NEAR-SURFACE CHEMICAL CHARACTERIZATION USING GRAZING INCIDENCE X-RAY FLUORESCENCE

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INTRODUCTION

External X-ray total reflection occurs when collimated X-ray beams impinge on a smooth, flat surface of matter at a small glancing angle, typically a few mrad.[1] With respect to the X-ray fluorescence technique, total reflection experiments have allowed the trace determination of solution samples using an X-ray mirror as a sample support.[2-5] The grazing incidence X-ray fluorescence technique (GIF) is also suitable for near-surface element analysis of the material, because the penetration depth of X-rays is 10-1000 Å around the critical angle. Besides the trace determination of impurities localized near surfaces[6], this technique is capable of a non-destructive depth profiling analysis using the angular dependence of the fluorescent X-ray intensity.[7-10] Recent studies show that synchrotron radiation (SR) is the most suitable X-ray source for such experiments.

For the near-surface characterization of materials, information on the chemical state is definitely as important as the identification/determination of elements. While electron spectroscopic techniques are very useful for surface characterization of less than several tens of angstrom depth, it is very difficult to get reliable information on deeper regions non-destructively. An ultra high vacuum environment is sometimes inappropriate for practical samples.

One of the promising procedures for near-surface chemical characterization is the GIF technique used in conjunction with the selectively induced X-ray emission spectroscopy (SIXES)[11,12], which employs

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absorption-edge shifts for chemical state analysis. The present paper demonstrates that chemical nature of elements near the surface can be analyzed clearly, separated from the bulk material information using an extremely low glancing angle.

EXPERIMENTAL

The experiment was carried out using SR at the Photon Factory on beam line 4A. The apparatus for chemical state analysis by SIXES is essentially the same as usual energy-dispersive X-ray fluorescence system using SR as reported in our previous paper.[11] This technique measures the X-ray absorption spectrum in terms of fluorescent X-ray intensity as a function of the incident energy scanned around the absorption edge of interest. In the present experiment, the GIF setup (Fig.1) was used for the surface sensitive measurement.

SR beams were monochromatized by a Si(111) double-crystal sagittal focusing monochromator. The energy resolution was about 1 eV at the absorption edge of chromium. The intensities of incident and reflected X-rays were measured by two ionization chambers. A Si(Li) detector was employed for the measurement of Kα fluorescent intensity, and was set at 90 deg. to the incident X-rays with an inclination of about 10 deg. from the horizontal plane. A slit was placed in front of the Si(Li) detector to eliminate X-rays from the edges of the sample. Optical alignment was optimized by the tranlational/rotational motion of the sample stage. The measurement was done in air.

The sample used was Cr[200Å]/Cr_2O_3[2000Å] thin film. It was prepared by vacuum evaporation with an electron beam gun and deposited on a flat,

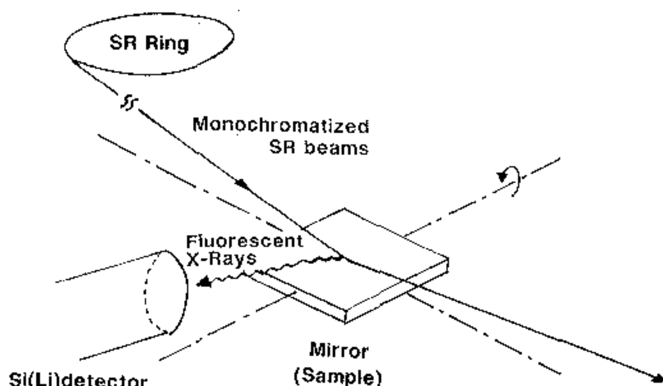

Fig.1 Schematic drawings of the experimental arrangement for grazing incidence X-ray fluorescence (GIF) measurement. Incident X-ray energy was scanned through the Cr K absorption edge.

