

Vanadyl Phthalocyanine Thin Film Prepared on a KBr Substrate by MBE Method

分子線エピタキシー法により KBr 基板上作製された バナジルフタロシアニン薄膜

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Abstract

Nonlinear optical materials are important in developing optical devices such as optical switch, modulation and memory. Therefore, they have recently attracted much attention. Vanadyl-Phthalocyanine (VOPc) is one of them. In this paper, we investigated not only the morphologies of VOPc thin film prepared on KBr substrate by molecular beam epitaxy (MBE) but also the conditions to prepared large single crystals. A 15nm-thick VOPc thin film prepared on a KBr substrate with a substrate temperature (T_s : 80°C), evaporating temperature (T_e : 300°C) and depositing time (t : 10 min.) has a uniform surface image of scanning electron microscopy (SEM). The film has an optical absorption peak at 810nm in the visible and infrared region. It was epitaxially grown. A VOPc thin film prepared on a KBr with another condition of T_s : 200°C and T_e : 300°C and t : 60 min. has discrete single crystals. Their average size are about $1 \times 0.5 \times 0.1 \mu\text{m}$. The single crystal is $3 \times 3 \text{R}45^\circ$ type and It was epitaxially grown judging from the images of SEM, atomic force microscopy (AFM), reflection high energy electron diffraction (RHEED) and the spectra measured with a UV/VIS spectroscopy. A VOPc thin film prepared on a KBr substrate with T_s : 250°C and T_e : 300°C shows the absorption peak around 830nm. Therefore, the shift of the optical absorption peak for the single crystal to a longer wavelength may be related to disorder in a film epitaxially grown and/or may be due to a phase transition under a high substrate temperature.

Keywords: Vanadyl- Phthalocyanine single crystal, Epitaxy growth, KBr substrate, Molecular beam epitaxy

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1. Introduction

Many researchers have reported that VOPc thin films prepared on alkali halide substrates by the molecular beam epitaxy were a

epitaxial grown. The VOPc thin film prepared on a KBr (100) substrate forms a single domain square lattice on the KBr substrate. It was named $3 \times 3R45^\circ$ type [1]. The distance between neighboring molecules is about 14Å [1]. The AlPcCl (Chloroaluminum-phthalocyanine) thin film evaporated on a NaCl substrate by MBE method forms the tetragonal phase. Its predominant phase on the NaCl (100) was a bidirectionally oriented tetragonal phase with $\sqrt{13} \times \sqrt{13} R \pm 11^\circ$. The phase of AlPcCl/KCl and AlPcCl/KBr were bidirectionally oriented tetragonal phase with $\sqrt{10} \times \sqrt{10} R \pm 27^\circ$ on KCl and with $\sqrt{10} \times \sqrt{10} R \pm 27^\circ$ on KBr, respectively. The predominant phase of AlPcCl/KI was an unidirectionally oriented tetragonal phase on KI (100) with $3 \times 3R45^\circ$. The phase of VOPc/KCl was bidirectionally oriented tetragonal phase on KCl with $\sqrt{10} \times \sqrt{10} \pm 27^\circ$ [2]. Hoshi et al. have studied the thickness dependence of the crystal structure of a VOPc film epitaxially grown on KBr(100) by optical absorption spectra and pointed out that the crystal structure changes around 64 nm in thickness. The VOPc thin film was an epitaxially grown film below 64 nm but not above 64 nm. The epitaxially grown film showed a second harmonic generation and the film with a bulk monoclinic phase did not [3]. Therefore, the epitaxially grown film is very important for a second harmonic generation. Morphologies of VOPc films on alkali halide substrates are important for their optical applications. However, there are some unknown things. VOPc thin films have not been prepared at a substrate temperature above 100 °C on alkali halide substrates so that there are few optical studies on them. Moreover, the growth mechanism of a single crystal on an alkali halide is not still clear enough. Here, we investigated the substrate temperature dependence of VOPc thin film prepared on a cleaved KBr substrate by MBE. The VOPc film prepared on the substrate of KBr kept at 80°C had a domain crystal and a large single crystal above 100°C. Morphologies of single crystals were studied by optical absorption spectroscopy, scanning electron microscopy

(SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED).

