Charge Generation Process in the Single Layer OPC

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Abstract

The charge generation process was studied for a single layered OPC comprising CGM pigments dispersed in the solid solution matrix of CTM in binder. This type of photoreceptor showed a unique bipolar photosensitivity. Since the major carrier in this system is the hole, the charge generation sites should be localized at the top surface of the layer when positively charged, and interface between the conductive substrate when negatively charged. Considering the difference of sensitivities by charging polarities in the actual single layer OPC, we assumed a model of photo-excitement of CGM in the bulk layer and diffusion of excited state as the phonon in the layer contributing the charge generation. By resolving the diffusion equation for free particles as well as the exciton diffusion in a crystal, we could estimate the diffusion length for this system as approximately 5μm and about 25% higher charge separating efficiencies at charge generation site of negative charging than that of positive charging. The theoretical result corresponded well to the experimental result for the relation between the sensitivities of both polarities.

Introduction

In recent years, the single layer OPC has been getting popularity again because of its advantages of simplified manufacturing and possibility of high-resolution imaging. Current development trend of the single layer OPC is mainly focused on the system comprising CGM pigment dispersed in CTM/binder matrix,[1-3] and nowadays, single layered OPCs of this type are actually employed in many electrophotographic printers and copiers.

As known well, the addition of electron acceptor or electron transport material (referred as ETM) into this system considerably improves the electrophotographic performances,[1, 2] and there is no doubt that recent progress in developments of various type of ETMs[4-6] with good performances made this type OPC much practicable.

In this system, it is known that OPC exhibits the bipolar photosensitivity,[1, 7] but the mechanism of the realization of bipolarity has not been studied in detail.

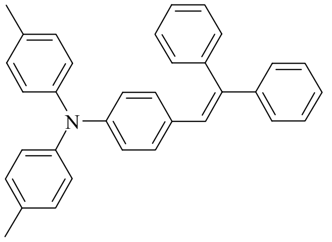
In this paper, we will present the charge generation mechanism of this type OPC studied by remarking this difference of photosensitivity by charging polarity with the assumption of different locations of photo-excitation and charge generation.

Experimental

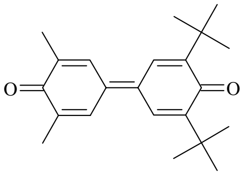
(a) OPC samples

As the CGM, x-form metal-free phthalocyanine (x-H_2Pc) pigment was employed.

At first, the pigment was added to the solution of polycarbonate-Z resin with chloroform and milled by a sand-mill to get homogeneous dispersion. Then, the appropriate amount of HTM (hole transport material) of the formula *(A)*,[8] ETM of the formula *(B)*,[5] and additional binder and solvent for adjusting the formulation were added to the dispersion and stirred until perfectly dissolved.



(A)



(B)

In order to compare the performances by addition of ETM, two kinds of formulation in following weight ratios were prepared:

Sample-1: CGM/HTM/ETM/binder = 3/40/10/50
Sample-2: CGM/HTM/binder = 3/40/60

These coating solutions were coated on bare aluminum tubes by ring-coating method and dried in an oven.

The thickness of obtained single layer OPCs was 13μm both in Sample-1 and in Sample-2.

(b) EP Properties

The EP properties were measured using a photoelectric drum tester, Cynthia-91 of GENTEC Co., Japan.

PIDC was measured in the static mode using 2μW/cm^2 monochromatic light exposure on the OPC surface. OPC was charged during rotation by a corotron then stopped at the measuring position, and when surface potential got 600V in absolute value, the light was exposed through a transparent probe of electrostatic voltmeter for 5 seconds, then an eraser light of 630nm LED was exposed for approximately 100μJ/cm^2 on the surface.

When measuring spectral sensitivity, same measurements of PIDC were repeated changing wavelength, where sensitivity ***S*** was defined as the deviation of initial light decay amplitude from dark decay amplitude,

$$S = \left| \frac{dV_D}{dt} - \frac{dV_L}{dt} \right| \qquad (1)$$

where $\boldsymbol{V_D}$ and $\boldsymbol{V_L}$ mean the surface potentials just before and after the start of light exposure respectively.

