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The Photovoltaic Effect in Naphthacene-Gold Layers

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The photovoltaic effect in gold–naphthacene thin layers has been studied. By excitation in the region of the visible absorption band of naphthacene (2.4—3.0 eV), it was found that the photovoltage consists of two components; one with a short response time, caused by the electron transfer across the boundary between gold and naphthacene, and the other with a long response time, attributable to a diffusion process in the naphthacene film. The lifetime of carriers produced by the former process was estimated to be 0.08 s at least, decaying by the recombination of trapped holes in naphthacene with electrons in gold. Photovoltage was also observed in a region of wavelengths greater than the visible absorption band of naphthacene.

Photovoltaic effects of organic compounds have been investigated by many authors.[1] It is known that the photovoltage for a semiconductor is produced by the transport of charge carriers across contact barriers.[2] Other processes such as the Dember effect[3] are also known. However, in the case of organic compounds such as anthracene and naphthacene, analysis of the phenomena is more difficult because of complicated features and poor reproducibility.

In order to clarify the mechanism of photovoltage by illumination in the region of the absorption band of naphthacene, we have made a detailed study of the photovoltaic effect across the gold-naphthacene interface. The photovoltage for a similar system was reported by Reucroft *et al.*[4] Ghosh and Feng investigated the photovoltage for a gold–naphthacene–aluminum system, attributing the photovoltage to the difference in the work function of the two electrode materials.[5]

Experimental

The specimens are made in the form of successive thin layers of gold(Au^1), naphthacene, inositol[$C_6H_6(OH)_6$], and gold (Au^2), obtained by evaporation onto a quartz substrate at less than 10^{-5} Torr (Fig. 1). The gold layers at the two ends, serving as electrodes, are semi-transparent. The deposition rate of naphthacene was about 2 nm/s. The thickness of the naphthacene layer was determined, by measurements of the optical density, to be in the range 0.05—1.0 μ. The area covered by both electrodes was about 0.2 cm^2. The photovoltage was measured by two methods, (a) with exciting light chopped at 30 Hz and a lock-in amplifier(NF circuit design block, LI-573), and (b) with a steady light and vibrating reed electrometer (Takeda Riken, TR-84M). Throughout this paper, the photovoltage is defined as the voltage at the Au^1 electrode taking that at the other electrode (Au^2) as zero. An Ushio 500 W xenon lamp and an Ushio 500 W halogen lamp were used as light sources. A Japan Jarrel-Ash, 0.25 m Ebert-type monochromator was used. The light intensity was measured with a thermopile (Eppley, Bismus-silver type). Most measurements were made under ordinary atmosphere.

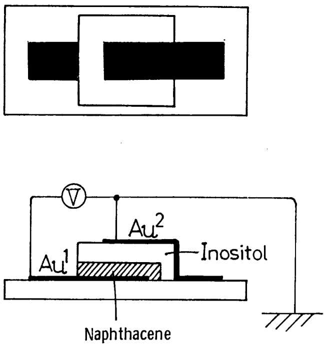

Fig. 1. A diagrammatic picture of a specimen used for photovoltaic measutements.

Results

The photovoltage of the Au^1–naphthacene–inositol–Au^2 system measured with the aid of a vibrating reed electrometer by exciting the visible absorption band of naphthacene is shown in Fig. 2. When the light was turned on, the photovoltage showed a quick negative response, followed by a slow rise toward the positive direction. When the light was turned off, it became more positive for an instant and then degraded slowly. It is obvious from this behavior that there are two components in the photovoltage (shown by broken lines): One has a negative polarity and a fast response and the other a positive polarity and a slow response. This photovoltaic behavior did not change with the direction of illumination, *i.e.*, illumination from either side of the Au electrodes. The response time and the intensity of

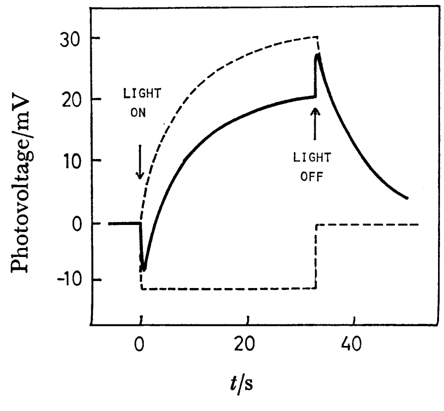

Fig. 2. The photovoltage measured as a function of time with steady illumination (λ=500 nm) by use of a vibrating reed electrometer.

