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Study of carrier blocking property of poly-linalyl acetate thin layer by electric-field-induced optical second-harmonic generation measurement

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Abstract

By using electric-field-induced optical second-harmonic generation (EFISHG) measurement, we studied the carrier-blocking property of poly-linalyl acetate (PLA) thin layers sandwiched in indium-zinc-oxide (IZO)/PLA/C_{60}/Al double-layer diodes. Results showed that the PLA layer totally blocks electrons crossing the C_{60} layer, and also blocks holes entering from the IZO layer. The EFISHG measurement effectively substantiates the hole-blocking electron-blocking property of the PLA layer sandwiched in double layer diodes.

Keywords: poly-linalyl acetate; non-synthetic polymer; electric-field-induced optical second-harmonic generation; Maxwell-Wagner effect

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1. Introduction

Organic electronic devices such as organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) have been paid much attention in electronics [1,2], and many device structures have been proposed to improve the device performance. Among them is the use of insulator-like layers that can assist carrier injection, carrier accumulation, carrier transport, carrier-blocking, and so forth. In many organic devices, the efficiency depends on the charge carrier transport through the layers. As an example, in OLEDs several functional layers are needed to transport charges, including hole and electron transport layers and the emissive layers (EML). In order to assure the hole flow into the emissive zone with a minimal barrier to injection, the Hole Transport Layer (HTL) needs to have its HOMO level aligned with the corresponding HOMO level of the host. In the meantime the HTL LUMO has to be sufficiently high to prevent electron leakage from the host into the HTL. In the case of OLED, an electron blocking layer (EBL) and HTL can promote hole injection from the anode into the EML while simultaneously preventing electrons from traversing the EML without radiative recombination, thereby greatly increasing the device efficiency. Therefore, it is vital to develop layers with specific charge transport and charge blocking property of insulator-like layer.

The carrier-blocking layers, i.e., hole-transport electron-blocking layers (EBL), electron-transport hole-blocking layers (HBL), are introduced in OLEDs where hole-electron balance should be optimized [2]. Analyzing the current-voltage (*I*-*V*) characteristics would be useful [4]. However, it is a hard task to analyze selectively the carrier transport across interface layers sandwiched in multilayer devices, e.g., OFETs and OLEDs. Therefore techniques that can directly probe carrier transfer across interface layers is helpful to study the carrier blocking property of interface layers in organic devices. We have developed the electric-field-induced optical second-harmonic generation (EFISHG) measurement technique that can directly probe carrier behavior in multilayer devices [5-9].

In this study, we analyzed the carrier blocking property of non-synthetic poly-linalyl acetate (PLA) layer. In our previous work, we showed that the polyterpenol (PT) layer is an insulator, and the layer functions as a hole-transport electron-blocking layer when incorporated in indium-zinc-oxide(IZO)/PT/C_{60}/Al diodes [10,11], by using the EFISHG measurement. Noteworthy that carrier blocking property of insulators is governed by materials attached to insulators [4].

2. Experimental

Figure 1a illustrates the experimental arrangement for the EFISHG measurement. The IZO/PLA/C_{60}/Al diode was prepared in a way similar to our previous study [10]; the surface of

IZO was UV/ozone treated to be free from organic residuals. Subsequently, the PLA layer (thickness 100 nm) was deposited on the IZO electrodes by using RF plasma polymerization, at a pressure of 100 mTorr, RF frequency 13.56 MHz, and RF power 75 W [12-14]. The fundamental properties of the PLA thin film is previously reported. The optically transparent films are characterized by smooth surface (roughness less than 0.4nm) and refractive index of 1.54 (at wavelength 500 nm). The PLA thin films have a dielectric strength E_B= 1.8 MV/cm. The relative dielectric constant is measured as a function frequency. Though at ambient conditions and frequency of 10 Hz, ε_r value is ~3.7, at higher frequencies (kHz and above) the ε_r value is 2.4 [12]. After that the C_{60} layer (thickness 100 nm) and Al electrodes (thickness 100 nm) were deposited successively by using vacuum evaporation technique under a pressure below 10^{-5} Torr, at an evaporation rate of 1 nm/min. Resulting diodes were sealed to avoid degradation during the current-voltage (*I-V*), capacitance-voltage (*C-V*) and EFISHG measurements. The *I-V* and *C-V* measurements were carried out in the dark. In the *I-V* measurements, DC voltage was applied to the IZO electrode in reference to the grounded Al electrode, at a rate of 0.3 V/s. In the *C-V* measurement, small AC voltage (amplitude 0.1 V, frequency 100 Hz) was superposed on the applied DC voltage. The capacitances of the PLA and C_{60} layers were C_1=0.95 nF and C_2=2.2 nF, respectively, where the electrode area was 4.1 mm^2.

