Photoinduced alteration of the inner electric field in a Zn-phthalocyanine/C_{60} heterojunction solar cell

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Abstract

Electroabsorption (EA) and photocurrent measurements are carried out for a Au/Zn-phthalocyanine(ZnPc)/C_{60}/In/Al heterojunction cell in order to elucidate the effect of photoexcitation of ZnPc or C_{60} on the inner electric field E_0. By a pumping excitation of either the ZnPc or C_{60} layer, the E_0 of the pumped layer is decreased and that of the other layer is increased. The photocurrent due to a probing-light illumination besides the pumping-light illumination has a good correlation with E_0 under the pumping excitation of ZnPc but has no correlation under the pumping excitation of C_{60}.

Keywords: Electroabsorption; Solar cells; Fullerenes and derivatives; Organic semiconductors based on conjugated molecules

1. Introduction

Organic thin-film solar cells have been studied as candidates for the practical devices based on organic semiconductors [1,2]. However, the mechanism of the photocurrent generation in the organic thin-film solar cells has not yet been clearly understood. The mechanism should be closely related to the distribution of the inner electric field (E_0) in the devices because E_0 can induce the dissociation of excitons as well as the drift of the photogenerated carriers. This is why the study of E_0 is important.

E_0 of organic devices is usually measured by electroabsorption (EA) technique in which an electric-field modulation is applied to the device and a synchronous change, $\Delta\alpha$, in the optical-absorption coefficient is detected at the fundamental modulation frequency [3]. Then, $\Delta\alpha$ is proportional to E_0. By using the EA technique, we have recently studied the correlation between E_0 and the photocurrent (I_{photo}) in phthalocyanine-based Schottky-junction and hetero-junction solar cells [4,5]. It was shown that the bulk E_0 in the devices has a good correlation with I_{photo}, indicating that the photoexcited carriers are generated by the electric field. The light intensity used in our previous studies was less than the order of 10 μW/cm^2 which was weak enough to avoid the disturbance of E_0. When the solar cells are practically used, however, much stronger light is illuminated. In such a situation, E_0 may be affected by the illumination. This paper deals with this problem. The EA and photocurrent measurements are carried out for a typical heterojunction cell Au/ZnPc/C_{60}/In/Al [6-9] with and without an illumination of a pumping light as well as a weak probing light. It will be shown that E_0 is affected by the pumping excitations of ZnPc and C_{60}, but the effect of the pumping excitation on I_{photo} is different for the two cases of the ZnPc- and C_{60}-excitations.

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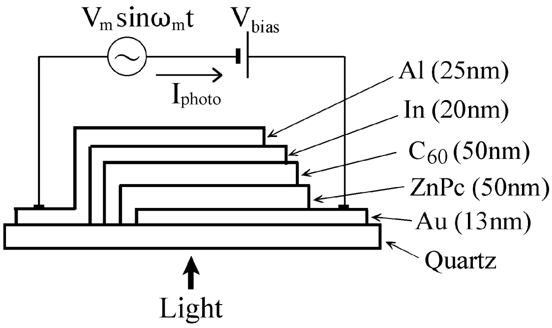

Fig. 1. Scheme of a Au/ZnPc/C_{60}/In/Al heterojunction and the electric circuit for the EA measurement.

2. Experiment

ZnPc was purchased from Kanto Chem. Co. Inc. and was used after subliming three times. C_{60} (99.95 %) was purchased from MER Corp. and was used after subliming two times.

The arrangement of the thin films in the Au/ZnPc/C_{60}/In/Al heterojunction system is shown in Fig. 1. On a quartz substrate of 9 × 24 × 1 mm^3, thin films were evaporated under a pressure of 1×10^{-4} Pa. The Al film is a supporting electrode for In because the conductivity of the In film is quite poor [10]. The thickness of each film is shown in Fig. 1. The speed of the evaporation was 0.02 nm/s for Au, 0.1 nm/s for ZnPc, C_{60} and Al, and 0.01 nm/s for In, monitored by a quartz oscillator (ULVAC CRTM-5000 and 6000). The active area of the device was 0.3 cm^2.

The electric circuit for the EA measurement is shown in Fig. 1. An electric-field modulation of 100 Hz was applied to the sample by using a function generator whose output signal was $V_m \sin\omega_m t$ with V_m = 0.5 V. The probing light for the EA measurement was entered normally to the active area of the device from the quartz side. The light source for the probing light was a 100 W halogen lamp followed by a monochromator. The cross sectional area of the beam was 0.06 cm^2. The intensity of the probing light depended on the wavelength but was always smaller than 1 μW. The transmitted light intensity T was detected by a photomultiplier tube. The change, ΔT, of the transmitted light intensity in the fundamental modulation frequency ω_m was detected by a lock-in amplifier. Then $-\Delta T/T$ is proportional to the inner electric field E_0 in the ZnPc and/or C_{60} layers depending on the wavelength of the probing light [5].