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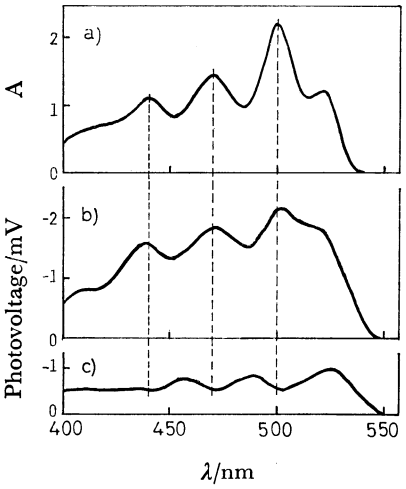

Fig. 3. (a) The absorption spectrum of a naphthacene film. (b) The photovoltage action spectrum, illuminated from the side of Au^1. (c) The photovoltage action spectrum, illuminated from the side of Au^2. The thickness of naphthacene layer is about 0.6 μ throughout. The photovoltage was measured by using a lock-in amplifier. The curves (b) and (c) are corrected so as to give photovoltages at the illumination intensity of 5.4×10^{13} photons/cm^2·s throughout the spectral region.

the slow component differed to some degree with specimen.

The visible absorption spectrum of a naphthacene layer deposited on a quartz glass plate is shown in Fig. 3a. The spectrum nearly coincides with the absorption spectrum of the single crystal of naphthacene assigned to a ^{1}La transition.[6]

The action spectra for the photovoltages measured with a lock-in amplifier are shown in Figs. 3b and c. It should be noted that only the component of photovoltage alternating at 30 Hz is given by this method and the resulting action spectra correspond to the fast-response component of the photovoltage shown in Fig. 2. Curve b, the action spectrum for illumination from the Au^1 side, closely resembles the absorption spectrum of curve a, while curve c, the action spectrum for illumination from the Au^2 side, is entirely different.

One of the action spectra for the photovoltage measured with the vibrating reed electrometer is shown in Fig. 4, with illumination from the Au^1 side and the wavelength scanned from short to long wavelengths at the speed of 25 nm/min. Contrary to the case shown in Fig. 3b, the action spectrum has a shape quite different from the absorption spectrum. The position of the minima indicated by arrows correspond well with the absorption peaks. Since there are two components in the photovoltage, the action spectrum should contain spectra for the positive and negative components. The fast-response, negative component should have a structure similar to the absorption spectrum, and therefore the action spectrum can be regarded as the difference between the slow-response, positive component, shown by the broken line, and the fast-response, negative component (hatched part).

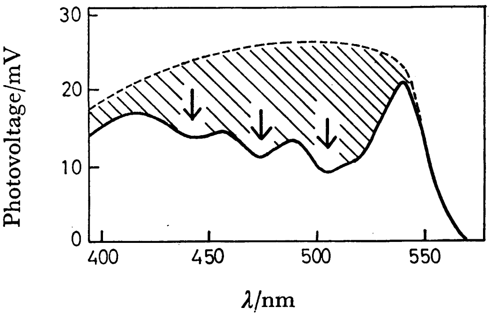

Fig. 4. The photovoltage action spectrum observed by using a vibrating reed electrometer under steady illumination.

The dependence of photovoltage on the exciting light intensity for each of the components is shown in Fig. 5. The photovoltage of the slow-response component (Fig. 5a) was measured with light at 535 nm and a vibrating reed electrometer. In the region where the light is weak, the photovoltage is proportional to light intensity,

