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Fluorescent-x-ray-interference effect in layered materials

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The interference of fluorescent x rays in a layered material has been observed in grazing exit experiments. The exit angular dependence of the x-ray fluorescence intensity of a Cr/Au layered thin film clearly shows an oscillation structure that represents the interference of emitted x rays. As predicted by the reciprocity theorem, the results obtained under the grazing exit condition agreed with the results obtained under the grazing incidence condition quite well.

X-ray analysis under the grazing incidence condition is now widely being used in various research fields. Grazing incidence x-ray diffraction has been commonly used in surface structure analysis in recent years.[1,2] Grazing incidence x-ray fluorescence (GIXRF) has made surface trace element analysis[3] and elemental depth profiling possible.[4,5] These techniques take advantage of the fact that the x-ray penetration depth depends on the angle of incidence, and is extremely shallow under the grazing incidence condition.

Becker, Golovchenko, and Patel[6] pointed out that grazing exit x-ray fluorescence (GEXRF) is also useful for surface characterization. They demonstrated experimentally the correlation between grazing incidence and grazing exit evanescent wave fields using a bulk Ge crystal, and explained their results by applying the reciprocity theorem. This GEXRF technique has been used to analyze the absorbate (Ag on Si) of less than one monolayer,[7] as well as to measure the ion-implantation profile.[8]

When a layered thin film is measured under the grazing incidence (GI) condition, the oscillation structure in the glancing-angle dependence of fluorescent x rays is observed as a result of the interference between incident and reflected x rays and is widely used in various application fields.[9] On the other hand, under the grazing exit (GE) condition, the oscillation structure is also expected in the exit-angle dependence as a result of the interference of fluorescent x rays themselves. Since the oscillation structure in the GE experiment is direct evidence of the reciprocity theorem, the experimental observation of the oscillation will extend the possibility of the GE experiment to get structure information of a layered material, such as the thickness and the density variation and the surface and the interface roughness.

In this paper, we describe the observation of a distinct oscillation structure in the exit-angle dependence of fluorescent-x-ray intensity from layered materials. The analytical procedure to get structure information is the same as that in the GI experiment.

Since the interference oscillation was hardly recognized in our previous experiment using an x-ray tube,[10] monochromated synchrotron x rays were used to get high angular resolution with good statistics.

Figure 1 depicts the experimental arrangement of the GEXRF spectroscopy. The experiment was performed at the Photon Factory on beamline 4A. The samples used were Cr (top)/Au (100 nm)/Cr (20 nm) layered thin films deposited on synthetic quartz substrates. Two types of sample with different top Cr layer (20 and 50 nm thick) were prepared. The Cr layer just above the substrate (20 nm thick) was deposited as a cohesive material for the Au layer. Synchrotron x rays were monochromated with a Si(111) double-crystal monochromator. 9.5- and 12.5-keV x rays were used for Cr excitation and Au excitation, respectively. A primary x-ray beam impinged on the sample surface at nearly normal incidence and the intensity of fluorescent x rays was measured as a function of the exit angle θ. Fluorescent x rays were detected by a Si (Li) detector. A receiving slit 80 μm wide was placed before the Si (Li) detector at a distance of 360 mm from the sample. The primary x-ray irradiated area was about 1×1 mm^2 at the sample position. This geometry attained an angular resolution of less than 0.28 mrad.

Figures 2(a) and 2(b) show the angular dependences of Cr $K\alpha$ intensity from Cr/Au-layered thin films under the grazing exit condition. Two samples have top Cr layers with different thickness, i.e., 20 and 50 nm. With the increase of the exit angle, the Cr $K\alpha$ intensity rises after 9 mrad, which is the critical angle of total external reflection for Cr $K\alpha$ radiation. Two broad peaks shown in Fig. 2(a) and four narrower peaks shown in Fig. 2(b) could be observed. These oscillation structures have not previously been observed in the GEXRF curve resulting from bulk or surface monolayer samples,[7,8] and are caused by the interference of fluorescent x rays on layered structures.