The EA measurement was carried out with or without a pumping-light illumination from the quartz side besides the probing-light illumination. The light source for the pumping excitation of ZnPc was a 5-mW He-Ne laser followed by a lens as a beam expander (λ = 633 nm, 3 mW/cm^2), and the light source for the pumping excitation of C_{60} was a 500-W Xe lamp with appropriate glass filters (400 < λ < 500 nm, 200 $\mu W/cm^2$).

The photocurrent measurement was carried out using the same probing- and pumping-light sources with the EA measurement. The probing light was chopped at 35 Hz and the synchronous change in the photocurrent was detected by a lock-in amplifier. The positive directions of the photocurrent (I_{photo}) and the applied bias voltage (V_{bias}) are defined in Fig. 1. All the measurements were carried out with the sample kept at room temperature in the air.

3. Results and Discussion

3.1. Electroabsorption

Figure 2 shows the EA spectrum of the Au/ZnPc/C_{60}/In/Al heterojunction cell and also the EA spectra of a Au/ZnPc/Al and a Pt/C_{60}/In/Al Schottky-junction cells. The latter spectra in Fig. 2(b) indicate that the EA signals of ZnPc and C_{60} distribute in the wavelength ranges of 530 nm < λ < 800 nm and 400 nm < λ < 600 nm, respectively, in which the optical absorption of ZnPc and

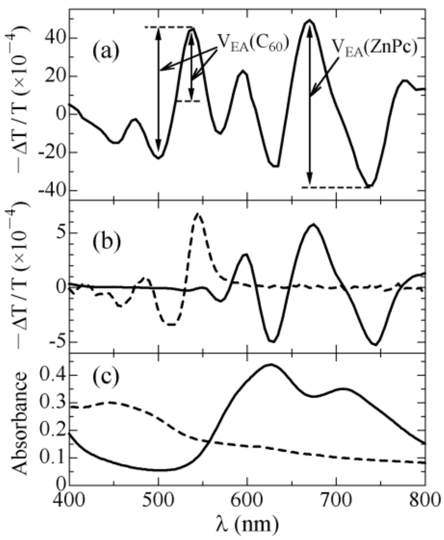

Fig. 2. (a) The EA spectrum of Au/ZnPc(50nm)/C_{60} (50nm)/In/Al with V_{bias}= −2 V. V_{EA} are the EA signal intensities for ZnPc and C_{60}. (b) The EA spectra of Au/ ZnPc(100 nm)/Al with V_{bias}= −2 V (solid curve) and of Pt/ C_{60}(100 nm)/In/Al with V_{bias}= 0 V (broken curve). (c) The optical absorption spectra of the thin films of ZnPc(50 nm) (solid curve) and C_{60}(50 nm) (broken curve).

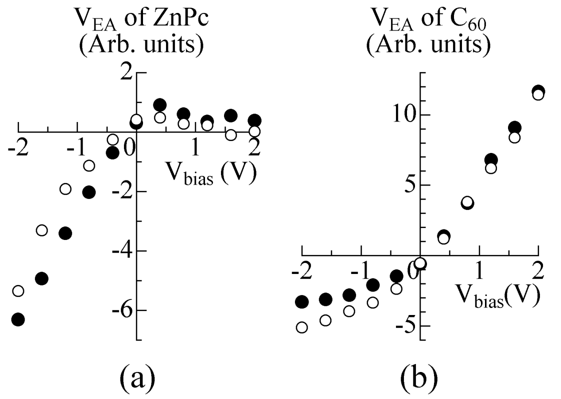

Fig. 3. The bias dependence of the EA signal intensity of (a) ZnPc and (b) C_{60} in Au/ZnPc/C_{60}/In/Al. ●: Without pumping excitation. ○: With the pumping excitation of ZnPc with a 633 nm light of 3 mW/cm^2.

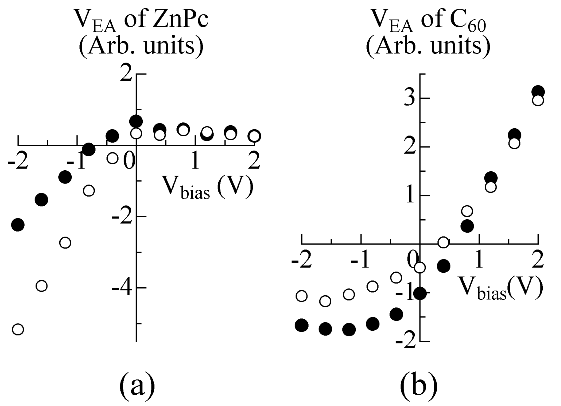

Fig. 4. The bias dependence of the EA signal intensity of (a) ZnPc and (b) C_{60} in Au/ZnPc/C_{60}/In/Al. ●: Without pumping excitation. ○: With the pumping excitation of C_{60} with a 400 nm < λ < 500 nm light of 200 μW/cm^2.