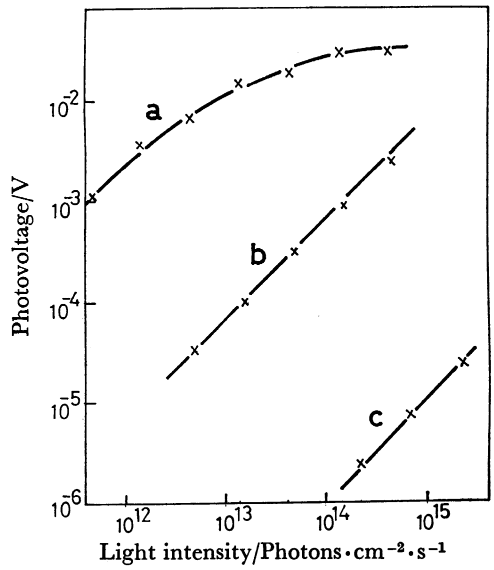

Fig. 5. The dependence of the photovoltages on light intensity. (a) Slow-response component, measured with a vibrating reed electrometer, λ 535 nm. (b) Fast-response component, measured with a lock-in amplifier, λ 500 nm. (c) Photovoltage in the long wavelength region, measured with a lock-in amplifier, λ 820 nm.

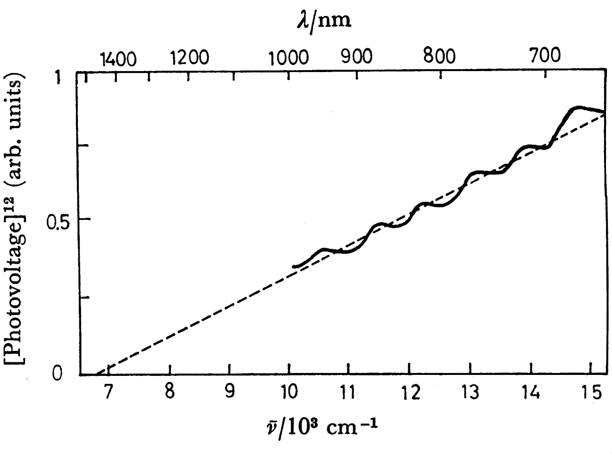

Fig. 6. Photovoltage action spectrum measured with the aid of a lock-in amplifier in the region of wavelength longer than the absorption band of naphthacene.

but shows saturation in the strong light region. The light intensity at which saturation began differed a little with specimen. It also shifted to the weaker intensity side day by day. The fast-response component of the photovoltage, measured with light at 500 nm and the lock-in amplifier, was proportional to the light intensity (Fig. 5b).

Weak photovoltages were also observed even with light at wavelengths longer than the absorption band of naphthacene. The action spectrum measured by using the lock-in amplifier is shown in Fig. 6. The dependence on light intensity is shown in Fig. 5c. The polarity was the same as that of the fast-response component observed for the excitation in the region of the absorption band.

Discussion

Mechanism for the Photovoltaic Effect. *a. The Fast-response Component*: The fast-response component makes the Au^1 electrode negative, and can be selectively measured by means of the chopped light method. When the light comes from the Au^1 side, the action spectrum agrees with the absorption spectrum of the naphthacene layer (Fig. 3b). When the light comes from the other side, the maxima of the action spectrum do not agree with the absorption peaks, but agree in wavelength with those of the absorption bottoms. In the case where the layer of naphthacene was thinner than 0.2 μ, the action spectra did not change with the direction of the illumination and agreed with the absorption spectra. These results suggest that the fast-response component of the photovoltaic effect takes place near the interface between gold (Au^1) and naphthacene, because the light coming from the side of Au^2 is absorbed more strongly at the absorption peaks in the naphthacene layer before reaching the naphthacene-Au^1 boundary than at the bottoms. The charge transfer process caused by the exciton at the interface may be suitable for explaining the results. The negative polarity shows electron trasfer from the naphthacene exciton to Au^1. A similar mechanism was proposed by Killesreiter and Baessler for an aluminum electrode-anthracene crystal system.[7,8] They attributed the photocurrent to a charge carrier generated by the exciton-metal interaction, and concluded that the electron transfer from the exciton takes place mainly within 20 Å from the boundary.

The depths of light absorption (the distance at which the light intensity becomes 1/e) of the naphthacene layer can be approximately estimated from the absorbances to be 0.12 μ at λ 500 nm (at the absorption maximum) and about 0.3 μ at the minima. When illuminated from the side of Au^2 into the naphthacene layer 0.6 μ or more in thickness, the exciting light hardly reaches the interface. The fact that we obtained photovoltage to a considerable magnitude under these conditions (Fig. 3c) shows that some species with long diffusion length (>0.1 μ) participate in the electron transfer process at the boundary. The diffusion length of the singlet exciton in naphthacene single crystal is determined to be 120 Å[9] by fluorescence studies, and that of triplet exciton to be 0.4 μ[10] by photocurrent studies. For a thin film made by evaporation, the values should be smaller. It might be concluded that the participation of triplet excitons formed from singlet excitons is predominant in the charge carrier generation for the case of excitation from the Au^2 side. When illuminated from the Au^1 side, both singlet and triplet excitons can participate in the electron transfer process.

