 

# Influence of Phthalocyanine Doping on Photoconductivity of $C_{60}$ Thin Films

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## Abstract

Influence of $H_2Pc$ doping and thermal annealing on photoconductivity of $C_{60}$ thin films were investigated. The photoconductive sensitivity increased remarkably over whole visible region in the $H_2Pc$-doped $C_{60}$ thin films before thermal annealing. While, the photoconductive sensitivity of the films increased remarkably in the wavelength region of 450-550nm after thermal annealing. The photoconductive sensitivity of $C_{60}$ thin films was high at low doping concentrations of $H_2Pc$, before thermal annealing. While, the photoconductive sensitivity was high at high doping concentrations of $H_2Pc$ after thermal annealing. The temperature dependence of the dark conductivity was measured to assess the conduction type of the $H_2Pc$-doped $C_{60}$ thin films, and mechanisms for carrier generation and transport were discussed.

## Introduction

$C_{60}$ has become a material of profound interest due to the progress of recent macroscopic preparation[1]. Especially, observation of superconductive transition increased much interest concerned with the electrical property of $C_{60}$ thin films[2]. Since $C_{60}$ molecule has orbitals corresponding to conduction and valence bands, it shows semiconductive properties[3]. In addition, these films have an optical absorption spectrum in the visible region and show photoconductivity. If highly sensitized, the photoconductive materials, like $C_{60}$ and its related molecules can be considered as a prospective candidate that can be used as an electrophotographic photoreceptor[4]. It was reported that $C_{60}$ has a high electron affinity and acts as an electron acceptor in combination with most conducting polymers[5]. In this respect, it is expected that the photoconductivity of $C_{60}$ thin film can be increased, if $C_{60}$ is doped with appropriate conducting polymers.

On the other hand, phthalocyanines (Pc) are green to blue pigment, which have an optical absorption spectrum in visible-IR region, and are practically used as a carrier generation material (CGM) in electrophotographic organic photoreceptors (OPC).

In this study, we used metal-free phthalocyanene as a dopant for $C_{60}$, and the photoconductivity of metal-free phthalocyanine-doped $C_{60}$ thin films was investigated in a quest for applying $C_{60}$ to electrophotograrphic photoreceptors.

## Experimental

Both $C_{60}$ and $\alpha$–form metal free phthalocyanine ($H_2Pc$) powders were used as evaporation sources. The purities of the $C_{60}$ and $H_2Pc$ were 99.98% and above 99%, respectively. Thin films were fabricated by conventional vacuum evaporation, and doping was carried out by coevaporation method. A pair of Au electrodes, which forms ohmic contact with both $C_{60}$ and $H_2Pc$, were deposited on Corning 7059 glass substrate before thin film deposition. The electrode spacing was 0.3mm. Doping concentration of $H_2Pc$ into $C_{60}$ was controlled by regulating each crucible temperature and was determined by calculating the weight fraction of $C_{60}$ and $H_2Pc$ from the optical absorption coefficient at 450nm (for $C_{60}$) and 630nm (for $H_2Pc$) in prepared thin films.

It should be noted that electronic and photoelectronic properties of $C_{60}$ are strongly influenced by oxygen[6,7], e.g. conductivity of $C_{60}$ thin films decreases by oxygen adsorption. While, conductivity of $H_2Pc$ thin films increases by oxygen adsorption. The vacuum deposited films were exposed to air before mounting in a cryostat for electrical measurements in this study. Therefore, measurements of photoconductivity were carried out before and after thermal annealing in vacuum to examine the influence of oxygen adsorption on the photoconductivity of $H_2Pc$-doped $C_{60}$ thin films. The thermal annealing of the specimens was carried out in vacuum by increasing temperature from 300 to 400 K, which took about 20 min.

All electronic and photoelectronic measurements were made in vacuum at room temperature except for temperature dependence measurements. The photoconductivity of the films was measured by applying dc voltage of 20V. Spectral response of photoconductivity of the films was determined by illumination of monochromatic light using a xenon lamp and a monochromator.

