Charge Generation in a Bisazo-Based Layered Photoreceptor

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Abstract

In the past papers, we had proposed a new model of the charge generation process in a single layer organic photoconductor, supposing indirect process of charge generation. In this study, we expanded this concept into more general dual layered system. Photoreceptors comprising a charge generation layer (CGL) of bisazo pigments dispersion into polyvinyl-butyral resin and a charge transport layer (CTL) of solid solution of donor molecule into polycarbonate resin were employed in the experiment. The change of electrophotographic characteristics by thickness of CGL in both conventional dual layer system and plus charging inversed dual layer system suggested the location of charge generation site at the interface of CGL and CTL and the energy diffusion from the bulk CGL. The estimated energy diffusion length was much longer than those ever reported as exiton diffusion. It was also found that whole discussion derived in the previous study upon single layer OPC was applicable to this dual layer system.

Introduction

The most organic photoconductors (OPC) currently commercialized have the dual layer (DL) structure with CTL covering CGL on substrate.

Umeda et al [1] and Niimi et al [2] studied the charge generation in the layered OPCs with specific azo pigments as charge generation materials (CGM) and stilbene compound as charge transport material (CTM) and concluded that photo-excited energy transferred in the CGM as the exciton diffusion, and free carrier dissociation from ion pair occurred only at the surface of CGM particle in the contact of CTM molecule supposing the penetration of CTM molecule into CGL when coating and the charge generation in the bulk CGL.

In the past papers [3, 4], we proposed a new model of charge generation process in the single layer (SL) OPC, supposing the photo-excitation in the bulk layer and charge separation only at the layer surface assisted by the energy diffusion in the layer as same as the exciton diffusion model in a thin melocyanine film proposed by Gosh et al [5]. Although the configuration of studied OPC was not so common as DL system, the adopted concept was essential and supposed to be applied to general OPC system.

In this paper, we will expand this model to the more general layered OPC comprising CGL and CTL, where a bisazo pigment known to be an *n*-type semiconductor is employed as the CGM. Since the major carrier in this CGL is supposed to be electron and that in CTL is hole, we will assume a charge generation model with the energy diffusion from the bulk CGL and the charge generation only at the layer interface of CGL and CTL, where CGL corresponds to total layer of SL OPC in function.

For the purpose of observing the effect of the incident light direction against the charge generation site in the same manner as previous study for the SL system, we prepared IDL samples with the CGL as top layer on CTL, in addition to the usual DL samples with CTL on CGL of same formulation.

Experiment

OPC Samples

Bisazo pigment in Fig. 1(a) structure [6] was dispersed in polyvinyl-butyral resin in 1:1 weight ratio with solvent by a ball-mill. Thus prepared dispersion liquid was coated on anodized aluminum drums by the ring-coating method and formed CGL. In order to compare the characteristic change by the CGL thickness, two samples with thin and thick CGLs were prepared in the same way. The estimated thicknesses from the relative light absorption against reference sample were approximately 0.4μm and 1.6μm respectively.

On the CGL, a solvent solution of a stilbene compound having high hole-mobility in Fig. 1(b) structure [7] and polycarbonate resin in 4/6 weight ratio was coated similarly and 17μm thick CTL was formed after drying.

Additionally, we prepared the IDL samples with two different CGL thicknesses by coating CGL on the 17μm CTL using the same coating liquids for DL samples as illustrated in Fig.2. In this case, the thickness of the thinner CGL estimated in the same way was 0.4μm and the thicker was 1.0μm.