(c) Absorbance Spectrum

For the measurement of absorbance spectrum of the pigment and OPC film, a UV-visible spectrometer, model 8453 of Agilent Technologies was used.

For the measurement of absorbance spectrum of the pigment, above dispersion liquid of pigment and binder was diluted properly with chloroform and measured in a quartz cell. In the measurement of film absorbance, a part of OPC film was peeled off from the Al substrate, and then measured its absorbance spectrum directly.

Experimental Results

Figure 1 shows the absorbance spectrum of the OPC film of Sample-1, where the absorbance of original pigment dispersion is drawn in thin line together for comparison. It is seen that the original spectrum of CGM was kept unchanged even in the dried film and there is no absorbance of HTM and ETM or their complex in the wavelength range longer than 500nm.

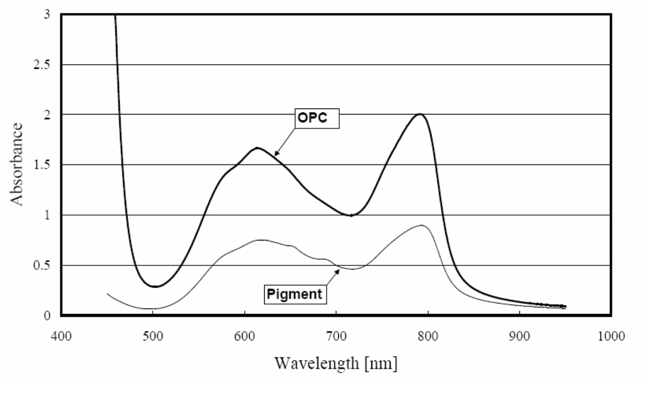
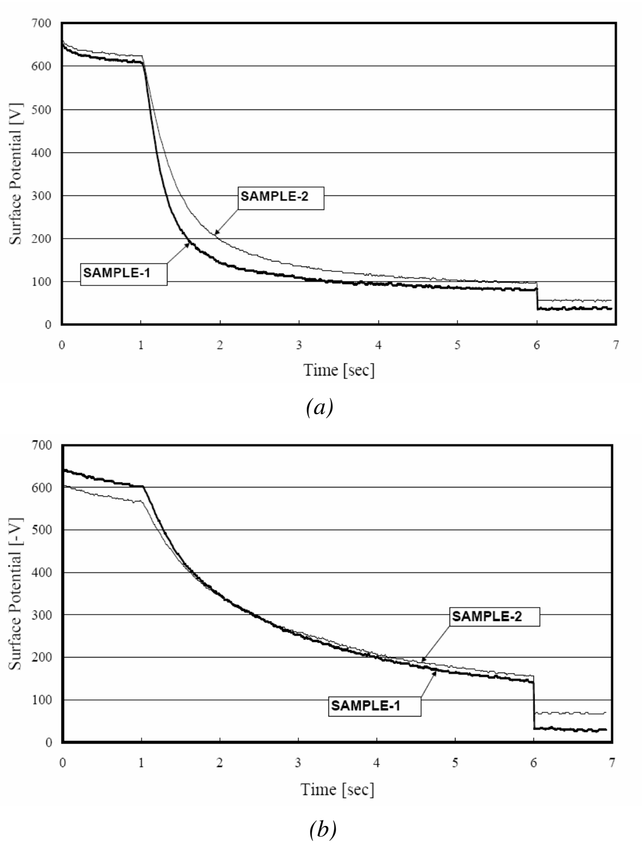


Figure 1. Absorbance spectra of OPC film and pigment dispersion. Bold line shows the absorbance of OPC film and thin line shows that of pigment dispersion in solvent.

Figures 2 (a) and (b) respectively show the positive and negative charging PIDCs by 780nm monochromatic light for both samples of the OPC with and without ETM.

Figure 3 shows the spectral sensitivities of Sample-1 single layer OPC for both polarities as defined by the equation (1).



