Indirect Charge Generation in OPC

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Abstract

A new model of charge generation, including an indirect process for single layer organic photoconductor (OPC), was proposed and verified through experiments using OPC samples with various formulations. In the proposed process, the charge generation occurs at the surface of the photosensitive layer and is assisted by the energy propagation from the bulk layer. We propose mathematical model to describe this behavior and provide experimental evidence showing charge generation only at the surface. The proposed model was applicable to various single layer OPC formulations employing a common parameter in that model. The analytical result of the experimental data showed the prominent dependence of energy diffusion length on CGM concentration. This dependence can be explained by proposing that the disturbance of phonon migration is due to CGM particles.

Introduction

In our previous paper [1], we proposed a new model for the charge generation process in single layer organic photoconductor (OPC). The proposed charge generation model is characterized by the following assumptions:

1. Charge generation takes place at the interface of photosensitive layer.
2. The incident light energy absorbed in the bulk propagates in the layer as the diffusion of an electrically neutral particle and contributes the charge generation at interface.

These assumptions are basically the same as the exciton diffusion process for the charge generation in a thin *p*-type film proposed by Gosh et al.[2], so we similar equations can be used to represent our suggested model. However, we assume a different energy carrier other than an exciton because the single layer OPC as the basis of our model consists mainly of an amorphous and transparent CTM/binder matrix, where free migration of exciton cannot be allowed and the layer is much thicker than the usual diffusion length of exciton in organic crystal. We propose that this carrier particle is a phonon.

If we define the sensitivity as the initial discharging speed when exposed to weak continuous light, the sensitivity of positive charging is given as

$$S_p = \frac{e\phi_p P_o \alpha}{h\nu(\beta+\alpha)} \qquad (1)$$

and the sensitivity of negative charging is given as

$$S_n = \frac{e\phi_n P_o \alpha}{h\nu(\beta-\alpha)}\{\exp(-\alpha l)-\exp(-\beta l)\} \qquad (2)$$

Therefore, the ratio of sensitivities of both polarities can be simply written as

$$\frac{S_n}{S_p} = r\frac{\beta+\alpha}{\beta-\alpha}\{\exp(-\alpha l)-\exp(-\beta l)\} \qquad (3)$$

where r is the total quantum efficiency ratio of both polarities, ϕ_n/ϕ_p.

The equation (3) is the representative formula of our proposed model derived from the stated assumptions, that is, the feasibility of this equation may prove the validity of supposed model. We showed a good correspondence of these equations with experimental values for a peculiar single layer formulation in the previous paper.

Contrarily, conventional charge generation model is based upon the assumption that charges separate at the CGM particles, which absorbed the incident light energy in the bulk. Supposing that model, Buettner et al.[3] explained the photo-discharging characteristic of positively charged *p*-type film by assuming immobile negative charges in bulk could be neutralized by the recombination with mobile holes. However, according to its model, the final state of charges after light exposure is supposed to be composed of surface positive charges and bulk negative charges just below the surface charges, which is substantially equivalent to that of our supposed model. The prominent difference of its model from ours is only the location of the charge generation site, that is, bulk versus surface.

To clarify this issue, we report experimental results examining the change of photo-discharging characteristics by changing the formulation of the interface. Moreover, we will present the experimental results for different formulations to verify the generality of the proposed model and show the analytical result for formulation dependence of the diffusion length.

This paper will clarify the remaining issues for the model we proposed in the previous paper using the recent experimental results.

