Growing process, surface morphology and nonlinear optical characteristics of vanadyl-phthalocyanine thin film fabricated on alkali halide substrate

Suguru Mototani[1], Shizuyasu Ochiai[1], Goro Sawa[1], Yoshiyuki Uchida[2], Asao Ohashi[1], Kenzo Kojima[1], and Teruyoshi Mizutani[3]

[1]*Department of Electrical Engineering, Aichi Institute of Technology, Toyota 470-0392, Japan*

[2]*Department of Information Network Engineering, Aichi Institute of Technology, Toyota 470-0392, Japan*

[3]*Department of Electrical Engineering, Nagoya University, Nagoya 464-8603, Japan*

Nonlinear optical materials adopting optoelectronics elements are required to have a third-order nonlinear optical susceptibility of 10^{-9} order [esu]. However, the relationship between nonlinear optical characteristics and the morphology of the meal-phthalocyanine thin film prepared on alkali-halide substrate remains unclear. Therefore, the growing process of vanadyl-phthalocyanine (VOPc) thin films fabricated on alkali-halide substrate were investigated by UV/Vis spectra, AFM images, and the incident angle dependence of second harmonic (SH) and third harmonic (TH) intensities measured by Marker fringe. It is recognized that VOPc thin film prepared on KBr (100) is an island-like growth, on KCl (100) it is step-terrace growth.

OCIS codes: 250.0250, 310.0310, 160.4330, 160.4890.

Vanadyl-phthalocyanine (VOPc) thin films prepared on alkali halide substrate grow with epitaxy and pseudomorphic layers. On an alkali halide substrate, however, VOPc thin films exhibit many kinds of epitaxial growth, and transform from an epitaxal to a pseudomorphic layer with increasing film thickness[1,2]. However, the growing process, morphology, and nonlinear optical characteristics of a vanadyl-phthalocyanine thin film fabricated on an alkali halide substrate remain unclear. In this paper, the nonlinear optical characteristics and morphologies of VOPc thin films prepared on KCl (100) and KBr (100) substrates are investigated by UV/V is spectra measured with an UV/V is spectrometer, scanning electron microscope (SEM), atomic force microscope (AFM) and the incident angle dependence of second harmonic (SH) and third harmonic (TH) intensities measured by Marker fringe. VOPc thin films were prepared as follows. The vacuum of the main chamber of the molecular beam epitaxy equipment was maintained at about 10^{-7}Pa, while the evaporating temperature of VOPc molecule depositing on KCl and KBr substrates was kept at 300 °C. The substrate temperatures of KCl and KBr substrates were kept at 150 °C. Table 1 lists the preparatory conditions for Sa-1—3 and Sb-1—3, respectively.

Figure 1 shows the Vis/UV spectra of Sa-1—3. Their Vis/UV spectra of Sa-1—3 have a peak at 780 nm and a shoulder at 810 nm. This indicates that the depositing process of Sa-1—3 firstly involves epitaxy deposition. Subsequently, increasing thickness prompts the growth of a pseudomorphic layer[1,2]. Figure 2 shows the AFM image of Sa-1. The surface of the VOPc thin film deposited on the KCl (100) surface clearly has terraces and steps from the AFM image. Figure 3 shows the AFM image of Sa-2 magnified 6 times greater than in Fig. 2. The VOPc thin film deposited with a thickness of 20 nm (Sa-1) forms plate-like crystals with terraces and steps present. These indicate that the activation energy of the thermal diffusion of the VOPc molecules adhering to the KCl (100) surface is significantly different at point of adherence on the KCl surface or the growth process of the VOPc thin film preparing on the KCl substrate relates to the surface stress of KCl.

Figure 4 shows the AFM image of Sa-3, and here, the terrace and step are not observable. This suggests that as the film thickness increases, the height of the step narrows until the step disappears. This also suggests that according to the increase of thickness, the VOPc molecules gather in the step region and the step disappears. Needle-like crystal growth is also observed from the AFM image. This indicates that VOPc molecules deposited on KCl (100) substrate are oriented parallel on the substrate.

