Observation of reflected X-rays from end face of organic thin film

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Abstract. During the irradiation of white X-rays of synchrotron radiation on copper phthalocyanine thin film on a Si wafer (CuPc/Si) under the grazing incidence condition, X-rays from the end face of the CuPc layer were observed by solid state detector. These were understood to be refractions through the CuPc layer and reflections from the CuPc/Si, because their energy variation as a function of the X-ray exit angle followed Snell’s law. We also discussed the similarities and differences between the observed phenomenon and X-ray waveguide phenomenon.

1. Introduction

When white X-rays impinge on organic films under the grazing incidence condition, some monochromatic X-rays are emitted from the end face of the organic layer due to X-ray waveguide phenomenon.[1-3] This emission has been explained as a total external reflection at the upper and lower interfaces of the guiding layers.[4] As a result of the multiple total reflections, the layer is capable of guiding a finite number of electromagnetic modes, which forms X-ray standing-wave in the direction of the plane.

One of the present authors (K. Hayashi) has insisted that the X-ray waveguide phenomenon is useful for the characterization of organic films, because the energies of monochromatic guided X-rays are sensitively varied by the thicknesses and densities of the films. To date, we have determined accurate film structures of paraffin and copper phthalocyanine by observing the guided X-rays in addition to the energy dispersive X-ray reflectivities.[2,3] This structural analysis method is considered to be promising for in-situ measurements during the film growth process. However, white
X-rays from X-ray tubes are too weak to allow to be measured in a few seconds. Therefore, intense white X-ray beams such as synchrotron radiation are needed for the in-situ measurements to be made.

As a preliminary study, we used white X-rays of synchrotron radiation in Photon Factory and observed X-rays emitted from the end face of copper phthalocyanine (CuPc) film in order to determine the details of the behavior of X-rays traveling in the CuPc layer.

2. Experimental

The CuPc film was prepared on a Si (001) wafer by the evaporation method. The evaporation was conducted at $10^{-4} - 10^{-5}$ Pa. The Si substrate during evaporation was kept at room temperature. Film thickness was controlled by a quartz oscillation monitor so as to be about 100 nm. After the evaporation, the film thickness was measured by a stylus surface profiler (ULVAC, Dektak3), and the obtained value was 110 nm. Surface morphology was checked by AFM.

The X-ray experiment was carried out at BL3C in Photon Factory. The experimental setup adopted here is displayed in Fig. 1. The size of the incident beam was adjusted to be $100 \times 100 \mu m^2$ by the slit. The X-rays from the end face of the CuPc film passed through two slits and were detected by a pure Ge-type solid state detector (SSD), which was connected to a digital signal processor and personal computer. The grazing incidence angle was fixed at 0.21º, and the X-ray exit angle varied from -0.14º to 0.18º via 0.05º steps. The data collection time for one spectrum was 20 sec. The reflected X-rays were also measured at a symmetrical reflection geometry of $\phi_1 = \phi_2 = 0.21º$.

3. Results and Discussion

Figure 2 shows the spectrum of the reflected X-rays. The displayed data are not normalized with the spectrum of the incident white beam, which could not be measured in the present work because of its extremely strong intensity. Some Kiessig fringes appeared in the energy range between 9 and 13 keV. Figure 3 shows the angular change of the spectrum. The arc indicated by A is the refraction through the Si wafer, because its energy increases with the increasing $\phi_2$, in accordance with Snell’s law. Snell’s law was expressed as the following equation,

$$ E_r = \frac{h c}{m c^2} \left(\frac{\sum_{a} N_a f_a}{\phi_1^2 - \phi_2^2}\right) $$

where $E_r$ is the energy of the refracted X-rays, $h$ the Planck constant, $c$ the light velocity, $e$ the electron charge, $m$ the electron mass, $f_a$ the real part of the atomic scattering factor of a type $a$ atom, and $N_a$ the number of type $a$ atoms per unit volume. Using this equation, the energies of refraction through the Si wafer were calculated with the density of $2.33 \, g/cm^3$ (crystalline bulk of Si), and they were plotted in Fig. 3. The calculated energies agree with those of arc A. In addition to arc A, two arcs symmetrical
with respect to $\phi_2 = 0.0^\circ$, which are indicated by B and C, were observed. Since these patterns were not observed for a simple Si wafer, it was considered that they were X-rays traveling in the CuPc layer.

