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ARTICLES

Observation of interference effects due to multiple reflection of fluorescent x rays in an organic thin film

Yoshio Suzuki, Yuji C. Sasaki, and Yasushi Tomioka
Advanced Research Laboratory, Hitachi Ltd., Hatoyama, Saitama 350-03, Japan

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An interference pattern of fluorescent x rays caused by multiple reflection in a thin film has been observed. The fluorescent x rays emitted from a zinc monatomic layer embedded in an organic thin film on an x-ray reflecting mirror are reflected both at air-film and at film-mirror interfaces. Interference due to multiple reflection appears at an angular distribution of fluorescent x rays just above the critical angle for total reflection from the air-film interface. Position of atoms emitting fluorescent x rays were determined by measuring interference patterns. [S0163-1829(96)06342-4]

I. INTRODUCTION

Characteristic x rays emitted from a thin layer deposited on a substrate have shown anisotropic distribution at a low take-off angle, as reported by Hasegawa *et al.*[1] when electron-impact excitation is used. When the deposited layer is thin enough, the intensity of characteristic x rays maximizes at the critical angle for total external reflection. The same phenomenon when fluorescent x rays are excited by x-ray beams has been reported by Sasaki and Hirokawa,[2] and is accounted for by the refraction and reverse total-reflection processes of fluorescent x rays.[3]

These phenomena, called the total-reflection-angle effect, can be explained by interference between directly emitted x rays and x rays reflected from the high-density substrate surface.[4] When the distance between the fluorescent x-ray emitter and x-ray reflecting surface is not zero, interference fringes should appear below the critical angle for total external reflection. This interference effect for fluorescent x rays (FXI, denoting fluorescent x-ray interference) has been observed in zinc-embedded organic thin film on a gold substrate, and it is confirmed that the distance between fluorescent x-ray emitting atoms and the substrate interface can be determined by analyzing measured interference fringes.[4,5] Similar phenomena for monochromatic x rays emitted from radioactive atoms by spontaneous emission processes after electron-capture decays have also been observed.[6] The interference of fluorescent (or characteristic) x rays is considered to be a time-inverse phenomena of x-ray standing wave (XSW) experiments,[7,8] and can also be regarded as a special case of x-ray holographic microscopy using a local reference beam.[9] Recently, experimental results of the three-dimensional local-beam holography have been demonstrated by Tegze and Faigel.[10] Their method is considered to be a powerful technique for determining the atomic-scale feature of neighboring atoms. Although the fluorescent x-ray interference described in this paper cannot be applied to analysis of three-dimensional atomic-scale structures, it is possible to determine one-dimensional long-range (~100 Å) interface structures.

These interference effects of fluorescent (or characteristic) x rays are considered to be caused mainly by reflection from the surface of high-density substrates. The distance of x-ray emitting atoms from the substrate surface can be determined by measuring interference patterns. Internal reflection from the film-air interface does not play an important role in these interference effects. This is because the reflectivity of x rays is usually very small except for total external reflection. Therefore, multiple-reflection effects are negligible except for stratified media such as multilayer structures.

When an x-ray beam propagates from a high-density medium into a low-density medium, or from organic film into air, total reflection conditions can never be satisfied. However, the reflectivity of x rays in internal reflection is not negligibly small for grazing incidence conditions. An x-ray beam that is internally reflected from thin film-air interface sometimes plays an important role in interference phenomena. As shown in Fig. 1, x rays emitted from a point source in the thin film deposited on the mirror substrate are reflected both from the film-air interface and film-substrate interface. Further, the interference between reflected beams causes interference fringes in an angular distribution of x-ray emission at a low take-off angle. In this paper, we describe multiple reflection effects for the interference of fluorescent x rays emitted from embedded atoms in an organic thin film

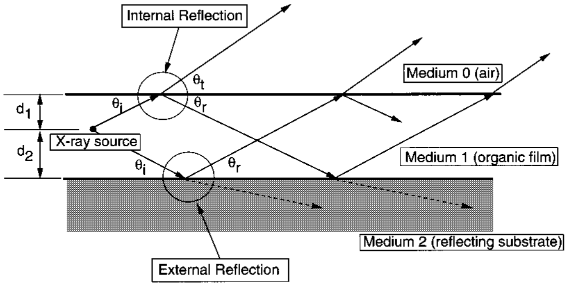

FIG. 1. Schematic diagram of multiple reflection.