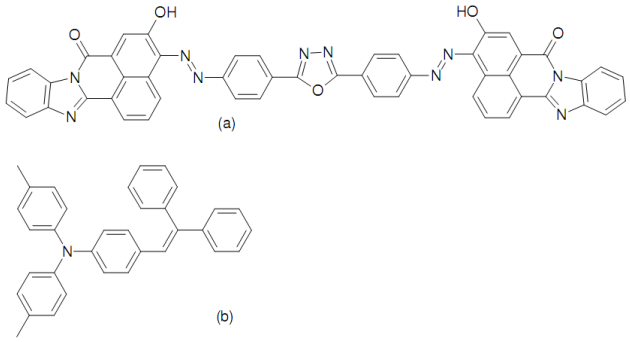

Figure 1. (a) Bisazo compound as CGM and (b) Stilbene compound as CTM

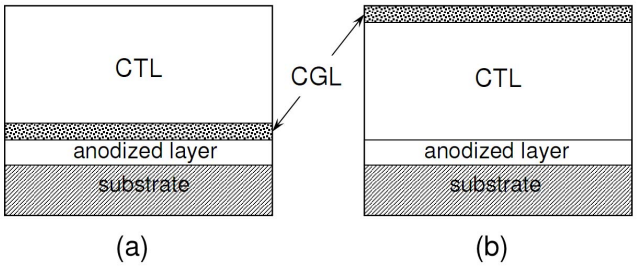

Figure 2. Schematic illustrations of OPC profile, (a) DL structure and (b) IDL structure.

Absorbance Spectrum

The UV-visible spectrum of CGL films were directly measured by a UV-visible spectrometer, Model 8453 from Agilent Technologies, for approximately 1.0μm thick samples prepared by spin-coating solutions on a PET sheet.

Spectral Sensitivities

The spectral sensitivities were measured using a photoelectric drum tester, Cynthia-91 of GENTEC Co., Japan in the same manner described in the previous paper [3].

PIDC was measured in the static mode using continuous exposure of 2μW/cm^2 monochromatic light on the OPC surface, which was charged 500V in absolute value.

The sensitivity $\boldsymbol{S}$ was defined as the deviation of initial light decay amplitude from dark decay as follows,

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

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

Experimental Results

Absorbance Spectrum

Fig. 3 shows the absorbance spectrum of the CGL film comprising bisazo pigment of formula Fig. 1(a) dispersed in polyvinyl-butyral. It exhibits strong absorption from UV region to around 600nm, and substantially no absorption at the wavelength longer than 700nm. The absorption peak (λ_{max}) is found at around 530nm.

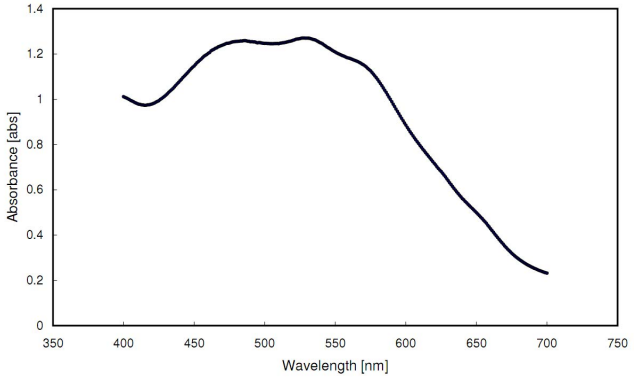

Figure 3. Absorbance spectrum of bisazo pigment film coated on PET sheet.

Spectral Sensitivities

Fig.4 shows the spectral sensitivities for DL samples with thick and thin CGLs, where prominent increase of sensitivity and shift of sensitivity peak to longer wavelength appear clearly by increasing CGL thickness. Not like the absorption spectra, the sensitivity shows rapid drop in the shorter wavelength than 450nm, where the absorption of CTM increases.

The results for IDL samples in Fig. 5 also show the similar sensitivity increase and wavelength shift of the peak, but no rapid sensitivity drop in shorter wavelength.

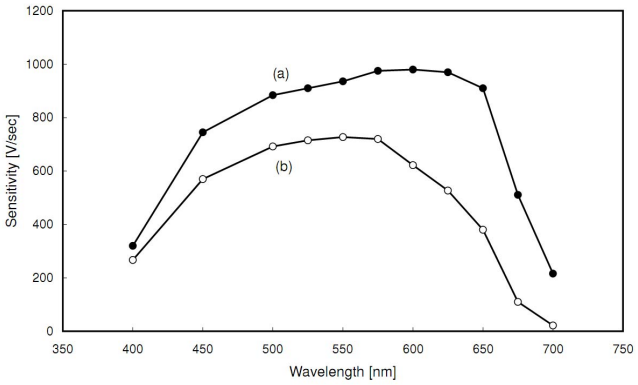

Figure 4. Spectral sensitivities of DL photoreceptors: (a) 1.6μm thick CGL, (b) 0.4μm thick CGL

(1)