C_{60} occurs as shown in Fig. 2(c). It is seen in Fig. 2(a) that the EA spectrum of the heterojunction is made by an overlap of the ZnPc- and C_{60}-spectra.

Figure 3 shows the bias dependence of the EA signal intensities (V_{EA}) of ZnPc and C_{60} for the heterojunction cell with and without the pumping excitation of ZnPc. V_{EA} was measured from the difference between the EA-peak heights at 670 and 740 nm for ZnPc and at 505 and 545 nm for C_{60}. We first inspect the results without the pumping excitation in Fig. 3. For V_{bias} > 0 V, V_{EA} of ZnPc, or the inner electric field E_0 in the ZnPc layer, is nearly quenched. This means that the forward bias is supplied only to the C_{60} layer. The similar result was reported when a perylene derivative PTCBI was used instead of C_{60} [5].

Next, the results with the pumping excitation of ZnPc in Fig. 3 are inspected. For V_{bias} > 0 V, no substantial difference is seen between the EA intensities with and without the pumping excitation. For V_{bias} < 0 V, on the other hand, $|V_{EA}|$, or the inner electric field $|E_0|$, is decreased for ZnPc (Fig. 3(a)) and is increased for C_{60} (Fig. 3(b)) by the pumping excitation of ZnPc.

Figure 4 shows the bias dependence of V_{EA} with and without the pumping excitation of C_{60}. In this case, V_{EA} of C_{60} was measured from the difference between the EA-signal heights at 520 and 545 nm instead of the peak heights at 505 and 545 nm, because the pumping light disturbed the detection of the 505-nm probing light. It is seen in Fig. 4 that, for V_{bias} < 0 V, $|V_{EA}|$, or $|E_0|$, is increased for ZnPc (Fig. 4(a)) and is decreased for C_{60} (Fig. 4(b)) by the pumping excitation of C_{60}.

Thus, under the reverse bias condition, the inner electric field E_0 in the pumped layer is decreased and E_0 in the other layer is increased. Figure 5 shows the deduced band diagrams under the reverse bias condition. A possible interpretation of the effect of the pumping excitation is that the carrier density in the pumped layer is increased to decrease the resistance, so that the fraction of the bias voltage supplied to the pumped layer is decreased and that supplied to the other layer is increased.

3.2. Photocurrent

Figure 6 shows the bias dependence of the photocurrent I_{photo} by the probing light illumination with and without the pumping excitation of ZnPc. It is noted that I_{photo} does not include the photocurrent due to the pumping excitation but is a change of the current due to the probing-light illumination. First, the results without the pumping excitation are inspected. For V_{bias} > 0.5 V,

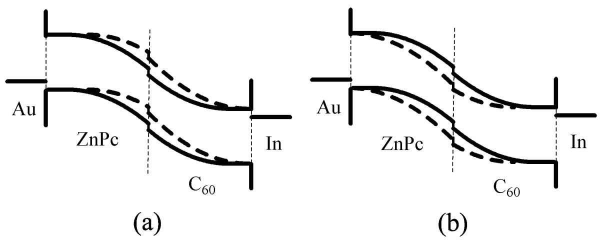

Fig. 5. The band diagrams of Au/ZnPc/C_{60}/In/Al for V_{bias} < 0 V deduced from the present EA results. The solid lines are for the case with no pumping excitation. The broken lines are for the case with the pumping excitation of (a) ZnPc and (b) C_{60}.

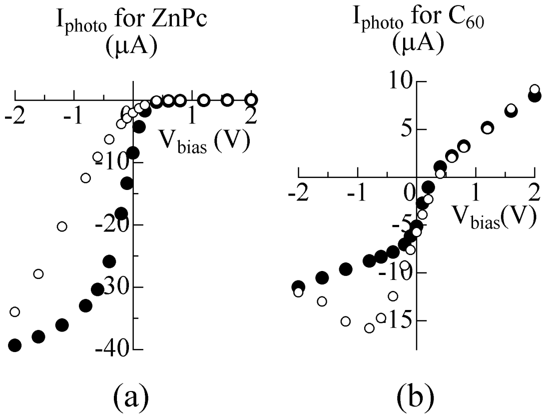

Fig. 6. The bias dependence of the photocurrent by the probing excitation of (a) ZnPc at 720 nm and (b) C_{60} at 450 nm for Au/ZnPc/C_{60}/In/Al. ●: Without the pumping excitation. ○: With the pumping excitation of ZnPc at 633 nm.

