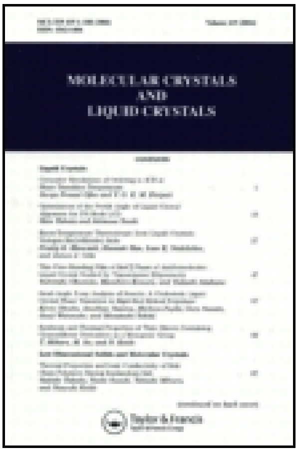

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Direct Probing of Internal Electric-fields in Fullerene Diodes Using Electric-field-induced Second-harmonic Generation Measurement

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By using electric-field-induced optical second-harmonic generation (EFISHG) measurement, we directly probed internal electrostatic fields formed in indium-zinc-oxide (IZO)/fullerene (C_{60})/Al diodes, which are electrically shorted. Results showed that an internal electric-field is formed in the direction from the IZO to Al electrode, whereas the electric-field points in the opposite direction by the use of an interlayer of bathocuproine (BCP) between C_{60} and Al. We concluded that the EFISHG measurement directly probes internal electric-fields formed in organic devices, and it is thus helpful for understanding the effect of an interlayer in diodes.

Keywords Carrier injection; double-layer diode; Electric-field-induced optical second-harmonic generation (EFISHG); fullerene; internal electric-field; work function difference

Introduction

Organic thin film devices have attracted much attention in electronics. Among them are organic light-emitting diodes (OLEDs) [1] and organic solar cells (OSCs) [2]. The device structure is basically the same with that of a metal-insulator-metal (MIM) diode with a thin organic layer. Owing to the difference of work function of the two electrodes, a non-zero internal electric-field is formed in these short-circuited devices. The presence of the non-zero internal electric-field assists carrier injection in OLEDs [3], whereas it assists charge separation in OSCs [4]. Accordingly measuring the internal field is an important research subject for understanding carrier mechanism in these devices. The electric-field-induced optical second-harmonic generation (EFISHG) measurement is capable of directly probing electric-fields in MIM devices [5, 6]. In the EFISHG measurement, nano (or femto) second pulsed laser is used as a probe light. Therefore, we can carry a time-resolved method in the EFISHG measurement, where the electric-field evolution induced by carrier injection and succeeding carrier transport is allowed to be traced. Until now, we have been using the time-resolved EFISHG measurement to probe carrier motion in organic devices, on paying attention to the presence of space charge fields generated from carriers [7]. In

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this paper, for further understanding carrier behavior in diodes, the time-resolved EFISHG measurement is employed to measure internal electric-fields formed in short-circuited MIM diodes.

Experimental

Figure 1 portrays an experimental arrangement of the time-resolved EFISHG measurement, where IZO/fullerene (C_{60})/Al and IZO/fullerene (C_{60})/bathocuproine (BCP)/Al diodes are used. These diodes were prepared on glass substrates with patterned IZO electrodes (device area 3.1 mm^2) as follows: Before the preparation, the substrates were UV/Ozone-treated, and the surface of the IZO electrodes was free of organic residues. On the UV/Ozone-treated substrates, the C_{60} layer (thickness $d = 200$ nm) and Al electrode were evaporated successively. The BCP layer was also evaporated with a thickness of 5 nm when we prepared the IZO/C_{60}/BCP/Al diodes.

In the time-resolved EFISHG measurement, the pulsed laser beam (duration 4 ns, repetition rate 10 Hz) was incident at an angle of 45° from the IZO side. The wavelength of the pulsed laser beam was 1000 nm, to selectively probe the SHG from the C_{60} layer [6]. In the presence of an internal d.c. electric-field $E_{0,}$ the second-harmonic nonlinear polarization wave $P_{2\omega}$ (wavelength $\lambda/2$) is induced due to electromagnetic coupling between the electric-field E_ω of laser beam (wavelength λ) and electrons in C_{60} molecules. As a result the EFISHG is generated and its intensity is given as

$$I_{2\omega} \propto |P_{2\omega}|^2 \propto \left|\varepsilon_0 \chi^{(3)} \vdots E_0 E_\omega E_\omega\right|^2 \tag{1}$$

where ε_0 is the vacuum permittivity, $\chi^{(3)}$ is the third-order nonlinear susceptibility. Equation (1) indicates that the EFISHG intensity is proportional to $|E_0|^2$. Here $E_0(= E_i + E_e)$ is given as sum of the internal electrostatic field E_i and the external electric-field E_e $(= V/d$, V: external voltage, d : distance between two electrodes). In the time-resolved EFISHG measurement, $I_{2\omega}$ is probed with a delay time t_d, upon application of step d.c. voltage V to the IZO electrode in reference to the Al electrode (see Fig. 1), in a manner as in our previous study [6].

