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Orientation of Tin-Phthalocyanine Film on Rubbing Substrates

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Optical properties of orientated tin-phthalocyanine (SnPc) films evaporated on two kinds of rubbing treated substrates (polyimide plates and polyamide plates, respectively) were studied by evaluating with absorption spectra, SEM and AFM techniques. On the polyimide plate, the orientation ratios of molecules with the perpendicular direction and with the parallel direction to the rubbing direction were 3 to 1. But, the direction of oriented molecules on the polyamide plate was parallel direction to the rubbing direction.

Keywords: SnPc; orientation; rubbing; absorption spectra; SEM

INTRODUCTION

Optical properties of a functional organic material with π-conjugated system depend strongly on as-prepared molecular orientation, stacking or packing with changing the substrate materials or substrate temperatures.
Phthalocyanine, especially, metallo-phthalocyanine (M-Pc) is one of the most interesting organic materials in optical and electrical applications. It has been known that M-Pc compounds whose center atoms are Ge, Sn and Pb have a shuttle-cock structure. In previous papers[1],[2], the values of optical third order electric susceptibility $\chi^{(3)}$ of evaporated tin-phthalocyanine (SnPc) films were 150×10^{-12}esu on the glass plate with coated rubbing treated polyimide thin film. The purpose of this study is to investigate the effects

of substrate materials to as-prepared molecular orientations of SnPc films. Microcrystals of as-evaporated SnPc films were formed on three kinds of glass plates: one was with coated rubbing treated polyimide thin film (called the polyimide plate), other with coated rubbing treated polyamide thin film (called the polyamide plate) and the other without coated (called the non-rubbing plate). Temperature of substrates was kept at 200℃ during the evaporated time.

EXPERIMENTAL

Orientations of SnPc films were evaluated with three methods; an absorption measurement, a scanning electron microscope (SEM) technique and an atomic force microscope (AFM) technique. Figure 1-a shows a SEM image for the non-rubbing plate and Figs.1-b and -c show for the polyimide plate and the polyamide plate, respectively. It was found from the figures that the microcrystals on both the polyimide plate and the polyamide plate were oriented respectively, but those on the non-rubbing plate were not oriented. On the polyimide plate, the orientation ratios of molecules with the perpendicular direction and with the parallel direction to the rubbing direction were 3 to 1. The anisotropy of the third harmonic generation (THG) intensities was also obtained[2]. On the contrary, the microcrystals on the polyamide plate were oriented parallel direction to the rubbing direction.

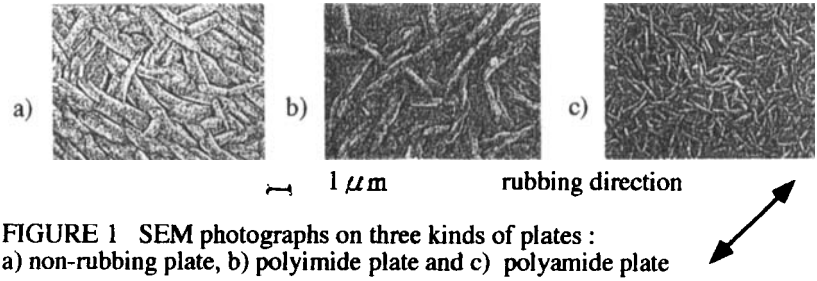

FIGURE 1 SEM photographs on three kinds of plates :
a) non-rubbing plate, b) polyimide plate and c) polyamide plate

From an usual absorption measurement, the wavelength ranges of Q-band of SnPc film formed on the substrate heated at 200℃ shifted toward longer wavelengths than those at room temperature. It is considered that

these phenomena will be caused by Dabydov splitting built up when some molecular orientations coexist in the microcrystals. It shifted from 700nm to 790nm. On the other hand, the wavelength of peak absorption spectra for the linearly polarized light perpendicular to the rubbing direction was 815 nm and that for the linearly polarized light parallel to the rubbing direction was 760nm, respectively. To obtain the reflectivity from refractive index and absorption coefficient, the reflective indices were calculated from absorption spectra by Kramers-Kronig transformation.
Figure 2 shows the reflective indices dependent on wavelengths for SnPc.

