分子線エピタキシーにより作製され、有機ガスで処理されたバナジルフタロシアニン薄膜の配向

Orientation of Vanadyl-Phthalocyanine Film Prepared by Molecular Beam Epitaxy and Treated in Organic Gas

Hiroyuki NAKANO†, Akinori MAEDA†, Hideo FURUHASHI††,
中野寛之　前田昭徳　古橋秀夫
Toshio YOSHIKAWA†††Yoshiyuki UCHIDA††, Kenzo KOJIMA†,
吉川俊夫　内田悦行　小嶋憲三
Asao OHASHI† and Shizuyasu OCHIAI†
大橋朝夫　落合鎮康

Abstract: In this paper, the VOPc film was prepared on KBr substrate by OMBD. After that, it was treated in organic gas. The thickness of VOPc film was 96 nm. The morphologies of VOPc film before and after the gas treatment were characterized with optical absorption (VIS/UV) spectra and SEM image. The third-harmonic generation (THG) of VOPc film before and after the gas treatment were also measured by Maker fringe method using a Nd-YAG laser.

Keywords: epitaxy, VOPc film, organic gas treatment, phase transition, THG

1. Introduction

Organic nonlinear optical materials, which can yield large third–order nonlinearties, have been widely studied to achieve optical devices like on optically gated optical switch. Organic thin films are promising for the application to various kinds of optical devices because of their excellent processability. However, most thin films are usually fabricated by spin casting or by the Langmuir-Blodgett method. These thin films do not necessarily take full advantage of the large nonlinearities of the materials, since these methods cannot be easily applied to molecules with poor solubility. Organic molecular beam deposition (OMED) has recently attracted a lot of interest because it is applicable to molecules with poor solubility and its deposition is easy to control (1-4). Moreover, OMED is considered to have other advantages to provide good crystal quality, high optical transmittance, and/or large optical nonlinearity. However, optical IC requires that the film thickness of nonlinear optical film is thicker than 1mm and that the film must be grown with epitaxy. The second and third harmonic generations of the film grown epitaxially are higher than those of the film grown pseudoepitaxially and the film thickness related to the performance of optical IC.

In this paper, we investigate the characterization and nonlinearities of the thick film prepared on KBr by OMBD and treated in organic gas.

2. Experiments

The source material used was VOPc powder supplied from Eastman Kodak Company. After VOPc powder was inserted into a Knudsen-cell, it was preheated at 300°C for two hours. The substrate of KBr was cleaved just before it was attached on the holder. The main chamber of OMBD was at about 10^{-7}Pa, and the KBr substrate was preheated for one hour. The preheating temperature of KBr substrate (Tp) was at 150°C. The evaporating temperature was kept at Te: 300°C. The substrate temperature (Ts) was at 200℃. The evaporating time (t), the film thikness (d), the time treated in organic gas (tv), the temperature treated in organic gas (Tv) and the organic gas used are at 240 minutes, 36nm, 25hrs, 24°C and 1,2-Dichloroethane, respectively.

2. Results and Discussion

Fig.1 shows the structure of a vanadyl-phthlocyanine molecule. The height is 0.2 nm and the diameter is 1.4nm. Fig. 2 shows VIS/UV spectra. The absorption spectrum of VOPc film has an absorption peak at 780nm before the organic gas treatment and at 810nm

† 愛知工業大学　電気工学科　（豊田市）
†† 愛知工業大学　情報通信工学科（豊田市）
††† 愛知工業大学　総合技術研究所（豊田市）

after the gas treatment, respectively. The peak shift suggests that the crystal structure of a VOPc film changes from a pseudoepitaxial growth to epitaxial growth during organic gas treatment. Fig 3 shows the SEM image of VOPc film before the gas treatment. The SEM image shows that the VOPc film consists of grains. The surface density of grain is high. Therefore, the grains deform in VOPc film so that the VOPc film pseudoepitaxially grows on KBr substrate. Fig. 4 shows the SEM image of VOPc film after the gas treatment. The SEM image shows a soomth surface of VOPc film. The grains disappear from the surface of VOPc film and a few single crystals exist there. The percentage of single crystal to the flat area of VOPc film is small. Therefore, we will not discuss the effect of single crystal in this paper. As mentioned above, the surface of VOPc film is smooth and the grains disappear during the gas treatment