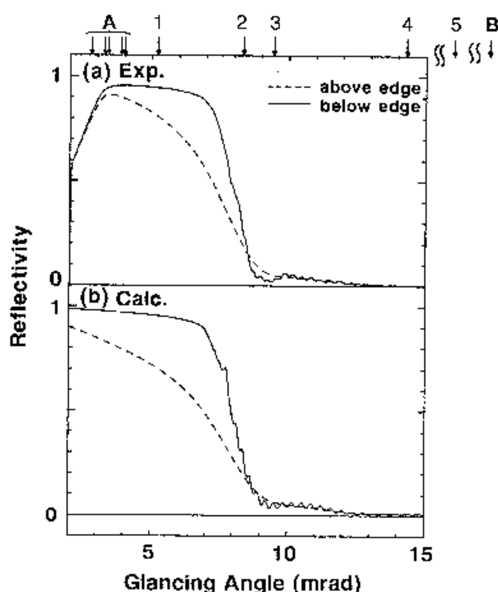

Fig.2

Angular dependence of the reflectivity at lower (solid line) and higher (dashed line) energy side of the absorption edge. Experimental (a) and calculated (b) results are shown.

smooth synthetic quartz plate. Pure Cr and Cr_2O_3 thin films of 2000Å were also prepared as reference samples.

RESULTS AND DISCUSSION

Figure 2(a) shows the experimental results of reflectivity near the Cr K absorption edge (5.9888 keV). The reflectivity calculation was performed using simple Fresnel's theory[1,13] for above (+41 eV) and below (-22 eV) the edge and is shown in Fig.2(b). Anomalous dispersion factors were taken from the table.[14] Reduced reflectivity in the experimental curve for extremely low angles of less than 3 mrad. is due to the decrease in the effective cross section of the sample. Below the absorption edge, high reflectivity is observed due to small absorption in the film. The curve also shows interference oscillations which can be mainly explained as the effect of reflection at the Cr_2O_3/SiO_2 interface. Such a structure has been observed usually when a light loose layer is on top of a heavy packed layer. However, it was confirmed that interference was also observed even if the order of the layers was reversed, below the absorption edge of the heavy element,as the present case. Good agreement was obtained between the experimental and calculated data. In contrast, above the absorption edge, strong absorption smears the angular dependence of the reflectivity. The difference between the experimental and calculated curves below the critical angle probably is due to the uncertainty of the theoretical refractive index parameters.

Cr Kα fluorescent intensity was measured at various glancing angles by scanning incident X-ray energy through the absorption edge. Figure 3

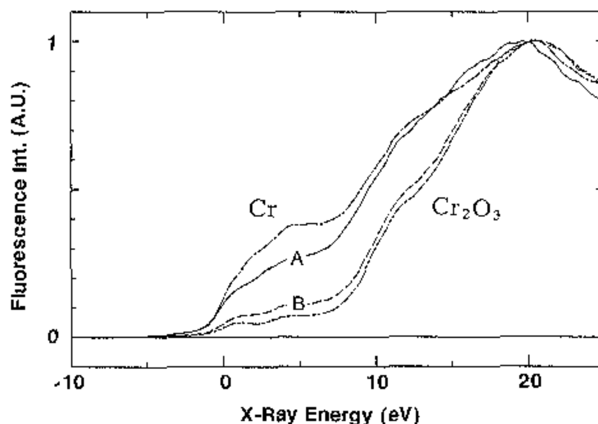

Fig.3 Near-edge absorption spectra of Cr[200Å]/Cr_2O_3[2000Å] thin film using the GIF setup. A: extremely small glancing angle, less than 4 mrad. (See, Fig.2), B: ordinary 45 deg. incidence angle. Standard spectra of chromium metal and its oxides measured at 45 deg. incidence angle are also shown as reference.

shows the near edge absorption spectrum measured at an extremely low angle of less than 4 mrad. (A, See also Fig.2) and the one obtained at 45 deg. incidence angle (B). The standard spectra of Cr metal and Cr_2O_3 thin films are also shown. Fluorescent X-ray intensity abruptly increases as the incident energy crosses the absorption edge. The Cr_2O_3 absorption curve locates higher energy side of the Cr curve, since the position of the absorption edge shifts to a higher energy as the oxidation number increases. The fine structure observed in the curve also contains chemical information, as discussed elsewhere.[12]

The curves **A** and **B** are clearly distinguished from each other, though the sample is the same. For the 45 deg. incidence angle, the penetration depth is in the order of μm above the absorption edge. Therefore B corresponds to information for the whole film, i.e., Cr metal 200 Å layer plus Cr_2O_3 2000 Å layer. From the quantitative analysis, it was found that curve **B** was in good agreement with the synthesis spectrum of Cr and Cr_2O_3 in the layer thickness ratio of about 1:10. On the other hand, in the grazing incidence condition, the penetration depth becomes extremely shallow and is estimated to be less than 100 Å for **A**. That is, curve **A** indicates the chemical state of the near-surface layer of the sample. Actually, it is close to the spectrum of Cr metal. The difference between **A** and the Cr metal spectrum might be explained by considering the formation of the surface Cr_2O_3 layer by natural oxidation. Assuming that curve **A** consists of two components, Cr and Cr_2O_3 spectra, the thickness of the surface Cr_2O_3 layer can be calculated and was estimated to be about 40 Å. From these results, it is concluded that we can analyze the near-