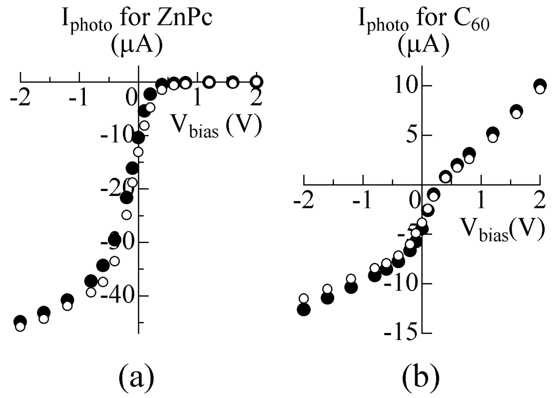

Fig. 7. The bias dependence of the photocurrent by the probing excitation of (a) ZnPc at 720 nm and (b) C_{60} at 450 nm for Au/ZnPc/C_{60}/In/Al. ●: Without the pumping excitation. ○: With the pumping excitation of C_{60} at 400 nm $< \lambda <$ 500 nm.

I_{photo} by the probing excitation of ZnPc is quenched (Fig. 6(a)), which has a good correlation with the quenching of E_0 observed in Fig. 3(a). This indicates that the photoexcited carriers are generated by E_0. Next, the results with the pumping excitation of ZnPc in Fig. 6 are inspected. For $V_{bias} > 0$ V, I_{photo} is not affected by the pumping excitation. For $V_{bias} < 0$ V, on the other hand, $|I_{photo}|$ by the probing excitation of ZnPc is decreased (Fig. 6(a)) and $|I_{photo}|$ by the probing-light illumination of C_{60} is increased (Fig. 6(b)) by the pumping excitation of ZnPc. The change of I_{photo} by the pumping excitation of ZnPc in Fig. 6 has a good correlation with the change of E_0 shown in Fig. 3.

Figure 7 shows the bias dependence of I_{photo} with and without the pumping excitation of C_{60}. In this case, I_{photo} is not affected by the pumping excitation in any bias region. This is in contrast to the substantial effect of the pumping excitation of C_{60} on E_0 shown in Fig. 4. It is noted that all the measurements have been carried out for two independent samples, and the results were qualitatively reproducible. The absence of the correlation between I_{photo} and E_0 under the pumping excitation of C_{60} suggests that I_{photo} is determined not only by E_0. A further study is needed on the mechanism of photocurrent generation under the pumping excitations.

4. Conclusions

Without the pumping excitation, the inner electric field and the photocurrent have a good correlation, indicating that the photoexcited carriers are generated by the inner electric field. With the pumping excitation, the inner electric field in the pumped layer is decreased and that in the other layer is increased under the reverse bias condition, which may be due to the change of the resistance of the pumped layer. The change of the photocurrent by the pumping excitation of ZnPc has a good correlation with the change of the inner electric field. On the other hand, the photocurrent is not affected by the pumping excitation of C_{60} while the inner electric field is affected substantially, which suggests that the magnitude of the photocurrent is determined not only by the inner electric field.

References

[1] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Adv. Funct. Mater. 11 (2001) 15.
[2] H. Spanggaard, F.C. Krebs, Solar Energy Mater. Solar Cells, 83 (2004) 125.
[3] I.H. Campbell, D.L. Smith, in Conjugated Polymer and Molecular Interfaces, W.R. Salaneck, K. Seki, A. Kahn, J.-J. Pireaux, (eds.), Marcel Dekker, New York, 2002, Chap. 21.
[4] I. Hiromitsu, Y. Murakami, T. Ito, Solid State Commun. 119 (2001) 357.
[5] I. Hiromitsu, Y. Murakami, T. Ito, J. Appl. Phys. 94 (2003) 2434.
[6] K. Murata, S. Ito, K. Takahashi, B.M. Hoffman, Appl. Phys. Lett. 68 (1996) 427.
[7] H. Yonehara, C. Pac, Thin Solid Films 278 (1996) 108.
[8] I. Hiromitsu, Y. Kaimori, M. Kitano, T. Ito, Phys. Rev. B59 (1999) 2151.
[9] I. Hiromitsu, M. Kitano, R. Shinto, T. Ito, Solid State Commun. 113 (2000) 165.
[10] F.-R. Fan, L.R. Faulkner, J. Chem. Phys. 69 (1978) 3334.