The thermally stimulated current of β-form oxotitanium phthalocyanine dispersed in polyester

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A thermally stimulated current (TSC) has been applied to estimate the trap properties on a thin film of β-form oxotitanium phthalocyanine (β-TiOPc) dispersed in polyester. The hole trapping levels derived from the activation energies (Eas) were obtained by an initial rising method and heating rate dependence on TSC peaks. The Eas for an electric field of 2.5×10^3 V/cm were distributed from 0.033 eV for shallow traps to 0.42 eV for deep traps.

I. INTRODUCTION

There have been many investigations on phthalocyanines (Pcs) since these materials have become important for practical use in various fields.[1-3] In the case of electrophotography, the photoreceptors are usually prepared by the dispersing of photoconductive materials in a solvent with a binder polymer and then coating onto a conductive substrate.[2] In these systems, the photoconductivity is influenced by the entrapment of photogenerated carriers to the trapping sites in the photoconductive films.

Infrared (IR) sensitive photoreceptors using oxotitanium phthalocyanine (TiOPc) have been actively developed in recent years to obtain highly sensitive photoreceptors; therefore, it is necessary to analyze the trapping characteristics of TiOPc responsible the charge carrier generation or transport abilities in photoconductive films.[4]

The analysis of trap levels and depth in photoconductive films has been investigated using a thermally stimulated current (TSC) technique. Hoshino has investigated the TSC of the trapping levels of copper phthalocyanine (CuPc) dispersed in polyurethane film in which the traps are presumed to exist at the interface of CuPc particles and polymer.[5]

In this study, we measured the TSC of a thin film of β-TiOPc, which is a very stable crystalline form in TiOPcs, dispersed in polyester film in order to investigate the behaviors of carrier traps. In particular, we discussed the reflectance of the appropriate trapping state as a function of the electric fields, the wavelengths of irradiated light and TSC peaks as a function of different thermal rising rates.

II. EXPERIMENT

A. Fabrication of cell

The β-TiOPc was prepared by a previously described method,[4] and the crystal structure has been determined to be monoclinic.[6] The photoconductive film (10 μm) was composed of 50 wt.% β-TiOPc dispersed in polyester (Toyobo; Vylon 200) and coated on the glass. The structures of TiOPc and polyester are shown in Fig. 1. The glass was previously deposited on a semi-transparent Au electrode. The semi-transparent Au electrode was then deposited on the top of the film. The transmittance of the Au electrodes was fixed at 60±2%.

B. TSC measurement

The TSC measurement was carried out as follows. The sample cell was placed in a cryostat under an Ar atmosphere at 10^{-4} Torr. If necessary, a bias voltage (Vb) was applied, and was cooled to 100 K. The cell was then irradiated by a 500-W Xenon lamp for 3 min at an appropriate wavelength with a band pass filter. The light and Vb were then turned off. The temperature of the film was raised at a constant rate, and the TSC was measured by an electrometer under the applying of the collecting voltage (Vc).

III. RESULTS AND DISCUSSION

A. TSC and applied voltage dependences

Figure 2 shows typical TSC curves. Curve (a) was obtained by irradiation of white light at 100 K, and curve (b) was not irradiated. The peak at 16 °C was measured for both (a) and (b). It was also obtained in the TSC of the polyester film, and depended on the applied Vbs. Therefore, this peak would be due to a relaxation of dipoles in the polyester. A peak at − 55 °C was considered to be the carriers detrapping, that is, the carriers were produced by light irradiation and held many traps in the photoconductive layer.

