eqs. (1) and (2). The interface charge $Q_s$ increases linearly in proportion to the applied dc voltage $V$, i.e., $Q_s = C_2 V$ ($C_2$: polyimide layer capacitance), suggesting that polyimide is serving as a good hole blocking layer. Note that the interfacial charge $Q_s$ in Au/pentacene/polyimide/IZO device obeys $Q_s = C_2 (V - V_{th})$ if threshold voltage $V_{th}$ is non-zero due to limited carrier injection and other factors [26]. The EFISHG directly probes $Q_s$, and the non-zero threshold voltage of devices does not give effect on the following analysis.

As shown in Fig. 2(b), the EFISHG measurement revealed the accumulation of interface holes $Q_s$ ($>0$) in the Au/pentacene/polyimide/IZO MIS diode. This situation is quite different from that of single-layer devices. In Au/pentacene/IZO single-layer device, holes are injected from Au electrode to pentacene while electrons enter from IZO electrode to pentacene. That is, in single-layer devices, hole and electron injection from the opposite electrode governs carrier mechanism of the diode. By contrast, in Au/pentacene/polyimide/IZO MIS diode, holes are injected from Au and go through the pentacene layer, and then accumulate at the pentacene/polyimide interface. These
accumulated holes are a source of space charge field which dominates the carrier mechanism in double-layer diodes as described in our previous studies [22, 27, 28]. Consequently, interfacial holes govern carrier mechanism of the Au/pentacene/polyimide/IZO MIS diodes. However, we are still not clear the energetics of these accumulated holes, i.e., whether the interfacial holes are at pentacene states or at polyimide states. In order to energetically identify the holes accumulated at the pentacene/polyimide interface of Au/pentacene/polyimide/IZO MIS diodes, we employed EL spectroscopy.

Figure 3(a) shows the EL spectrum of the Au/pentacene/polyimide/IZO diodes at $V = +20$ V. The EL spectrum shows a peak at $\lambda = 700$ nm with broad shoulder distributed in the region from 400 nm to 900 nm in wavelength. The EL peak observed at $\lambda = 700$ nm is assigned due to the recombination of a pair of hole and electron in a pentacene molecule, on the basis of the photoluminescence spectrum of the pentacene film that has been found at 700 nm [29]. Figure 3(b) shows the EL spectra of the Au/pentacene/IZO and Au/polyimide/IZO single-layer devices at $V = +5$ and +12 V, respectively. The EL intensity integrated in the region from $\lambda = 400$ to 900 nm was normalized to be unity. The spectra appeared in the same manner for pentacene at $V = -31$ V and for polyimide at -12 V (not shown). Results suggest that the EL spectrum of
Au/pentacene/polyimide/IZO MIS diodes was the sum of EL spectra from the pentacene and polyimide single-layer devices. In other words, the EL emission from the Au/pentacene/polyimide/IZO diode was due to recombination of electrons and holes in the pentacene and in the polyimide, but probably not due to recombination via states crossing-over between pentacene and polyimide. We fitted the EL spectrum of the MIS diode by summing up the EL spectra of the Au/pentacene/IZO and of Au/polyimide/IZO single-layer devices, at a proper ratio. Figure 3(a) shows the obtained best fitted spectrum where the EL spectra of pentacene and polyimide were combined with the percentage ratio of pentacene:polyimide = 40:60. Results clearly indicate that the EL spectrum of the Au/pentacene/polyimide/IZO diodes is mainly due to the recombination process of electrons and holes in pentacene and polyimide layers. That is, holes that are accumulated at the pentacene/polyimide interface are not merely located in the pentacene layer, but they are transferred to the polyimide states.