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deposited on a mirror substrate. A method of positional determination for x-ray emitting atoms not only in terms of the mirror surface but also the film-air interface will be presented.

II. THEORETICAL BACKGROUND

Suzuki and Hasegawa[4] interpreted the angular distribution of x-ray emission by the interference effects of fluorescent x rays. Fluorescent x rays emitted from an atom on a mirror substrate can travel along two optical paths, a directly traveling wave (E_D) and one reflected from the surface (E_R). Anisotropic emission is caused by the interference between these two waves.

This model shows that fluorescent x-ray interference fringes are observed when the fluorescent source is away from the surface. The angular distribution of fluorescent x rays can then be given by

$$I(\theta_t,d)=|E_D+E_R|^2,$$

where θ_t is the take-off angle of fluorescent x rays, and d is the distance between the source point (atom) and reflecting surface. E_D and E_R are the direct and reflected E-field plane waves of fluorescent x rays. The geometrical path difference Δ between E_D and E_R is described as

$$\Delta=2d\ \sin\theta_t.$$

Therefore, the interference pattern depends on distance d between the source atom and reflecting surface. Positional information on the source can be obtained by observing the take-off angle dependence of fluorescent x-ray emission. Although the reflectivity of x rays is usually very small (generally about 10^{-10}) under normal incidence conditions, it is nearly 100% below the critical angle for total external reflection (θ_c). Thus, interference fringes can clearly be observed only when the observation angle is smaller than θ_c.[4,5]

As it is impossible to hold source atoms in a vacuum above the substrate, Langmuir-Blodgett (LB) films on heavy metal substrates (usually gold or platinum) are usually used for XSW and the FXI experiments.[5–8] Source atoms are embedded in the LB film. This system is approximately equal to that with source atoms above the substrate. This is because (1) density of the LB film is much smaller than that of the substrate, so that total external reflection occurs on the LB-substrate interface, and (2) the absorption loss in the film is negligibly small because of the low linear absorption coefficient for the LB film. We have already observed interference fringes caused by distance d, and the experimental results show good agreement with calculations.[5,6] Therefore, the basic effect of interference is considered to be caused by direct emission and totally reflected radiation at the mirror surface.

However, fluorescent x-ray emission from these layered structures is somewhat deformed by reflection from the air-LB interface. As shown by Fig. 1, when an x-ray beam propagates from a high-density medium (medium 1) into a low-density one (medium 0), a portion of the incident radiation is reflected at the interface. Under normal-incidence conditions, of course, reflectivity is extremely low. However, when the glancing angle approaches zero, reflectivity is not negligibly small. Reflectivity and phase change can be calculated by the Fresnel formula.[11]

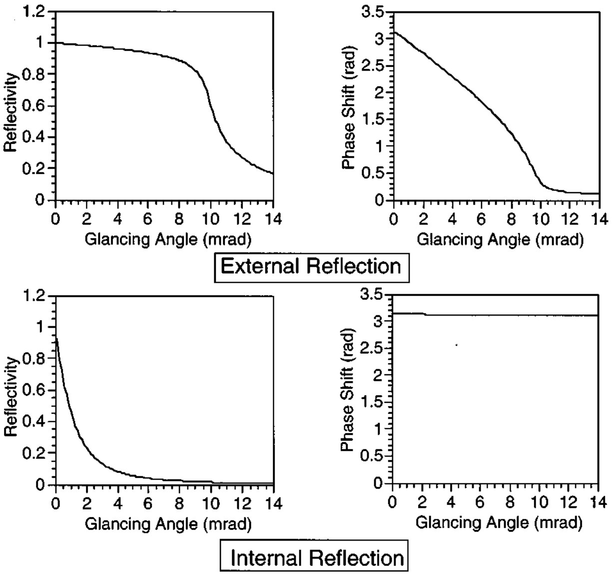

FIG. 2. Calculated reflectivity and phase shift at external reflection and internal reflection.