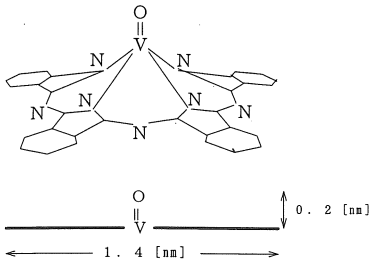

Fig. 1 Structure of vanadyl-phthalocyanine molecule

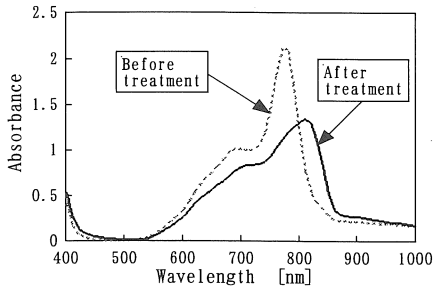

Fig. 2 Absorption spectra of VOPc film after and before the gas treatment.

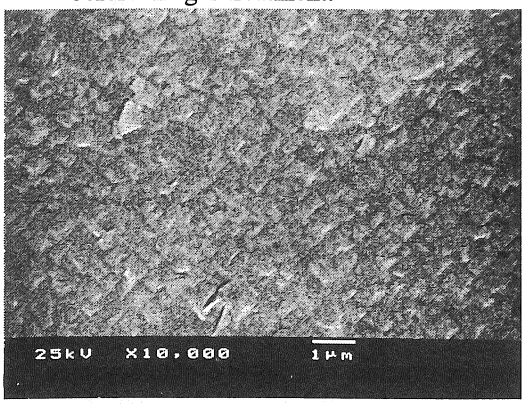

Fig. 3 SEM image of VOPc film before the gas treatment in organic gas.

Therefore, the gas treatment may relax the deformation in VOPc film and induce the change in film from a pseudoepitaxial growth to epitaxial growth.

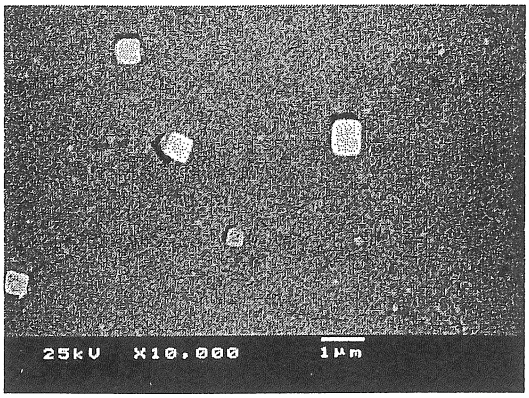

Fig. 4 SEM image of VOPc film after the gas treatment.

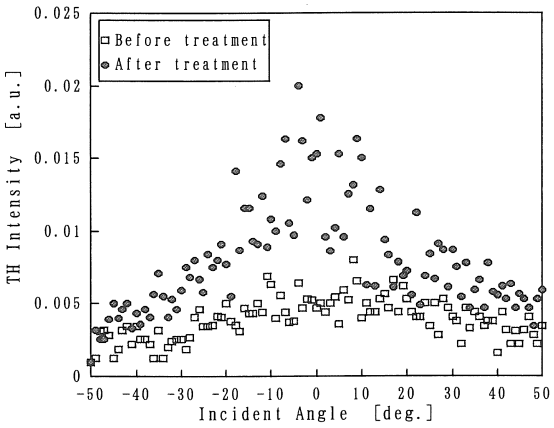

Fig.5 SH intensity vs. incident angle of VOPc film. (P polarized laser light)

Fig.5 shows the third harmonic (TH) intensity vs. incident angle of VOPc film. The gas treatment improves the TH intensity. It suggests that the phase transition from pseudoepitaxy to epitaxy of VOPc film is closely related to the improvement of the third-order harmonic intensity of VOPc film.