## Results and Discussion

The doping concentration of $H_2Pc$ into $C_{60}$ was characterized by using an UV-visible spectrophotometer. Figure 1 shows the optical absorption spectra of $C_{60}$ thin films doped with $H_2Pc$ of several concentrations. The absorption of the $C_{60}$ film increases sharply around 550nm and shows a peak at 450nm. On the other hand, the absorption of the $H_2Pc$ film is located in a longer wavelength region and increases slowly around 850nm, and shows a peak at 630nm. It is confirmed that the optical absorption occurs in different region in $C_{60}$ and $H_2Pc$ films.

It is assumed here that the absorption spectra of $H_2Pc$-doped $C_{60}$ thin films are superposition of the two components of $C_{60}$ and $H_2Pc$. The concentrations of $H_2Pc$ were calculated from the peak intensities at 450nm and 630 nm originated from $C_{60}$ and $H_2Pc$, respectively. As the concentration of $H_2Pc$ increases, the peak at 630nm originated from $H_2Pc$ increases, while the peak at 450nm originated from $C_{60}$ decreases. The absorbencies of the spectra in Figure 1 are normalized.

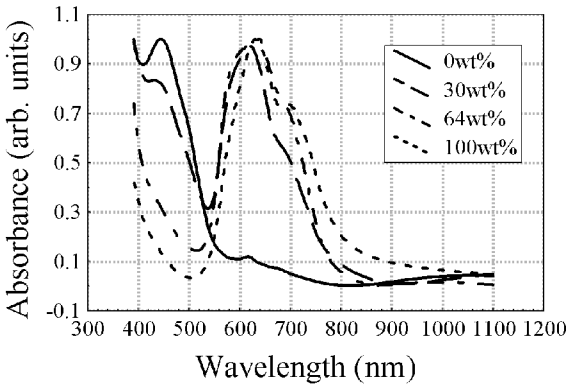


*Figure 1. Optical absorption spectra of $C_{60}$ thin films doped with several concentrations of $H_2Pc$.*

Next, the photoconductivity was examined for the $H_2Pc$-doped $C_{60}$ thin films. Doping concentration of $H_2Pc$ was changed from 0 to 76wt%. The photoconductivity was evaluated by measuring the transient photocurrent of $C_{60}$ thin films doped with $H_2Pc$ of several concentrations. The phorocurrent increased sharply as the illumination started, and then showed saturation. The steady state photocurrent $I_p$ was defined as the saturation value. In this paper, the photoconductive sensitivity was defined as $(I_p - I_d)/I_d$ using dark current $I_d$. Figure 2 shows the spectra of the photoconductive sensitivity for the $H_2Pc$-doped $C_{60}$ thin films before thermal annealing in vacuum. The photoconductive sensitivity of 11wt% $H_2Pc$-doped $C_{60}$ thin film showed a highest sensitivity over whole visible region. However, the photoconductive sensitivity of the heavily doped thin films (76wt%) was lower than that of the undoped $C_{60}$.

Figure 3 shows the spectra of the photoconductive sensitivity after thermal annealing. The photoconductive sensitivity of the 64wt% $H_2Pc$-doped $C_{60}$ thin film showed the highest sensitivity. This value increased remarkably in the wavelength region of 450-550nm with the increase in $H_2Pc$ concentration. It is seen from Figures 2 and 3 that the photoconductive sensitivity spectrum varied with the thermal annealing.

The photoconductive sensitivities of the films at 480 and 640nm as a function of $H_2Pc$-concentration were shown in Figures 4 and 5, respectively. It is vivid from those figures that before thermal annealing, the films of low concentration of $H_2Pc$ show high sensitivity comparing with the films of high $H_2Pc$ concentration. While, the films, which show high sensitivity before the thermal annealing, show low sensitivity after thermal annealing. The spectra peak of the sensitivity, doped with higher concentration of $H_2Pc$, shows a shift of value to a higher concentration, after thermal annealing.

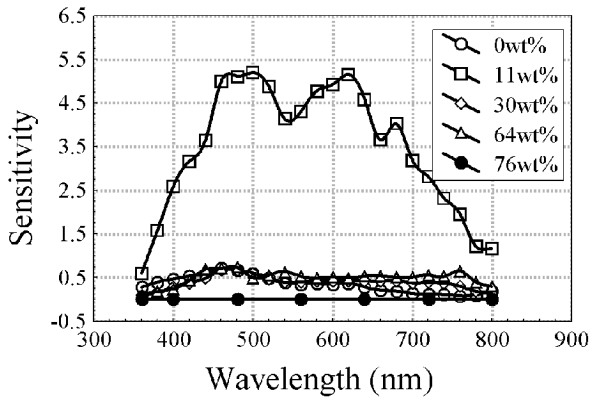


*Figure 2. Spectral responses of photoconductive sensitivity for the $H_2Pc$-doped $C_{60}$ thin films before thermal annealing.*

