

Effects of Organic Gas on Third-order Nonlinear Optical Intensities and Morphologies of Vanadyl-Phthalocyanine Thin Films Prepared on Polyimide Substrate

ポリイミド基板の上に作成されたバナジルフタロシアニン薄膜の3次非線形光学強度と形態への有機ガス効果

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Abstract Vanadyl-phthalocyanine (VOPc) thin films were prepared by a molecular beam epitaxy on a polyimide (PI) substrate at 150°C, and then they were exposed to dichloroethane vapor for 25 hours. Their morphologies were investigated with Vis/UV spectra and the surface images observed by an atomic force microscope (AFM). The Vis/UV spectrum of VOPc thin film before the organic gas treatment has a broad absorption shoulder between 640 and 740nm and an absorption peak at 840nm in the Q band region. It has been known so far that VOPc thin film has Phase I, II and III. Phase I has two absorption peaks at 680 and 740nm. Phase II and Phase III are characterized with absorption peaks at 820 and 830nm, respectively. Therefore, the morphology having an absorption peak at 840nm is different from that of Phase III. The Vis/UV spectrum of VOPc thin film after the organic gas treatment has a broad absorption shoulder between 640 and 740nm and an absorption peak at 830nm in the Q band region. The absorption peak at 840nm shifts to 830nm by the organic gas treatment. This means that the phase morphology of VOPc thin film changes into Phase III during the gas treatment. On the other hand, VOPc molecules deposited on PI substrate before the organic gas treatment form needle crystals. This indicates that VOPc molecules deposited on PI substrate are perpendicular to PI substrate. The surface image of VOPc thin film after the gas treatment is smooth. This suggests that VOPc molecules are parallel to PI substrate. The third-order optical susceptibilities after and before the gas treatment are 3.75×10^{-9} and 3.25×10^{-9} esu, respectively. The molecular orientation of VOPc thin film is improved during the organic gas treatment.

1. Introduction

A vanadylphthalocyanine (VOPc) molecule is a dye's molecule. Its π conjugated length is relatively long as compared with other phthalocyanine derivatives and its crystal morphology has a lot of crystal phases. VOPc thin films as nonlinear optical materials were prepared by molecular beam epitaxy¹⁻³⁾. Especially, VOPc thin films have been fabricated on substrates of alkali halide crystals where VOPc molecules are deposited epitaxially⁴⁻⁵⁾. VOPc molecules deposited form a commensurate square lattice of $3 \times 3 R45^\circ$ on KBr substrate and $10^{1/2} \times 10^{1/2} R \pm 27^\circ$ type and bidirectional orientation for epitaxial square lattice on KCl

substrate¹⁾. On the other hand, polymer materials have excellent high transparency, smooth surface, flexibility and low price as compared with a fused quartz and also an excellent flexibility and low price as compared with alkali halide single crystal substrates. However, few dye's thin films have been prepared so far on polymer substrates in the field of nonlinear optical materials. In this paper, the morphologies and nonlinear optical properties of vanadylphthalocyanine (VOPc) thin films prepared on polyimide substrate were studied with Vis/UV spectra, XRD profiles, AFM image, SEM image and third order nonlinear optical susceptibility.

2. Experiments

VOPc films were fabricated on polyimide substrates by the molecular beam epitaxy (MBE) method. The source material used was VOPc powder supplied from Eastman Kodak Company. Fig. 1 shows

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the VOPc molecular structure. The molecule is 1.4nm in diameter and 0.2nm in height. 25 μ m-thick polyimide film was adopted as a substrate. After VOPc powder was inserted into a Knudsen-cell, it was preheated at 300°C for two hours. The substrate of polyimide was attached on the holder just after the cleaning with acetone.

