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Internal electric field of the Schottky-barrier solar cells ITO/pentacene/H_2-phthalocyanine (H_2Pc)/In/Al (cell A) and ITO/H_2Pc/In/Al (cell B) was studied by electroabsorption spectroscopy under white light illumination. The H_2Pc films in the two cells have different crystal orientations. Under short-circuit condition, the average internal field in the H_2Pc layer of cell A is increased by 2.5 times by an illumination of $40\,mW/cm^2$ white light, which is due to a trapping of photogenerated holes and a resulting dipole layer formation at the H_2Pc/In interface, while that of cell B is not affected by the white light illumination. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4835096]

The organic thin-film solar cell (OSC) is widely studied in recent years as a candidate of the next generation solar cell.[1–3] The energy conversion efficiency η of OSC has been greatly improved in the last decade. However, further improvements of η and stability are required for the commercial use of OSC. To achieve the further improvements, study of the internal electric field of OSC should be important because electric field is a driving force of the photovoltaic effect. It is well known that electroabsorption (EA) spectroscopy is a technique to measure the internal field of organic electronic devices.[4–6] In EA, an electric-field modulation $F_m \sin \omega_m t$ is applied to the device, and the synchronous change in optical absorption coefficient, $\Delta\alpha$, is detected. The response $\Delta\alpha$ in the fundamental frequency ω_m is proportional to the static internal electric field F_0 in the device[4–6]

$$\Delta\alpha \propto F_0 F_m \mathrm{Im}\chi^{(3)}, \tag{1}$$

where $\mathrm{Im}\chi^{(3)}$ is the imaginary part of the third-order electric susceptibility. Using the EA technique, much information has been obtained on the mechanism of photocurrent generation in OSC.[7–11]

In all the past EA studies of the electric field, weak monochromatic light was entered into the device and the transmitted light intensity was detected to measure $\Delta\alpha$. Since the light intensity of the incident light was very weak, the observed electric field was approximately that in the dark. In the present study, we tried a new type of EA measurement, i.e., EA under white light illumination (EAWL), by using a white incident light of relatively strong intensity instead of the weak monochromatic light, which enables the measurement of the internal field of OSC under operation. The measurement of EAWL becomes possible by a very simple modification of the usual EA spectrometer, i.e., by placing

the sample *before* the monochromator as in Fig. 1, instead of *after* the monochromator in the usual spectrometer. In this paper, we call the usual EA spectroscopy using the weak monochromatic incident light as EA under monochromatic light illumination (EAML).

It is expected that the internal electric field of OSC is affected by the white light illumination when the photogenerated carriers are trapped in the device, so that EAWL should be especially useful to elucidate the role of carrier traps in the photovoltaic effect. In the present study, two types of Schottky-barrier OSC's, ITO/pentacene/H_2-phthalocyanine (H_2Pc)/In/Al (cell A) and ITO/H_2Pc/In/Al (cell B), shown in Fig. 2, were chosen to test the ability of EAWL. In these devices, a Schottky barrier is formed at the H_2Pc/In interface. In cell A, the (31-3) crystal plane of α-form H_2Pc is aligned parallel to the substrate plane; in other words, the *b*-axis (the current-easy axis) of α-H_2Pc stands on the substrate plane as shown in Fig. 2.[12] In cell B, on the other hand, the *b*-axis lays parallel to the substrate plane.[12] Since the current in OSC flows between the two electrodes, it is expected that cell A should have a higher performance than cell B. However, Naito and co-workers[13] showed that a ITO/pentacene/H_2Pc/C_{60}/bathocuproine/Ag heterojunction cell had a lower performance than a cell without the pentacene buffer layer. The lower performance of the former was attributed to a larger resistance at an interface.[13] In the present study, the performance and the internal electric field of simpler cells, i.e., the Schottky-barrier cells, were studied to elucidate the effect of insertion of the pentacene buffer layer. It will be shown by a combination of the
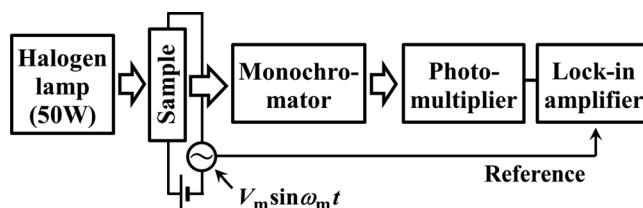

FIG. 1. Block diagram of EAWL spectrometer.