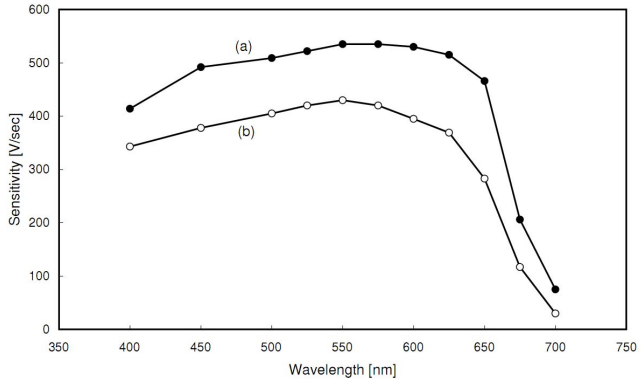

Figure 5. Spectral sensitivities of IDL photoreceptors: (a) 1.0μm thick CGL, (b) 0.4μm thick CGL

Discussion

Generation Model:

It is characteristic that not only the absolute value of sensitivity increases, but also the spectral dependence of sensitivity changes by increasing the CGL thickness of DL OPC, where the sensitivity spectra becomes broader and the sensitivity peak shifts to the longer wavelength. Similar phenomena also can be observed for IDL samples.

Supposing the charge generation only at CGL/CTL interface and energy transfer from the bulk CGL, this phenomenon can be simply explained.

In the very thin CGL sample, the distance of light absorption and the charge generation site is so close that the effect of energy diffusion can be small and spectral dependence will be similar to the absorption spectra. When the CGL is thick, the light with large penetration depth will excite deeper bulk CGM and the energy diffusion from there contributes the sensitivity increase and the change of spectral dependence. This concept is utterly the same with our model previously adopted in the charge generation in SL OPC when positively charged, where we regard the CGL/CTL interface to be the photoreceptor surface [3]. In this model, when the energy diffusion length is smaller enough than layer thickness,

the sensitivity will be approximately expressed in the following simple equation.

$$S_p = \frac{e\phi_p P_o \alpha}{Ch\nu(\beta+\alpha)} \quad (2)$$

where C is the capacitance of the total layer, α is the absorption coefficient, ϕ_p is the quantum efficiency, P_0 is the power of incident light and β is the reciprocal of diffusion length. In the case of DL OPC, the diffusion length would be so comparable to the CGL thickness that the term including layer thickness cannot be neglected. The original equation before eliminating the term including layer thickness parameter should be adapted to our DL model as follows.

$$S_{DL} = \frac{e\phi_{DL} P_o \alpha}{Ch\nu(\beta+\alpha)}\{1-\exp(-\beta l-\alpha l)\} \quad (3)$$

where l is the thickness of charge generation layer.

In this equation, all parameters except for β and ϕ_{DL} are already known. Supposing the quantum efficiency ϕ_{DL} is constant for wavelength, we can simulate the spectral sensitivity for any proposed β value using the absorbance spectrum data for 1.0μm thick CGL. Fig. 5 shows the spectral sensitivities thus calculated for by changing the value of β/ln10 from 0 to 1×10^4 supposing the CGL thickness l to be 1.6×10^{-4}cm as the experimental value for thicker CGL. Fig.5 simultaneously shows the experimental data of DL OPC with thick CGL so as to fit to the calculated curve optimally.

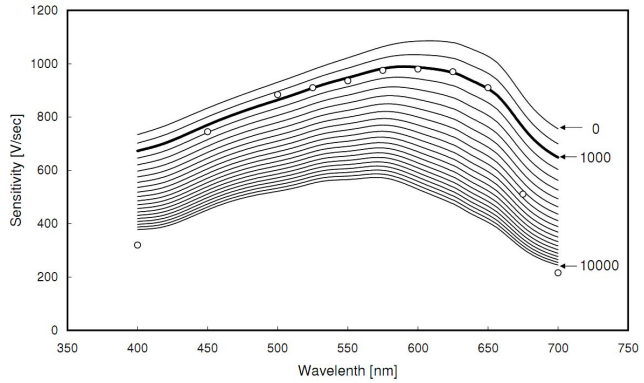

Figure 6. Calculated spectral sensitivities of DL for 1.6μm thick CG with various β values fitting to experimental results shown as circles.

