ポリイミド基板上に作製されたVOPc薄膜の形態と非線形光学特性へのコロナ帯電効果

Effects of Corona Charging on Nonlinear Optical Property and Morphology of VOPc Thin Film Prepared on Polyimide Substrate by Molecular Beam Epitaxy

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Abstract: — One important factor for a nonlinear optical thin film having high second and third nonlinear optical susceptibilities is a high packing density. Vanadyl-phthalocyanine (VOPc) thin films were prepared on non-charged and corona-charged polyimide substrates by the molecular beam epitaxy (MBE). The VIS/UV spectrum of Sample 1 on a non-charged substrate had a maximum absorption peak at 835nm. According to Griffiths et al., the VOPc thin film has a maximum absorption peak at 830nm, after prepared on a glass at room temperature and heated at 325 ^{O}C for 2 hours. He called the morphology of Phase III. The maximum absorption peak of Sample 1 shifted longer by 5nm than that reported by Griffiths. This means that the packing density of Sample 1 is higher than that of the VOPc thin film reported by Griffiths. A maximum absorption peak in Q band region of Sample 4 on a corona charged substrate appeared at 845nm, which is longer by 10nm than that of Sample 1. This suggests that a strong interaction between VOPc molecule and electric charge on polyimide substrate makes a high molecular packing of Sample 4. The third harmonic (TH) generations of Samples 1 and 4 were measured by Maker fringe with P polarized laser light. The peak value of TH intensity of Sample 4 was larger by 2 times than that of Sample 1. This means that the nonlinear optical property of VOPc thin film is improved by corona charging.

Keywords: epitaxy, VOPc film, corona charging, phase transition, THG

1. Introduction

Nonlinear optical materials are important to develop optical devices such as laser, optical switch, modulation, and memory. Therefore, they have recently attracted much attention. Vanadyl-Phthalocyanine (VOPc) is one of them. Many researchers have reported that VOPc thin films were epitaxially grown on alkali halide substrates by MBE [1)-4)]. Moreover, Ochiai et al pointed out that the single crystal (pesudomorphic layer) having absorption peak at 790nm in Q band have not been investigated for the third-order nonlinear optical properties and the morphologies[5)]. The polyimide (PI) film is more flexible, better optical transmittivity and much cheaper than KBr substrate and also is a heat-resistant polymer film. They mean that the VOPc film prepared on polyimide film will be able to use as a substrate to prepare VOPc thin film. Therefore, we investigated the morphologies and nonlinear optical properties of VOPc thin films prepared on polyimide film. Possible ways to improve the nonlinear optical susceptibility of VOPc thin film are to increase the film thickness, to improve the orientation of molecules on the substrate and to increase the molecular packing density. Therefore, we will discuss the difference between the nonlinear optical properties of VOPc thin films prepared on a non-corona charged and corona charged PI substrate. We will also investigate the relation between the morphologies and nonlinear optical properties of VOPc thin films by VIS/UV spectroscopy, Scanning electron

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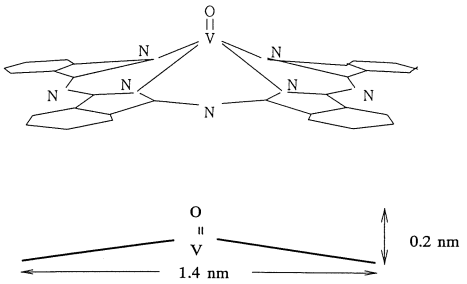
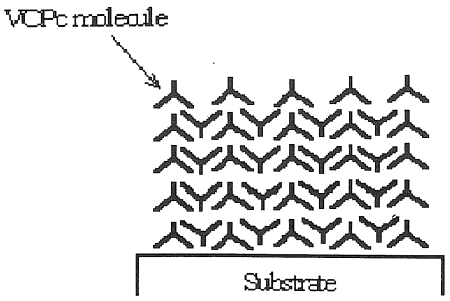
microscopy (SEM) and Maker fringe.

