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Photoconductivity of C_{60}-H_2Pc Coevaporated Thin Films

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Abstract

Changes in electronic and photoelectronic properties of fullerene (C_{60}) and metal-free phthalocyanine (H_2Pc) coevaporated thin films were investigated by changing their mixing ratio. The influences of thermal annealing and oxygen adsorption on the properties were also investigated. The electronic and photoelectronic properties changed by incororation of H_2Pc into C_{60}, and thermal annealing changed their properties dramatically. Thin films in which one component was doped lightly into the other showed high photoconductive sensitivity in comparison with that of C_{60} or H_2Pc alone in over all visible region. Existence of sensitization center and process caused from minority carrier trapping was confirmed from thermal quenching of photoconductivity. Mechanisms for carrier generation and transport were discussed using a model in which photons of high and low energies were absorbed in C_{60} and H_2Pc molecules, respectively, followed with majority carrier injection and trapping.

Introduction

A great deal of effort has been made on studies for the electronic and photoelectronic properties of C_{60} thin films in recent years. It is known that C_{60} shows semiconductive properties, including photoconductivity,[1] and the majority carrier of C_{60} thin films is electron. Because of its photoconductivity, it is expected that C_{60} works well as a charge generation or transport material in an electrophotographic organic photoreceptor. Hosoya et al. reported a study of an application of C_{60} to electrophotographic photoreceptor.[2] Furthermore, it is also known that C_{60} molecule has a high ability as an electron acceptor.

On the other hand, phthalocyanines (Pc) have an optical absorption spectrum in visible-IR region, and are practically used as a carrier generation material in organic photoreceptors. The majority carrier of Pc thin films is hole.

In this paper, we describe that incorporation of H_2Pc into C_{60} will be effective on increasing the majority carrier of the C_{60}. Therefore, the electronic and photoelectronic properties of C_{60} and H_2Pc coevaporated thin films were investigated to clarify the mechanisms of carrier generation and transport.

Experimental

Thin films were fabricated by conventional vacuum coevaporation method. The purities of C_{60} and H_2Pc powders were 99.98% and above 99%, respectively. A pair of Au electrodes, which form ohmic contact with C_{60} and H_2Pc, were deposited on Cornig 7059 substrate before thin film deposition. The electrode spacing was 0.3mm. The fraction of C_{60} and H_2Pc was defined as $N_p/(N_f+N_p)$ [mol%], where N_f, N_p is the concentration of C_{60} and H_2Pc, respectively, and was determined from the optical absorption coefficient of coevaporated thin films at 500nm (for C_{60}) and 630nm (for H_2Pc).

The electronic and photoelectronic properties of C_{60} and H_2Pc thin films were strongly influenced by oxygen. The conductivity decreases by adsorption of oxygen for the C_{60} films, while it increases for the H_2Pc films. The vacuum deposited films were exposed to air before mounting on a cryostat for electrical measurements in this study. The electrical and photoelectrical measurements were carried out before and after thermal annealing in vacuum to examine the influence of oxygen adsorption on the photoconductivity of coevaporated thin films. The thermal annealing was carried out under vacuum by increasing temperature of the films from room temperature to 400K, which took about 20min. All electrical and photoelectrical measurements were made in vacuum at room temperature except for the measurement of thermal quenching in photoconductivity. The transient photocurrent was measured with irradiating monochromatic light through the glass substrate using a xenon lamp and a monochrometer.

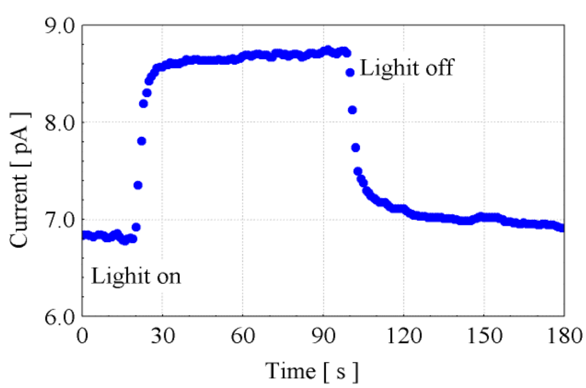

Figure 1. Characteristic of transient photocurrent for C_{60} thin film at 480nm.

Results and Discussion

Figure 1 shows the transient photocurrent for the undoped C_{60} thin film at 480nm before the thermal annealing. The photocurrent showed a rapid increase, followed with a slowly increase with beginning of illumination, and then was saturated. This characteristic implies that majority carriers are transported via trapping and thermal detrapping. Transient photocurrent showed a similar characteristic for another wavelength light in the range of 400-800nm.