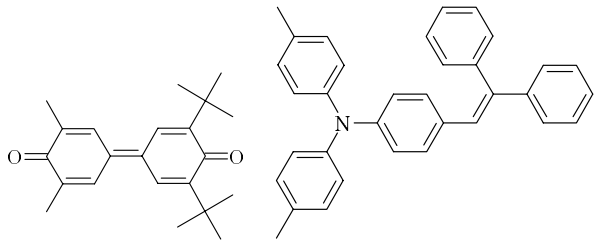
Experimental

(a) OPC samples

(1) Verification of surface generation model

At first, a thin solution of electron transport material (ETM) of formula *(A)* [4] was coated on the lower half part of an aluminum drum substrate making about 0.2μm thickness film after drying. Then, a coating liquid of single layer OPC without ETM in the formulation, CGM/HTM/binder = 3/40/57, was coated on the entire outer surface of drum substrate including uncoated area of ETM layer by ring coating method, where X-form metal-free phthalocyanine (X-H_2Pc) [5] pigment, compound of formula *(B)* [6] and polycarbonate Z resin were employed as CGM, hole transport material (HTM) and binder, respectively.

Thus, we could get a sample OPC where the lower one-half of the drum is undercoated with an ETM layer. The dried thickness of OPC layer was about 13μm.



(A) (B)

Figure 1. *Charge transport materials*

Since ETM of the formula *(A)* is soluble in the solvent used in the coating liquid of the outer layer, the ETM layer was presumed to be partially or wholly dissolved into the upper layer during the coating and drying process until the layer fully cured. However, the coating solution of upper layer was so viscous (about 200cps) that no convective mixing would occur and the contact time of lower and wet upper layer was very short, thus the penetration of ETM into the upper layer should be limited only to a very narrow depth. It means this OPC with ETM undercoated has an area of high ETM concentration at the interface with the substrate as schematically illustrated in Fig.2.

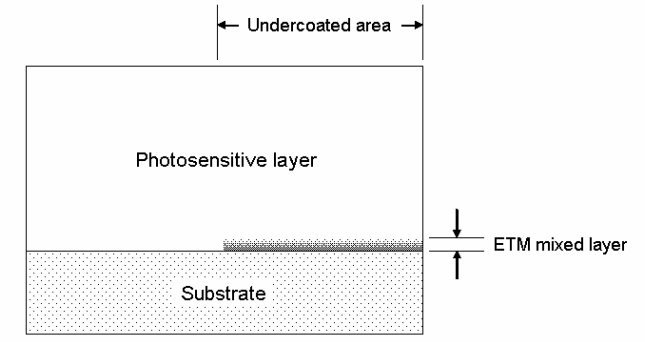


Figure 2. *Schematic illustration of the profile of single layer OPC for the experiment (1)*

(2) Formulation dependence

OPC samples with four different formulations were prepared in order to clarify the universality of the proposed model and to detect the parameter change due to formulation variety. The formulations contained the same components as mentioned in the proceeding experiment.

Table 1: Formulations by weight ratio

Sample	CGM	HTM	ETM	Binder
I	0.6	40	10	49.4
II	1	40	10	49
III	2	40	10	48
IV	4	40	10	46

The thicknesses of dried films of these samples were measured to be in the range of 14~15μm.

(b) EP Properties

The EP properties were measured using a photoelectric drum tester, Cynthia-91 of GENTEC Co., Japan in the same manner described in the previous paper.

PIDC was measured in the static mode using continuous exposure of 2□W/cm^2 monochromatic light on the OPC surface.

The sensitivity S was defined as the deviation of initial light decay amplitude from dark decay as follows,

$$S = \left| \frac{dV_D}{dt} - \frac{dV_L}{dt} \right| \qquad (4)$$

where V_D and V_L mean the surface potentials just before and after the start of light exposure respectively.