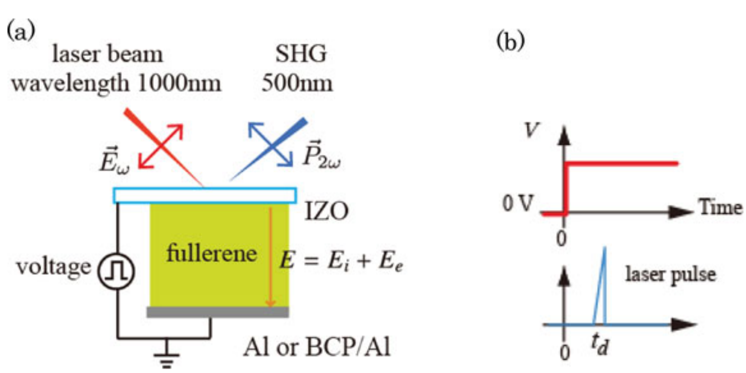

Figure 1. (a) Experimental illustration for the time-resolved EFISHG measurement. (b) Timing chart of step-voltage application and laser pulse irradiation.

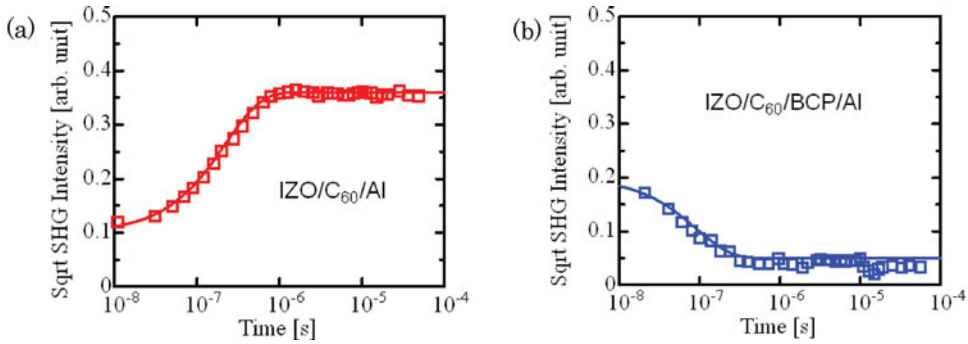

Figure 2. EFISHG response recorded by the application of a step voltage at $t = 0$, (a) for the IZO/C_{60}/Al diode with a step voltage V of +1 V, and (b) for the IZO/C_{60}/BCP/Al diode with a step voltage V of + 0.5 V.

Equation (1) shows that $I_{2\omega} = 0$ when $E_0 = E_i + E_e = 0$. Therefore, the internal field is estimated as $E_i = -E_e$, by choosing the applied external voltage V to be $I_{2\omega} = 0$. Upon application of a step-voltage V at $t = 0$, the electric-field E_e in the C_{60} layer in diodes increases with time as $E_e = V/d(1-\exp(-\mathrm{t}/\tau))$, with a single relaxation time $\tau = RC$ (R: electrode and lead-wire resistance, C: sample capacitance). Accordingly, the electric-field E_0 increases, though the E_0 is shifted with E_i from E_e.

Results and Discussion

Figures 2a and 2b show the time-resolved EFISHG response of the IZO/C_{60}/Al and IZO/C_{60}/BCP/Al diodes, respectively, where a step-voltage was applied at $t = 0$. The EFISHG response with a single relaxation time τ of 100 ns, which agrees well with the circuit RC with electrode resistance $R = 100\ \Omega$ and device capacitance $C \sim 1$ nF. Results suggest that external electric-field is applied to the C_{60} layer in proportion to $V/d(1 - \exp(-t/\tau))$. In more detail, for the IZO/C_{60}/Al diode (see Fig. 2a), the EFISHG signal was non-zero at $t = 0$, but increased with time upon application of a step-voltage of +1V to the IZO electrode. The result suggested that there is an internal field E_i in the C_{60} layer in the direction from the IZO to the Al electrode, and additionally the field in the C_{60} layer increases in proportion to $V/d(1 - \exp(-t/\tau))$ by the applied step-voltage. On the other hand, for the IZO/C_{60}/BCP/Al diode (Fig. 2b), the EFISHG signal was again non-zero at $t = 0$, indicating the presence of non-zero internal field E_i' in the C_{60} layer, but $E_i' \neq E_i$. Interestingly the field formed in the C_{60} layer decreased in proportion to $V/d(1-\exp(-t/\tau))$ by the applied step-voltage of +0.5V. Results suggest that the polarity of E_i' is opposite to the E_i. That is, the internal electric-field E_i' points in the direction from the Al to IZO electrode, as a result of the insertion of the interlayer between C_{60} and Al electrodes. Consequently, the application of the step-voltage of +0.5 V resulted in the decrease of the electric-field E_0 $(= E_e + E_i')$.