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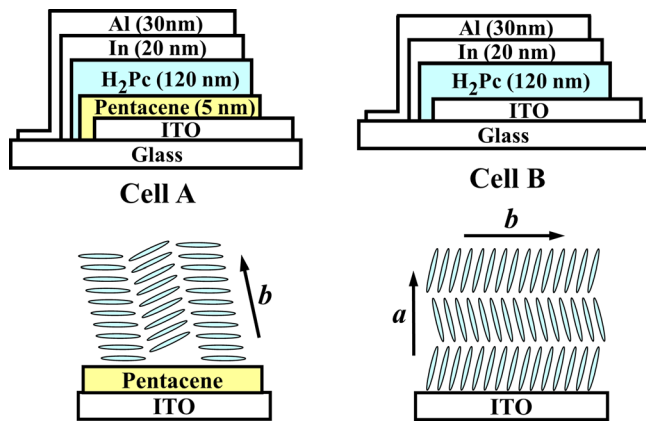[b]Author to whom correspondence should be addressed. Electronic mail: hiromitu@riko.shimane-u.ac.jp

FIG. 2. Schemes of cell A and B, and molecular orientations of H_2Pc in the two cells.
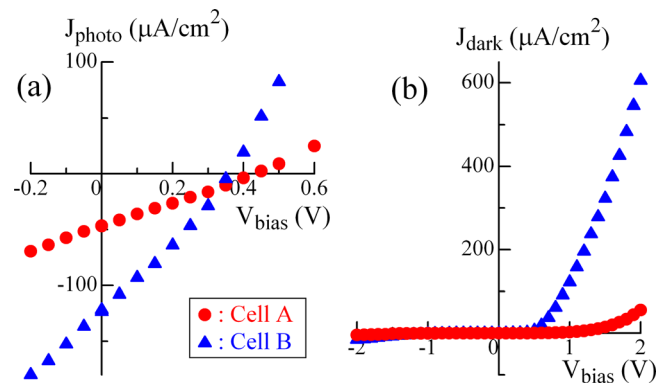

FIG. 3. Bias voltage dependence of the current densities of cell A and B (a) under an illumination of 100 mW/cm^2 light of AM1.5 spectrum and (b) in the dark.

EAWL and EAML measurements that the photovoltaic performance of cell A is strongly affected by a trapping of photogenerated carriers.

H$_2$Pc and pentacene were purchased from Acros and Aldrich, respectively, and used after three and two sublimations in vacuum. The ITO substrate of flat-ITO grade with a 9 Ω/sq. sheet resistance was purchased from Geomatec, and used after polishing,[12] which was performed by rubbing the ITO surface manually in one direction with a plastic eraser (PLUS Statonary AIR-IN) 10 000 times. The force applied on the ITO surface by the eraser was roughly 2N. The average roughness R_a of the polished ITO surface was $\sim$1.0 nm. Then, the ITO substrate was washed with tetrahydrofuran, acetone, and dichloromethane and cleaned by illuminating it by UV light from a Hg lamp.

Pentacene, H$_2$Pc, In, and Al films were deposited on the ITO substrate by vacuum evaporation under a pressure of 1×10^{-4} Pa. The speeds of evaporation were 0.02 nm/s for pentacene and In, 0.05 nm/s for H$_2$Pc, and 0.1 nm/s for Al, as monitored using a quartz oscillator (ULVAC CRTM-5000 or CRTM-6000). The effective area of the device was 0.35 cm^2.

The block diagram for the EAWL measurement is shown in Fig. 1. A white light from the 50 W halogen lamp was entered into the sample, and the transmitted light was entered into the monochromator. In the EAML measurement, on the other hand, the sample was set between the monochromator and the photomultiplier. In both EAWL and EAML, the electric-field modulation was applied to the device using a function generator whose output signal was $V_m \sin \omega_m t$ with a modulation frequency $\omega_m/(2\pi)$ of 1 kHz and an amplitude V_m of 0.25 V. The transmitted light intensity T was detected using the photomultiplier. The amplitude of the change in the transmitted light intensity, ΔT, with frequency ω_m was detected using the lock-in amplifier. Then, $-\Delta T/T$ is proportional to the change in optical absorption coefficient, $\Delta \alpha$. The intensities of the white light for EAWL and the monochromatic light for EAML were 40 mW/cm^2 and less than 0.1 mW/cm^2, respectively. The photocurrent-voltage measurement was carried out under an illumination of 100 mW/cm^2 light of AM1.5 spectrum. All the measurements were performed with the sample kept in air at room temperature.