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2. Experimental and Results

Material used is VOPc powder supplied from Eastman Kodak company. Figure 1 shows the molecular structure of VOPc. The molecule has the size of 1.4 nm in diameter and 0.20 nm for the b axis. The main chamber of MBE is at about 10^{-7} Pa. After VOPc

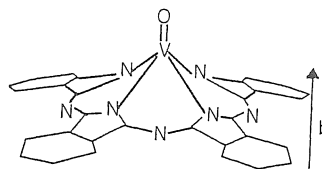


Fig.1 Molecular structure of VOPc.

Table 1 : Conditions to prepare VOPc film on KBr substrate

	Ts(°C)	t(min)	d(nm)
S-1	80	10	15
S-1	80	60	40
S-3	80	120	80
S-4	100	10	-
S-5	100	60	-
S-6	100	120	-
S-7	150	10	-
S-8	150	60	-
S-9	150	120	-
S-10	200	10	-
S-11	200	60	-
S-12	200	120	-
S-13	250	10	-
S-14	250	60	-
S-15	250	120	-

powder is inserted into a Knudsen-cell, it is preheated at 300°C for two hours. The substrate of KBr is cleaved just before setting to a holder. After the main chamber of MBE becomes about 10^{-7} Pa, the KBr substrate is preheated at 150°C for one hour. The evaporating temperature is 300 °C. Table 1 shows the conditions to prepare VOPc films on KBr substrate. Symbols of T_e , T_s , t and d express an evaporating temp., substrate temp., evaporating time and thickness, respectively. Figure 2 shows the XRD spectra of KBr alone (V), S-1 and VOPc powder (A), respectively. The spectra of S-1 and KBr alone have a peak at $2\theta = 27^\circ$ which does not exist in the spectrum of VOPc powder. Moreover, the peak intensity of S-1 is larger than that of KBr alone. This reveals

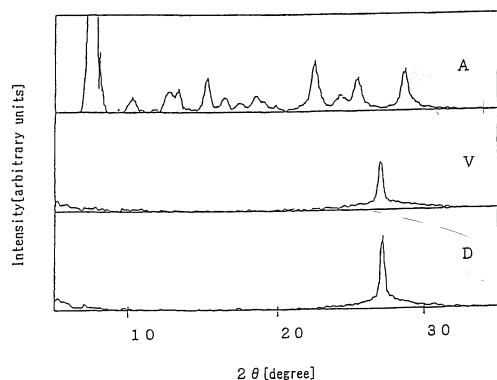


Fig. 2 XRD spectra of KBr alone (V), S-1 and VOPc powder (A) respectively.

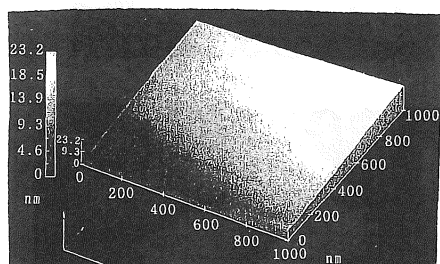


Fig. 3 AFM image of S-1.

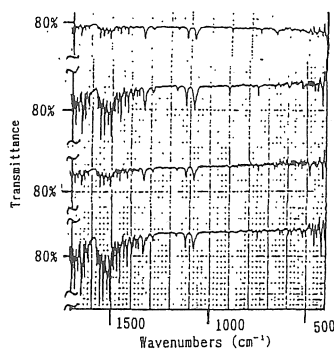


Fig. 4 FT-IR spectra of S-1, 5, 8 and 11.

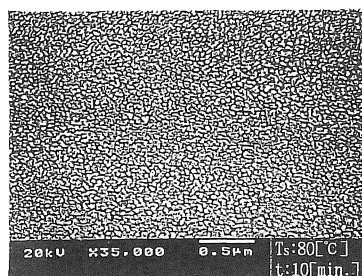


Fig. 5 SEM image of S-1.