(a)

(b)

Figure 2. PIDCs for (a) positive charging and (b) negative charging. Exposure: 780nm, 2μW/cm^2

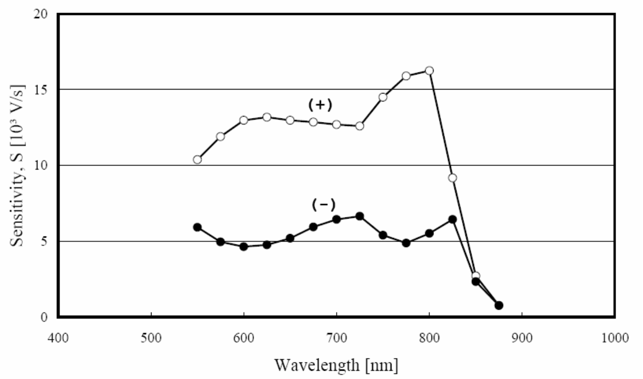
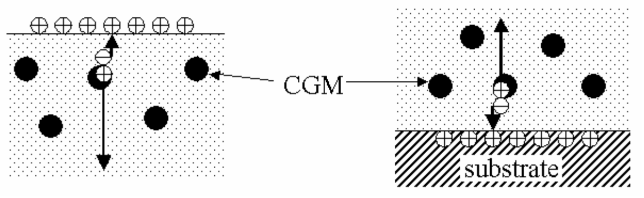


Figure 3. Spectral sensitivities of Sample-1 for both polarities. Open circles show the positive charging sensitivities and solid circles show the negative charging sensitivities.

Discussion

(a) Model of Charge Generation

Observing the results shown in Fig. 2, it is found that the existence of ETM contributes a little to increase the sensitivities of both polarities but remarkably affects on the absolute values of residual potential. From the result that sensitivity defined as the photocurrent in this study is not affected so much by the electron mobility in the layer, it is suggested that the number of free positive carrier is constant regardless of the existence of ETM. Namely, only the CGM pigments closest to the surface having strong interaction with surface positive charges but isolated from them by the CTM/binder matrix, where separated electron can make the ion pair with the positive charge on the surface, can be the charge generation sites in this system. And these negative charges need to be neutralized by electron motion in the matrix for reducing the residual potential as illustrated in Figs. 4.



(a) *(b)*

Figure 4. Schematic illustration of charge generation sites in Sample-1, where (a) shows the charge generation of positively charged state, and (b) shows that of negatively charged state.

As shown in the result of spectral sensitivities at Fig. 3, the spectral dependence of photosensitivity of this single layer OPC differs very much by charging polarity, where the spectral dependence of positive charging is very similar to the absorbance spectrum of CGM, but that of negative charging is unique showing valley at the wavelength of absorption peak of CGM and peak at the shoulder slope or valley of that absorbance spectrum. Similar phenomena have been reported for several past photoreceptors in single layer construction.[7, 9]

This phenomenon readily reminds us the similar spectral dependence of photocurrent in some organic solar cell.[10] In that case, the spectral dependence of photocurrent when illuminated from the opposite side of charge generation site corresponds to photosensitivity of negatively charged single layer OPC in this study, which suggests too that the charge generation site in negative charging exists at the opposite side of light exposure, i.e., the interface between OPC layer and substrate.

The literature[10] explained this phenomenon well by the theory of exciton diffusion in the thin melocyanine cell. In the present case, the concept of exciton diffusion hardly seems to be applicable because the layer of OPC is hundreds or thousands times thicker than that of solar cell, and the whole system is the mixture of small part of crystalline CGM, which accepts incident light, and majority part of transparent and purely amorphous CTM/binder matrix. But, the similarity of the apparent phenomena makes us suppose a similar principle of charge generation process, i.e., bulk CGM excitation by incident light, propagation of excited state to the charge generation site and charge generation only at the layer surface area.

The existence of the coupling of exciton and phonon in polymer film is known well for various organic materials.[11,12] And it seems appropriate to assume here the phonon as the carrier of excited state of this system, because it may have the long diffusion length, which can realize the energy transfer of long distance like OPC film, and rapid propagation of energy, as shown in the quick response of photo-decay for both charging polarities without delay.

(b) Determination of Parameters

If we assume the model of charge generation in this system as mentioned above where the distance of charge generation sites from layer surfaces are short enough to be negligible compared with layer thickness, we can determine the carrier number at the charge generation site in the same way of Ghosh-Feng model[10] for exciton diffusion.