In this study, photoconductive sensitivity σ_p was defined as

$$\sigma_p = \frac{\int_{t_s}^{t_e} \frac{i_p(t) - I_d}{I_d} dt}{L_N} \qquad (1)$$

In this study, photoconductive sensitivity σ_p was defined as

$$L_N = (t_e - t_s) \cdot \left(\frac{L(\lambda)}{2.0\times10^{15}} \right)^{\gamma}$$

where I_d[A]; dark current, $i_p(t)$[A]; transient photocurrent as a function of time t[s], t_s, t_e[s]; the time when irradiation is turned on and off, $L(\lambda)$[photons/s·cm^2]; incident photon flux at λ [nm], γ; power index on light intensity dependence of photocurrent.

Figure 2 shows a spectral response of photoconductive sensitivity for the undoped C_{60} thin film. The optical absorption spectrum is also given in the same figure. The photoconductive sensitivity was high before thermal annealing. The C_{60} thin film absorbs photons of high energies mainly and the photoconductive sensitivity is high in the high absorption region. Although the energy gap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of C_{60} molecule is 1.5-2.0eV, the C_{60} thin film shows weak absorption and weak photoconductive sensitivity in the wavelength region corresponding to the energy, because optical transition between these orbits are forbidden.

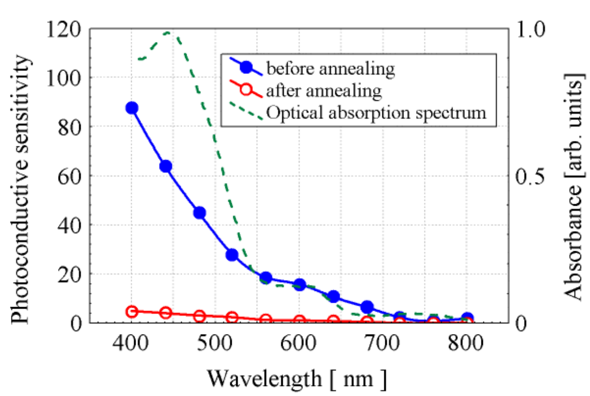

Figure 2. Spectral response of photoconductive sensitivity for C_{60} thin film.

Characteristic of transient photocurrent for thin film of undoped H_2Pc were similar to that for the thin film of C_{60}, that is to say, the majority carriers are transported via trapping and detrapping. Photoconductive sensitivity for H_2Pc thin film is shown in figure 3. The undoped H_2Pc thin film absorbs photons of lower energies mainly than C_{60}, and its photoconductive sensitivity is high in the high absorption region. The photoconductive sensitivity was somewhat high before thermal annealing.

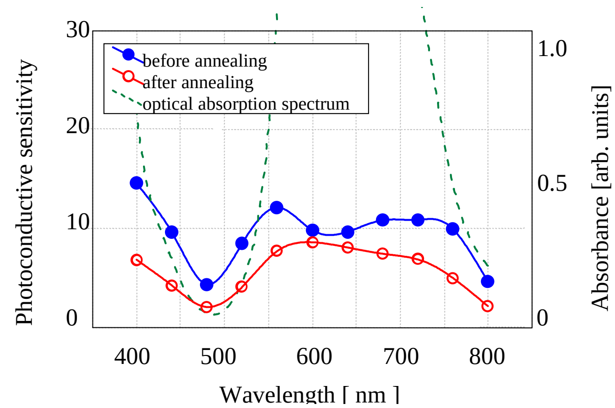

Figure 3. Spectral response of photoconductive sensitivity for H_2Pc thin film.

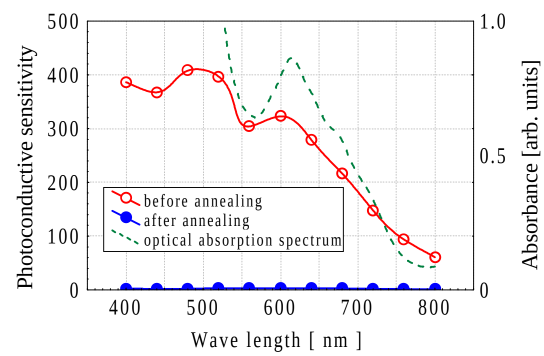

Figure 4. Spectral response of photoconductive sensitivity for C_{60} thin film doped with 10mol% of H_2Pc.