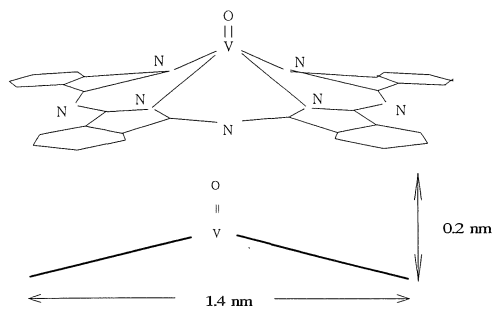


Fig. 1 Molecular structure of VOPc molecule

The main chamber of MBE was at about 10^{-7} Pa. The preparing conditions of samples are listed in Tables 1 and 2. Symbols in Tables 1 and 2 are evaporating temperature: T_e evaporating time: t and substrate temperature: T_s . S-1~12 means Samples 1-12. The thickness of S - 1~6 are 96, 102, 108, 95, 98 and 104nm, respectively. The thickness of S - 7~12 are 96, 108, 139, 94, 97 and 108nm, respectively. The incident angle dependence of third

Table 1 Preparing conditions of VOPc thin films.

Sample no.	1	2	3	4	5	6
T_e [°C]			300			
T_s [°C]			25			
t [min.]	60	120	180	60	120	180
Organic gas Treatment	N	N	N	Y	Y	Y

Table 2 Preparing conditions of VOPc thin films.

Sample no.	7	8	9	10	11	12
T_e [°C]			300			
T_s [°C]			150			
t [min]	60	120	180	60	120	180
Organic gas Treatment	N	N	N	Y	Y	Y

harmonic (TH) intensities of S - 1~12 are measured by Maker fringe with Nd : YAG laser. Its specifications are output 455mJ,

wavelength 1064nm, pulse width 5ns and repeating frequency 10Hz, respectively. The third harmonics is detected with a photomultiplier.

3. Results and Discussion

Fig. 2 shows the Vis/UV spectra of Samples 1 to 3 before organic gas treatment and Samples 4 to 6 after. Samples 1 to 3 have two absorption shoulders at 680 and 820 nm and an absorption peak at 740 nm. The morphology having a long broadband around 730 nm and an absorption peak at 680 nm was named Phase I by Griffiths et. al.. The morphology having a long broadband around 730 and two absorption peaks at 680 and 820 nm was also named Phase II. Therefore, they indicate that the VOPc thin films of Samples 1 to 3 were deposited initially with Phase II, and then with Phase I on Phase II. On the other hand, the VOPc thin films of Samples 4 to 6 after the organic gas treatment have an absorption peak at 820nm and a flat absorption band from 650 to 780 nm. As described above, the morphology of Samples 4 to 6 is near Phase II. The absorption

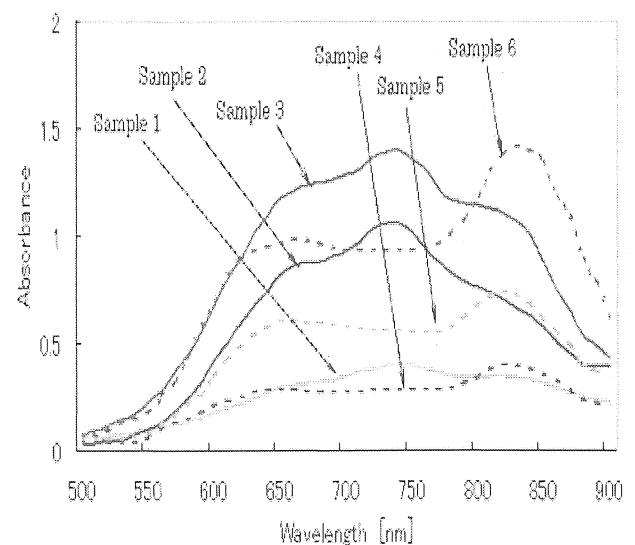


Fig. 1 Vis/UV spectra of Samples 1 to 6.

shoulder at 820 nm of Samples 1 to 3 before the organic gas treatment changes into an absorption peak at 820nm after the organic gas treatment. VOPc molecule is donor⁶⁾. If 1,2-Dichloroethane is acceptor⁷⁾, the donor-acceptor interaction between VOPc molecule and 1,2-Dichloroethane causes a higher molecular diffusion after the organic gas treatment and it accelerates to change from Phase I to Phase II.