Figure 3 shows the photo- and dark-current densities (J_{photo} and J_{dark}) vs. bias voltage (V_{bias}) of cell A and B. In

Fig. 3(a), the short-circuit current density (J_{sc}) of cell A is substantially smaller than that of cell B. In Fig. 3(b), J_{dark} under $V_{bais} > 0$ V of cell A is much smaller than that of cell B, which indicates that the series resistance of cell A is much larger. The lower photovoltaic performance of cell A is caused by the larger series resistance.

Figure 4(a) shows the EAWL spectra of cell A with $V_{bias} = 2$, 0, and -1 V. The lineshape is characteristic of the EA spectrum coming from the bulk of phthalocyanine film.[7,9,11] It is observed that the intensity of the spectrum has a strong bias dependence. This indicates that the internal electric field in the H$_2$Pc layer strongly depends on the bias voltage, because the EA signal intensity is proportional to the internal field as shown in Eq. (1).

Figure 4(b) shows the EAWL spectra of cell B. The lineshape for $V_{bias} = 0$ and -1 V is nearly the same with that of cell A in Fig. 4(a). For $V_{bias} = 2$ V, on the other hand, a new peak appears at 560 nm. The signal of this new peak is phase-shifted from that of the usual EA signal, because the peak at 560 nm could be observed even when the phase of the lock-in detection was shifted by 90°. This indicates that the peak at 560 nm is due to excited-state absorption of
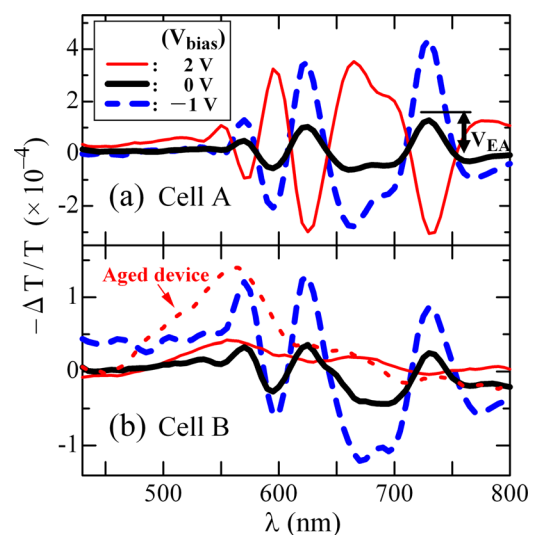

FIG. 4. EAWL spectra of (a) cell A and (b) cell B under the applied bias voltages (V_{bias}) of 2, 0, and -1 V. The dotted curve in (b) is the EAWL spectrum of cell B after 2 month-aging measured under $V_{bias} = 2$ V. The EA signal intensity V_{EA} is defined in (a).

trapped charges in the H₂Pc film.[14,15] This assignment is supported by the energy of the excited-state absorption of Zn-phthalocyanine which was reported to be 2.3 eV, i.e., 540 nm.[16] From the ratio $I_y/I_x = 0.65$, where I_x and I_y are the heights of the 540 nm peak for the phases of 0° and 90°, respectively, the lifetime τ of the excited state is estimated to be $\tau = (I_y/I_x)/\omega_m = 1.0 \times 10^{-4}$ s.[14] The excited-state absorption is usually accompanied by a ground-state bleaching,[14,15] which is expected to be observed at 550–750 nm for H₂Pc. However, the signal of the ground-state bleaching is not clearly identified in Fig. 4(b) probably because of an overlap of the EA signal. The peak at 560 nm of cell B was detectable only for $V_{bias} \geq 2$ V because the number of the trapped charges is large enough under this bias condition due to enhanced charge injection. The dotted curve in Fig. 4(b) shows the EAWL spectrum of cell B after 2 month-aging measured under $V_{bias} = 2$ V. It is observed that the intensity of the 560 nm peak became significantly large by the aging, which indicates that the number of the carrier traps was increased. The peak at 560 nm was not observed for cell A because the carrier injection is much less efficient as observed in Fig. 3(b).