As a result of the TSC measured at various Vc's, the TSC peaks, resulting from the detrapping, shift to a lower temperature with increasing electric field. They are explained by the lowering of the trap activation energy (Ea) due to the Poole–Frenkel effect.[7] The polarity of the TSC peak with the detrapping was not affected by Vc. The polarity was measured at reverse polarity of the applied Vb. Thus, the applied Vb produced polarized dipoles and internal electric fields were formed in the layer. As a result of calculations using TSC curves at various applied Vc's, the

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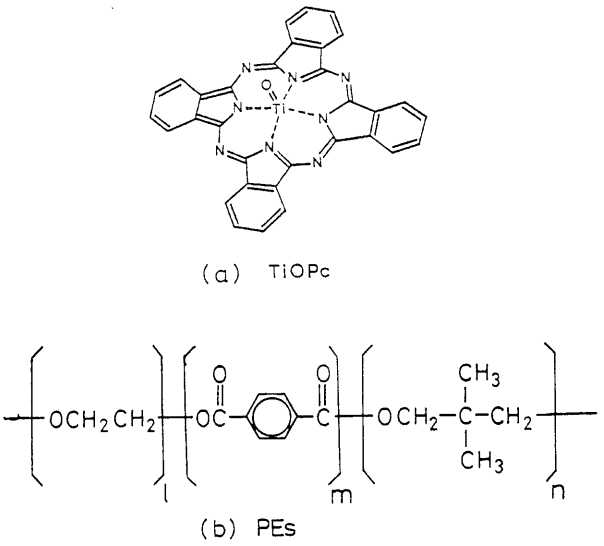

FIG. 1. Structures of β-TiOPc and polyester.

temperature dependences on the internal electric field agreed with relaxation of polarization obtained by the TSC.

B. Wavelength dependences of photoinduced TSC

Figure 3 shows the TSC measured at various wavelengths of irradiated light. As shown in Fig. 3, the wavelengths of 340, 679, and 780 nm are the peaks of absorption on the β-TiOPc film, respectively. The absorption at 483 nm shows the minimum of the energy level. The amounts of TSC were significantly affected by the wavelength irradiated; however, the temperatures of all TSC peaks were -55 °C. That is, the amounts of photocarriers captured in trapping sites depended on the wavelength of the irradiated light, and the trapping levels, of course, were still the same

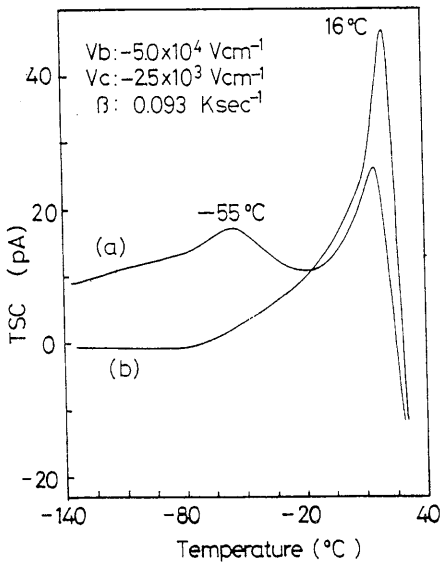

FIG. 2. Measured TSC curves. Curve (a) is a result of irradiated light at 100 K, and curve (b) is not irradiated. Vb: 5×10^4 (V/cm), Vc: 2.5×10^3 (V/cm), β: 0.093 (K/s).