2. Experiments

The source material used was VOPc powder supplied from Eastman Kodak Company. Figure 1 shows the molecular structure of VOPc molecule. Its powder was inserted into a Knudsen-cell and preheated at 300°C for one hour. The surface of PI substrate was cleaned up with acetone. After that, the substrate was attached on the holder. The main chamber of MBE was at about 10^{-7}Pa, and the PI substrate was preheated at 300°C for one hour. The evaporating temperature (T_e) was kept at 300°C. Symbols used are T_s: substrate temperature, t : evaporating time and d : film thickness, respectively.



(a)



(b) Phase II

Figure 1 (a) Molecular structure of VOPc molecular
(b) Structure of Phase II

The charging on PI substrate was done by a corona charging method using a needle-plate electrode. The distance between the needle and the plate electrode was 2 cm. The tip radius of the needle was 260 μm. The PI substrate was put on the plate just under the needle and 8 kV was applied to the needle for 30 minutes.

3. Results and discussions

Firstly, the morphologies of VOPc thin films prepared on PI substrate were investigated by VIS/UV spectra and SEM images observed under different conditions. Figure 2 shows the VIS/UV spectra measured under different conditions. Sample 1 shows a broad band from 550nm to 780nm and an absorption peak at 835nm. According to Grifffiths, the phase having one peak at 820 nm in Q band region is called Phase II [6)-7)]. Its structure is shown in Figure 1. Phase II has a triclinic crystal structure, the space group P and is identified as a slipped stack arrangement. The absorption peak at 835nm of Sample 1 shifts by 15nm the longer wavelength side than that of Phase II. It reveals that the phase morphology of Sample 1 is not Phase II but has a different phase. The phase having an absorption peak at 830nm is called Phase III [6)-7)]. Phase III has a tetragonal crystal structure. Sample 1 has an absorption peak at 835nm in Q band region. Therefore, its phase is close to Phase III and may also include a deformation in VOPc thin film. Sample 2 has an absorption peak at 840nm in Q band region. This means that the packing density of VOPc thin film is higher than that of Sample 1. In other words, it suggests that island crystals grow in VOPc thin film by molecular diffusion. Sample 3 has the absorption peak at 845nm in Q band region. The substrate temperature of Sample 3 is higher than that of Sample 2. Therefore, it suggests that island crystals in the VOPc thin film of Sample 3 are much lager than those for Sample 2.

