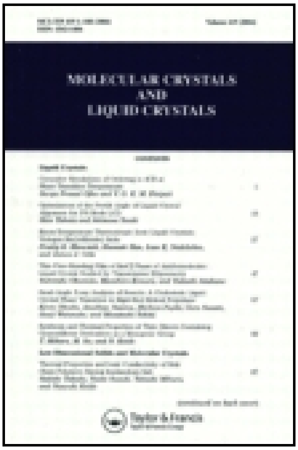

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Molecular Size Dependence in Third Order Susceptibility of Evaporated Tin-Phthalocyanine Thin Film

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Molecular Size Dependence in Third Order Susceptibility of Evaporated Tin-Phthalocyanine Thin Film

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Abstruct Molecular size dependence in third order optical susceptibility $\chi^{(3)}$ for evaporated tin-phthalocyanine thin film was examined by methods of a scanning electron microscope technique (SEM) and an optical third harmonic generation (THG) Maker-fringe technique. Evaporated molecular size influenced greatly the values of $\chi^{(3)}$. The thicker molecular size grew, the greater values of $\chi^{(3)}$ were. The values were greater with increasing the order orientation $O_A = A_\perp/(A_\perp + A_{II})$, whose preferential direction was parallel to the major axis of microcrystals.

INTRODUCTION

Phthalocyanine, especially, metallo-phthalocyanine(M-Pc) is one of the most interesting organic materials in optical and electrical applications$^{1)}$. But, these properties are different from size and shape of Pc molecular structures$^{2-4)}$. It has been known that M-Pc compounds whose center atoms are Ge, Sn and Pb have a shuttle-cock structure$^{5)}$.

In previous paper$^{6)}$, the values of optical third order electric susceptibility $\chi^{(3)}$ of evaporated tin-phthalocyanine (SnPc) on two kinds of glass plates were measured. The values were 30~50 × 10^{-12}esu on a boro-silicated glass plate at room temperatire and 150 × 10^{-12}esu on the glass plate with coated rubbing treated polyimide thin film heated at 200°C, respectively. The purpose of this study is to clarify a relation between size or orientation of evaporated SnPc molecules from the observations of SEM (scanning electron microscope) photographs and the values of $\chi^{(3)}$ from the measurements of THG (third-harmonic generation) Maker-fringe intensities, respectively.

EXPERIMENTAL AND DISCUSSIONS

The structure of specimens for studing was shown in Fig.1. Four kinds of specimens were prepared: types A and B were evaporated on a boro-silicated glass plate (called the glass plate) and types C and D on the glass plate with coated rubbing treated polyimide thin film (called the rubbing plate). The substrates of types A and C were not heated, but types B and D were heated at 200°C. The temperature was monitored and controlled by a thermo-couple. Film thickness was monitored by a quartz oscillator and evaporation rate was 0.1nm/s constant. Al (aluminum) heater was a flat panel to make the temperature uniform.

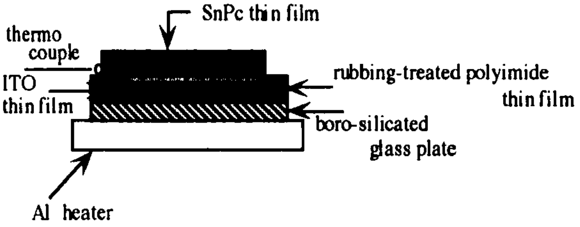
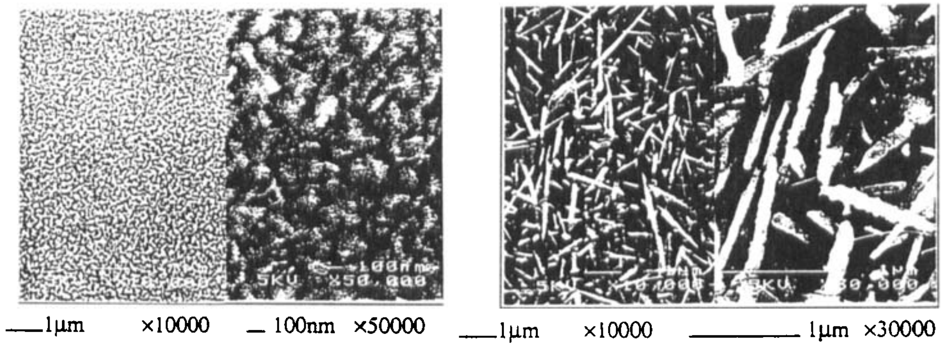


FIGURE 1. Structure of specimen (called the rubbing plate).



a) type A

b) type B

FIGURE 2. SEM photographs of two kinds of specimens :
a) type A (130µm) and b) type B (130µm).