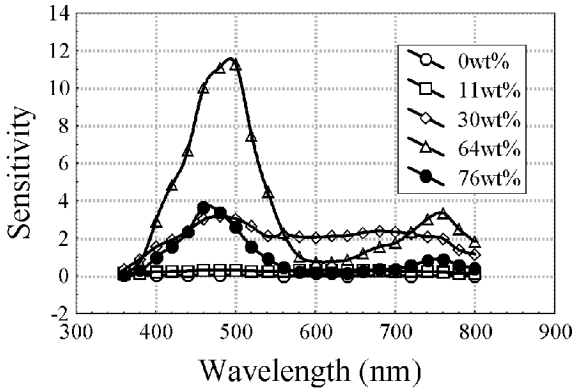


*Figure 3. Spectral responses of the photoconductive sensitivity for the $H_2Pc$-doped $C_{60}$ thin films after thermal annealing.*

It is known that the majority carrier in undoped $C_{60}$ thin films is electron. The dark conductivity of undoped $C_{60}$ thin films decreases while exposed to air, because oxygen ions grab the electron from the bulk. If it is assumed that the increase in carrier concentration by light irradiation and the carrier mobility are not changed under thermal annealing for the undoped $C_{60}$ films, it can be said that the sensitivity of the films show a decrease by the annealing. On the other hand, it is known that the majority carrier in $H_2Pc$ thin films is hole. Since oxygen ions act as an electron acceptor, dark conductivity of $H_2Pc$ thin films increases while exposed to air. So, it will not be improper to mention that the conduction type of the $H_2Pc$-doped $C_{60}$ thin film is depended on with the sensitivity change caused by thermal annealing. Therefore, we can say that the conduction type of $C_{60}$ thin films doped with $H_2Pc$ of less than about 10wt% is n-type, and the films doped with $H_2Pc$ of over 60wt% are p-type.

It can be considered that the type of majority carrier in $C_{60}$ thin films change from electron to hole, while doped with $H_2Pc$ and the step of concentration increases from 10 to 60wt%.

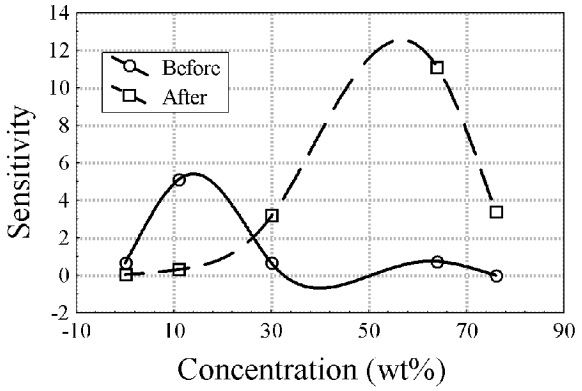


*Figure 4. Photoconductive sensitivity of the films at 480nm as a function of $H_2Pc$-concentration.*

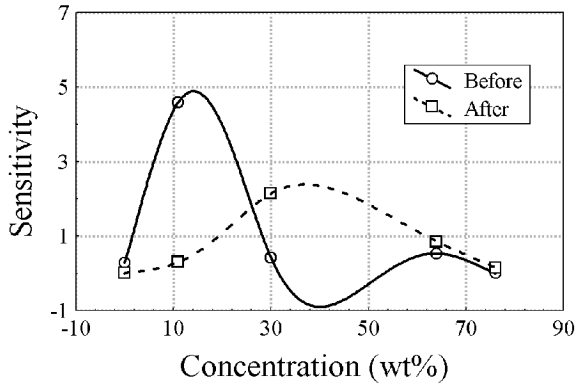


*Figure 5. Photoconductive sensitivity of the films at 640nm as a function of $H_2Pc$-concentration.*