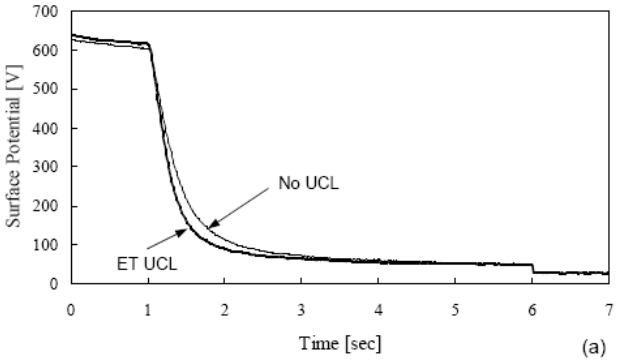
(c) Absorbance Spectrum

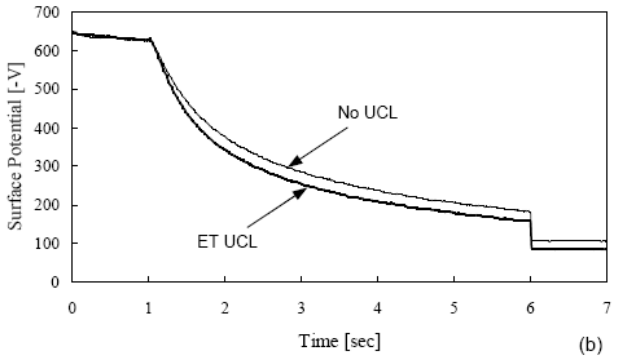
The UV-visible spectrum of OPC films were directly measured by a UV-visible spectrometer, Model 8453 from Agilent Technologies, for 17~18μm thick samples prepared by spin-coating solutions on a glass substrate.

Experimental Results

(1) Effect of ETM undercoating

Figs.3 (a) and (b) respectively show the positive and negative charging PIDCs by 780nm monochromatic light for both regions in the sample, i.e., with and without an undercoated ETM layer.



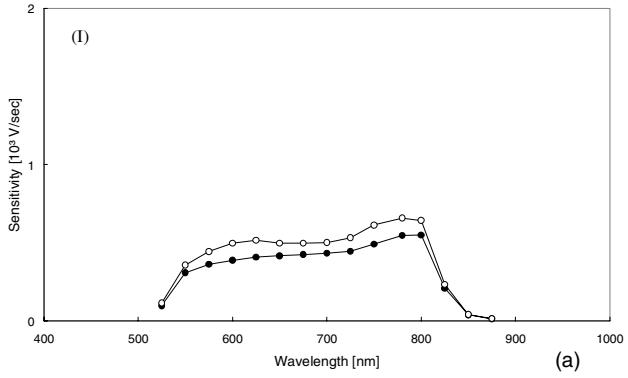


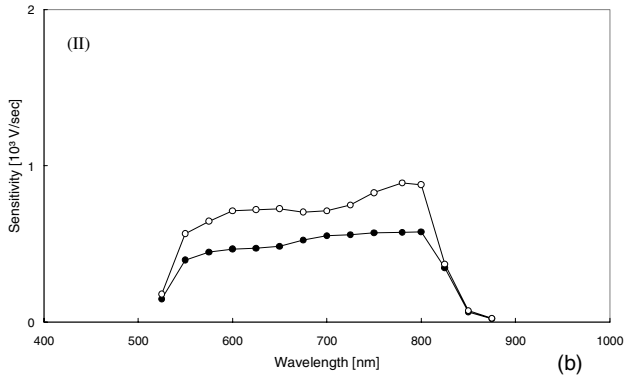
Figures 3 (a) - (b). *PIDCs for (a) positive charging and (b) negative charging. Exposure: 780nm, 2μW/cm^2*

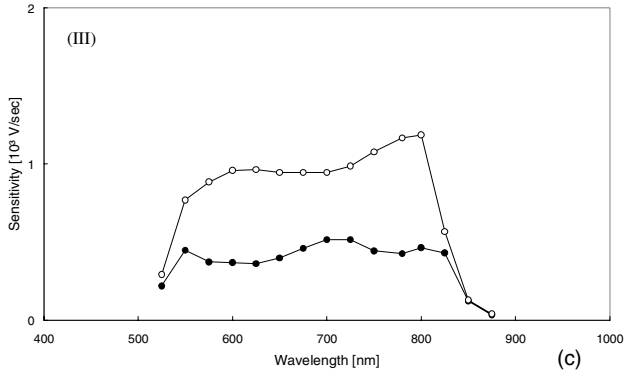
In spite of the very small amount of ETM possibly less than 2wt% for the total layer, the EP property was prominently improved by its undercoating. Almost a 20% increase in the sensitivity was observed for the both charging polarities.