Figure 2 shows SEM photographs of two kinds of specimens. It was clear from type A specimen that fine-grain microcrystals grew closely and had disorder orientations. From type B specimen, fine-needle-like microcrystals grew and they had a little order orientation.

We used the rubbing plate, and the surface of the plate was observed by using a method of AFM (atomic force microscope) technique. Photograph of the surface state was shown in Fig.3 and many linear oblique grooves were formed by rubbing the polyimide film. SnPc was performed on this plane.

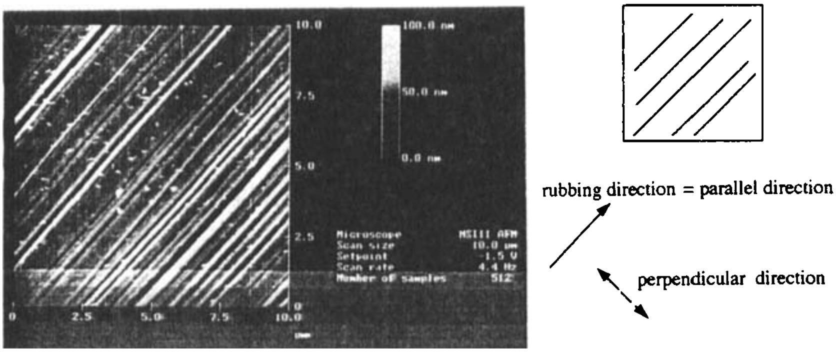
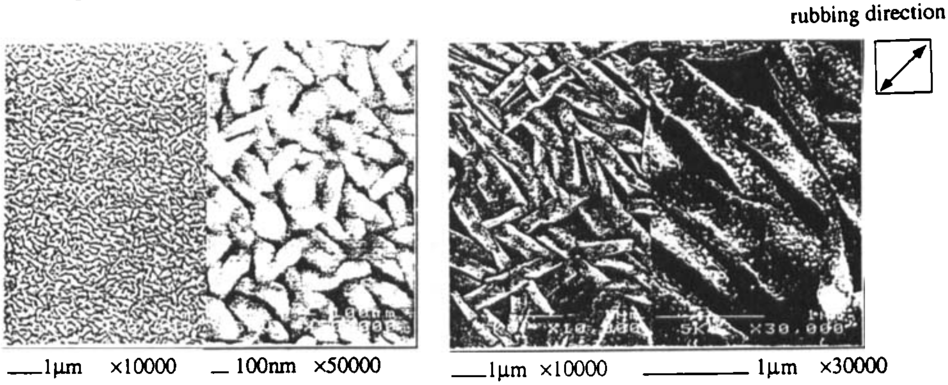


FIGURE 3. AFM photograph of surface state of the rubbing plate

Figure 4 shows SEM photographs of two kinds of specimens, It was clear from type C specimen that fine-grain microcrystals grew thicker than those from type A and the direction of their major axis which had a little order orientations was perpendicular to the rubbing direction. From type D specimen, fine-needle-like microcrystals grew more thicker than those from type B. They had an order orientation whose major axis was perpendicular to the rubbing direction.



a) type C

b) type D

FIGURE 4. SEM photographs of two kinds specimens :
a) type C (80µm) and b) type D (100µm).

Then, it could be said that thicker and orderd microcrystals would grow on the rubbing plate heated because it would be easy for evaporated molecules to migrate on the rubbing plate.

On the other hand, the values of $\chi^{(3)}$ were measured by using a method of THG Maker-fringe technique. Three fundamental wavelengths were selected for entrance laser beams: 1890nm, 2100nm and 2190nm. Quartz crystal was used as a reference material and the measurements were carried out in the air. The changes of $\chi^{(3)}$ dependent on the rotation angle of SnPc specimen were shown in Fig.5, where 0° was the rubbing direction parallel and 90° the direction perpendicular to the direction of linear polarized incident light, respectively. Maximum values took the angle 90°.