In the case of positive charging, it will be

$$n_p = \frac{\phi_p N_o \alpha}{\beta + \alpha} \tag{2}$$

where $\boldsymbol{\phi_p}$. is the total quantum efficiency for positive charging, $\boldsymbol{N_o}$ is the incident photon number, $\boldsymbol{\alpha}$ is absorption coefficient, and $\boldsymbol{\beta}$ is the reciprocal of the diffusion length $\boldsymbol{L}$.

In the case of negative charging, using $\boldsymbol{\phi_n}$ as the corresponding quantum efficiency, it will be

$$n_n = \frac{\phi_n N_o \alpha}{\beta - \alpha}\{\exp(-\alpha l) - \exp(-\beta l)\} \tag{3}$$

where $\boldsymbol{l}$ means the layer thickness.

Since $\boldsymbol{N_o = E_o/h\nu}$, where $\boldsymbol{E_o}$ is the light energy, $\boldsymbol{h}$ is the Plank's constant and $\boldsymbol{\nu}$ is the wave number, the sensitivities for both polarities, $\boldsymbol{S_p}$ and $\boldsymbol{S_n}$, which are defined as photocurrents, can be written as

$$S_p = e\frac{dn_p}{dt} = \frac{e\phi_p P_o \alpha}{h\nu(\beta + \alpha)} \tag{4}$$

and

$$S_n = \frac{e\phi_n P_o \alpha}{h\nu(\beta - \alpha)}\{\exp(-\alpha l) - \exp(-\beta l)\} \tag{5}$$

where $\boldsymbol{P_o}$ means the light power and we assume the photocurrent is purely emission-limited here. Therefore, the ratio of sensitivities of both polarities can be simply written as

$$\frac{S_n}{S_p} = r\frac{\beta + \alpha}{\beta - \alpha}\{\exp(-\alpha l) - \exp(-\beta l)\} \tag{6}$$

where $\boldsymbol{r}$ means total quantum efficiency ratio of both polarities, $\boldsymbol{\phi_n/\phi_p}$.

Hence, we can obtain the actual values of diffusion length $\boldsymbol{L}$ and quantum efficiency ratio $\boldsymbol{r}$ from the relation (6) by applying the obtained experimental values.

Substituting absorption coefficients, film thickness and sensitivity values at two different wavelengths into equation (6), we can get the approximate value for $\boldsymbol{\beta}$, for example, by substituting the experimental values at 600nm and 775nm, we can get 1994 [cm^{-1}] as $\boldsymbol{\beta}$, i.e., diffusion length $\boldsymbol{L}$ is about 5μm.

Then, using the obtained value of $\boldsymbol{\beta}$, we can verify the equation (6) by plotting the correlation of

$$\left(\frac{S_n}{S_p}\right) \quad vs. \quad \left[\frac{\beta+\alpha}{\beta-\alpha}\{\exp(-\alpha l)-\exp(-\beta l)\}\right]$$

for the experimental result of spectral sensitivities as shown in Fig. 5, where good linearity can be seen proving the good applicability of equation (6) to actual system.

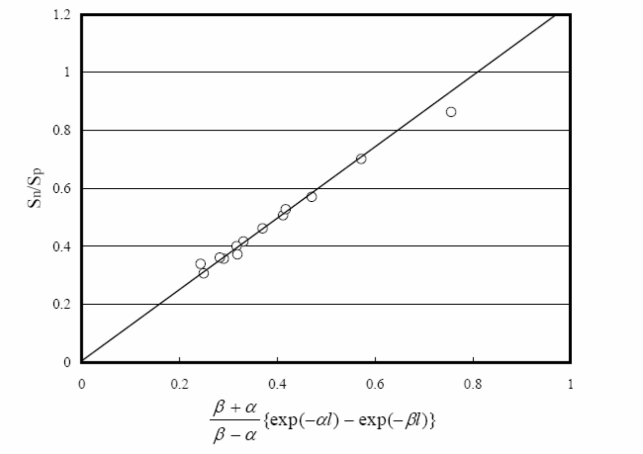


Figure 5. $\left(\frac{S_n}{S_p}\right) \quad vs. \quad \left[\frac{\beta+\alpha}{\beta-\alpha}\{\exp(-\alpha l)-\exp(-\beta l)\}\right]$

Dots are the calculated values from the data of spectral sensitivities of both polarities. Line is the approximation by the linear proportion.