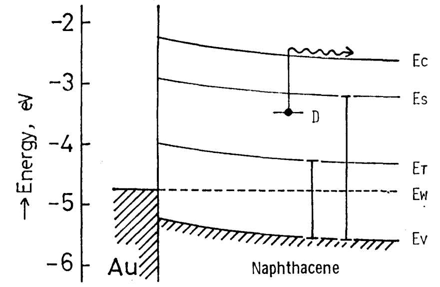

Fig. 7. A band model for the gold-naphthacene interface. E_C, E_V, and E_W designate the energies of the conduction band, the valence band and the work function of gold, respectively. E_S and E_T are the energies of the singlet and triplet excitons of naphthacene. D indicates a hypothetical donor level.

The work function of gold (E_w) is about 4.8 eV,[11] the ionization potential of naphthacene (I_P) is about 5.25 eV[12] and the band gap of naphthacene (E_g) is 3.0 eV.[13] If one takes the position of the valence band of naphthacene (E_v) to be 5.25 eV, then, that of the conduction band (E_c) is 2.25 eV. The energies of the singlet exciton (E_S) and the triplet exciton (E_T) from the valence band are 2.4 eV[13] and 1.25 eV,[14] respectively (Fig. 7). The electron transfer from naphthacene to gold requires an energy higher than E_v-E_w, *viz.*, 0.45 eV. For the case of the electron transfer from gold to naphthacene, the energy of E_w-E_c, *viz.*, 2.55 eV or more, is required. The energies of both singlet and triplet excitons are therefore large enough to cause an electron transfer from naphthacene to gold, but not to cause an electron transfer from gold to naphthacene. This conclusion is compatible with the polarity of photovoltage observed.

b. The Slow-response Component: The photovoltage curve in Fig. 4 can be interpreted to be the superposition of a slow-response, positive component and a fast-response, negative one. When the light is not very strong, the two components of the photovoltage are nearly proportional to the light intensity, as shown in Figs. 5a and b. One can therefore conclude that the action spectrum when illuminated from the Au^1 side should have the same fine structure as that of the absorption spectrum. But the slow-response component is strong in the region of the tails of absorption band of naphthacene (Fig. 4), which implies that the slow component of the photovoltaic effect takes place, not at the interface but inside the naphthacene layer.

Jortner proposed an exciton-exciton interaction mechanism for free carrier generation in the bulk.[15] This mechanism, however, does not explain the dependence on light intensity we obtained. The exciton-impurity (electron donor or electron acceptor) interaction or exciton-trapped carrier interaction, leading to carrier formation as indicated in Fig. 7, seems to be a plausible mechanism for the slow response component.

As is usual in the band theory for semiconductors, we assume that the naphthacene energy bands are bent near the boundary due to the difference of work functions between gold and naphthacene. Since the work function of naphthacene is reported to be 4.51 eV,[16] we can assume that the bands for naphthacene are bent downwards toward the interior as shown in Fig. 7 by an amount of (4.87—4.51) eV. When free carriers are produced in the naphthacene, the electrons move to the interior of the naphthacene layer and the holes move to the gold electrode according to the energy gradient. It is therefore expected that the polarity of the photovoltaic effect becomes positive at the electrode, regardless of the species of the mobile carrier. Thus we can conclude that the slow-response component arises from the charge carrier generation in the interior of naphthacene layer.

