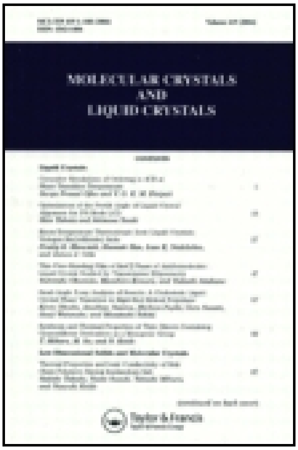

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Evaluation of Thin Films of Functional Organic Materials by Total Reflection X-Ray Diffraction

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EVALUATION OF THIN FILMS OF FUNCTIONAL ORGANIC MATERIALS BY TOTAL REFLECTION X-RAY DIFFRACTION

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Abstract The crystal structure and molecular orientation of lead phthalocyanine (PbPc) thin films onto a silicon (Si) and potassium bromide (KBr) were *in-situ* observed by using the new system combined a total reflection X-ray diffraction (TRXD) with an organic molecular beam deposition (OMBD). When the substrate was kept at a temperature of 25°C, the deposited films consisted of monoclinic crystals and the PbPc molecules tend to orient with the column axis parallel to the surface. Further, the films deposited on Si at 100°C consisted of the triclinic crystals with the column axis parallel to the surface. While, the thin films on KBr exhibited much higher crystallinity than on Si, and same structures even if the substrate temperature of 180°C was raised after deposition.

1. INTRODUCTION

It is currently interested in the highly ordering of organic molecules epitaxially grown on single crystal, semiconductor, and metal surfaces because of the potential for organic ultrathin films with the new electrical and optical properties. Also, the monolayer films of organic functional molecules such as metal-phthlocyanines, perylene dye, fullerene have been prepared by organic molecular beam depotion (OMBD) techniques [1-5]. OMBD is a kind of physical vapor deposition techniques under an extreme clean atmosphere in a ultrahigh vacuum (UHV) and is expected to prepare high crystalline organic ultrathin films. Thus, it is important to elucidate the growth mechanism and to control precisely the deposition condition such as substrate temperature and deposition rate. For the purpose of the *in-situ* observation of the cohesive process of organic molecules, we employed the new system of energy dispersive type total reflection X-ray diffraction (TRXD) combined with OMBD (TRXD-OMBD).

Lead phthalocyanine (PbPc) has been investigated for the curious electrical properties and gas sensitivities such as the electrical switching, electrical rectifying, NO2 gas sensor, etc.[6-8] PbPc molecule has an unique shuttlecock-shape and it is known that there are two types of the monoclinic and triclinic crystal structures as shown Fig. 1.[9, 10] Although it was confirmed that the crystal structures of deposited thin films could be controlled by the deposition condition, all the *exo-situ* measurements were done.[11-14]

In this study, *in-situ* observations of the crystal structure and molecular orientation in the PbPc film were performed by using TRXD-OMBD.

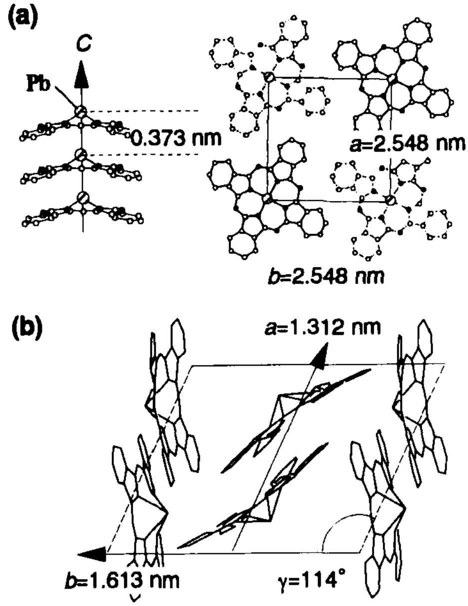

Fig. 1 Crystal structures of (a) monoclinic and (b) triclinic PbPc.