Fig. 3 shows AFM image of Sample 3. The surface of VOPc thin film deposited on the polyimide substrate kept at 25°C is smooth. It was reported that the activation energy of desorption of VOPc

molecules deposited on a polyethylene-terephthalate (PET) substrate is 31kcal/mol⁸⁾. Its value is higher than that of the hydrogen bonding. Polyimide and polyethylene-terephthalate films are aromatic polymer. Therefore, the activation energy of desorption of VOPc molecules on the PI substrate is expected to be near the value on the PET substrate. Moreover, the interaction of between VOPc molecules on the PI substrate is below 10 kcal/mol and the molecular diffusion of VOPc molecules on the PI substrate kept at 25 °C is low. These reveal that VOPc molecules deposited on the PI substrate are parallel on the substrate.

Fig. 4 shows the AFM image of Sample 6. A lot of island crystals are observed on the PI substrate. The molecular diffusion of VOPc molecules occurs on the PI substrate kept at 150°C. Therefore, it indicates that a lot of island crystal grow with merging grains of

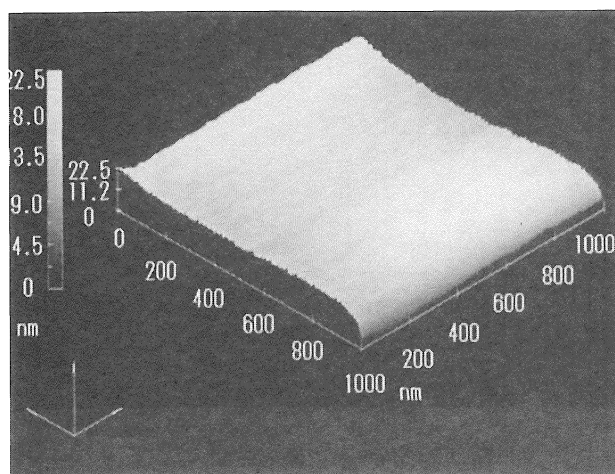


Fig. 3 AFM image of Sample 3.

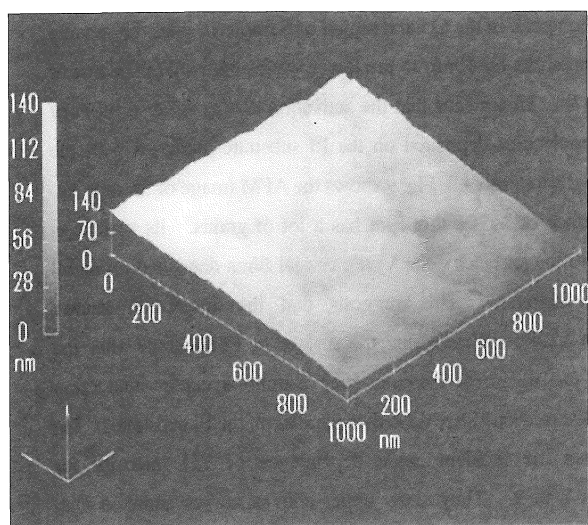


Fig. 4 A AFM image of Sample 6.

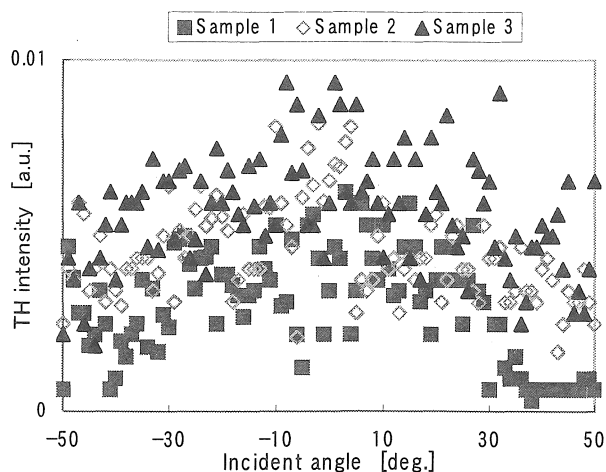


Fig. 5 TH intensity vs. incident angle of Samples 1 to 3.