Figure 1a shows the optical set-up for the EFISHG measurement. A laser pulse generated from the third-order harmonic light of a Nd:YAG laser coupled with an optical parametric oscillator was used as an optical probe (average power 1 mW, repetition rate 10 Hz, duration 4 ns). *p*-polarized laser pulses were irradiated on the diode from the IZO electrode side at an incident angle of 45°. The wavelength of the laser beam was set at 1000 nm (the wavelength of EFISHG at 500 nm) to selectively probe electric field in C_{60} layer [15]. The laser pulses impinged onto the diode, and EFISHG was radiated from C_{60} molecules due to the electromagnetic coupling of the laser beam and electrons in the molecules. Note that generation of EFISHG signals from IZO, PLA, and Al is negligibly small at this wavelength. The EFISHGs radiated from the diode were detected by the photomultiplier tube (PMT), whereas laser pulses reflected from the diode were eliminated using optical filters attached in front of the PMT.

The EFISHG process is a third-order nonlinear process, and its intensity is given as $I_{2\omega} \propto |\varepsilon_0 \chi^{(3)} \vdots E_0 E_\omega E_\omega|^2$ [7,16] (ε_0: vacuum permittivity, $\chi^{(3)}$: the third-order susceptibility, E_0: electrostatic field, E_ω: electric field of the laser beam). That is, EFISHG intensity is in proportion to the square of the electrostatic field as $I_{2\omega} \propto |E_0|^2$. In the layers sandwiched between parallel electrodes, E_0 is given by the sum of the electric field E_m originated from charges $\pm Q_m$ on electrodes and the electric field E_s from charges Q_s in the diode, i.e., $E_0 = E_m + E_s$. The two charging processes for Q_m and Q_s are well reflected in the EFISHG transients that traces electric field E_0 in the layer [17]. In detail, after positive voltage application to the IZO electrode, charges $+Q_m$ and $-Q_m$ are induced on the IZO and Al electrodes, respectively, with a response time $\tau_{RC}=R_sC$ (R_s: resistance of the circuit corrected to the diode in series, C: capacitance of the diode). As a result, the electric field E_m increases as $E_m=Q_m'/\varepsilon_r\varepsilon_0(1-\exp(-t/\tau_{RC}))$, where $Q_m'=CV$ is the electrode charge induced by voltage V and ε_r is the relative dielectric constant of C_{60} layer. After that, charges on electrodes are allowed to be injected, if C_{60} and PLA layers are not working as a carrier blocking layers. In the IZO/PLA/C_{60}/Al diode, electrons on the Al electrode are expected to be injected into C_{60} layer, transported through C_{60}, and accumulated at the C_{60}/PLA interface. The accumulated charge Q_s is a space charge, and thus produces a space charge field in the C_{60} layer as $E_s=1/d_2\cdot Q_s'/(C_1+C_2)$ $(1-\exp(-t/\tau_{MW}))$, where d_2 is the C_{60} layer thickness and Q_s' is charges accumulated at the C_{60}/PLA interface in the limit $t\rightarrow\infty$. This interfacial charging process is well known as the Maxwell-Wagner (MW) effect [7]. Modeling the MW effect based on electric circuit analysis gives the time-constant as $\tau_{MW}=(C_1+C_2)/(G_1+G_2)$ (G_1: conductance of PLA layer, G_2: conductance of C_{60} layer). Accordingly, the second transient phenomenon appears at $t = \tau_{MW}$ in the trace of EFISHG measurement, if the interfacial charging proceeds. Figure 1b portrays a timing-chart for the time-resolved EFISHG measurement. The AC square-wave voltage was applied to the IZO electrode at $t = 0$, and laser pulse was incident at a time t_d (=10 ns ~ 25 ms). The applied voltage was V_a = 10 ~ 20 V, while pre-biasing V_b (see Fig. 1b) was set at -10 V to deplete electrons from the diode as a pre-condition. The time-constant was determined from EFISHG transients by using a filtering technique in the way same as in our previous study [17].