Some of the carriers might be captured by shallow traps. The trapped carriers can be thermally excited and recombine slowly with the counter charge carriers. The decay of the slow-response component can be interpreted by such a thermal recombination process.

c. Photovoltaic Effect in the Region of Long Wavelength: A very weak photovoltage was observed in the region of wavelength longer than the absorption band of naphthacene with a lock-in amplifier. The polarity and the light intensity dependence are the same as those of the fast-response component caused by light in the region of the absorption band. The action spectrum is shown in Fig. 6, where the square root of the photovoltage is plotted against wave number. The photovoltage could be observed even with light at 1000 nm. The small humps in the spectrum are due to the interference of light in the sample. No peak can be observed which corresponds to S–T absorption band of naphthacene. It is seen that the plot lies roughly on a straight line (dotted line). From the intersection of the straight line with abscissa, the threshold energy for the photovoltage is found to be about 6800 cm^{-1} (0.84 eV). Williams and Dresner reported the threshold value of photoemission of holes from gold to anthracene crystal to be 1.17 eV[17] from the photocurrent measurement. Based on their result, 0.77 eV is estimated as the threshold of photoemission of holes from gold to naphthacene, since naphthacene has an ionization potential 0.40 eV smaller than anthracene. This nearly coincides with the value derived experimentally by us. Our result also shows that the photoemission occurs for an organics-metal system without external electric field.

A slow-response, positive component of the photovoltage was observed with the light at wavelengths greater than the absorption edge of naphthacene, in addition to the fast-response, negative one. The former component might be caused by the direct excitation of the trapped carriers.

Since the photovoltage measured with the aid of a lock-in amplifier gives only the alternating part of the voltage caused by chopped light, there should be no effect by an additional steady illumination, if the photovoltage is proportional to light intensity. Contrary to expectation, the photovoltage remarkably increased by steady illumination in the region of the absorption band of naphthacene in addition to the chopped light at wavelengths greater than that of absorption band. It was also observed that this enhancement grew slowly on application of the steady light, as in the case of the slow-response component. It is plausible that the long wavelength light stimulates the detrapping of the trapped carriers produced by the steady light in naphthacene layer.

Carrier Formation and Recombination at the Boundary. The excitons at the boundary between gold and naphthacene inject holes into the naphthacene layer.

The rate of transfer is formulated as

$$\mathrm{d}N/\mathrm{d}t = I\Phi\eta - kN, \tag{1}$$

where N is the density of holes in the naphthacene layer [holes·m^{-2}], I the light intensity [phtons·m^{-2}·s^{-1}], Φ the quantum yield of the excitons which can reach the boundary per photon, η the efficiency that the exciton causes electron transfer, and k is the rate constant for the recombination of holes with the electrons in the gold electrode [s^{-1}].

In the stationary state, N is given by Eq. 2 taking $\mathrm{d}N/\mathrm{d}t=0$

$$N = I\Phi\eta/k, \tag{2}$$

For the sake of simplicity we assume that the holes lie on a plane parallel to the boundary with a distance d. Then the photovoltage (V_{ph}) can be given by

$$V_{\mathrm{ph}} = Ned/\varepsilon\varepsilon_0, \tag{3}$$

where e is the elementary electronic charge, ε the dielectric constant of naphthacene, and ε_0 the vacuum permittivity. From Eqs. 2 and 3, we find that V_{ph} is proportional to the light intensity, in agreement with the experimental result (Fig. 5b). The experimental value of V_{ph} was obtained to be 20 mV, at $I=10^{18}$ photons·m^{-2}·s^{-1}, at $\lambda=500$ nm, measured with the aid of a vibrating reed electrometer and using the specimen whose slow-response component was weak. η and ε can be taken to be 0.2[7] and 3.8,[18] respectively, according to Baessler *et al.* d can be reasonably assumed to be 5 Å, and Φ 0.5 at most. We can then get k to be 12 s^{-1} or less. This corresponds to a lower limit of the lifetime of the holes produced at the boundary of 0.08 s. The lifetime thus obtained is much longer than the value of 1.2—2.0 μs[19] reported by Bogus. Bogus derived the lifetime of the hole produced at the boundary between an anthracene crystal and silver from measurement of the photocurrent, where free carriers only participate. It should be noted that the photovoltage is caused not only by free carriers but also by trapped carriers. Thus it is concluded that the holes produced in our experiment are trapped within a few microseconds, and the trapped holes then recombine with electrons in the metal within some hundreds of milliseconds. Although no detailes on the state of trapped holes are known, they might either be localized on naphthacene cation or impurity cation stabilized near the boundary. Our studies on the photovoltaic effect have thus revealed the existence of trapped holes with a long lifetime at the boundary between an organic substance and a metal.

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