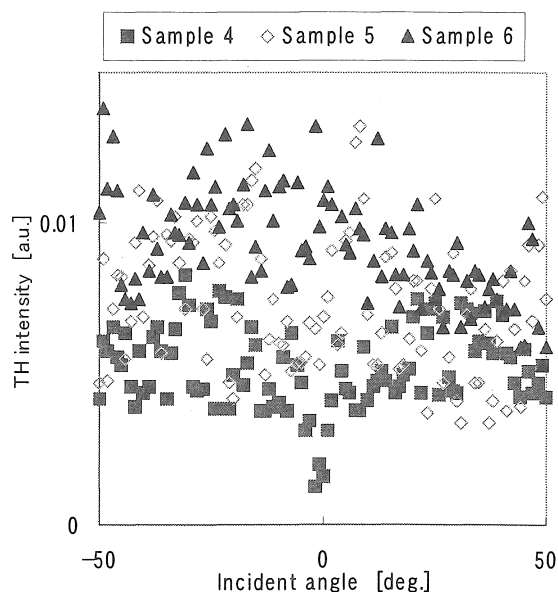


Fig. 6 TH intensities vs. incident angle of Samples 4 to 6.

VOPc molecules on the substrate. This indicates that the packing density of crystals of Sample 6 is higher than that of Sample 3. In other words, Sample 3 is a VOPc thin film deposited dominantly with Phase I and Sample 6 is deposited dominantly with Phase II. From Vis/UV spectra and AFM images, the phase morphology of Samples 1 to 3 are dominated with Phase I and Samples 4 to 6 are dominated with Phase II. The distance between layers of Phase I is larger than that of Phase II. This means that the electron density of Phase I is lower than that of Phase II. The third

harmonic intensity depend upon the electron density between layers of Phase. Therefore, it is expected that TH intensity of Phase II is larger than that of Phase I. If Samples 1 to 3 are dominated with Phase I and Samples 4 to 6 are dominated with Phase II, the third harmonic intensity of Samples 1 to 3 are lower than those of Samples 4 to 6. Fig. 5 shows TH intensity vs. incident angle of Samples 1 to 3 irradiated with P polarized laser light (Laser source: ND: YAG laser, Wavelength: 1064 nm). Fig. 6 shows TH intensity vs. incident angle of Samples 4 to 6. Samples 1, 2 and 3 have small TH intensities as compared with Samples 4, 5 and 6, respectively. These indicate that Samples 1 to 3 have Phase I and Samples 4 to 6 have Phase II.

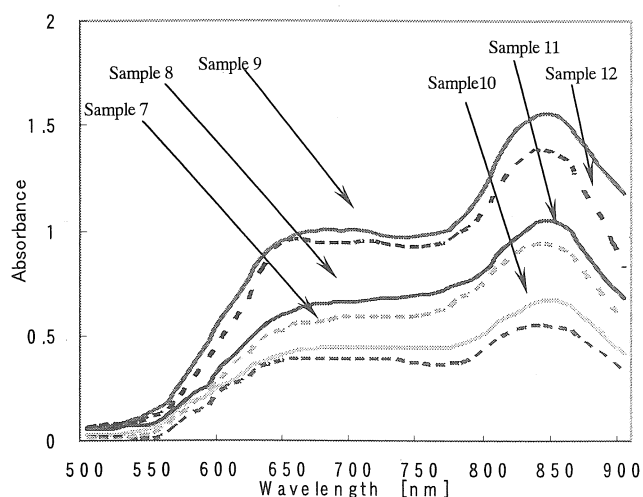


Fig. 7 Vis/UV spectra of Samples 4 to 9.

Fig. 7 shows the Vis/UV spectra of Samples 7 to 12. The Vis/UV spectra of Samples 7 to 9 have a similar pattern. The Vis/UV spectrum of Sample 7 has an absorption peak at 840 nm and a flat broad band from 650 to 780 nm. The absorption peak of Samples 7 to 9 shifts by 20 nm to the longer wavelength side than those of Samples 10 to 12. Therefore, the molecular diffusion of VOPc molecules deposited on PI substrate kept at 150°C may reduce the activation energy of absorption between VOPc molecule and PI substrate so that the interaction between VOPc molecules is larger than that between VOPc molecule and PI substrate, and VOPc molecules are perpendicular on PI substrate because of the interaction between VOPc molecules. This means that the molecular packing density of the VOPc molecules perpendicularly oriented on PI substrate is higher than that of parallel-oriented one. Fig. 8 shows the AFM image of Sample 9. A lot of needle crystals are observed. This reveals that VOPc molecules are perpendicular