3. Results and Discussion

Figure 2a shows the *I*-*V* characteristics of the IZO/PLA/C_{60}/Al diode. DC current flowing through the diode is very small (< 10 nA), but leakage current > 10 nA flows in the region higher than 10 V. Figure 2b portrays the *C*-*V* curve of the diode. At -20 V, the capacitance was 0.64 nF, corresponding to the series capacitance of C_{60} and PLA layer, C ($=C_1C_2/(C_1+C_2)$) = 0.66 nF. Results show that the C_{60} layer blocks hole injection from the Al electrode, whereas the PLA layer blocks electron injection from the IZO electrode. On the other hand, with increasing DC voltage from -20 V to +20 V, the capacitance increases and saturates. At 20 V, the capacitance was $C = 0.96$ nF, corresponding to the capacitance of single layer PLA ($C = C_1$). This result suggested that electrons enter from the Al electrode, then travel across the C_{60} layer, and finally accumulate at the C_{60}/PLA interface. Taking this into account, we may argue as that main source of the leakage current at $V > 10$ V is the accumulated electrons.

Figure 3a shows the EFISHG transients under AC square-wave voltage application. The EFISHG responded at times, corresponding to $t = \tau_{RC}$ and τ_{MW}, in a manner as described in section 2. The first response at $t = \tau_{RC}$ is due to charge accumulation onto the IZO and Al electrode, $+Q_m$ and $-Q_m$, respectively. The time-constant τ_{RC} = 190 ns estimated from the EFISHG transients corresponded well to the circuit RC time constant of $\tau_{RC}'=R_sC$~190 ns (C=0.96 nF and R_s~200 Ω). At $t = 10^{-6}$ s, the electrode charging completes, where charges induced on the electrode is given as $Q_m'=CV$. The EFISHG intensity $I_{2\omega}$ ($\propto|E_m|^2$) at $t= 10^{-6}$ s is proportional to V^2, because of $E_m \propto Q_m \propto V$. The second response at $t = \tau_{MW}$ is due to the interfacial charging due to the MW effect. At $t = 10^{-6}$ s, EFISHG intensity $I_{2\omega}$ ($\propto|E_0|^2$) decreases and finally reaches nearly zero at $t > 10^{-3}$ s. The zero EFISHG indicates that electric field is zero (E_0=0) in the C_{60} layer. That is, electrons $Q_s = -C_1V$ are accumulated at the C_{60}/PLA interface, and the induced space charge field E_s totally cancels out the electric field in the C_{60} layer. In Fig. 3b, the time-constants, τ_{RC} and τ_{MW}, were plotted as a function of voltage. The time-constant for electrode charging τ_{RC} was independent of the voltage, which is the general characteristic behavior of this process [17]. On the other hand, τ_{MW} shows voltage-dependence reflecting transport mechanism of layers. Results showed that τ_{MW} (= 2.0×10^{-4} s) is constant. One possible way to explain the result is that the PLA layer well blocks electron injection from the C_{60}/PLA interface, while the PLA layer also blocks hole injection from the IZO electrode. That is, the conductance of the PLA is nearly zero $G_1 = 0$. On the other hand, conductance of C_{60}, G_2, is about 10^{-5} S [18]. Using these conductance and capacitance of the PLA and C_{60} layer, τ_{MW}

$=(C_1+C_2)/(G_1+G_2) = 3.2\times10^{-4}$ s is estimated, which agreed well with the result. Note that, the time-constant τ_{MW} is a function of applied voltage depending on transport mechanism of the device [4]. The time constant is inversely proportional to the applied voltage ($\tau_{MW} \propto 1/V$) when electron-blocking hole-blocking insulator is used and carrier transport in an active layer is governed by the carrier transit across the layer, in a manner as for ITO/polyimide/pentacene/Au [19]. The time constant is inversely proportional to the square of the applied voltage ($\tau_{MW} \propto 1/V^2$) when hole-transport electron-blocking insulator is actively working, in a manner as for IZO/PT/C_{60}/Al diodes [10]. The voltage-independent τ_{MW} of the IZO/PLA/C_{60}/Al diode clearly demonstrates that the PLA is an excellent electron-blocking hole-blocking insulator, and that the C_{60} layer can be regarded as an Ohmic conductor. In conclusion, EFISHG measurement effectively verified the hole-blocking electron-blocking property of the PLA layer.

4. Conclusion

By using EFISHG measurement, we analyzed the carrier-blocking property of poly-linalyl acetate (PLA) thin film sandwiched in IZO/PLA/C_{60}/Al double-layer diodes. Results showed that the PLA film totally blocked electrons travelling across the C_{60}, meanwhile, the PLA never allowed holes entering from the IZO. This behavior of the PLA layer is contrast to PT layer, which functioned as a hole-blocking electron-blocking layer when used in IZO/PLA/C_{60}/Al diodes, whereas PLA layer blocks both electrons and holes. The PLA is a non-synthetic environmentally friendly polymer that is suitable as a hole-blocking electron-blocking insulating layer and hence can be used in applications which require perfect insulators.