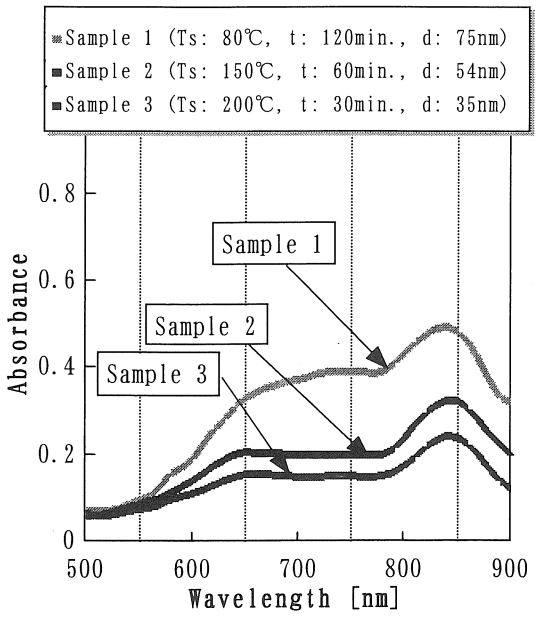


Figure 2 VIS/UV spectra of Samples 1, 2 and 3

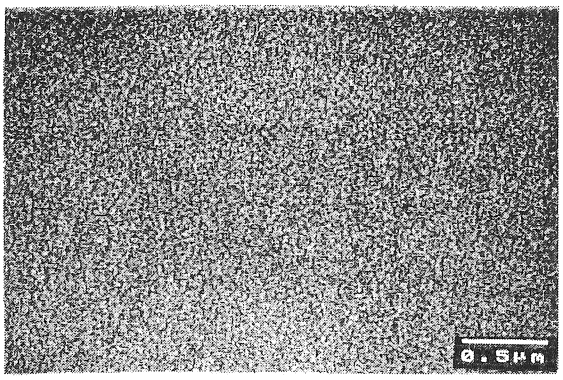


Figure 3 SEM image of Sample 1.

Figure 3 shows the SEM image of Sample 1. The surface of the thin film is smooth and a lot of grains are formed. This suggests that the molecular diffusion of VOPc molecule on PI substrate is low and the interaction between adsorped molecule and the PI substrate is strong. These are closely related to the phase morphology of Sample 1. Figure 4 shows the SEM image of Sample 2. A lot of island crystals grow on PI substrate. This reveals that the molecular diffusion of VOPc molecule on PI substrate is higher than that of Sample 1 and the interaction between deposited molecules and the PI substrate is weaker than that of Sample 1. These are closely related to the phase morphology of Sample 2. Figure 5 shows the SEM image of Sample 3. Island crystals grow bigger in Sample 3 than in Sample 2. It suggests that the molecular diffusion of VOPc molecule on PI substrate is higher in Sample 3 and that

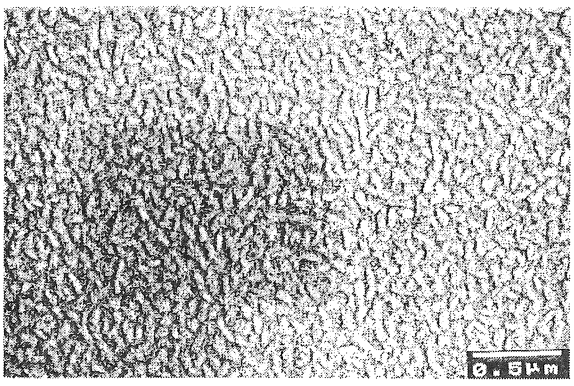


Figure 4 SEM image of Sample 2.

the interaction between deposited molecules and the PI substrate is weaker in Sample 3. These are closely related to the phase morphology of Sample 3. Figure 6 shows the VIS/UV spectra of Samples 1 and 4. Sample 1 is a non-charged VOPc/PI. Sample 4 is a VOPc/PI charged with corona charging. As described above, Sample 1 has the morphology of Phase III.

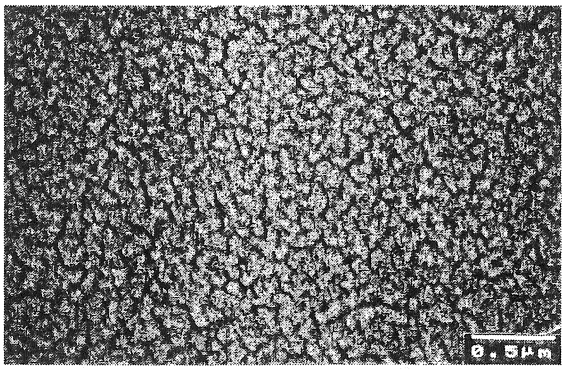


Figure 5 SEM image of Sample 3.

The absorption peak in Q band region of Sample 4 shifts by 10nm to the longer wavelength side and it is larger than that of Sample 1. The wavelength of the absorption peak in Q band region of Sample 2 and 3 agree with that of Sample 4. The VOPc thin film prepared on PI substrate charged with corona charging at 80°C has island crystals and the molecular diffusion of VOPc molecules on PI substrate is much higher than that of Sample 1.