We can determine the quantum efficiency ratio from the slope of the regression line in Fig. 5 as $\boldsymbol{r} = 1.25$. Since the value $\boldsymbol{r}$ means the ratio of total quantum efficiencies for both charging polarities, but there may not be any difference in the photon-phonon or exciton-phonon transfer efficiency by charging polarity, $\boldsymbol{r}$ simply means the ratio of charge separation efficiencies at the both sites.

The reason of better quantum efficiency for negative charging than for positive charging is supposed to be due to the strong local field at the interface between PC layer and substrate where charge generation site of negative charging system exists, and there may not be supposed to be such a strong field at the top surface of the OPC layer for positive charging.

Thus, knowing all parameters for the model of charge generation in single layer OPC, we can simulate the spectral sensitivity by the absorbance spectrum using the equations, (4) and (5), because the sensitivity can be regarded as the simple function of absorption coefficient and wavelength by these equations. Figure 6 shows the simulated spectral sensitivities by the equations (4) and (5) and actual experimental values for them.

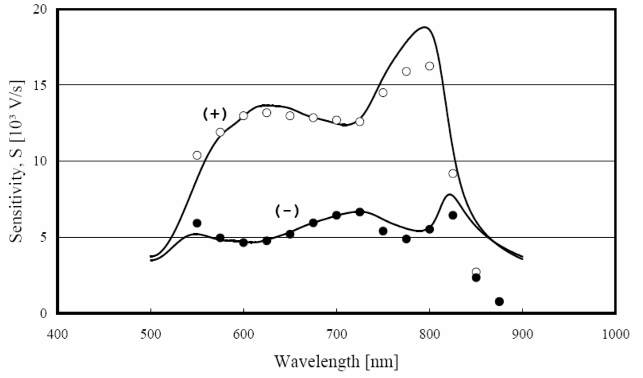


Figure 6. Simulated spectral sensitivities of both polarities. The curved lines are the results of calculation and the circles are the experimental values of sensitivity.

Except for the gradual deviation at the wavelength longer than 750nm, the plot shows excellent agreement of theoretical simulation and experimental result not only in relative magnitude but also in shape of spectral dependence, which verifies the supposed model for charge generation process suggested in this study. This deviation at longer wavelength seems to be due to the photon energy dependence of the quantum efficiencies, ϕ_p and ϕ_n, which we supposed to be constant in this study. For more precise agreement of calculation and experimental results, it is supposed that the wavelength dependence of quantum efficiencies should be taken into account.

Conclusion

The present results clarify the charge generation process of single layered OPC comprising CGM pigments dispersed in CTM/binder matrix. Experimental results suggested the different location but similar conformation of charge generation sites for positive and negative charging polarities, and the process of bulk excitement and surface charge generation system of the photosensitivity. That is, the incident light penetrates deeply into PC layer and excites the bulk CGM, and excited state propagates by the phonon diffusion to the charge generation site according to its charging polarity. The unique spectral dependence of negative charging sensitivity was perfectly explained by the suggested model of charge generation process. Numerical analysis by the suggested equations for both sensitivities applying estimated parameters precisely corresponded to actual data of spectral sensitivity, which verified well the model employed.

Although only a single layered model with peculiar formulation has been studied here, we believe the basic concept employed in this study can be applicable to various types of photoreceptors.

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Biography

Saburo Yokota received his Ph.D. in Physics from the Science University of Tokyo, Tokyo, Japan in 1982. From 1982 to 2000, he worked on the development of various types of OPC and experimental studies for them at Dainippon Ink & Chemicals, Inc., Japan. Since 2001, he has worked as a principal engineer at Digital Printing Division of Samsung Electronics, Korea. Currently, his main research activities focus on development and evaluation of materials related to electrophotographic photoreceptor. He is the member of the Imaging Society of Japan and the Japan Society of Applied Physics. yokota@samsung.com