Table 1. Preparatory Conditions for the VOPc Thin Film Deposited on KCl and KBr Substrates

Sample No.	Sa-1	Sa-2	Sa-3
Substrate	KCl (150 °C)		
Sample No.	Sb-1	Sb-2	Sb-3
Substrate	KBr(150 °C)		
Vacuum (Pa)	10^{-7}		
Evaporating (°C)	300		
Evaporating Time (min)	10	30	60
Preheating (°C)	300		
Thickness of KCl (nm)	20	30	54
Thickness of KBr (nm)	6	22	53

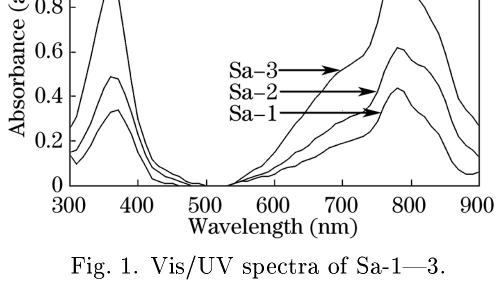

Fig. 1. Vis/UV spectra of Sa-1—3.

1671-7694/2005/0s0028-03 http://www.col.org.cn

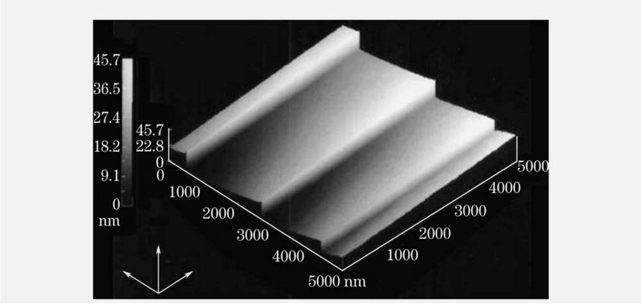

Fig. 2. AFM image of Sa-1.

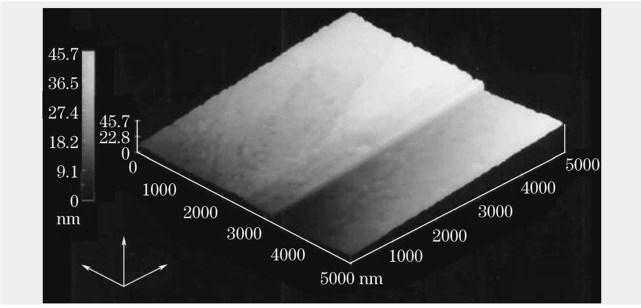

Fig. 3. AFM image of Sa-2 magnified 6 times greater than in Fig. 2.

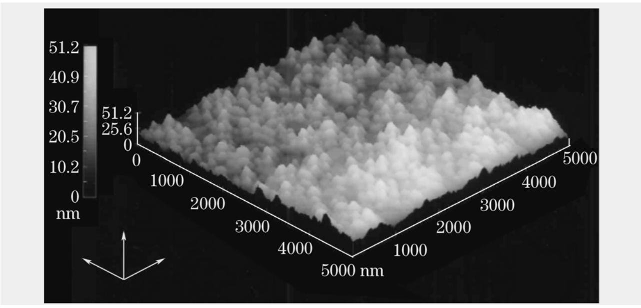

Fig. 4. AFM image of Sa-3.

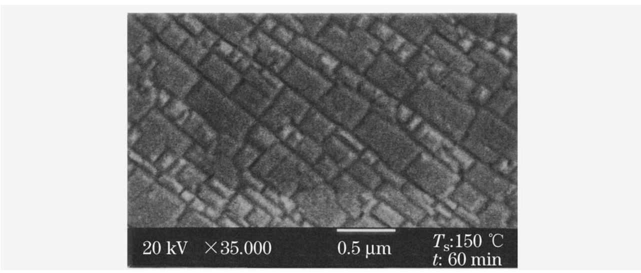

Fig. 5. SEM image of Sb-2.

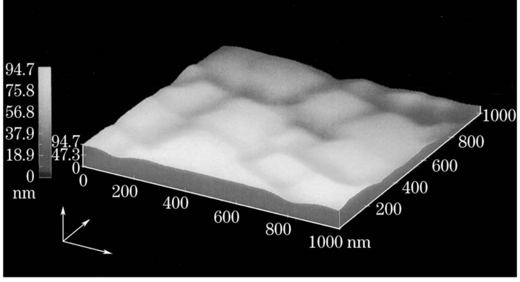

Fig. 6. AFM image of Sb-2.

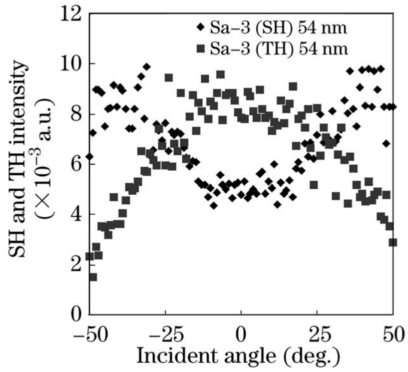

Fig. 7. Incident angle dependence of the SH and TH intensities of VOPc thin film fabricated on the KCl substrate.