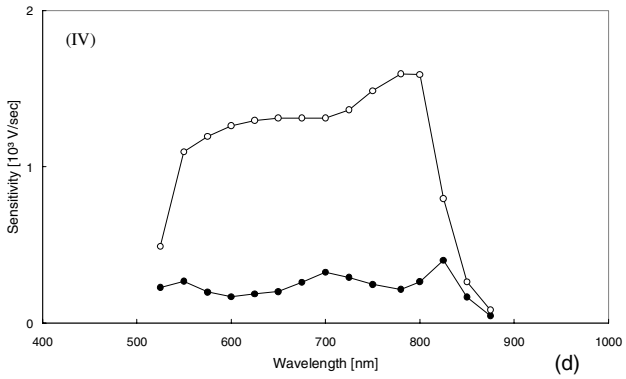
(2) Spectral sensitivities by formulations

Figs. 4(a) - (d) are the spectral sensitivities of all samples for both polarities. In the very thin CGM concentration system, both sensitivities were comparable in absolute values and spectral dependences were similar. However, the difference of both sensitivities became clearer with increasing CGM concentration. The positive charging sensitivity increased almost linearly and the characteristic spectral dependence of negative charging sensitivity appeared showing significant peaks at the absorption valley and shoulder slopes as described in the previous paper.









Figures 4 (a) - (d). *Spectral sensitivities of both polarities: Open circles show the positive charging sensitivities and solid circles show the negative charging sensitivities.*

Discussion

(1) Verification of surface generation model

The experimental result shown in Figs.4 (a) and (b) indicates the important role of the formulation at the interface between the photosensitive layer and substrate in photo-sensitivities of both polarities. The bulk generation model has no ability of explaining this result, because the difference of formulation is supposed to be limited only at the area close to the interface where the incident light can be reached only by about 1% of the total energy.

Contrarily, our model can explain this result very simply. For the negative charging photo-discharge, the interface between the photosensitive layer and substrate is the main charge generation site in our model, so the existence of ETM here should be the very definite factor for the charge separation efficiency.

For the positive charging, the charge generation at the interface could have no effect on photo-discharge when no ETM contained in the layer, because electron could not move upward from substrate to surface. When the layer had rich-ETM region near the interface, charge generation would take place there because generated electrons could move upward through the ETM rich region. Thus, in the case of ETM undercoated, the energy of incident light could contribute charge generation at both sides of photosensitive layer efficiently.

(2) Formulation dependence of charge generation process

As shown in our previous paper, we can estimate the energy diffusion length by resolving the equation (3). Fig. 5 shows the dependence of inversed diffusion length, β on CGM concentration obtained by applying the data shown in Figs. 4 (a) – (d). A clear correlation can be observed showing linear increase of β value by increasing CGM concentration.

This result suggests that the energy propagation in the CTM/binder matrix is strongly disturbed by the existence of CGM pigments, where the magnitude of the disturbance seems to be proportional to the density of CGM, and the diffusion length decreased as increasing CGM concentration.