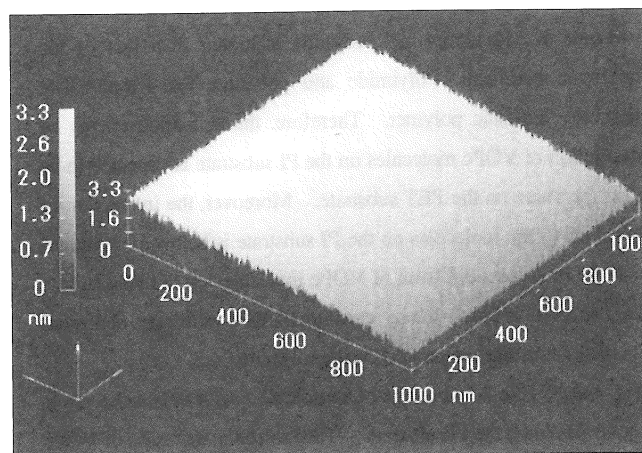


Fig. 8 AFM image of Sample 9.

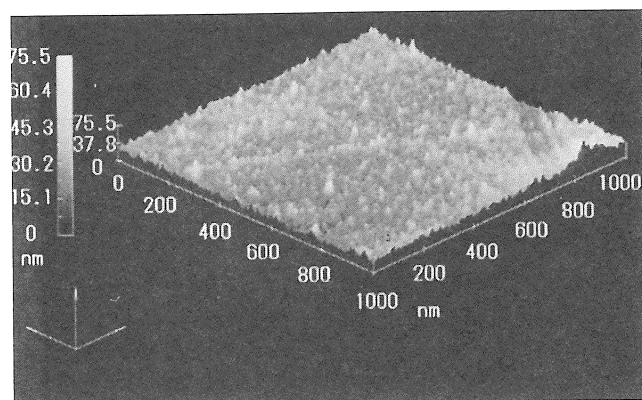


Fig. 9 AFM image of Sample 12.

on the PI substrate. Vis/UV spectra of Samples 10 to 12 have a similar pattern. For example, Sample 10 has an absorption peak at 830 nm and a flat broad band from 650 to 780 nm. An absorption peak in the Q band region of Sample 10 after the organic treatment shifts by 10 nm to the lower wavelength side than that of Sample 9. This means that the activation energy of absorption of VOPc molecules deposited on the PI substrate increases with the organic gas treatment. Fig. 9 shows the AFM image of Sample 12. The surface of VOPc thin film has a lot of grains. Its surface is similar to the surface of the VOPc crystal films deposited on alkali halide substrates. This suggests that the absorption energy between VOPc molecule and the surface of PI substrate after the organic gas treatment increases with a donor-acceptor interaction and VOPc molecules are deposited parallel on the PI substrate. Fig. 10 shows the incident angle dependence of TH intensity for Samples 7 to 9. They show upper convex curves centered at 0 degree and increase with increasing the thickness of Sample. These indicate that the orientation of VOPc molecules deposited on the PI substrate

of Samples 7 to 9 is a higher order orientation than Sample 1 to 3 and a higher packing density than that of Samples 1 to 3. Fig. 11 shows the incident angle dependence of TH intensity for Samples 10 to 12. As mentioned above, the orientation of Samples 10 to 12 has an excellent molecular arrangement as compared with Samples 7 to 9. Therefore, TH intensities of Samples 10, 11 and 12 are larger than those of Samples 7, 8 and 9, respectively.

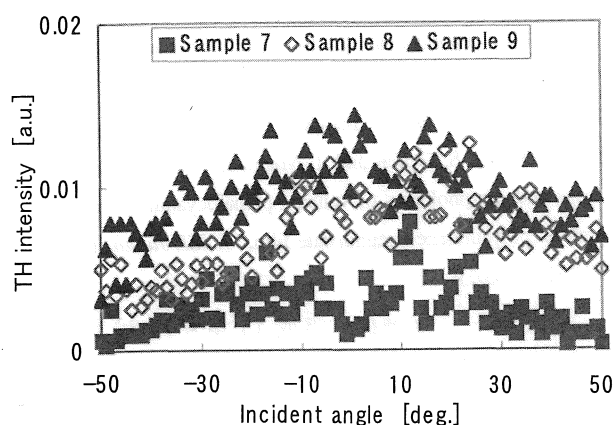


Fig.10 TH intensity vs. incident angle of Samples 7 to 9.