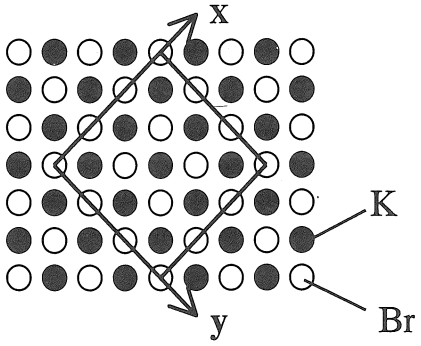

Fig.6- (a) Crystal coordinates.

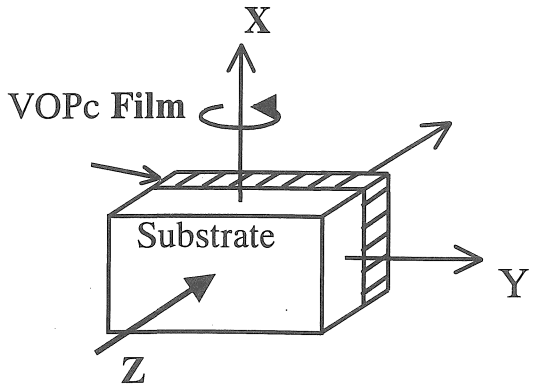

Fig 6-(b) Laboratory system of Cartesian coordinate.

The VOPc film treated with organic gas is epitaxy and has the 4mm structure with C_4 axis along the KBr surface normal [5].
Fig. 6 (a) shows the epitaxial structure of VOPc square lattice on KBr(001) where KBr ions are shown as open and solid circles. The x and y in Fig. (a) are the crystal coordinates. To describe an experimental condition, a Laboratory system of Cartesian coordinates (X, Y, Z) is introduced, where the Z in Fig. (b) is in the direction of the incident laser beam and X is the rotation axis of Maker fringe experiment.
The tensor components of χ obey the following equation for our film [6].
For the irradiated laser beam polarized S,

$$\chi'_{1111} = \chi_{1111} \quad \cdots\cdots (1)$$

In the case of the irradiated laser beam polarized P,

$$\chi'_{2222}=\cos^4\theta\ \chi_{1111}+3\cos^2\theta\sin^2\theta\ \chi_{1331}+3\cos^2\theta\sin^2\theta\ \chi_{3113}+\sin^4\theta\ \chi_{3333} \quad \cdots\cdots (2)$$

The comparison between calculated and experimental values of the third harmonic (TH) intensity vs. incident angle in Fig. 7 suggests that the TH intensity is dominated by a χ_{1111} in tensor components.

4. Theoretical Analysis of Tensor Components of $\chi^{(3)}$

The third order tensor components of VOPc film grown with epitaxy were expressed by equation (1) and (2). The third harmonic intensity is given by as following equation (3).

$$I_3=\frac{4\omega^2 I_1^3}{(nc)^4\varepsilon_0^2}\{\chi^{(3)}\}^2 d^2 T_1^3 T_3 \frac{\sin^2(\Delta kd)/2}{(\Delta kd/2)^2} \quad \cdots\cdots (3)$$

where $I(3\omega)$ is the third order harmonic intensity, $I(\omega)$= 1.20E+8 J/m^2 fundamental laser light intensity, n_1=2.82 refractive index of the sample for fundamental laser light, n_3= 2.86 refractive index for third-order harmonics, λp=1064 [nm] fundamental wavelength, lc=4.43E-6 [m] coherence length of the sample, d=lcosθ effective length, l≒100E-9 [m] film thickness, T1≒1 transmission factor of KBr, T2 ≒1 transmission factor of VOPc film, $\chi^{(3)}$=6.2E-17 [m^2/V^2] third-order optical susceptibility and ΔK phase mismatch between the fundamental and the harmonic frequencies inside the film. The ΔK is given by,

$$\Delta K=\pi/l_c=6\pi\ (n_1-n_3)/\lambda_P$$

The incident angle dependence of the third order harmonic intensity was calculated by using equations (1), (2) and (3) and values described above.