It is noted that the EA signal intensity of cell A in Fig. 4(a) is significantly larger than that of cell B in Fig. 4(b). This is mainly attributed to the difference in the sensitivity of the EA detection between cell A and B caused by the difference in the molecular orientation of H₂Pc shown in Fig. 2. The H₂Pc film of cell A has a 3.0 times larger absorption coefficient α than that of cell B because of the different molecular orientation.[12] The EA spectrum of H₂Pc is close to the 2nd derivative of the absorption spectrum. In this case, the following relationship is fulfilled[17]

$$\Delta\alpha \approx \frac{1}{2}\frac{\partial^2\alpha}{\partial E^2}(\Delta E)^2 = \frac{1}{2}(\boldsymbol{m}\cdot\boldsymbol{F})^2\frac{\partial^2\alpha}{\partial E^2}, \quad (2)$$

where $\Delta\alpha$ is the change of α by the electric field $\boldsymbol{F}$, E is the optical transition energy of the molecule, ΔE is the 1st order Stark shift, and $\boldsymbol{m}$ is the dipole moment induced by the optical transition. When α becomes 3.0 times larger with the spectral line shape unchanged, $\partial^2\alpha/\partial E^2$ also becomes 3.0 times larger. Assuming that the dependence of $\boldsymbol{m}\cdot\boldsymbol{F}$ on the molecular orientation is weak, $\Delta\alpha$, which correlates with the EA signal intensity, becomes substantially larger.

The EA signal intensity, V_{EA}, is defined in Fig. 4(a) as the difference between the signal heights at 760 and 730 nm. This wavelength region was chosen for the definition of V_{EA} because the disturbance by the spectra coming from the excited-state absorption and ground-state bleaching is negligible. The bias voltage dependence of V_{EA} by EAWL and EAML is shown in Fig. 5. First, we examine the results of EAML. The plot of the EAML intensity of cell A in Fig. 5(a) crosses the abscissa at 0.18 V which corresponds to the built-in potential (V_{bi}) in the dark. On the other hand, V_{bi} of cell B in the dark is 0.59 V as observed in Fig. 5(b). In the present cells, a Schottky barrier is formed at the H₂Pc/In interface, but not at the pentacene/H₂Pc and ITO/H₂Pc interfaces because no rectification was observed in the devices ITO/pentacene/H₂Pc/CuI/Au and ITO/H₂Pc/CuI/Au, where CuI/Au gives an ohmic contact with H₂Pc. The smaller V_{bi}
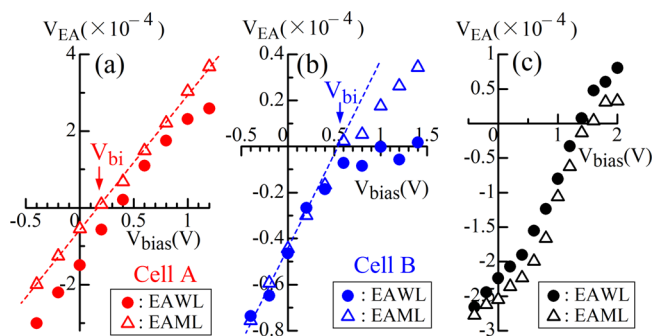

FIG. 5. Bias voltage dependence of EAWL and EAML intensities of (a) cell A, (b) cell B, and (c) a ITO/pentacene (5 nm)/H₂Pc (120 nm)/Al (30 nm) cell.

of cell A indicates that the Schottky-barrier height at the H₂Pc/In interface of cell A is smaller than that of cell B, as illustrated in Fig. 6 for the case of $V_{bias} = 0$ V in the dark. The difference in the barrier height between cell A and B may be explained by the difference in the crystal orientation in the H₂Pc film which may cause a difference in the vacuum level at the surface.[18]

Next, the result of EAWL for cell A in Fig. 5(a) is examined. V_{EA} at $V_{bias} = 0$ V by EAWL is -1.5×10^{-4}, while that by EAML is -0.6×10^{-4}. This indicates that the internal electric field in the H₂Pc layer becomes 2.5 times larger by the white light illumination. Under the present modulation frequency of 1 kHz, the observed electric field by EA is the average field in the H₂Pc layer, because the modulation voltage is applied to the whole H₂Pc layer, which was checked by a capacitance measurement:[9] The capacitance of cell A was independent of the bias voltage between $V_{bias} = -2$ and 1 V, with a value of 10 nF which corresponds to the value for a capacitor with an inter-electrode distance of 120 nm, an area of 0.35 cm², and a dielectric constant of 3.9. The increase of the average electric field in the H₂Pc layer by the white light illumination indicates that an interface dipole is induced by a trapping of photogenerated charges. Figure 6(a) shows the proposed band diagrams of cell A. In the dark with $V_{bias} = 0$ V, the electric field exists near the H₂Pc/In interface due to the Schottky-barrier formation. By the white
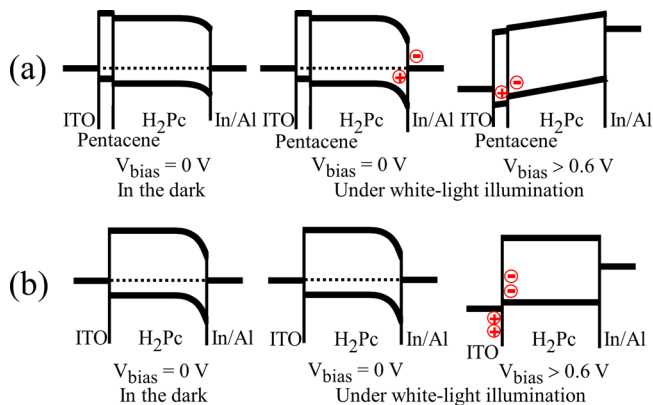