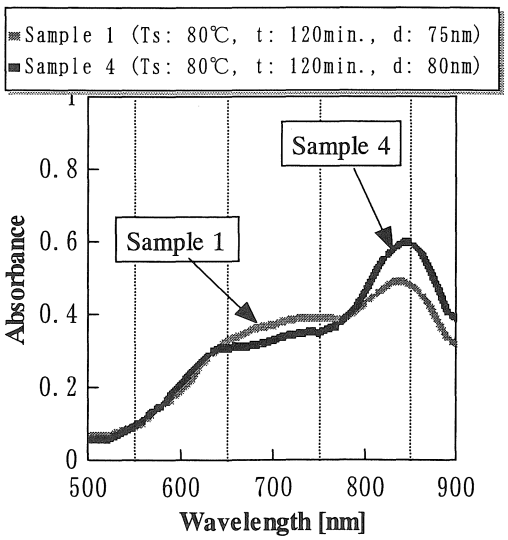


Figure 6 spectra of Samples 1 and 2.

Figure 7 shows the incident angle dependence of third harmonic (TH) intensity for Samples 1 and 4 irradiated with P polarized laser light. The maximum TH intensity of Sample 4 is

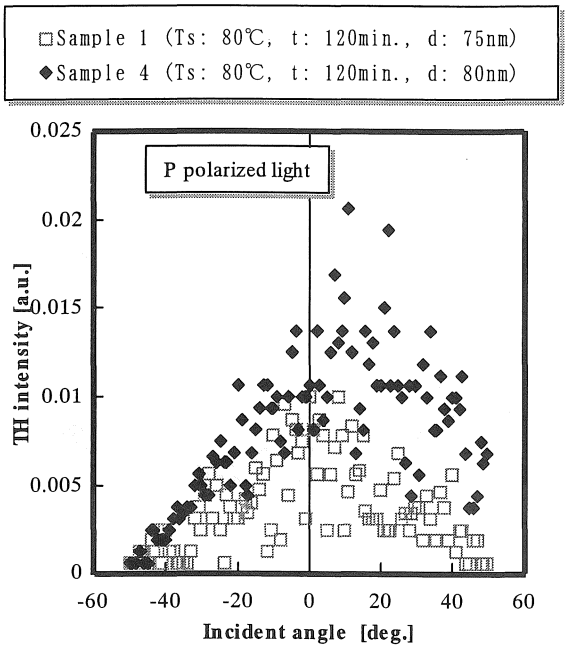


Figure 7 Incident angle dependence of TH intensity for Samples 1 and 4 irradiated with P polarized laser light.

larger by 2 times than that of Sample 1. This means that the third order nonlinear optical property of VOPc thin film is improved by the corona charging of PI substrate at 80°C. The TH intensity versus incident angle is an upper convex curve having a maximum TH value at 0 degree. It suggests that VOPc molecules deposited on the PI substrate are parallel to the PI substrate.

4. Conclusions

VOPc thin films have a lot of grains at the substrate temperature of 80°C and a lot of island crystals at the substrate temperatures of 150 °C and 200 °C. The films having the grains or island crystals are closely related to the red shift of the absorption peak in Q band region. The red shift is larger for corona-charged PI substrate than non –charged one. The shift of the absorption peak in Q band region of the VOPc thin film prepared at the substrate temperature of 80°C is similar to that at 150 °C or 200 °C. This suggests that the molecular diffusion of VOPc molecules deposited on the PI substrate charged by corona charging is higher than that of a non-charged VOPc/PI. On the other hand, it is suggested that the packing density of island crystal is higher than that of grain. The TH intensity of the VOPc thin film prepared on the PI substrate charged by corona charging is higher by 2 times than that of a non-charged VOPc/PI. The TH intensity versus incident angle is an upper convex curve having a maximum TH value at 0 degree. The former means that the packing density of the VOPc thin film prepared on the PI substrate charged by corona charging is higher than that of a non-charged VOPc/PI and the latter suggests that VOPc molecules deposited on the PI substrate are parallel to the PI substrate.

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