Results of numerical calculation both for external and internal reflection are shown in Fig. 2. Here, external reflection means that the x-ray beam propagates from a relatively low-density medium (medium 1) into a high-density medium (medium 2), and internal reflection means the propagation of an x-ray beam from a relatively high-density medium (medium 1) into a low-density one (medium 0). Calculation for internal reflection has been done in the case of a cadmium-arachidate LB film-air interface, and external reflection has been calculated for an air-platinum interface. As shown in Fig. 2, reflectivity for external reflection is nearly 100% below the critical angle for total external reflection, and sharply drops to zero above the critical angle. The phase difference at reflection changes from π to zero. The reflectivity for internal reflection, on the contrary, is nearly 100% at a glancing angle of zero, and rapidly drops to 0% as the glancing angle increases. An important feature of internal reflection is that reflectivity is not zero at very small glancing angles (less than a few mrad), and the film-air interface acts as a half-mirror in these grazing incidence regions.

As described above, fluorescent x-ray emitting atoms embedded in LB film are sandwiched by two reflecting interfaces, i.e., one is the substrate surface and the other is the air-film interface. Therefore fluorescent x-ray interference is caused by both reflections: external reflection at the film-substrate interface and internal reflection at the air-film interface. The effects of multiple reflection must be observed during the fluorescent x-ray interference experiment. Wang *et al.* have already reported the special effect of multiple reflection on x-ray standing wave experiments.[8] When target atoms are at the center of deposited thin film, a sharp peak is observed in fluorescent x-ray yield as a function of the incident angle of the primary x-ray beam, and this phenomenon is called a resonance enhanced x ray. However, their experiment was done only when the probe layer was at the center of the LB film. Therefore, interference fringes on FXI or XSW experiments caused by multiple reflection were not