We can neglect the large drop of the experimental sensitivities in shorter wavelength than 450nm since it is obviously due to the light absorption by CTM. In the same way, we can also neglect the sensitivity drop in the wavelength longer than 650nm, because actual light absorption in this area by this pigment is supposed to be much smaller than observed. Since OPC shows almost no sensitivity in the longer wavelength area, the apparent absorbance spectra may includes the effect of surface reflection or scattering and being lifted the baseline up.

Comparing the curves of Fig.6 with the data of thicker CGL in Fig.4, the spectral sensitivity of thick CGL almost fits to the calculated curve of β/ln10 = 1×10^3 in the wavelength range 450 – 650nm. Therefore, we will roughly determine β to be about 400cm^{-1}, that is, the diffusion length D is about 2.5μm, which is longer even than actual CGL thickness.

Simulation of experimental data:

We can simulate the spectral sensitivity by using obtained β value.

Fig. 7 shows calculated spectral sensitivities using fixed β value and various CGL thicknesses into equation (3). Clear increase of sensitivity and sensitivity shift to longer wavelength can be seen by the increase of CGL thickness as same as the experimental result shown in Fig. 4.

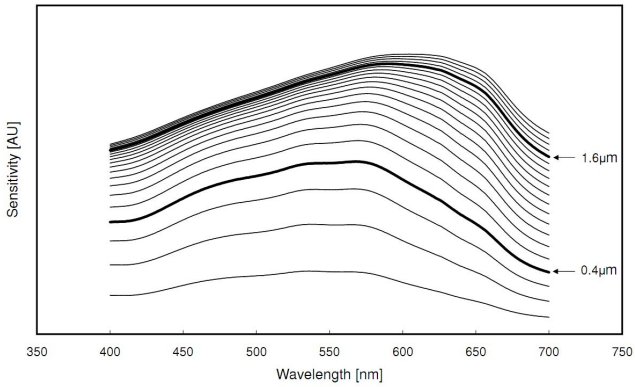

Figure 7. Simulated spectral sensitivities of DL photoreceptors for fixed β with various CGL thicknesses. The bold lines show those of 0.4μm and 1.6μm thick CGLs corresponding to actual photoreceptors

On the other hand, the spectral sensitivity of IDL samples showed similar spectral shift by increasing CGL thickness, but the increase of relative sensitivity was not so large as in DL system. Supposing same charge generation only at the CGL/CTL interface, we can consider the sensitivity of IDL system to be same with that of SL OPC when negatively charged as follows.

$$S_{IDL} = \frac{e\phi_{IDL} P_o \alpha}{Ch\nu(\beta-\alpha)}\{\exp(-\alpha l)-\exp(-\beta l)\} \quad (4)$$

Supposing the β value to be 400cm^{-1} as suggested above, we can simulate the spectral sensitivity of IDL photoreceptor using the equation (4) and absorbance spectrum data as shown in Fig. 8.

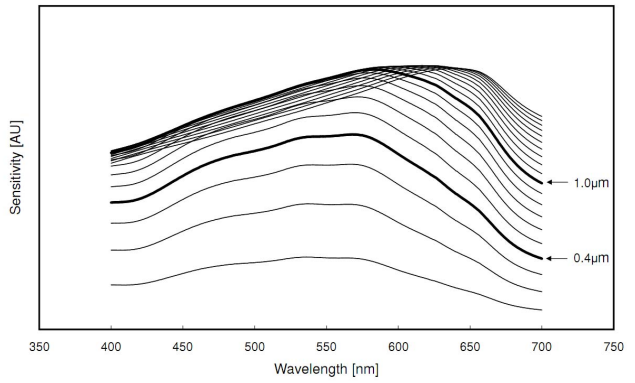

Figure 8. Simulated spectral sensitivities of IDL photoreceptors for fixed β with various CGL thicknesses. The bold lines show those of 0.4μm and 1.0μm thick CGLs corresponding to actual photoreceptors

Not like the case of SL OPC, the spectral dependence of IDL OPC is apparently similar to that of DL OPC. It shows similar tendency of sensitivity increase and wavelength shift as same as the simulation for DL OPC and experimental result shown in Fig. 5 corresponds well to it. But, it shows a definite difference in the point that sensitivity gets down when CGL thickness becomes thicker than a critical value.