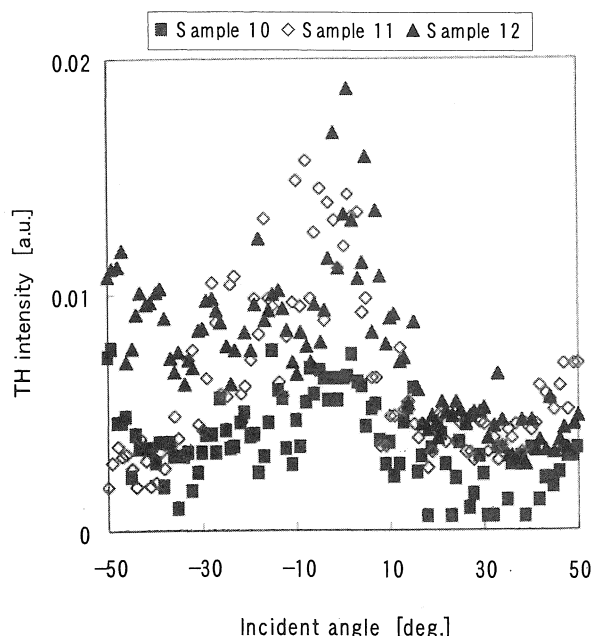


Fig. 11 TH intensity vs. incident angle of Samples 10 to 12.

Fig. 12 shows the maximum TH intensity as a function of thickness. The maximum TH intensity for VOPc thin films prepared on the PI substrate at 25°C has a tendency to saturate with the increase of

thickness. On the other hand, for the VOPc thin films prepared at 150°C, it saturates with the increase of thickness before the organic gas treatment (Sample 7, 8 and 9), but not after the gas treatment. This means that Samples 10 to 12 have an excellent high order orientation. The third order susceptibility ($\chi^{(3)}$) of Samples 9 and 12 prepared on the PI substrate kept at 150°C are estimated from the maximum TH intensity at 0 degree. The $\chi^{(3)}$ values after and before the gas treatment (Samples 9 and 12) are 3.75×10^{-9} and 3.25×10^{-9} esu, respectively. This indicates that the orientation of VOPc thin film is improved by the organic gas treatment.

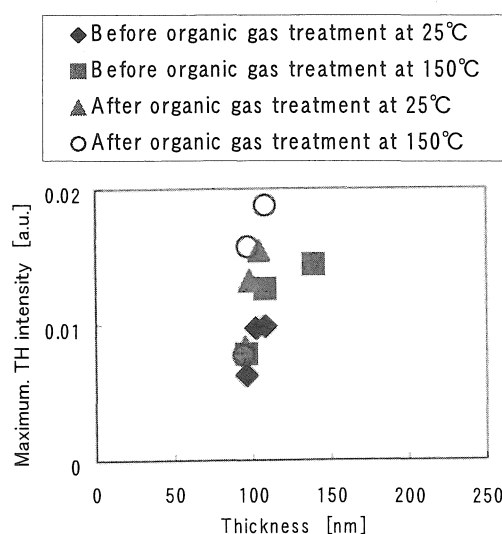


Fig. 12 maximum TH intensity vs. thickness.

4. Conclusions

The phase morphology of VOPc thin film on PI substrate changes from Phase I to Phase II by the organic gas treatment. The absorption energy between VOPc molecule and the surface of PI substrate increases with gas treatment. The VOPc thin film prepared on PI substrate kept at 150°C is dominated with perpendicular molecular orientation but changes to parallel molecular orientation after the gas treatment. The $\chi^{(3)}$ value of VOPc thin film prepared on PI substrate kept at 150°C is estimated from the maximum TH intensity measured by Maker fringe. The $\chi^{(3)}$ values before and after the gas treatment are 3.25×10^{-9} and 3.75×10^{-9} esu, respectively. It is improved during the organic gas treatment. This paper was published by APOC2002 held on China.

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