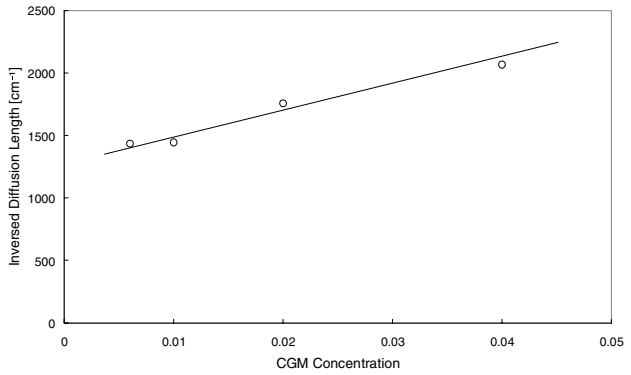


Figure 5. *Inversed diffusion length* β *as the function of CGM concentration.*

Here, let us assume the existence of two different disturbance coefficients for energy propagation, D_M of the CTM/binder matrix and D_P of CGM pigment and naturally $D_M < D_P$. The transmittance of phonon for the length d would be proportional to $\exp[-\{(1-\rho)D_M + \rho D_P\}d]$ using the value of CGM density ρ, so that the inversed diffusion length β should be represented in the following relation.

$$\beta \propto \{D_M + (D_P - D_M)\rho\} \qquad (5)$$

Thus, the linear dependence of β on CGM concentration can be simply explained.

Then, using the obtained value of β, we can verify the equation (3) by plotting the relation,

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

for the experimental result of spectral sensitivities as shown in Fig.6. A good linear relationship is seen proving the good applicability of equation (3) to whole actual systems.

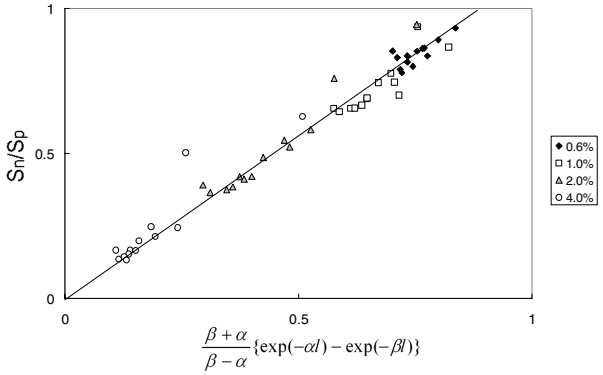


Figure 6. $(\frac{S_n}{S_p}) \quad vs. \quad [\frac{\beta+\alpha}{\beta-\alpha}\{\exp(-\alpha l) - \exp(-\beta l)\}]$ *: Dots are the calculated values from the data of spectral sensitivities of both polarities. Line is the approximation by the linear proportion.*

Fig. 6 also shows that the data of different formulations and wavelengths are aligned on one line crossing at origin point, which would indicate that relation (3) is consistently valid in the different formulations of single layer OPCs evaluated in this study. Since slope of the regression line, which denotes the ratio of charge separation efficiency of negative charging to positive charging, is larger than ***1***, then this suggests that the separation efficiency for negative charging is larger than that for positive charging due to the different locations of charge generation sites as suggested in the previous paper.

Conclusion

The present results verified the proposed model for charge generation at layer surface and not in bulk in the single layered OPC comprising CGM pigments dispersed in CTM/binder matrix. A change of the formulation at the layer interface causes prominent change in both sensitivities for positive and negative charging, which may be the direct proof of surface generation.

This model is consistently applicable to different formulations of photoconductive layer. The numerical analysis of the positive and negative charging sensitivities for various formulations suggests the strong dependence of energy diffusion length on the CGM concentration. This dependence can be simply explained by assuming a disturbance of energy propagation due to the existence of CGM pigments in the CTM/binder matrix.

References

1. S. Yokota, J. Imaging Sci. Tec. **49**, 629 (2005)
2. A. K. Ghosh and T. Feng: J. Appl. Phys. **49**, 12 (1978)
3. A. V. Buettner and W. Mey, Photogr. Sci. Eng., **26,** 80 (1982)
4. Y. Yamaguchi, H. Tanaka and M. Yokoyama: Chem. Materials **3**, 709 (1991)
5. R. O. Loutfy, B. S. Ong and J. Tadros, J. Imaging Sci. **29**, 69 (1985)
6. US Pat. 5,336,577

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.