2. EXPERIMENTAL

The *in-situ* system is constructed by an UHV chamber (base pressure less than 5 × 10^{-9} Torr) and TRXD as shown in Fig.2. TRXD method is developed for the effective observation of organic thin films. When the incident X-rays are set up at a glancing angle

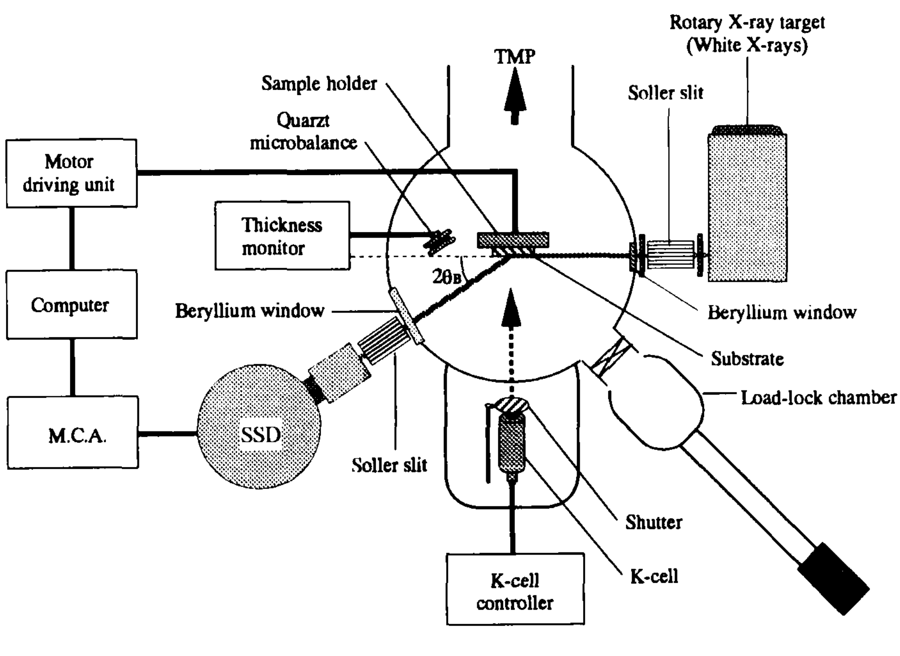

Fig. 2 Schematic illustration of TRXD-OMBD system (top view).

of about 0.2°, a total reflection phenomenon of X-rays at the interface between the films and substrate occurrs. As made use of this effect, the obstructive X-rays from the substrate considerably decrease and the diffracted X-rays of thin films are able to be detected sensitively. Also, there are two type geometries of X-ray measurements, which are "in-plane type" for the observation of in-plane structure and "vertical type" for the layered structure. The details of TRXD are described elsewhere.[16, 17] Because the energy dispersive type system is employed, the X-ray diffraction measurement is quickly performed at a fixed angle. Thus, this system is most proper to apply to *in-situ* measurement. In our system (TRXD-OMBD), the high power rotary anode target of tungsten as a X-ray source and the pure germanium type SSD as a detector were used for the high sensitive measurement. The incident and diffracted X-rays were introduced in and out the UHV chamber through thin beryllium windows. In the UHV chamber, the organic molecular beams were precisely controlled by the Knudsen cell (K-cell). Also, the substrate holder could be moved by the motor driving units and the temperature was controlled between -50 and 200 °C. During the deposition, the film thickness was monitored by a quartz oscillator beside the substrate.

Lead phthalocyanine (PbPc, 98%) was purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification. Also, the substrates were optically-flat silicon wafer [Si (111), Shin-etsu Chem. Ltd.] and potassium bromide [KBr (100), Furuuchi Chem. Ltd.]. Just before the deposition, Si (111) wafer was simply cleaned by acetone and ethanol, and KBr (100) substrate was air-cleaved. Further, both substrates were baked during 2 hours in UHV chamber. PbPc was deposited as following conditions: pressure of 3×10^{-8} Torr, deposition rate of 0.002 nm/sec, total thickness of 100 nm, and substrate temperatures of 25 °C and 100 °C.

In order to evaluate the crystal structure and molecular orientation just after the deposition, the *in-situ* measurements of thin films were performed by in-plane and vertical type TRXD.