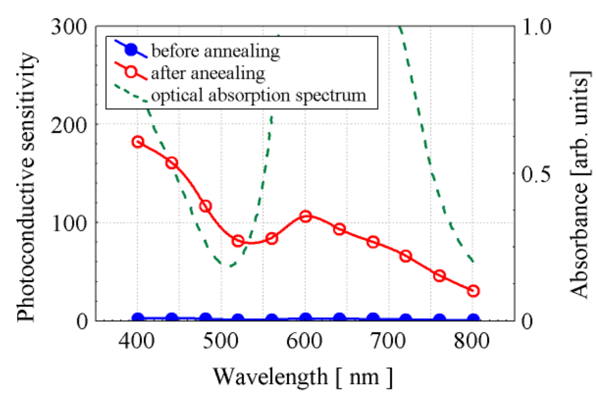

Figure 5. Spectral response of photoconductive sensitivity for C_{60} thin film doped with 81mol% of H_2Pc.

Figure 4 shows photocnductive sensitivity for C_{60} thin film doped with 10mol% of H_2Pc. The sensitivity increased dramatically by the H_2Pc doping over whole visible region and decreased by the thermal annealing.

Figure 5 shows photoconductive sensitivity for C_{60} thin film doped with 81mol% of H_2Pc (H_2Pc thin film doped with 19mol% of C_{60}). The C_{60} doping also increased the sensitivity of the H_2Pc thin film dramatically over whole visible region.

The spectral responses of photoconductive sensitivity for those films are shown in figure 6. It should be noted that the thin films, in which one component was doped lightly into the other, showed high photoconductive.

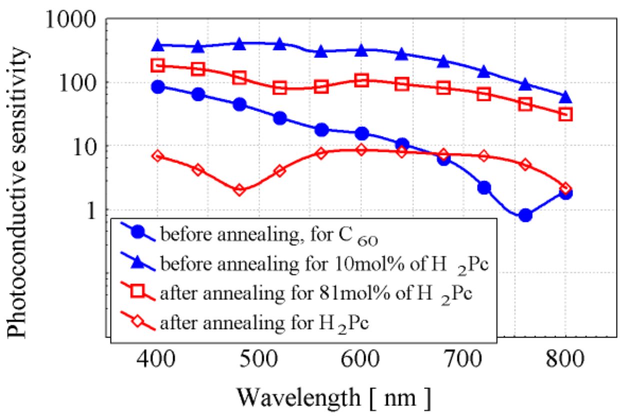

Figure 6. Spectral response of the photoconductive sensitivity for the C_{60}-H_2Pc coevaporated thin films.

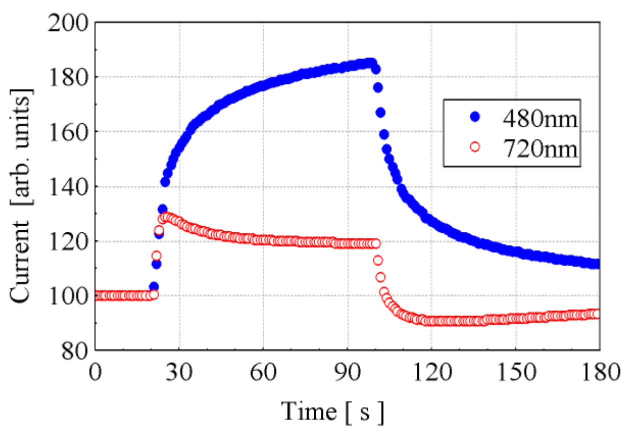

Figure 7. Characteristics of transient photocurrent for C_{60} thin film doped with 81mol% of H_2Pc at room temperature.

Transient photocurrent showed different characteristics for short and long wavelength regions in the C_{60} thin film doped with 81mol% of H2Pc. Figure 7 shows the characteristics of transient photocurrent for the film at 480 and 720nm at room temperature. The transient photocurrent at 480nm increased slowly associated with the light irradiation, and then showed saturation. This characteristic indicates that the majority carriers are transported via trapping and detrapping. On the other hand, the photocurrent increased rapidly at 720nm with beginning of the light irradiation, and then decreased slowly. This characteristic suggests minority carrier trapping and recombination in the film due to thermal excitation of minority carriers.

Therefore, photoconductivity measurements at high temperatures were carried out to confirm the existence of minority carrier trapping. Figure 8 shows the transient photocurrent for C_{60} thin film doped with 81mol% of H_2Pc at 720nm at several high temperatures.

Figure 8 indicates that the increase in current with light irradiation (photocurrent) becomes smaller as the temperature increases. Furthermore, the current decreases with light irradiation (less than the dark current) with further increase in temperature. Thus, the photoconductivity of C_{60} thin film doped with 81mol% of H_2Pc showed thermal quenching. Therefore, the enhancement of photoconductivity can be attributed to the effect of sensitization center, which traps minority carrier to prevents recombination. These results indicate that C_{60} molecule acts as a sensitization center in H_2Pc thin films.