To further verify the direction of the internal electric-field formed in the C_{60} layer, we carried the time-resolved EFISHG measurement at various step-voltages, in the range from −1.5 V to 1.5 V. To avoid the influence of carrier injection, we plotted the results at $t = 200$ ns, as shown in Fig. 3. Note that at $t = 200$ ns the time-resolved EFISHG signal saturates in a similar manner as shown in Fig. 2, suggesting no other electric-field

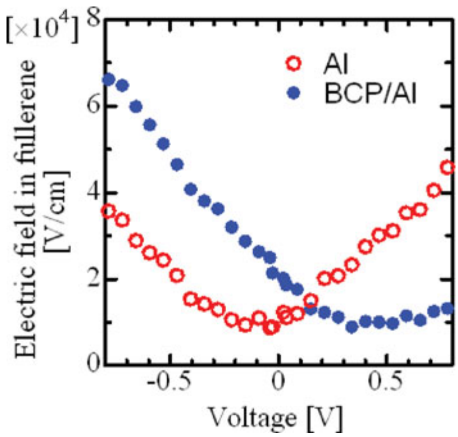

Figure 3. Plots of the electric-field in the C_{60} layer probed by the EFISHG measurement.

formation such as by carrier injection. The y-axis represents the electric-field E_0, Here the value of the electric-field was determined using Eq. (1), with reference to the EFISHG intensity at $V = -1$ V. The electric-field in the C_{60} layer gives a minimum at $V = -0.1$ V for the IZO/C_{60}/Al diode, whereas at $V = +\ 0.42$ V for the IZO/C_{60}/BCP/Al diode. As we mentioned in EXPERIMENTAL section, the EFISHG intensity should be a minimum when we applied external voltage V to satisfy $E_i = -E_e$ $(= -V/d)$. Accordingly, the internal field in the C_{60} layer is $E_i = 5 \times 10^3$ V/cm in the direction from the IZO to Al electrode for IZO/C_{60}/Al diode, whereas $E_i' = -\ 2.1 \times 10^4$ V/cm in the direction from the Al to IZO electrode, for the IZO/C_{60}/BCP/Al diode. Noteworthy that the work-function-difference between IZO ($\phi_1 = 4.8$ eV) and Al ($\phi_2 = 3.4$ eV) is about 1.4 eV, and an internal field $E_i = (\phi_2 - \phi_1)/ed = -7 \times 10^4$ V/cm (e, elementary charge) is assumed to be formed in the C_{60} layer, in the direction from the Al to IZO. The results of the EFISHG measurements of the IZO/C_{60}/BCP/Al diode agreed well with the assumption. On the other hand, in the IZO/C_{60}/Al diode, electrons transfer from the Al to the C_{60} layer at the Al/C_{60} interface, where electrons are accumulated. As a result, an electrostatic space charge field is additionally formed in the C_{60} layer, and the internal field is thus in the direction from the IZO to Al.

Conclusion

By using the EFISHG measurement, internal electric-fields in IZO/C_{60}/Al and IZO/C_{60}/BCP/Al diodes were determined. Results showed that the direction of the probed internal field was from the Al to IZO electrodes for the short-circuited IZO/C_{60}/BCP/Al diode, in a manner as expected from the work-function-difference between the IZO and Al electrodes. On the other hand, the result showed that the direction changes without a BCP interlayer between the C_{60} layer and Al electrode. The EFISHG measurement is helpful for further understanding of carrier motion in organic devices by the introduction of an interlayer, where an internal electric-field makes a significant contribution such as in OSCs and in OLEDs.

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