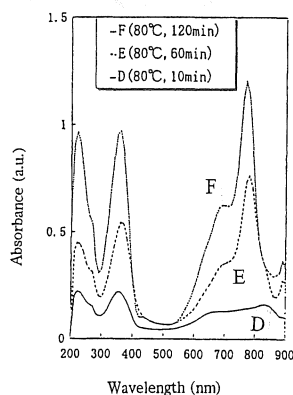


Fig. 6 Optical absorption spectra of S-1, S-2 and S-3 respectively.

that VOPc molecules pile with the interval of 0.33 nm. Therefore, this also indicates that VOPc molecules pile along the b axis of molecule normal to a substrate because the diameter of molecule is 14 Å. The XRD spectra of S-1 to 10 show a similar pattern so that VOPc molecules under other producing conditions pile up with the b axis normal to the substrate. Figure 3 shows the AFM image of S-1. Multi-layers are observed at an edge on the film so that the film shows the layer growth. Figure 4 shows the FT-IR spectra of S-1, 5, 8 and 11, respectively. The FT-IR spectra were measured with the incidence normal to samples. A VOPc molecule has a V-O stretching mode at 1000 cm^{-1} . Samples measured have no absorption peak at 1000 cm^{-1} . This means that VOPc molecules in the VOPc/KBr pile up with the b axis normal to a substrate. Figure 5 shows the SEM image of S-1. The film is a uniform film with small grains. Figure 6 shows the optical absorption spectra of S-1, S-2 and S-3, respectively. The optical absorption

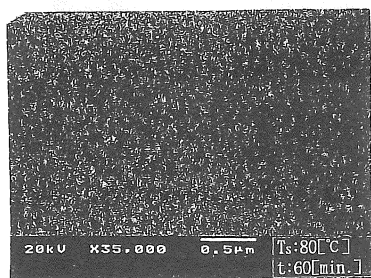


Fig. 7 SEM image of S-5.

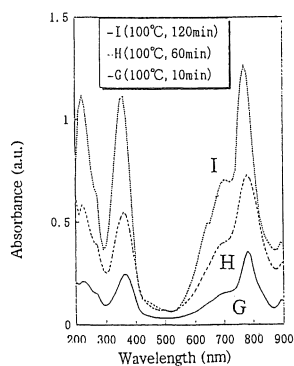


Fig. 8 Optical absorption spectra of S-4 to 6.

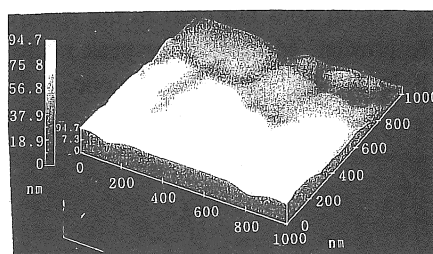
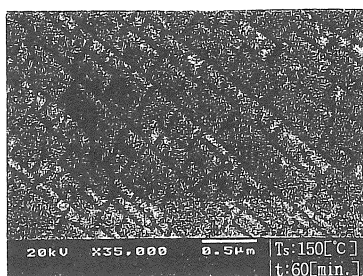


Fig. 9 SEM and AFM images of S-8.

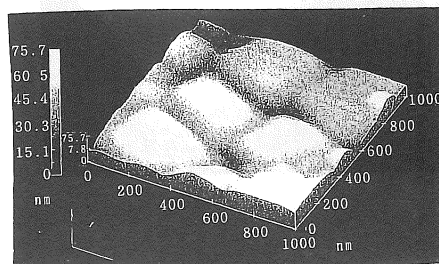
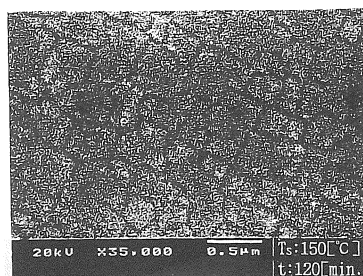


Fig. 10 SEM and AFM images S-9.

spectrum of S-1 shows an absorption peak at 810 nm. Other samples show an absorption peak at 780 nm. This means that only film of S-1 is epitaxially grown [3]. The films of S-2 and S-3 have a monoclinic structure [3]. Figure 7 shows the SEM image of S-5. The film is nonuniform with unidirectionally oriented grains. Figure 8 shows the optical absorption spectra of S-4 to 6. Each sample has a dominant absorption peak at 780 nm. This suggests that the films of S-4 to 6 have a monoclinic structure [4].

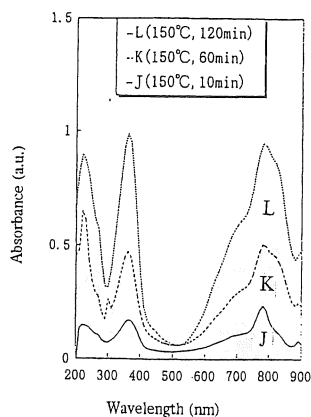


Fig. 11 Optical absorption spectra of S-7 to 9.