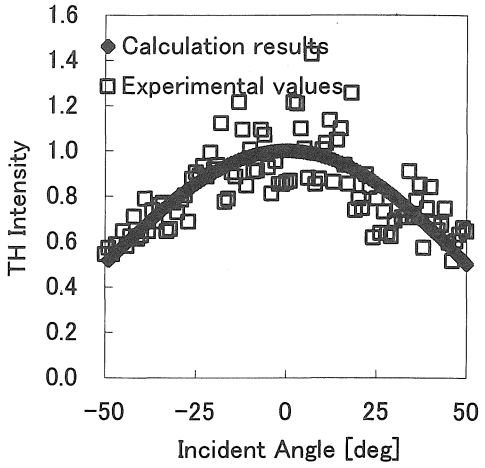

Fig. 7 Insident angle dependence of TH intensity and calculated value (Irradiated laser beam polarized S)

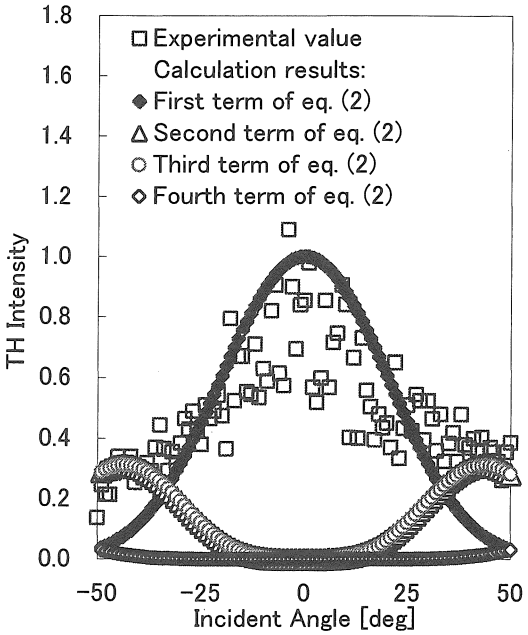

Fig. 8 Incident angle dependence of TH intensity and calculated value (Irradiated laser beam polarized P)

The calculated values are normalized with TH peak intensity. From the results of calculated curves and experimental values in Fig. 8, the tensor components of epitaxial VOPc film are not only dominated by χ_{1111}, but also are related to the nonlinear optical susceptibilities of χ_{1331} and χ_{3113}. It means that the VOPc film treated with organic gas is grown with epitaxy.

COCLUSIONS

From experimental and calculated results, we suggested the VOPc film grown epitaxially was dominated by the nonlinear optical susceptibility of χ_{1111}. The gas treatment improves the TH intensity. It suggests that the phase transition from pseudoepitaxy to epitaxy of VOPc film is closely related to the improvement of the third-order harmonic intensity of VOPc film. This paper was published by Photonics-2000 held on India.

1. M. Hara, H. Sasabe, A. Yamada and A. F. Garito:, Jpn. J. Appl. Phys. 28, L306 (1989)
2. A. J. Dann, H. Hoshi and Y. Maruyama:, J. Appl. Phys. 67, 1371 (1990)
3. H. Tada, K. Saiki and A. Koma:, Jpn. J. Appl. Phys. 30, L306 (1991)
4. L. K. Chau, C.D. England:, S. Chen and N. R. Armstrong, J. Phys. Chem. 97, 2699 (1993)
5. H. Hoshi, K. Hamamoto, T. Yamada, K.Ishikawa, H. Takezoe, A. Fukuda, S. Fang, K. Kohama and Y. Maruyama:, Jpn. J. Appl. Phys. 33, L1555 (1994)
6. H. Hoshi, N. Nakamura, and Y.Maruyama, J. Appl. Phys. (1991) 7244

(Received March 19. 2001)