3. RESULTS AND DISCUSSION

3.1. The PbPc thin films formed on Si

The PbPc thin films on Si substrate were prepared at the substrate temperature of 25°C, and the thickness of 100 nm. Figure 3 shows the vertical type TRXD profiles of PbPc thin films at the diffraction angle of 4.8°. Except for the fluorescence X-rays from the sample and instrument such as Pb-Lα, Pb-Lβ, Mo-Kα, Compton scattering of Mo-Kα, etc., only one peak corresponding to the (320) diffraction of monoclinic

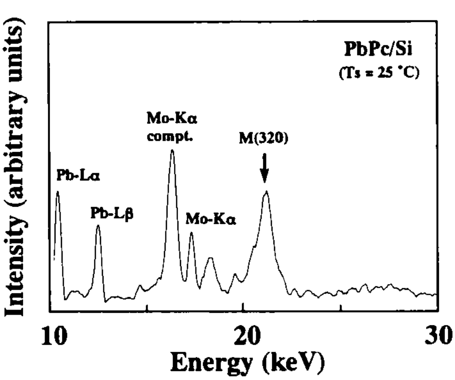

Fig. 3 Vertical type TRXD profile at 2θ=4.8° of the PbPc thin films deposited on Si at the substrate temperature of 25°C.

crystals [M(320)] was observed.

The PbPc thin films deposited at 100°C were measured at the diffraction angle of 2.6, 4.5, 5.6°. Figures 4 and 5 show the vertical and in-plane type TRXD of the thin films, respectively.

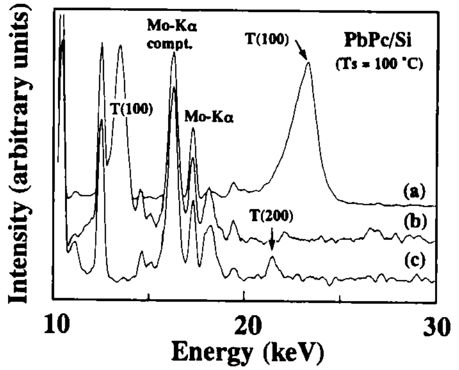

Fig. 4 Vertical type TRXD profiles at (a) 2θ=2.6°, (b) 4.5°, (c) 5.6° of the PbPc thin films deposited on Si at the substrate temperature of 100°C.

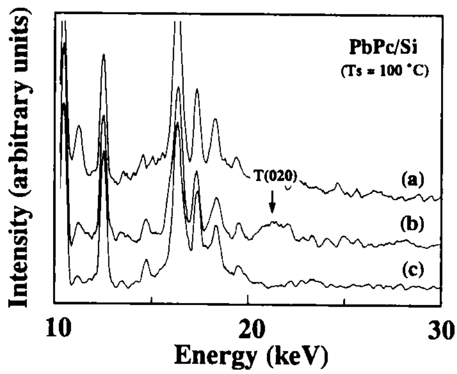

Fig. 5 In-plane type TRXD profiles at (a) 2θ=2.6°, (b) 4.5°, (c) 5.6° of the PbPc thin films deposited on Si at the substrate temperature of 100°C.

In Fig. 4 (a) and (b), the sharp peaks are corresponding to the (100) diffraction of triclinic crystals [T(100)], and its secondary order diffraction (200) [T(200)] is observed in Fig. 4 (c). On the other hands, the (020) diffraction of triclinic crystals [T(020)] is only observed in the in-plane TRXD profiles as shown in Fig. 5.

As above results, The films deposited at 25°C mainly consisted of monoclinic crystals, and the column axis (c-axis) were parallel to the substrate as shown in Fig. 6 (a). On the other hands, it is considered that the thin films at 100°C formed triclinic crystals, and the column direction, namely b-axis of triclinic, was almost parallel to the substrate as illustrated in Fig. 6 (b).