The EFISHG measurement indicated that the accumulated holes at the interface are being with a charge density of $Q_s = 3.8 \times 10^{-7}$ C/cm$^2$, meanwhile the EL spectrum of the diode suggested that 40% of the interface holes $Q_s$ are located in the pentacene states and 60% of the $Q_s$ occupied the polyimide states, under assumption that holes accumulated at pentacene/polyimide interface govern EL emission. Note that, in general,
many factors such as hole-electron balance, exciton generation efficiency, fluorescence quantum efficiency, and outcoupling efficiency contribute to EL emission. In the present calculation, we tentatively assumed that the interfacial holes govern EL emission, and other factors are the same for polyimide and pentacene. Accordingly, we normalized the EL intensity so that the area of the pentacene and polyimide EL spectra have the area of $0.4 \times Q_s$ and $0.6 \times Q_s$, respectively. Figure 3(c) displays the calculated interface state density at the pentacene/polyimide interface of the Au/pentacene/polyimide/IZO diodes. We obtained electronic energy state of the accumulated holes by converting the EL wavelength $\lambda$ to photon energy as $E = h \cdot c / e \lambda$ ($h$: Planck constant, $c$: speed of light in vacuum, $e$: elementary charge). The energy states in pentacene distribute in the region from 1.5 to 1.8 eV with the interface state density > $10^{12}$ cm$^{-2}$eV$^{-1}$. This energy states’ distribution well agrees with those observed by using photo-conductance and photoluminescence spectroscopies [30-32]. Results showed that the accumulated holes are stored at the valence band-like state of pentacene and recombined with electrons injected from polyimide to the conduction band-like state of pentacene. On the other hand, energy state distribution in polyimide is broader than that of the pentacene and ranges from 1.7 to 2.4 eV. The polyimide has a large optical energy gap $E > 4.3$ eV [33] which is far larger than $E \sim 2$ eV obtained from the analysis of EL spectrum. This
result indicated that the accumulated holes are stored in electronic donating states of polyimide that are positioned in the energy gap region, and recombined with electrons located at the electron accepting states of polyimide [34, 35]. Note that energy distributions of the highest occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) also contribute to EL spectrum for hole-electron recombination through these states.

It is instructive here to discuss carrier mechanism for the observed EL emission. As the EFISHG result clearly indicated, holes are injected from the Au electrode, and transported through the pentacene, and then accumulated at the pentacene/polyimide interface. The polyimide layer blocked hole transport in the layer, resulting in the interfacial hole accumulation with charge density $Q_s \sim C_2V$. On one hand, these accumulated holes occupy both energy states at pentacene and those at polyimide as evidently shown by the EL spectrum measurement. On the other hand, these holes are a source of electrostatic field in the polyimide layer and assist electron injection from the IZO electrode into the polyimide. The injected electrons migrate along the electrostatic field in the polyimide. As the result, electrons are transferred toward the holes accumulated at the interface and recombine with these holes to emit EL. That is, the interface holes are a source of EL emitted from the Au/pentacene/polyimide/IZO diode.
Note that the carrier mechanism described here also accounted for the EL emission from double-layer organic light-emitting diodes in our previous studies [36-38]. It is also noteworthy that, we recently got similar results as that holes can be trapped into polyimide interface energy states beyond the pentacene layer, by using $C-V$ measurement coupled with charge modulation spectroscopy (CMS), where diodes with TIPS-pentacene/polyimide double-layers were used [14]. The EL-EFISHG measurement of Au/pentacene/polyimide diode studied here showed good agreement with our recent study on TIPS-pentacene/polyimide diodes.

4. Conclusions

By using the EL–EFISHG measurement, we studied the interfacial energy states of Au/pentacene/polyimide/IZO diodes. The EFISHG well probed accumulated holes at the pentacene/polyimide interface, where the hole density was $Q_s = 3.8 \times 10^{-7}$ C/cm$^2$. The EL spectroscopy showed that the energy states with a density of $10^{12}$ /cm$^2$eV distributed in the region $E = 1.5–1.8$ eV for pentacene and $1.7–2.4$ eV for polyimide. The EL–EFISHG measurement is helpful to study the status of accumulated charges at organic-organic layer interfaces and thus available for determining interface energy states in electronic devices.
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References


Figure Captions

Figure 1: $I$–$V$ and $EL$–$V$ characteristics of the Au/pentacene/polyimide/IZO diode. The inset shows the structure of the diode and experimental arrangement for the EL measurement.

Figure 2: EFISHG measurement of the Au/pentacene/polyimide/IZO diode. (a) The EFISHG intensity measured under pulse and dc voltages for probing electrostatic field $\vec{E}_1$ formed in the pentacene layer. The inset shows the optical setup for the EFISHG measurement. (b) The interfacial charge density $Q_s$ obtained by using the EFISHG measurement (blue circles) and that calculated by using the linear relation $Q_s = C_2 V$ (solid line).

Figure 3: (a) EL spectrum of the Au/pentacene/polyimide/IZO diode measured by using the EL spectroscopy (blue curve) and that obtained by summing up EL spectra of Au/pentacene/IZO and Au/polyimide/IZO single-layer devices with the percentage ratio of pentacene:polyimide = 40:60. (b) The EL spectra of Au/pentacene/IZO and Au/polyimide/IZO single-layer devices. The EL spectrum was normalized as the area below the spectrum gives unit area. (c) Interface state density of pentacene and polyimide which are occupied by holes accumulated at the pentacene/polyimide interface of
Au/pentacene/polyimide/IZO diodes.
Figure 1: D. Taguchi et al.
Figure 2: D. Taguchi et al.
Figure 3: D. Taguchi