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Figure captions

Figure 1: (a) Optical setup for the EFISHG measurement and IZO/PLA/C_{60}/Al diode used here.

Figure 2: (a) *I-V* and (b) *C-V* characteristics of the IZO/PLA/C_{60}/Al diode.

Figure 3: (a) EFISHG transients of the IZO/PLA/C_{60}/Al diode. (b) Voltage dependence of response time for electrode charging process (τ_{RC}) and interfacial charging process (τ_{MW}).

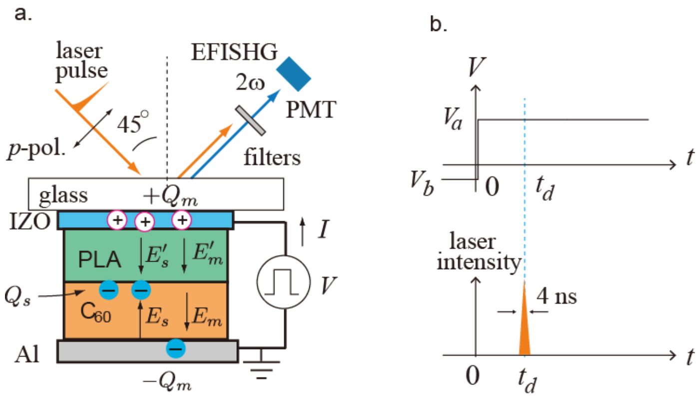

Fig. 1: D. Taguchi et al.

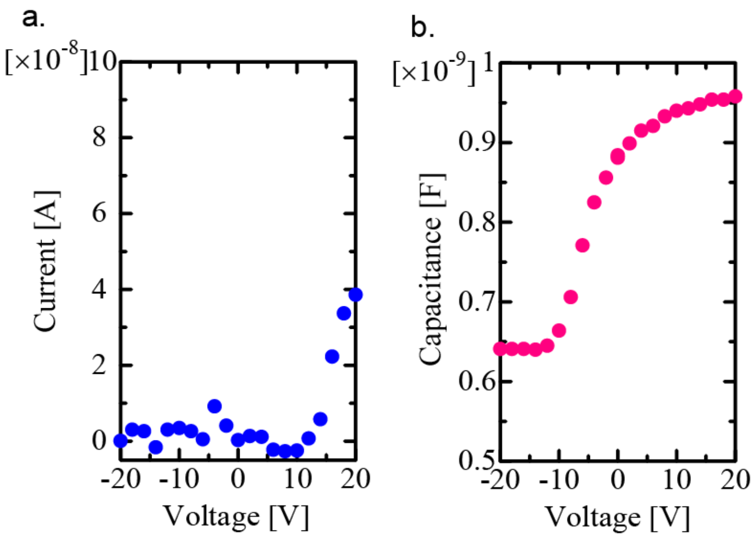

Fig. 2: D. Taguchi et al.

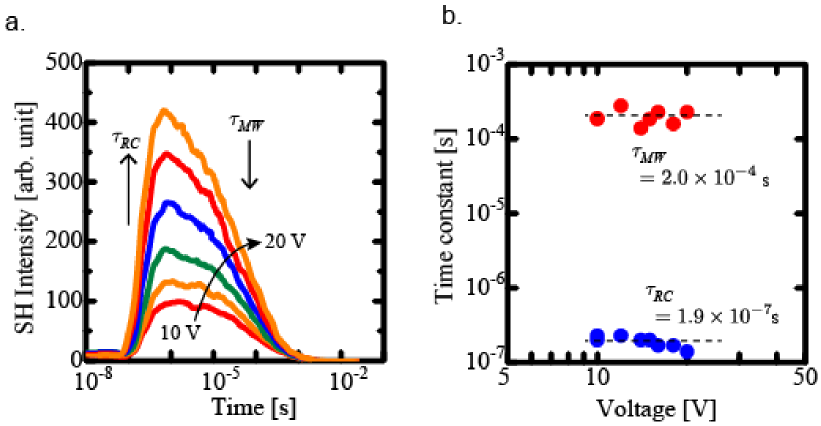

Fig. 3: D. Taguchi et al.