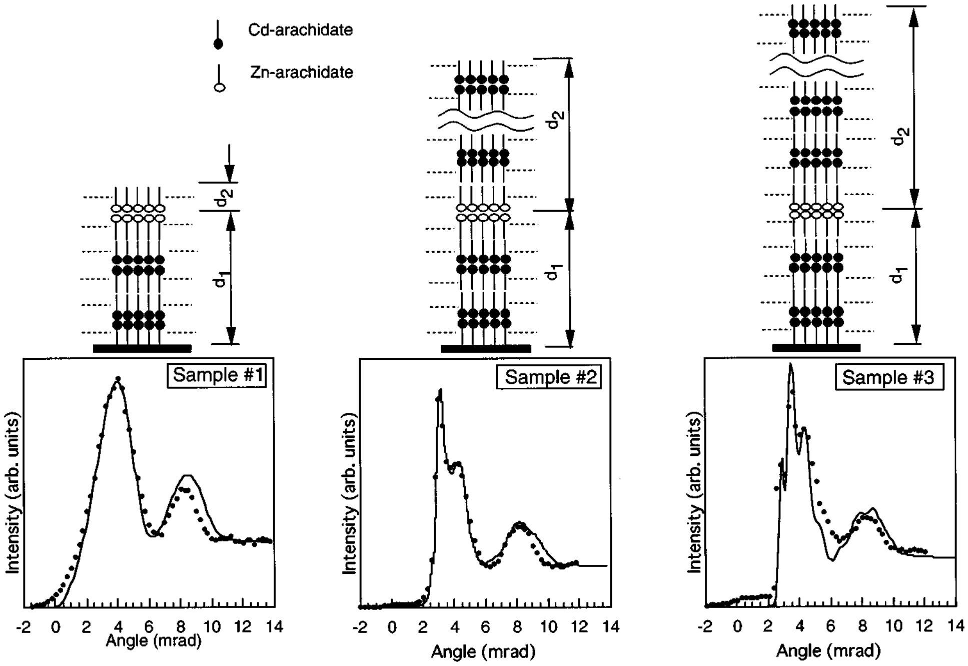

FIG. 3. Cross-sectional view of sample structures, and measured and calculated angular distribution of fluorescent x rays. The solid circles are measured data, and the solid lines are theoretical calculation. Angular distribution of Zn $K\alpha$ radiation is measured by slit scan. Measured data points are 64, and angle step is 0.25 mrad per data point. Signal integration time is 200 s per data point.

explicitly observed. We prepared some zinc-embedded LB film samples with different film thicknesses to observe multiple-reflection effects.

III. EXPERIMENT

Platinum film deposited on an optically flat chromium-coated glass was used as the x-ray reflecting mirrors. The thickness of the chromium buffer layer was about 300 Å, and a platinum film, 2000 Å thick, was evaporated on the chromium layer. The glass plate was 30 mm in diameter, and its flatness was better than 300 Å. LB films were then deposited on the platinum surface. We prepared three samples as shown in Fig. 3. The zinc-arachidate bilayer is allocated in the cadmium-arachidate bilayers, and zinc atoms are used as fluorescent x-ray sources. For all samples, distances between the mirror surface and the zinc-monatomic layer (d_1) are equal, with a different structure for the distances from the zinc layer to the air-film interface (d_2). Designed values of d_1 and d_2 are listed in Table I.

The experiment was carried out at experimental station BL-8C2 of the KEK Photon Factory 2.5 GeV storage ring. The experimental setup is similar to that of the previous experiment.[6] Synchrotron radiation from a normal bending magnet was monochromatized with a Si (111) double crystal monochromator, and tuned at an x-ray energy just above the Zn K absorption edge to maximize the intensity of Zn $K\alpha$ radiation. The output beam from the monochromator was confined to 200 μm (vertically)×6 mm (horizontally) by a cross slit. The intensity of monochromator output was monitored using an ionization chamber. The incident beam was linearly polarized, and its electric vector was in the horizontal plane. Consequently, fluorescent x rays were able to be measured at a 90° scattering angle in the horizontal plane to minimize background signals due to elastic scattering.

TABLE I. d_1 denotes the distance between substrate-thin film interface and Zn monolayer. d_2 denotes the distance between Zn monolayer and LB film-air interface. Fully extended and untilted molecule alignment is assumed.

	d_1	d_2
Sample no. 1	137.5 Å	27.5 Å
Sample no. 2	137.5 Å	247.5 Å
Sample no. 3	137.5 Å	467.5 Å

The primary x-ray beam impinges on the sample surface at a glancing angle of a few mrad, and was totally reflected to reduce background signals. Total intensity of the fluorescent x rays is strongly dependent on the glancing angle because of standing wave effects. Therefore, the incident angle of the primary beam was set at a fixed angle where the total intensity of fluorescent x rays is maximized. The exposed area for the sample was 6 mm×30 mm.

Angular distribution of Zn $K\alpha$ fluorescent x rays were measured using a pure-germanium detector combined with a slit. The slit 50 μm (vertical)×10 mm (horizontal) was placed in front of the detector at a distance of 200 mm from the sample to determine the take-off angle (θ_t). The angular distribution of fluorescent x rays was measured by scanning the slit along the vertical direction. Angular resolution estimated from this geometrical configuration was less than 0.5 mrad below the θ_t of 8 mrad.

IV. RESULTS AND DISCUSSION

Experimental results are shown in Fig. 3. Interference patterns clearly vary as the thickness of overcoat layer (d_2)

changes from 27.5 to 467.5 Å. The first maximum around 3 mrad for sample no. 1 (d_2=27.5 Å) is a single peak. The first maximum for sample no. 2 (d_2=247.5 Å) splits to double peaks, and that for sample no. 3 (d_2=467.5 Å) divides into triple peaks. These splits in peak are considered to be caused by multiple reflection between the air-LB film interface and LB film-substrate interface.