This indicates that VOPc molecules misfit with the substrate at 100°C (S-4 to 6). Figure 9 shows the SEM and AFM images of S-8. The film is non-uniform with unidirectionally oriented crystals from SEM image and it is the $3 \times 3 R45^\circ$ type from AFM image. Figure 10 shows the SEM and AFM images S-9. Crystals are much larger than those of S-8. However, the unidirectional orientation is disturbed at the crystal boundary, as compared with S-8. The crystal boundary may depend upon the properties of a cleaved KBr substrate. The film thickness is about 60 nm from the AFM image. Figure 11 shows the optical absorption spectra of S-7 to 9. Each sample has the absorption shoulder at 810 nm. This suggests that the films of S-7 to 8 are mixed with epitaxially grown and monoclinic one [3]. The optical absorption spectrum of S-9 shows the absorption peak at 780 nm, suggesting a monoclinic structure. Figure 12 shows the

RHEED patterns of S-8 and KBr alone. The RHEED pattern of S-8 shows the crystal growth of $3 \times 3 R45^\circ$. As described above, the type of crystal growth depends upon a substrate temperature. This indicates that molecules on the substrate kept for the long time at a high temperature (S-7 to 9) are possible to migrate. This explains that misfitted molecules disappear in the film of S-8. Figure 13 shows the SEM image of S-11. The crystals on KBr substrate are $1 \times 0.5 \mu\text{m}$ square crystals and their average thickness is about $0.1 \mu\text{m}$ from the AFM image. Figure 14 shows the SEM image of S-12. Crystals are much smaller than those of S-11. The unidirectional orientation is disturbed at the crystal boundary, as compared with S-12. Remarkable crystal boundaries appear in S-12 as shown Fig. 15 since strains between crystals may suppress the epitaxial

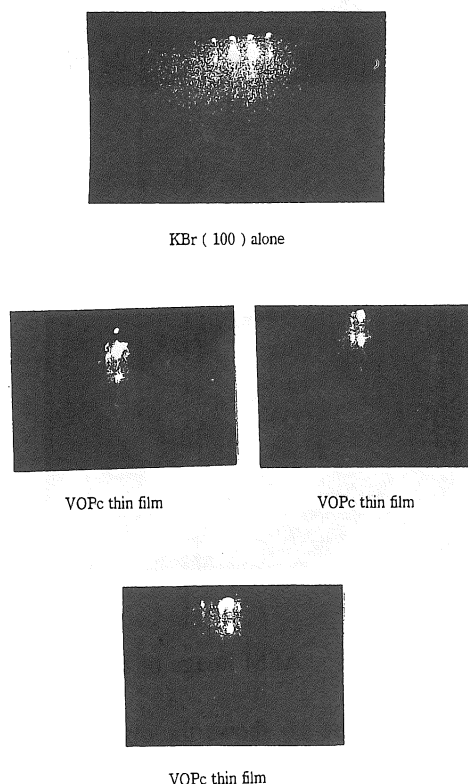


Fig. 12 RHEED patterns of different places of VOPc film of S-8 and KBr alone.

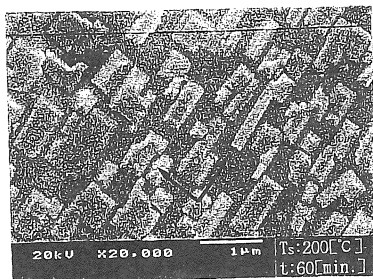


Fig. 13 SEM image of S-11.

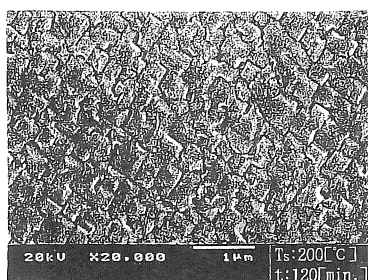


Fig. 14 SEM image of S-12.