Finally, the temperature dependence of the dark conductivity was measured to examine the electronic energy states and assess the conduction type for the $H_2Pc$-doped $C_{60}$ thin films. The dark conductivity σ can be expressed as

$$\sigma = \left( \frac{I/(l \cdot d)}{V/g} \right) \quad (1)$$

where *V* is applied dc voltage, *I*; dark current, *g*; electrode spacing, *l*; electrode length, and *d*; film thickness. Thin films of $C_{60}$ mounted in the cryostat were thermally annealed by increasing temperature from 300 to 400K in vacuum, under an applying dc voltage of 5V. Figure 6 shows the Arrhenius plots of the dark conductivity for the undoped $C_{60}$ thin film. The circles and squares correspond to 1st and the following 2nd annealings after exposed to air. The change in the temperature dependence of dark conductivity with the thermal annealing can be attributable to the degassing of oxygen from the specimen. It is also seen that the dark conductivity of the film increased by the degassing. The dark conductivity of the $C_{60}$ thin films doped with 11, 30, and 64wt% of $H_2Pc$ showed the similar change with thermal annealing. To emphasize in the other way, the dark conductivity of the films at room temperature increases with degassing of oxygen and this phenomena can be observed up to the concentrations of about 60wt% of the doped $H_2Pc$.

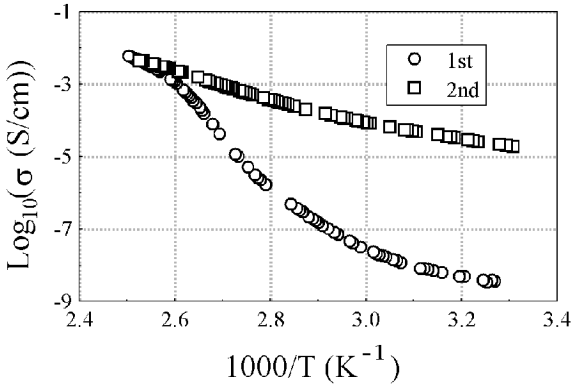


*Figure 6. Arrhenius plots of the dark conductivity of the undoped $C_{60}$ thin film.*

However, the dark conductivity at room temperature decreased by the thermal annealing for the $C_{60}$ film doped with 76wt% of $H_2Pc$ as shown in Figure 7. It should be noted that the dark conductivity of the film decreases with desorption of oxygen.

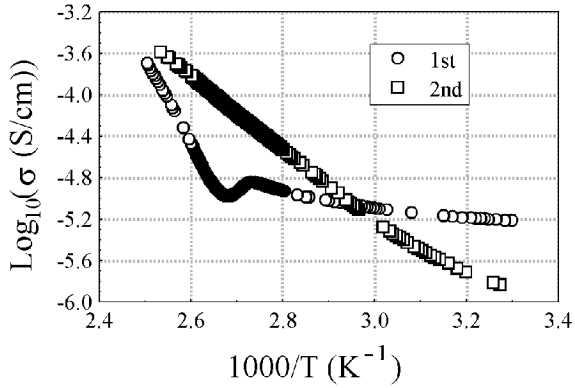


*Figure 7. Arrhenius plots of the dark conductivity for the $C_{60}$ thin film doped with 76wt% of $H_2Pc$.*

According to these results, the majority carrier of the $H_2Pc$-doped $C_{60}$ thin films change from electrons to holes as the set of concentration of the doped $H_2Pc$ increase from 60-80wt%.

## Conclusions

The photoconductivity of $H_2Pc$-doped $C_{60}$ thin films was investigated. The photoconductive sensitivity of $H_2Pc$-doped $C_{60}$ thin films is high at low doping concentrations of $H_2Pc$ before degassing of oxygen from the specimen, while the sensitivity of films is high at high doping concentrations of $H_2Pc$ after degassing of oxygen. The photoconductive sensitivity of the $C_{60}$ thin films increased

remarkably over whole visible region with doping of $H_2Pc$ before degassing of oxygen. For the degassed film, the photoconductive sensitivity increased remarkably in the wavelength region of 450-550nm. It is assumed that the conduction type of $H_2Pc$-doped $C_{60}$ thin films changes from n to p type at the $H_2Pc$ doping concentration of 60-80wt%.

## References


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## Biography

Ryoichi Yasuda received the B.E. degree from Ibaraki University in 1997. He is currently a master course student of Electrical and Electronic Engineering at Ibaraki University. His research interest includes fundamental study on carrier transport in organic semiconductors and development of electrophotographic photoreceptors.