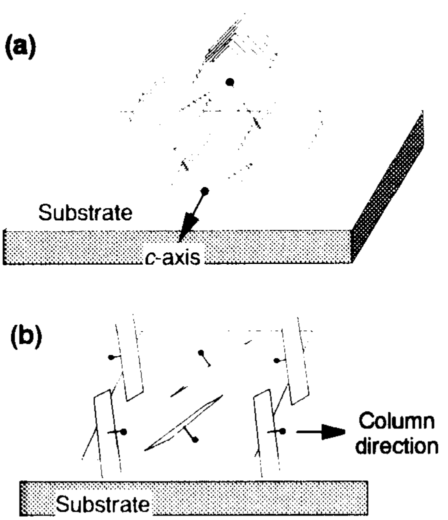

Fig. 6 Illustrations of molecular orientations in thin films deposited at (a) 25°C (*M*) and (b) 100°C (*T*).

3.2. The PbPc thin films formed on KBr

Next, it was attempted to prepare the PbPc thin films on KBr substrate, and characterize the crystal structure and molecular orientation by *in-situ* measurements. Figure 7 shows the vertical type TRXD profile of the PbPc thin film deposited onto KBr(100) at the substrate temperature of 25°C. Only one peak corresponding to the M(320) diffraction was observed the same as thin films on Si(111) at 25°C. Thus, it was confirmed that the deposited thin films on KBr formed monoclinic crystals and the column axis was parallel to the substrate.

Tada et al. [15] reported that the PbPc ultrathin films of monolayer or a few monolayers epitaxally-grown on the KBr(100) with the molecular planes were parallel to the substrate surface, namely the column axis was normal to the substrate. However, in our case, the column axis was parallel to the substrate. It is considered that the the molecular orientation changed as the thickness increased, or the very slow deposition rate affected the orientation. The further elucidation is now in progress.

Also, the crystallinity of the deposited thin films on KBr(100) was much higher than that on Si(111). Thus, it is anticipated to promote the growth of monoclinic crystals on alkali halide because of the epitaxial growth at the initial process. Further, the thermal stability of the deposited thin films on KBr was examined by *in-situ* measurements during annealing. Figure 8 shows the changes of the M(320) peak at the annealing temperature of (a) 25, (b) 60, (c) 100, (d) 140, (e) 180°C. The initial peak located at 20.9 keV (the lattice spacing; 0.70 nm) slightly shifts to the side of low energy upon heating, namely the lattice spacing become a little longer. However, it was not observed below the annealing temperature of 200°C that the T(020) peak corresponding to the lattice spacing of 0.73 nm located at 20.0 keV in this profile occurred because of the crystal transformation from monoclinic system to triclinic. Furthermore, Fig. 9 shows the changes of the M(320) peak (a) at 25°C before annealing, (b) just after annealing during 9 hours at 180°C, and (c) at 25°C after annealing. Similarly, it was confirmed that the M(320) peak only shifted and the

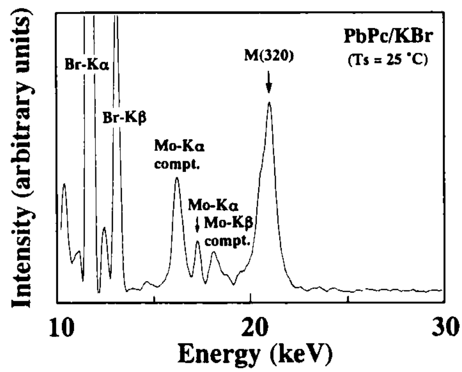

Fig. 7 Vertical type TRXD profile at 2θ=4.8° of the PbPc thin films deposited on KBr at the substrate temperature of 25°C.

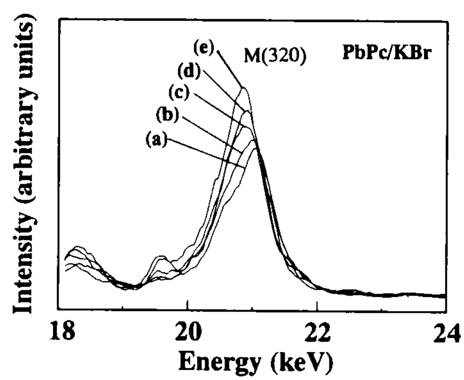

Fig. 8 Vertical type TRXD profiles of the monoclinic PbPc thin films deposited on KBr at (a) 25, (b) 60, (c) 100, (d) 140, (e) 180°C upon heating.