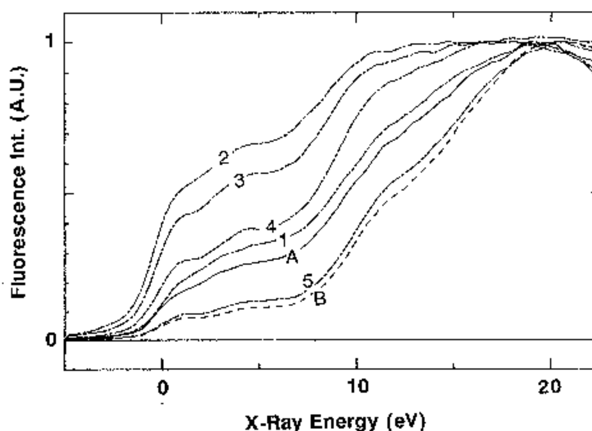

Fig.4

Near - edge absorption spectra around the critical angle. The numbers in the drawing correspond to the glancing angles shown in Fig.2. (1: 5.05 mrad; 2: 8.12 mrad; 3: 9.33 mrad; 4: 14.18 mrad; 5: 5 deg.) A and B are the same as in Fig.3.

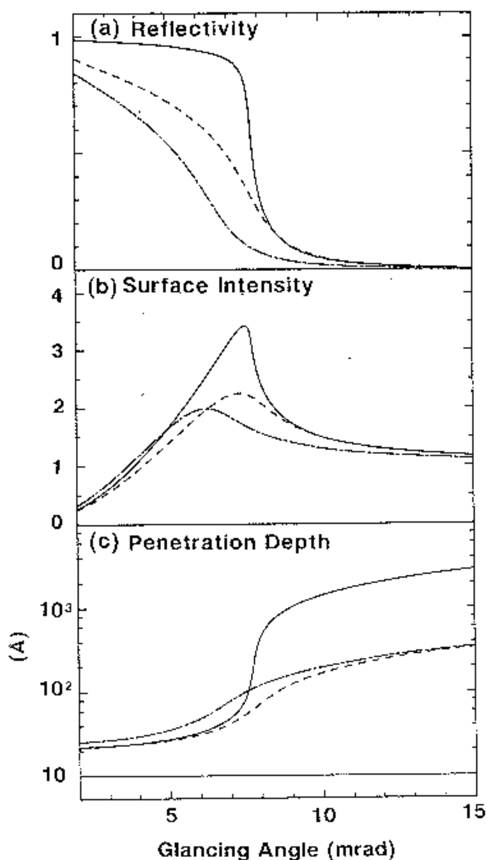

Fig.5

The calculated angular dependence of the reflectivity (a), surface X-ray intensity; (b), and penetration depth; (c) for pure chromium metal near the absorption edge. Calculation was made for +41 eV from the absorption edge (broken line), -22 eV (solid line), and +1 eV (dot-dash line). Anomalous scattering factors were taken from the table[14] for the calculation of the refractive index.

surface layer separated from the bulk material information by using the grazing incidence condition.

Generally, total - reflection experiments are affected by the significant change in anomalous dispersion factors near the absorption edge.[15,16] Figure 4 shows a series of near-edge spectra around the critical angle. They are strongly distorted from the real absorption spectra. To understand the essentials of the situation, it is convenient to consider a pure, homogeneous Cr metal sample. Figure 5 shows the calculated results of the angular dependence of the reflectivity, surface intensity and penetration depth for the three incident energies near the edge. It is clearly seen that they have strong energy dependence especially near the critical angle. Since the fluorescent intensity is largely proportional to the product of the surface intensity and the penetration depth, the low energy side of the absorption spectra is relatively enhanced compared with the high energy side, consequently deforming the shape of the spectra. Therefore, careful analysis is needed when the absorption spectrum is measured near the critical angle.

SUMMARY

The GIF technique using SR is a promising tool for near-surface characterization. Not only trace determination and depth profiling, but also chemical state analysis can be performed non-destructively. The chemical nature of the near-surface is analyzed clearly separated from the bulk-material information using an extremely low glancing angle.

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