Until now, we have measured X-rays emitted from the end face of the organic layers.[1-3] However, their X-ray energies have been discrete depending on the resonant modes of the X-ray waveguide phenomenon. Thus, X-rays guided in the organic layer due to the X-ray waveguide phenomenon have been observed as stripes in the 2D plot of the intensity as functions of X-ray energy and $\phi_2$.[5] However, streaks are not seen here. Therefore, we tried to explain the energy variation of

**Fig. 2 Spectrum of reflected X-rays from CuPc film.**

**Fig. 3 Intensity distribution of X-rays emitted from the end face of the CuPc layer as a function of X-ray energy and X-ray exit angle $\phi_2$.**
arc B by Snell’s law analogously to arc A. Figure 4 shows an illustration of the behaviors of the refraction and the reflection inside and outside the sample. First, we calculated the refraction curve through the CuPc layer with a bulk density of 1.62 g/cm$^3$.[6] However, the calculated curve shifted slightly toward higher energy. Thus, we changed the parameter of the CuPc density so as to fit the calculated data to the experimental data. Best fit was obtained when using the density parameter of 1.52 g/cm$^3$, which is 94% of the bulk density. From these considerations, it is known that arc B is attributable to the refracted X-rays emitted from the end face of the CuPc layer. The arc B corresponds to the refracted X-rays indicated by B in Fig. 4.

Using the obtained parameters of the thickness and density of the CuPc layer, we calculated the energy dispersive reflectivity curve and plotted it in Fig. 2. Kiessig fringes are reproduced to a certain extent; however, the dip structures below 8 keV are quite different from those in the experimental data. Although we suppose that this discrepancy correlated to the non-uniformity of the CuPc layer, the details are not clear now.

On the other hand, arc C can be interpreted as consisting of the X-rays emitted from the end face of the CuPc layer after being reflected at the CuPc/Si interface, which correspond to the reflected X-rays indicated by C in Fig. 4. The energy of arc C is limited to the range between 7.2 and 8.6 keV, which are the critical energies for total external reflection at the CuPc surface and the CuPc/Si interface, respectively. This energy limitation of arc C supports the assumption that arc C corresponds to the reflection only at the CuPc interface. Most reports on the X-ray reflectivity studies involve analyses of reflected X-rays from sample surfaces. As far as we know, reflected X-rays emitted from the end face of the layer were observed for the first time in the present experiment. Measurement of the reflected X-rays from the CuPc/Si interface may provide additional information on the buried interface.

![Fig. 4 Illustration of behaviors of refracted and reflected X-rays with sample.](image)

**4. Conclusion**

X-rays emitted from the end face of the CuPc layer were observed under the grazing incidence condition using white X-rays of synchrotron radiation. Using Snell’s law, the behaviors of two kinds of beams were well explained as refracted and reflected X-rays traveling in the CuPc layer. On the other hand, the spectra that typically resulted from the X-ray waveguide phenomenon were not observed in the present study. However, there were some similarities between the pattern of arcs B and C and the pattern of the guided X-rays brought by X-ray waveguide phenomenon; that is, symmetry with respect to $\phi_2 = 0.0^\circ$, widely separating of X-ray exit angles with the increase of the energy.[5] Thus, we can consider that the whole pattern of arcs B and C resembles to the patterns of guided X-rays, although the former and latter patterns are continuous and discrete, respectively. Therefore, the refraction and reflection phenomenon observed here might also be explained by the theory of the waveguide phenomenon. Further analysis is now in process.
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References
[1] K. Hayashi, J. Kawai, Y. Moriyama, T. Horiuchi and K. Matsushige, Spectrochim. Acta B 54 (1999) 227-230.
[2] K. Hayashi and J. Kawai, Physica B 283 (2000) 139-142.
[3] K. Hayashi, Physica B 357 (2005) 227-231.
[4] W. Jark, S. Di Fonzo, S. Lagamarsino, A. Cedola, E. di Fabrizo, A. Bram, C. Riekel, J. Appl. Phys. 80 (1996) 4831-4836.
[5] K. Hayashi, K. Sakai and H. Takenaka, Thin Solid Films 515 (2007) 5728-5731.
[6] M. Ashida, N. Uyeda, E. Suito, Bull. Chem. Soc. Japan 39 (1966) 2616-2624.