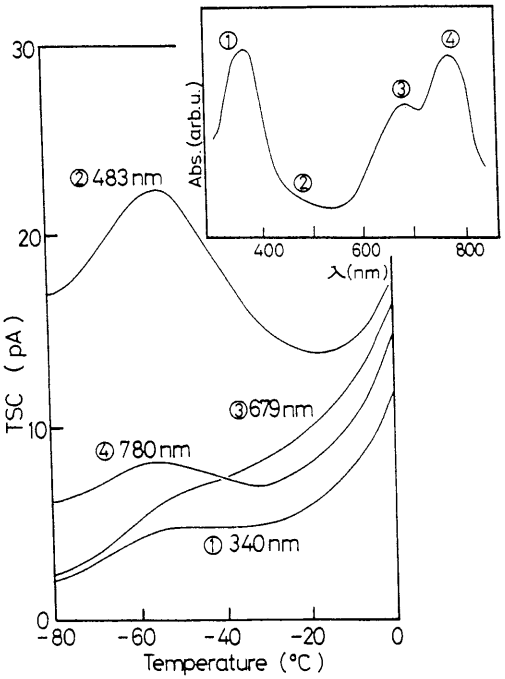

FIG. 3. Photoinduced TSC curves at various wavelengths. Vb: 5×10^4 (V/cm), Vc: 2.5×10^3 (V/cm), β: 0.093 (K/s). Numerals in figure indicate the wavelengths of irradiated light.

energy levels. Because of the high absorption efficiencies at 340 and 679 nm, many carriers yield at the surface of a film; therefore, the carrier density and the probability of recombinations would increase in the surface vicinity. On the contrary, the carriers produced at 483 nm would be uniformaly distributed in the bulk. Therefore, carriers could be sufficiently captured in trap sites. Since an absorption of 780 nm is predicated on the aggregation of TiOPc molecules, the trapping mechanism will be different. From the result of a small peak at 780 nm, we assumed that the probability of recombinations were reduced by the aggregation; therefore, a few carriers can be held in the trap site of the bulk.

C. Trapping sites analysis by activation energy

Since the dipole polarizations of polyester is significantly affected by the TSC peaks resulting from the detrapping, the trap Eas could not be exactly estimated. Therefore, TSC was measured under a nonpolarized field. 483-nm light was used to avoid the Dember effect. Figure 4 shows the TSC curves at various heating rates at a collecting voltage of 2×10^3 V/cm. The peaks were shifted to higher temperatures with increasing heating rates. The Ea1, which indicated deep trap depths, could be determined from the slope of the curve $\ln(\beta/\mathrm{Tm}^2)$ vs $1/k\mathrm{Tm}$, where Tm is the temperature of the maximum of the TSC peak, β is the heating rate, and k is the Boltzmann constant. The plots of this relation in Fig. 4 are shown in Fig. 5. The trap Ea1 determined from the slope of the curves is 0.42 eV, which means a main trapping level. In addition, Ea2 was obtained by an initial rising method reflecting

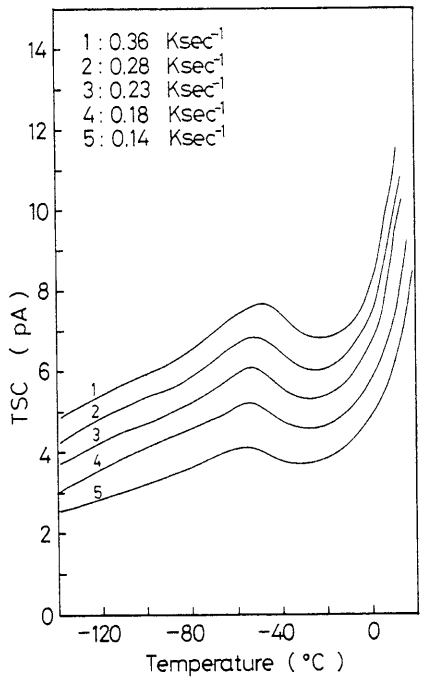

FIG. 4. TSC curves of various heating rates at 2.5×10^3 V/cm.

shallow trapping levels. From the equation of $\ln(I) = -(\mathrm{Ea2}/kT) + C$, where I is the measured TSC and C is a constant, Ea2 = 0.033 eV was calculated from the relation of [$\ln(I)$ vs $1000/T$] as shown in Fig. 6. The possible trap sites are classified into three domains in this film, that is: (1) within the β-TiOPc particles, (2) within the polyester, (3) at the interface. These trapping levels will be large distributions. In fact, they would be distributed from shallow traps (0.033 eV) to relative deep traps (0.42 eV). Hoshino has investigated the trap Ea of ϵ-CuPc dispersed in polyurethane as a function of electric field dependence.[5] He proposed the deep traps of Ea (0.4 eV) in the same electric field, and obtained TSC curves also similar to that of β-TiOPc. However, β-TiOPc has two trapping levels of shallow and deep. The photocarrier generating ability of the β-TiOPc is superior to that of ϵ-CuPc. The reason can