The angular dependence of Au $L\alpha$ intensity from the Cr (50 nm)/Au/Cr layered structure is shown in Fig. 3. The angular dependence does not show the interference

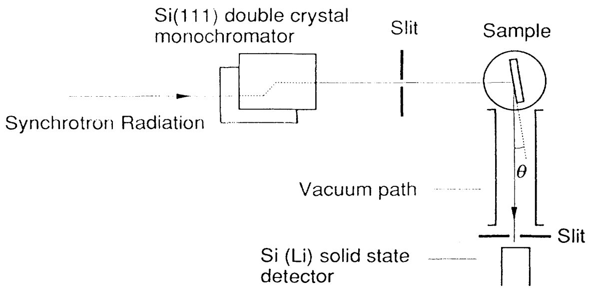

FIG. 1. Experimental arrangement of the GEXRF spectroscopy. The SR beam was monochromatized by a Si (111) double-crystal monochromator. A Si (Li) solid-state detector measured fluorescent x rays from the sample. The XRF intensity dependence of the exit angle θ was measured by rotating the sample.

oscillations. The x-ray-fluorescence (XRF) intensity increases as the exit angle increases just as in the case of bulk materials. The Au layer is thick enough to mask the radiation from lower layers, under the grazing exit condition.

Theoretical curves were obtained by the model on the basis of the reciprocity theorem, which dictates that the radiation propagation process has a source that is

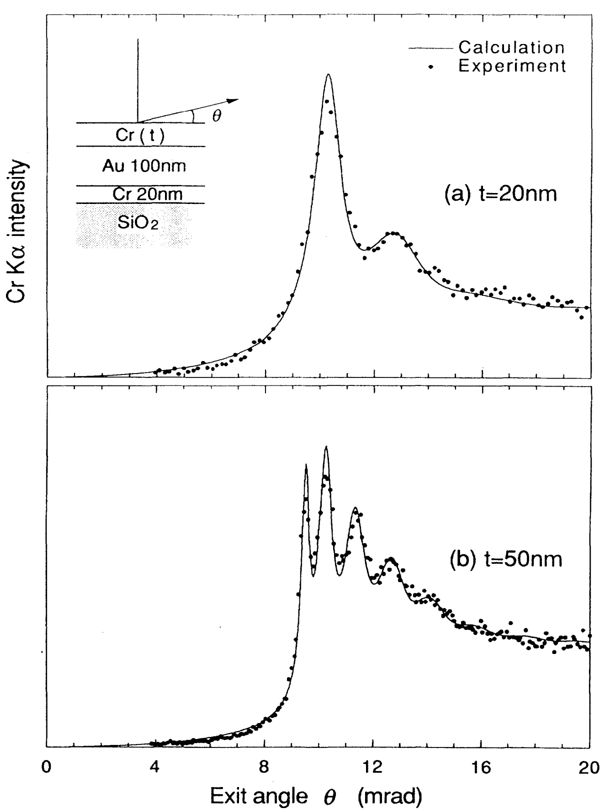

FIG. 2. Measured and calculated angular dependences of the Cr $K\alpha$ fluorescence intensity of (a) Cr (20 nm)/Au (100 nm)/Cr (20 nm) and (b) Cr (50 nm)/Au (100 nm)/Cr (20 nm) layered structures. The excitation energy was 9.5 keV.