FIG. 6. Proposed energy band diagrams of (a) cell A and (b) cell B. For $V_{bias} = 0$ V in the dark, the built-in potential is smaller for cell A. Under white light illumination with $V_{bias} = 0$ V, a dipole layer is formed in cell A at the H₂Pc/In interface. For $V_{bias} > 0.6$ V under white light illumination, a dipole layer is formed at the ITO/H₂Pc interface for cell B and at either the pentacene/H₂Pc or ITO/pentacene interface for cell A.

light illumination, some of the photogenerated holes in the H_2Pc layer are trapped at the surface of the H_2Pc layer. These trapped holes induce negative charges at the surface of the In electrode, forming an interface dipole layer. Since the energy level of the H_2Pc near In is lowered by the dipole formation, the average electric field in the H_2Pc layer is increased. The location of the dipole layer formation is the H_2Pc/In interface but not the pentacene/H_2Pc interface, an evidence of which is given by a result for a ITO/pentacene/H_2Pc/Al cell shown in Fig. 5(c). When Al cathode is used instead of In/Al, no substantial difference is observed between the EAML and EAWL intensities, which indicates that no dipole layer formation occurs. The increase of the built-in potential of cell A by the white light illumination should enhance the photovoltaic performance of cell A, although it is still poorer than that of cell B even after the enhancement.

In the case of cell B, on the other hand, V_{EA} at $V_{bias} = 0$ V by EAWL is nearly the same with that by EAML, as observed in Fig. 5(b). This indicates that the internal field at $V_{bias} = 0$ V in cell B is not affected by the white light illumination, in contrast to the case of cell A. It is interpreted that the density of the carrier traps at the H_2Pc/In interface in cell B should be much lower than that in cell A. The difference between cell A and B may be attributed to the difference in the molecular orientation at the surface of H_2Pc layer, as observed in Fig. 2, which may cause the different trap densities at the H_2Pc/In interface.

For $V_{bias} > 0.6$ V, on the other hand, the internal electric field of cell B is strongly altered by the white light illumination in contrast to the case of $V_{bias} = 0$ V. In Fig. 5(b), V_{EA} by EAWL is nearly zero for $V_{bias} > 0.6$ V, while V_{EA} by EAML increases monotonically. The difference between EAML and EAWL is again explained by a formation of an interface dipole layer due to carrier trapping. However, the dipole for $V_{bias} > 0.6$ V should have a different origin from that for $V_{bias} = 0$ V. Since the dipole for $V_{bias} = 0$ V was generated at the H_2Pc/In interface, the dipole for $V_{bias} > 0.6$ V may be generated at the ITO/H_2Pc interface, as illustrated in Fig. 6(b). Electron traps exist at the surface of the H_2Pc layer, and the photogenerated electrons are effectively trapped by these traps for $V_{bias} > 0.6$ V because the electrons drift toward ITO. The similar band flattening due to a trapping of the injected carriers in the dark has been reported before.[9,19] For cell A, the difference in V_{EA} between EAML and EAWL becomes smaller by increasing V_{bias} from 0 to 0.6 V, and again increases for $V_{bias} > 0.6$ V, as observed in

Fig. 5(a). The increase for $V_{bias} > 0.6$ V is explained by the dipole layer formation at either the pentacene/H_2Pc or ITO/pentacene interface under the white light illumination.

In conclusion, the effect of white light illumination on the internal electric field of cell A and B was studied by EAWL and EAML measurements. In cell A, the average electric field in the H_2Pc layer under $V_{bias} = 0$ V was increased by 2.5 times by the white light illumination, which is explained by a formation of a dipole layer at the H_2Pc/In interface. In cell B, on the other hand, the internal field in the H_2Pc layer was quenched for $V_{bias} > 0.6$ V under the white light illumination, which is explained by a formation of a dipole layer at the ITO/H_2Pc interface. It was demonstrated that EAWL is a powerful technique to investigate the internal electric field of OSC under operation.

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