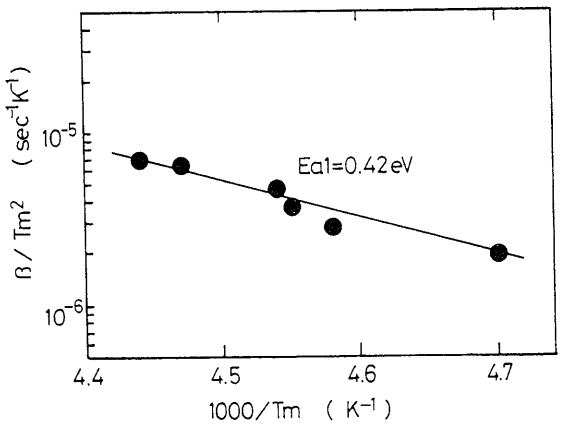

FIG. 5. ln β/Tm^2 vs 1000/Tm. Tm is the temperature corresponding to a peak current for a given TSC curve with a heating rate (β).

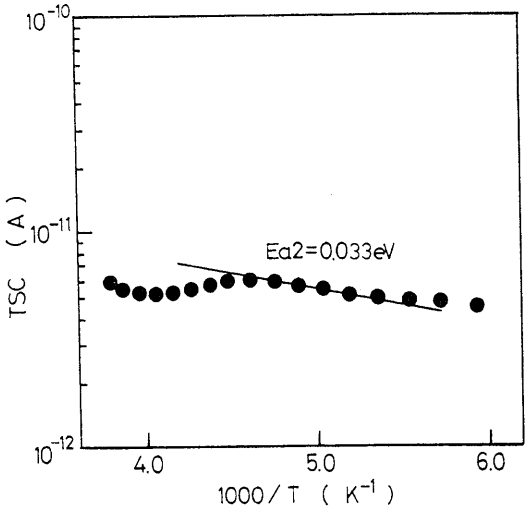

FIG. 6. Arrhenius plot of TSC peaks at 2.5×10^3 V/cm.

be considered that the photocarrier generation and the transport of carriers are not inhibited by these shallow traps; however, deep traps would control the mobility and life time of the carriers.

IV. CONCLUSION

This investigation shows the estimations of trap levels by the TSC technique on a thin film of β-TiOPc dispersed in polyester. The trap levels were derived from the Ea measured by an initial rising method and heating rate dependence.

A TSC peak at 16 °C was considered to be the relaxation of dipoles in polyester due to the dependences on bias voltage. The carriers were produced by the irradiation of light at an appropriate electric field. A TSC peak at −55 °C was a result of carrier detrapping from trap sites, probably in β-TiOPc or at the interface of β-TiOPc and polyester.

The amounts of TSC were significantly affected by the wavelength of the irradiated light, however, all the measured TSC peaks were at the same temperature in the same electric field. That is, the amounts of photocarriers captured in trapping sites would depend on the light absorbances in the photoconductive film. In the case of a large absorbance, most of the photocarriers are generated at the vinicity of light-irradiated surface, and recombinations do occur. On the contrary, for the case of low absorbance, the injected light can generate many photocarriers before recombination at a long distance; therefore, many carriers can be captured in the trapping sites, and measured by TSC analysis.

As a result of an initial rising method and heating rate dependences, we can estimate the shallow traps of 0.033 eV and deep traps of 0.42 eV, which are distributed in this photoconductive film. The photocarrier generation and the transport of carriers are not inhibited by these shallow traps, however, deep traps would control the mobility and life of the carriers in bulk.

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