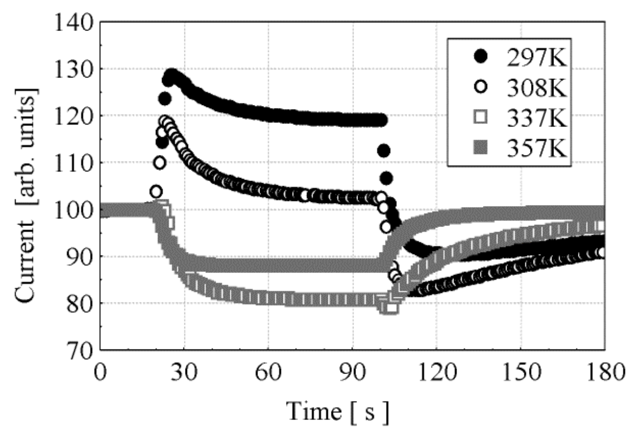

Figure 8. Characteristics of transient photocurrent for C_{60} thin films doped with 81mol%of H_2Pc at 720nm at various temperatures.

Here, we present a model for the role of C_{60} molecule as a sensitization center in H_2Pc thin films, and assume that the energy levels of the thin films are determined as follows. The energy level of HOMO for C_{60} molecule located 6.8eV under vacuum level corresponds to the ionization energy[3] of C_{60} molecule. Because the energy gap between HOMO and LUMO is 1.5-2.0eV, LUMO of C_{60} molecule is located 4.8-5.3eV under vacuum level. Considering that the C_{60} thin film absorbs photons of higher energies than 2.0eV mainly, there are some unoccupied molecular orbital over LUMO level. On the other hand, it is known that the HOMO and LUMO of H_2Pc thin film are located 5.2 and 3.2eV, respectively. It is assumed that energy levels, which originated from C_{60} molecule, are formed in the gap of H_2Pc. The energy diagram is shown in figure 9.

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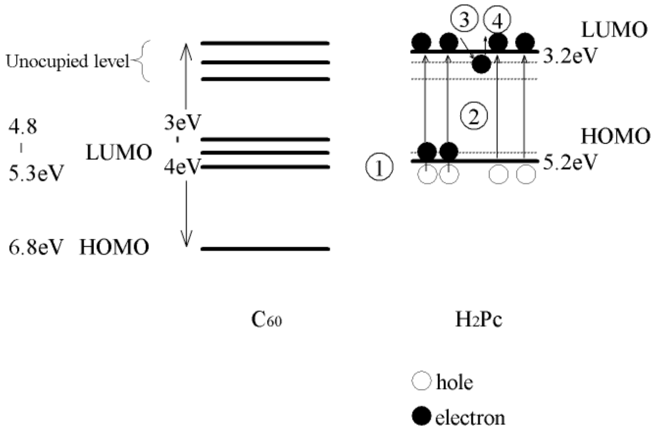

Figure 9. Schematic energy diagram for C_{60}–H_2Pc coevaporated thin films.

Since some electrons are thermally exited from the HOMO of H_2Pc to the level originated form unoccupied level of C_{60} at room temperature, the majority carries (hole) of H_2Pc are enhanced. When irradiated with light, electrons at the level originated from C_{60} molecule and electrons at HOMO of H_2Pc are exited to LUMO. The electrons that are minority carriers of H_2Pc are trapped by the levels originated from C_{60} molecule. The lifetime of hole at HOMO is increased because trapping of the minority carriers prevents recombination. Some electrons at the trap level are thermally exited, and recombination occurs, bringing about slow decrease in concentration of majority carrier. Since the rate of thermal excitation of minority carriers to LUMO increases at higher temperatures, hole concentration decreases by promotion of recombination.

Conclusions

Changes in electronic and photoelectronic properties of fullerene (C_{60}) and metal-free phthalocyanine (H_2Pc) coevaporated thin films were investigated by changing their fraction. The influence of thermal annealing and adsorption of oxygen on those properties was also investigated.

In conclusion, photoconductive sensitivity of the films was increased largely by a light-doping of one component to the other for both the C_{60} and H_2Pc. The thermal quenching of photoconductivity suggests that C_{60} molecule acts as a sensitization center in H_2Pc thin film.

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Biography

Manabu Takeuchi received his B. Sc., M. Sc. and D. Sc. degrees in Applied Physics from Tokyo Institute of Technology, Tokyo, Japan, in 1966, 1968 and 1971, respectively. Since 1972, he has worked in the department of electrical and electronic engineering at Ibaraki University. His research interest includes static electrification of electrophotographic developers and photoelectronic properties of semiconductor layers. He is a member of the IS&T, the Imaging Society of Japan, the Institute of Electrostatics of Japan and the Japan Society of Applied Physics.