Results of theoretical calculation are shown in Fig. 3. The calculation procedure of has been described in a previous paper.[5] Parameters for calculation were set as follows.

(1) Distance between substrate surface and Zn monatomic layer: d_1=97.5 Å. This value is common for all samples (no. 1, no. 2, and no. 3).

(2) Refractive index of air (medium 0 in Fig. 1): $n=1$.

(3) Refractive index of LB film (medium 1 in Fig. 1) for Zn $K\alpha$ radiation: $n=1-3.19\times10^{-6}+7.66i\times10^{-8}$.

(4) Refractive index of Pt substrate (medium 2 in Fig. 1) for Zn $K\alpha$ radiation: $n=1-4.76\times10^{-4}+4.08i\times10^{-6}$.

(5) Wavelength of Zn $K\alpha$ radiation: $\lambda=1.436$ Å (average of Zn $K\alpha_1$ and $K\alpha_2$).

(6) Standard deviation for depth distribution of Zn atom: σ=25 Å, Gaussian distribution is assumed.

(7) d_2=27.5 Å for sample no. 1, d_2=247.5 Å for sample no. 2, and d_2=467.5 Å for sample no. 3.

Although the fitted value of d_1 (97.5 Å) is slightly shorter than that derived from fully extended molecular length, the calculations show good agreement with experimental results.

These results are considered to be clear evidence of the interference effects of fluorescent x rays caused by multiple reflection from the film-substrate interface and film-air interface. By precise measurement of interference patterns, we can analyze not only fluorescent x-ray source to substrate distance (d_1) but also source to topmost interface distance (d_2). Thus the multiple-interference effect of fluorescent x rays can be applied to the one-dimensional structural analysis method for organic thin films.

Although reflection from the film-air interface is not total external reflection, reflectivity is sufficiently high at low glancing angles. The interface between the low-density medium and high-density medium works as a half-mirror at small glancing angles. The experimental results suggest the characteristic of fluorescent x-ray interference effects can be applied to a new structural analysis method. For structural analysis using interference effects such as FXI and XSW experiments, heavy metal substrate was used as the x-ray reflecting mirror surface, and structural information concerning the mirror surface was derived from measured interference patterns. For these experiments, total-external reflection at the interface from the low-density medium to high-density medium has been considered to be indispensable for measuring interference fringes. However, as shown in the present experiment, any interface works as a half-mirror when the glancing angle is extremely small, and reflectivity approaches nearly 100% as the glancing angle becomes zero. Therefore, if the angular distribution of fluorescent x rays is measured precisely around the critical angle for total external reflection, it is possible to observe interference fringes without the reflecting mirror substrate of heavy elements.

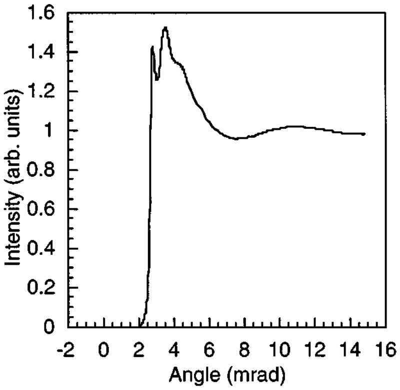

FIG. 4. Theoretical calculation for x-ray interference pattern of Zn $K\alpha$ x rays from Zn monatomic layer embedded in free standing LB film. Structure of film is the same as sample no. 3 except for the absence of Pt substrate.

We have calculated the interference pattern for LB thin films without a heavy element substrate. Theoretical simulation is shown in Fig. 4. Structure of the LB film is exactly the same as sample no. 3 except for the absence of the platinum substrate. Interference fringes caused by the reflection of fluorescent x rays can clearly be recognized just above the total external reflection angle for the air-LB film interface. Consequently, the structure of free standing polymer membranes can be analyzed by labeling specific sites with a metal element. This method could be used for the structural analysis method in the future.

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