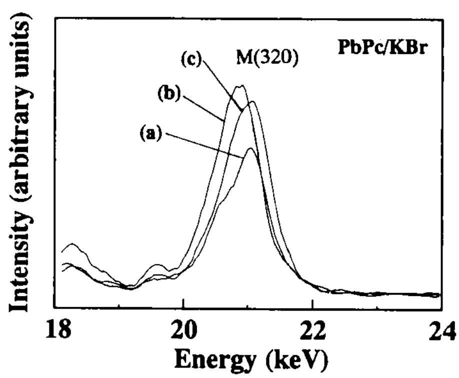

Fig. 9 Vertical type TRXD profiles of the monoclinic PbPc thin films deposited on KBr (a) at 25°C before annealing, (b) just after annealing during 9 hours at 180°C, (c) at 25°C after annealing.

transformation did not occur during annealing. The M(320) peak intensity after annealing somewhat increased because of the recrystallization of amorphous region in the deposited thin films. It was reported that the crystal transformation from monoclinic system to triclinic occurred when the deposited film on quartz glass annealed at 100°C during 2 hours. [14] However, it is thought that the high crystalline thin films with monoclinic crystals are thermally stable up to 200°C. Thus, it is imprtant to prepare much high crystalline films with monoclinic crystals from the view point of the application to an electrical device.

4. SUMMARY

In this study, it was attempted to examine the crystal structure and molecular orientation of PbPc films deposited on Si and KBr substrates by using TRXD-OMBD for *in-situ* measurements.

At the substrate temperature of 25°C, PbPc grew as monoclinic crystals with the column axis parallel to the substrate. Also, the crystallinity of the deposited films on KBr was much higher than on Si, and were thermally stable. Further, it was observed that the deposited films on Si at the substrate temperature of 100°C consisted of the triclinic crystals with the column axis parallel to the substrate.

REFERENCE

1. M. Hara, H. Sasabe, A. Yamada, and A. F. Garito, Jpn J. Appl. Phys., 28, L306 (1989)
2. M. Mobus, M. Schreck, and N. Karl, Thin Solid Films, 175, 89 (1989)
3. A. J. Dann, H. Hoshi, and Y. Maruyama, J. Appl. Phys., 67, 1371 (1990)
4. H. Tada, K. Saiki, and A. Koma, Jpn. J. Appl. Phys., 30, L306 (1991)
5. C. D. England, G. E. Collins, T. J. Schuerlein, and N. R. Armstrong, Langmuir, 10, 2748 (1994)
6. A. Heilmann, M. Muller, C. Hamann, V. Lantto, and H. Torvela, Sensors and Actuators B, 4, 511 (1991)
7. Y. Machida, Y. Saito, A. Taomoto, K. Nichogi, K. Waragai, and S. Asakawa, Jpn. J. Appl. Phys., 28, 297 (1989)
8. D. Campbell, and R. A. Collins, Thin Solid Films, 261, 311 (1995)
9. Y. Ukei, Acta Cryst., B29, 2290 (1973)
10. Y. Iyechika, K. Yakushi, I. Ikemoto, and H. Kuroda, Acta Cryst., B38, 766 (1982)
11. R. A. Collins, and A. Belghachi, Mater. Lett., 8, 349 (1989)
12. R. A. Collins, K. R. Strickland, M. J. Jeffery, K. Davidson, and T. A. Jones, Mater. Lett., 10, 170 (1990)
13. R. A. Collins, A. Krier, and A. K. Abass, Thin Solid Films, 229, 113 (1993)
14. A. Miyamoto, K. Nichogi, A. Taomoto, T. Nambu, and M. Murakami, Thin Solid Films, 256, 64 (1995)
15. H. Tada, K. Saiki, and A. Koma, Surf. Sci., 268, 302 (1992)
16. T. Horiuchi, K. Fukao, and K. Matsushige, Jpn. J. Appl. Phys., 26, L1839 (1987)
17. K.Ishida,K. Hayashi, Y. Yoshida, T. Horiuchi, and K. Matsushige, J. Appl. Phys., 73, 7338 (1993)