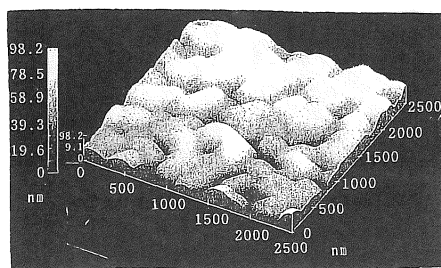


Fig. 15 AFM image of S-12.

growth. Figure 16 shows the optical absorption spectra of S-10 to 12. The optical absorption spectra of S-10 to 11 show the absorption peak at 810 nm in the Q band region and S-12 has the absorption peak at 780nm. These suggest the epitaxial growth

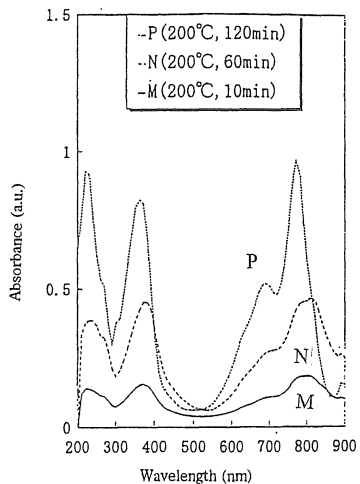
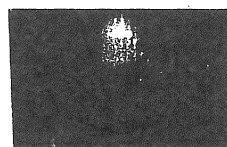
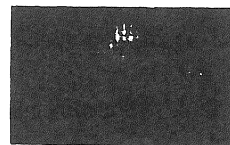


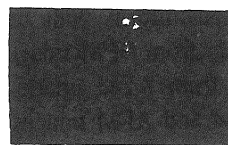
Fig. 16 Optical absorption spectra of S-10 to 12.



VOPc thin film



VOPc thin film



VOPc thin film

Fig. 17 RHEED patterns at different places of VOPc film of S-11.

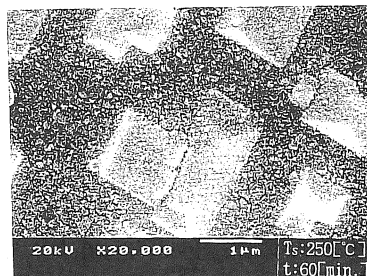


Fig. 18 SEM image of S-14.

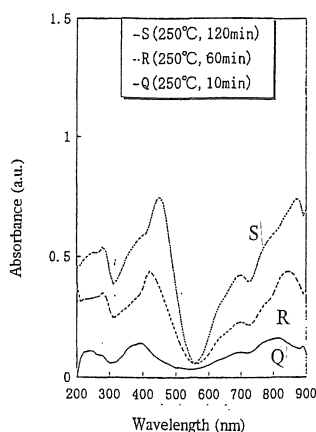


Fig. 19 Optical absorption spectra of S-13 to 15.

for S-10 and 11 [4] and the monoclinic growth for S-12. Figure 17 shows the RHEED patterns of S-11, suggesting the crystal growth of $3 \times 3 \times R45^\circ$. This suggests that misfitted molecules completely disappear in the film of S-11. Figure 18 shows the SEM image of S-14. The crystals on KBr substrate are a rooflike type, their size is above $1 \mu\text{m}$ square, about $0.15 \mu\text{m}$ in the thickness from an atomic force microscopy. Figure 19 shows the optical absorption spectra of S-13 to 14. The optical absorption spectra of S-13, 14 and 15 show the absorption peaks at 810, 830 and 860 nm in the Q band region. The VOPc thin film prepared on the glass substrate of at room temperature changed from phase I (780 nm) to phase II (850 nm) by the annealing treatment above 100°C [1, 5]. Therefore, S-13 has epitaxial growth crystals. Crystals of S-14 and S-15 may experience the phase transition from phase I (monoclinic structure) to phase II

(triclinic crystal structure). The triclinic crystal has a higher third harmonic generation coefficient than the monoclinic crystal [1]. Therefore, films with large triclinic crystals are important for the third harmonic generation devices.

3. Conclusions

(1) Films prepared on a KBr substrate temperature at 80°C are uniform and layer growth.

(2) Films prepared on a KBr substrate above 100°C are nonuniform.

(3) Crystals on a KBr substrate at a high temperature ($T_s : 150^\circ\text{C}$) or ($T_s : 200^\circ\text{C}$) are $3 \times 3 \times R45^\circ$ grown epitaxially.

(4) Crystals on a KBr substrate of a high temperature ($T_s : 250^\circ\text{C}$) are a rooflike type and the phase transition from a monoclinic to a triclinic crystal structure occurs.

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