Comparing previous SEM photographs with THG results, it could be said that the angle which showed the maximum values $\chi^{(3)}$ and the direction of microcrystal's major axis agreed closely. Thus, the values of $\chi^{(3)}$ were measured at only two angles, i.e., 0° and 90°. The values at 0° and 90° were represented by $\chi^{(3)}{}_{II}$ and $\chi^{(3)}{}_{\perp}$, respectively, which were parallel and perpendicular susceptibility of microcrystals to the rubbing direction.

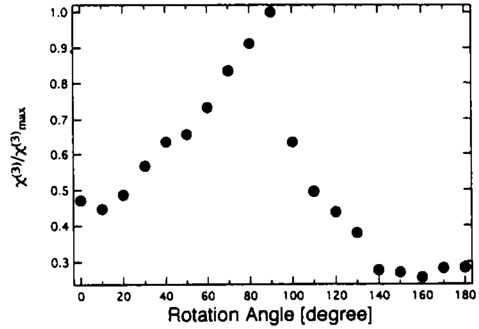


FIGURE 5. Normalized values of $\chi^{(3)}$ as a function of rotation angle. fundamental wavelength λ=2100nm, film thickness l_S=100μm

A new definition as a degree of order orientation O_A expressed by Eq.1 was introduced,

$$O_A = \frac{A_{\perp}}{A_{\perp} + A_{II}} , \qquad (1)$$

where $A_{\perp}$ was the gross area of microcrystals whose major axis was perpendi-

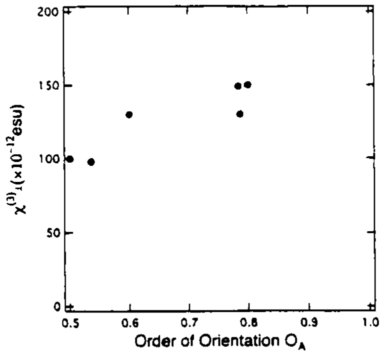


FIGURE 6.
Values of $\chi^{(3)}$ as a function of order orientation O_A.

cular and A_{II} the area parallel to the rubbing direction, respectively.

Figure 6 shows the values of $\chi^{(3)}$ as a function of order orientation O_A. If the orientation of molecules on the substrate would be randam, the values of $\chi^{(3)}_{\perp}$ would have maximum when $O_A=1$. Since intensity of THG beam J is related to stimulated light field E and third order nonlinear polarizability of γ by

$$J \propto \sum_{i} \gamma E^3 \cos^4\theta_i = <\cos^4\theta> \gamma E^3 \ , \qquad (2)$$

$\chi^{(3)}_{max}$ will become $8/3 \times \chi^{(3)}_{randam}$. Then, $\chi^{(3)}_{\perp max}$ will be 200×10^{-12}esu. On the other hand, an anisotropy of susceptibility $\Delta\chi^{(3)}$ was expressed by

$$\Delta\chi^{(3)} = | \ \chi^{(3)}_{\perp} - \chi^{(3)}_{II} \ | \ . \qquad (3)$$

$\Delta\chi^{(3)}$ increased with increasing O_A, i.e., the gross area of microcrystals whose major axis was perpendicular to the rubbing direction increased, but the gross area parallel to the rubbing direction decreased conversely.

Considering the orientation of molecules, a model presumed is shown in Fig.7, and the direction of molecular column will be parallel to the major axis of

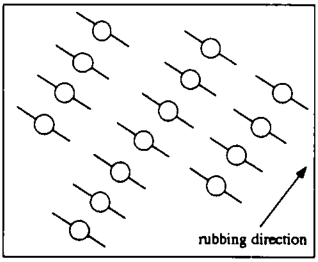


FIGURE 7.
Relation between directions of molecular column and rubbbing direction.

needle-like microcrystals. π-electron clouds would be super-imposed with each other, and the values of $\chi^{(3)}$ would increase.

CONCLUSIONS

SnPc molecular size and shape evaporated on the glass plate with coated rubbing treated polyimide thin film were observed by SEM technique and the values of $\chi^{(3)}$ were measured by THG technique. $\chi^{(3)}$ depended strongly on molecular size. From SEM photographs, evaporated SnPc molecules grew in the preferential direction, which was perpendicular to the rubbing direction. Thicker needle-like microcrystals, higher order orientation was formed on the substrate heated at 200°C. Higher order orientation O_A, larger values of $\chi^{(3)}{}_{\perp}$ and $\Delta\chi^{(3)}$ were obtained. If $O_A = 1$, both values will be a maximum.

There is a hope for SnPc compounds to be one of promising materials for application potentials. This study was partially supported by a scientific grant from Science University of Tokyo.

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