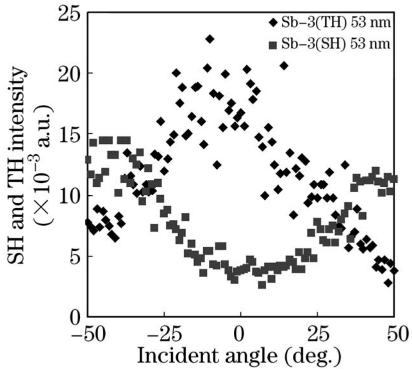

Fig. 8. Incident angle dependence of the SH and TH intensities of VOPc thin film fabricated on KBr substrate.

The growing process of the VOPc thin film prepared on the KCl (100) substrate for which a terrace/step structure does not exist, exhibits a needle-like crystal growth on the substrate. The growing processes of Sa-1—3 markedly depend upon the activation energy of thermal diffusion of the VOPc molecule on the KCl (100) surface. In other words, the surface stress of the KCl surface is strongly related to the growing process.

Figure 5 shows the SEM image of Sb-2. It is recognized that island-like crystal grows on the KBr (100) substrate. Moreover, the island-like crystals form a uni-directional orientation. This means that the VOPc thin film of Sb-2 grows epitaxy. Figure 6 shows the AFM image of Sb-2. The growth process of the VOPc thin film is an island-like crystal growth and the island-like crystals are also in a uni-directional orientation. The growth process of the VOPc thin film on the KBr substrate markedly depends upon the activation energy of the thermal diffusion of the VOPc molecule on the KBr (100) surface. In other words, the KBr surface stress is strongly related to the growth process. Figure 7 shows the incident angle dependence of the SH and TH intensities of the VOPc thin film fabricated on KCl substrate. The incident angle dependence of the SH intensity has a lower convex curve with symmetry against a center axis of 0 degree.

This indicates that VOPc molecules deposited on the KCl substrate are oriented parallel thereto. However, the SH intensity of 0 degree is not a zero value, indicating that the surface orientation exists in the surface neighborhood of the VOPc thin film or that an incident laser beam is scattered upon the surface of the VOPc thin film.

Under the Sa-3 preparatory conditions, the surface of the VOPc thin film is not smooth. Therefore, this indicates that the incident laser beam is scattered on the surface of VOPc thin film; hence the SH intensity of 0 degree not being a zero value. The incident angle dependence of TH intensity has an upper convex curve with symmetry against the center axis of 0 degree. This indicates that the VOPc thin film has a high orientation on the KCl substrate. Figure 8 shows the incident angle dependence of the SH and TH intensities of the VOPc thin film fabricated on the KBr substrate. The SH intensity of 0 degree is near zero, indicating that the surface orientation does not exist in the surface neighborhood of the VOPc thin film. The maximum TH intensity of its incident angle dependence is larger than that of the VOPc thin film prepared on the KCl (100) substrate. This indicates that the VOPc thin film prepared on the KBr substrate has a superior orientation to that of the VOPc thin film prepared on the KCl substrate.

In conclusion, VOPc thin films fabricated on KCl substrate under the preparatory conditions of Sa-1 and Sa-2 grow with a terrace/step structure and that under the preparatory condition of Sa-3 is a needle-like crystal growth, while those fabricated on KBr substrate grow with island-like crystals. These differences are closely related to the difference in surface stress between KBr and KCl. The SH and TH intensities of the VOPc thin film prepared on the KBr substrate are far superior to those on the KCl substrate. This is a factor strongly dependent on the morphology of the VOPc thin film.

The present work was carried out as part of the research project "Materials for the 21st Century—Materials Development for Environment, Energy and Information" (for fiscal years 2002—2006) supported by Ministry of Education, Science, Sports, and Technology. S. ochiai is the author to whom the correspondence should be addressed, his e-mail address is ochiai@aitech.ac.jp.

References

1. H. Hoshi, K. Hamamoto, T. Yamada, K. Ishikawa, H. Takezoe, A. Fukuda, S. Fang, K. Kohama, and Y. Maruyama, J. Appl. Phys. Part 2 **33,** 11A (1994).
2. Y. Tanabe, A. Kaito, K. Yase, K. Ueno, H. Okumoto, N. Minami, H. Nozoe, H. Kondoo, Y. Yumura, and H. Yanagishita, Phys. Chem. **2,** 235 (1994).