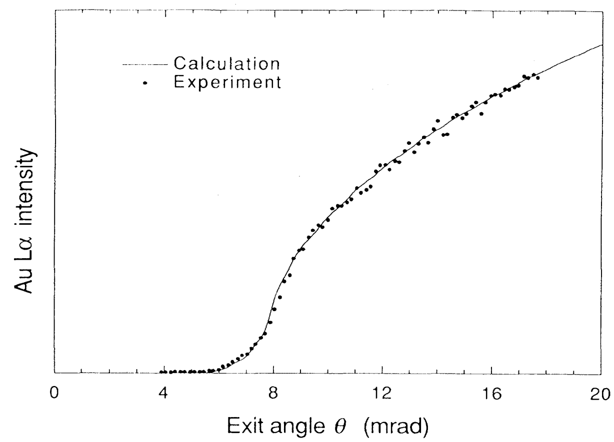

FIG. 3. Measured and calculated angular dependences of the Au $L\alpha$ fluorescence intensity of the Cr (50 nm)/Au (100nm)/Cr (20 nm) layered structure. The excitation energy was 12.5 keV.

symmetrical to the point of observation.[11] Let us assume that the fluorescent radiation is detected at a point outside the sample under the grazing exit condition. The intensity distribution of fluorescent x rays is the sum of the contribution from atoms within the excited region, as illustrated in Fig. 4. According to the reciprocity theorem, the intensity contribution from individual atoms is the same as the wave intensity at the position of each atom, which is induced by incident radiation of the same wavelength under the grazing incident condition. The wave amplitude $E(\theta,z)$ at depth z in the layered structure, which is induced by the incident radiation with glancing angle θ, can be calculated according to Fresnel's recursion formula.[12] The fluorescent-x-ray intensity $I_F(\theta)$ in GEXRF at exit angle θ is given by

$$I_F(\theta)=K\int_0^d C(z)|E(\theta,z)|^2 dz \ , \tag{1}$$

where $C(z)$ is the elemental concentration at depth z, d is the thickness of the layered structure, and K is the proportional coefficient. In the case of layered structures, $I_F(\theta)$ oscillates as θ increases. The basic idea behind this treatment is almost the same as that of Kossel lines by Laue, in which fluorescent radiation from the source within a crystal is diffracted by its crystal lattice.[13]

To analyze the observed angular dependence of fluores-

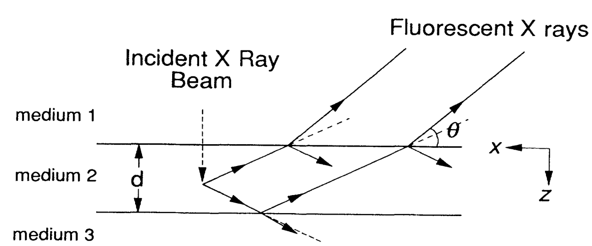

FIG. 4. Conceptual drawing of the grazing exit x-ray fluorescence from a layered material.

cent x rays, according to Eq. (1), a parameter-fitting procedure similar to one used in the grazing incidence experiment is necessary. Since it is expected that the Cr_2O_3 layer was formed by natural oxidation at the surface, a thin surface oxide layer was added in the calculation. The thickness of the surface oxide layer of Cr was estimated to be 4 nm, which is just the same as the thickness estimated by the GIXRF experiment.[14]

The theoretical curves (solid lines) in Figs. 2 and 3 can be obtained using Eq. (1) and assuming structures Cr_2O_3 (4 nm)/Cr (17 nm) [Fig. 2(a)] and Cr_2O_3 (4 nm)/Cr (46 nm) [Figs. 2(b) and 3]. These curves agree with the experimental data very well. The roughness of boundaries was taken into account by the Debye-Waller factor. As a result it was estimated to be 0.5 nm (standard deviation) for both samples.

In the case of a Au layer, the interference effect is so weak that the oscillation structure can hardly be observed on the theoretical curve (Fig. 3). In these theoretical curves, the effect of detector resolution was not taken into consideration.

In conclusion, we have measured the angular dependence of the GEXRF intensity for layered materials, and have obtained direct evidence of an interference effect on fluorescence intensity. We have also shown that the GEXRF experiment gives the same information with respect to the interference effect as did the GIXRF experiment, which was conducted using layered materials.

The grazing exit configuration can be used in conjunction with x-ray microprobe excitation. Present results are being applied to our goal of making it possible to analyze the surface or near surface region with several micrometers of lateral resolution.

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