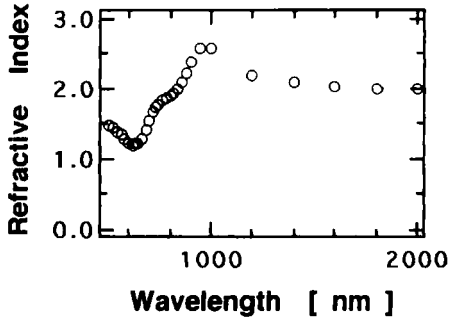

FIGURE 2 Refractive indices for SnPc (on quartz substrate)

Table I shows the reflectivities of α -type and β -type morphologies of the as-evaporated thin films calculated with the refractive index and the absorption coefficients at 790 nm. It became clear that the difference of reflectivities between α -type and β -type morphologies was nearly 10 %.

TABLE I Reflectivities of α -type and β -type morphologies of SnPc films at 790nm

Morphology	Reflectivity (%)
alpha-SnPc	20
beta-SnPc	29

Figure 3 shows the absorbance dependent on the direction of linearly polarized light as a function of wavelength. The direction of polarized light for the maximum absorbance was perpendicular to the rubbing direction and the wavelength of maximum absorbance blue-shifted. On the other hand,

the wavelength which showed the maximum absorbance for the parallel direction red-shifted.

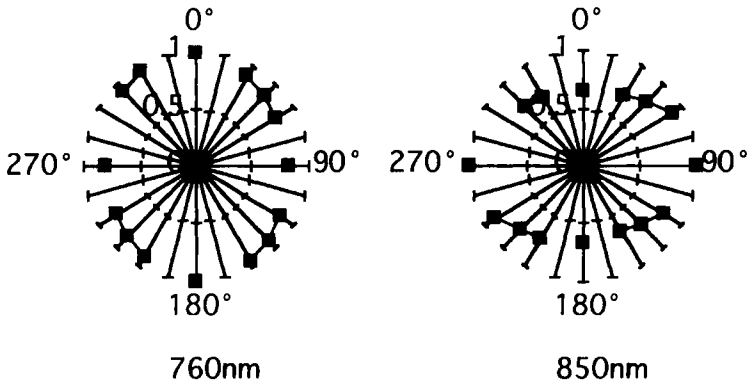

FIGURE 3 Anisotropy of absorbance as a function of wavelength.

Table II shows the anisotropy of reflectivity oriented SnPc films calculated with both the refractive indices and the absorption coefficients at 830 nm. The difference of the reflectivities for the linearly polarized light perpendicular and parallel to the rubbing direction was more than 10 %.

TABLE II The anisotropy of reflectivity of oriented SnPc film at 830nm

Polarized light direction	Reflectivity (%)
perpendiclar	15
parallel	31

DISCUSSIONS

We have reported that the grooves formed by rubbing were effective for SnPc molecules to have a high order orientation[2]. At first, the evaporated molecules will diffuse or migrate on the substrate and be held by the portions of the groove edges. The following molecules will stack on the first molecules and thus, the microcrystals grow to the direction of stacking. It is presumed that the azimuth of molecular major axis held originally by the active portions should decide the direction of the molecular orientation. Since

the direction of polarity in polyimide molecules may be different from that in polyamide molecules, the direction of SnPc molecular major axis will be changed by the conjugated states of these polarities and the polarity in SnPc molecules. However, this is unclear physically. We should therefore consider in detail the meaning of the different directions of their major axis. Further study of this is now in progress.

For the oriented films with β-type morphology (on the polyimide plate),
the reflectivity for the linearly polarized light perpendicular to rubbing direction was very different from that parallel to rubbing direction. When the values of two reflectivities are detected with high sensitivity, the ratios between two reflectivities for the oriented films will be different from those for the random films and will be not affected by the light-intensity changes.

So, it is expected that the ratios between two reflectivities can be used as the signal for the optical disk.

CONCLUSIONS

SEM images and the characteristics of spectroscopy were observed and evaluated for the as-evaporated SnPc films. The grooves made by rubbing affect strongly to the orientations of microcrystals. The direction of orientation was perpendicular to rubbing direction for polyimide plate, parallel for polyamide plate, but random for non-rubbing plate. On the polyimide plate at 790nm, the difference of reflectivity between α-type and β-type morphologies was large. At 830nm, the reflectivity for the linearly polarized light perpendicular to the rubbing direction was different from that parallel to the rubbing direction. The ratios between reflectivities for two directions on the oriented SnPc films were different from those on the random film. There is a hope for SnPc film in one of optical functional materials.

References

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