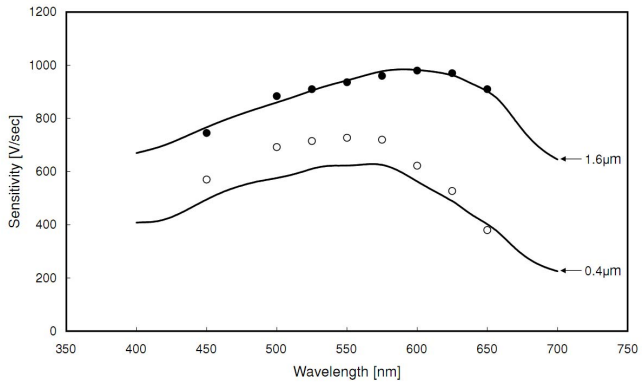

Figure 9. The fitting of calculated curves of spectral sensitivity in DL OPC to experimental values for both 0.4μm and 1.6μm thick CGLs

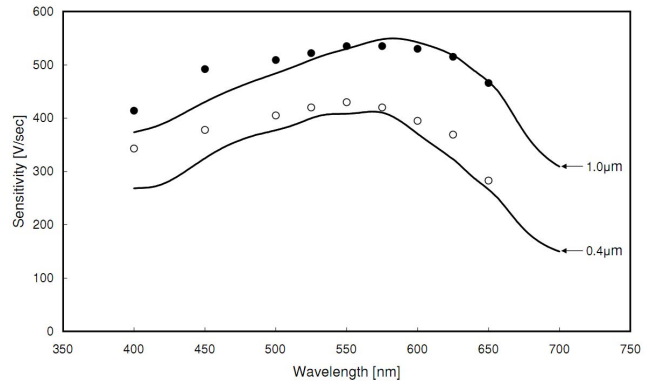

Figure 10. The fitting of calculated curves of spectral sensitivity in IDL OPC to experimental values for both 0.4μm and 1.0μm thick CGLs

Figs. 9 and 10 shows that spectral dependences of calculated sensitivities fit best to the experimental data of thick CGL samples of both DL and IDL systems in the wavelength range from 450nm to 650nm. On the other hand, the absolute values of thin CGL samples are rather larger than calculation. The reason of this deviation of experimental values from theoretical ones is supposed to be due to the reflection of penetration light from the substrate, which will be much effective when the thin CGL with higher transparency is used.

The quantum efficiencies for both DL and IDL systems were calculated in order to fit the simulation curves to experimental data. The obtained values are; $\phi_{DL} = 0.17$ and $\phi_{IDL} = 0.11$. Thus, the quantum efficiency of DL system is much larger than that of IDL system. This result is reasonable because the solvent of CTL is also a good solvent for CGL binder, so that the penetration of CTM molecule into CGL may easily occur in DL system when it is coated as suggested by Niimi et al [2] generating some hole mobility in CGL. On the other hand, since the solvent of CGL is not such a good solvent for CTL binder, the penetration of CTM molecule at the interface of IDL OPC may be much smaller than that of DL system, which causes the large difference of quantum efficiencies by coating order of the layers after all.

Conclusion

As shown above, by assuming a same charge generation model proposed for SL OPC, we can explain every phenomenon observed in spectral study for layered photoreceptors without any contradiction such as wavelength shift of maximum sensitivity, change of spectral curve shape, change of absolute value of sensitivity and so on.

Obtained result can be summarized as follows.

i) Our model of charge generation for SL OPC perfectly can be applied to that of layered system without any contradiction.
ii) The charge generation occurs only at the interface of CGL/CTL in both DL and IDL systems.
iii) Estimated energy diffusion length is about 2μm and a little smaller than that of SL OPC, but much larger than those in prior studies as the exciton diffusion [5].
iv) The quantum efficiency of DL system is larger than that of IDL system possibly due to the increase of hole mobility in CGL by CTM penetration into CGL.

Since the numerical analysis shown here were carried out in a very rough way, more precise analysis would be necessary for a detailed numerical discussion in future.

References

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Author Biography

Saburo Yokota received his Ph.D. in Physics from the Tokyo University of Science, 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.