ANALYSIS OF SPECIFIC INTERFACES IN THIN FILMS BY X-RAY FLUORESCENCE USING INTERFERENCE EFFECT IN TOTAL REFLECTION

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ABSTRACT

It has been proposed that the interference effect in grazing incidence/exit X-ray fluorescence can be used as an analytical tool. Though these total reflection related measurements have been widely used because of their inherent high sensitivity to the surface of materials, the interference in case of thin films is most likely to be considered difficult to analyze. The present paper describes the use of the interference effect to provide additional capability to enhance information on a specific interface of a thin film. Detailed interpretation of the angular resolved fluorescence tells us at which interface an element of interest is localized. It can be applied to the thin film of only a few layers or non-periodic multilayers where a regular standing wave is not generated.

INTRODUCTION

Grazing incidence and exit X-ray techniques using total reflection have been used extensively for characterization of material surfaces and thin films.1) As is often the case in multilayers, specular reflectivity, fluorescent X-rays and other signals from thin films sometimes show a complex angular dependence because of the interference effect.2-6) This is due to the strong modulation of the X-ray electric field in a film caused by multiple reflection of incident X-rays at each interface. In addition, in the grazing exit case, fluorescent X-rays generated in a thin film interfere during exit process, and exhibit a similar angular dependence.7,8) While specular reflectivity provides information on layer thickness and surface/interface roughness, angular resolved X-ray fluorescence gives the elemental depth

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distribution. This is because the penetration depth, or more exactly, the internal X-ray electric field intensity distribution is a function of the angle.[9,10] The depth profile of impurity elements can be determined, when the sample is assumed to be a uniform material (no interference, evanescent wave)[11,12] or a periodic multilayer (extreme case of interference effect, standing wave).[13,14] However, a non-periodically layered thin film, which is of practical importance to science and industry, has not been considered as a good target because of the complicated appearance of the interference effect. In the present paper, use of the interference effect in grazing incidence[15] and exit X-ray fluorescence measurements is described from an analytical point of view for this type of thin film.

INTERFACE SENSITIVE X-RAY FLUORESCENCE MEASUREMENT[15]

The experiment was done using synchrotron radiation on beam line 4A at the Photon Factory, Tsukuba, Japan, in order to get tunable monochromatic X-rays with both high collimation and sufficiently high flux density. Figure 1 shows the equipment used for grazing incidence X-ray fluorescence measurements and its schematical layout. Synchrotron radiation was monochromatized by a Si(111) double-crystal sagittal focusing monochromator. Optical alignment was optimized by the translational and rotational motion of the sample stage. Reflectivity and fluorescence intensities were measured by two ionization chambers and a Si(Li) detector . Measurement was done in air.

In general, X-ray fluorescence spectra depend on the angular position in the grazing incidence X-ray experiments. Figure 2 shows the angular dependence of fluorescent intensities of a copper[235Å]/gold[500Å] thin film on a silicon substrate, which is prepared by the sputtering technique. Extremely small quantities of iron and titanium are evaporated as

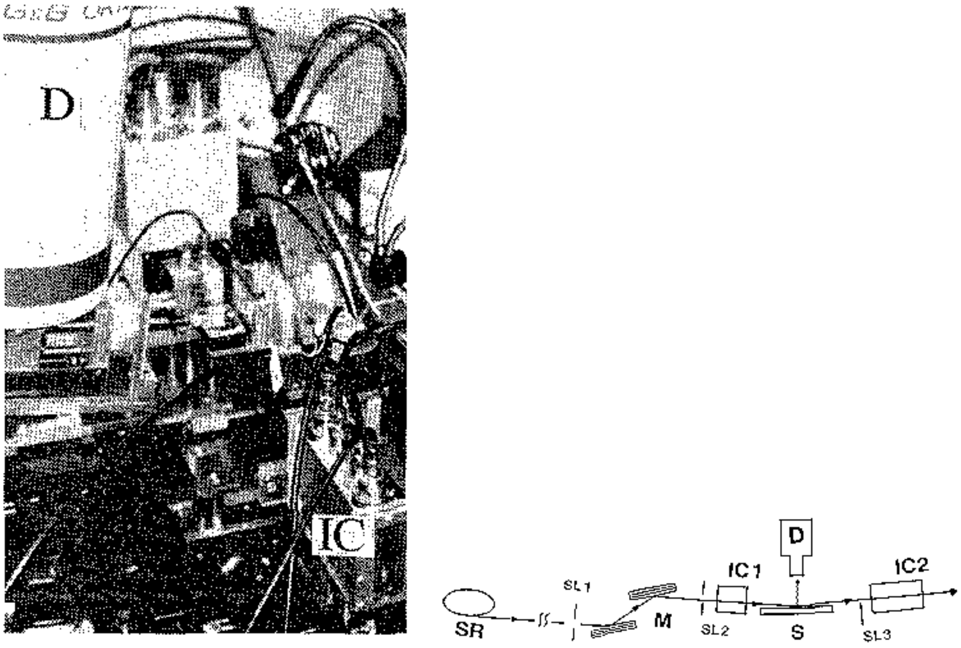

Figure 1. Schematic layout and photograph of the apparatus. SR; storage ring, M; monochromator, IC; ionization chamber, D; Si(Li) detector, S, sample SL; slit.

makers of the surface and the interface between copper and gold layers, respectively. It is obvious that iron fluorescence intensity was strong at about 7 mrad, near the critical angle, because it reflects the X-ray intensity at the surface. However, the titanium intensity dependence is interesting. It peaks at about 7.5 mrad, slightly higher than that of iron. This should not be simply interpreted as a result of the monotonic increase of penetration depth, as both intensities show some oscillation due to the interference effect.

Another example of the interference effect is shown in Figs 3 and 4. The sample is a Cu[100Å]/Ag[230Å]/Au[500Å]/Si thin film, and iron[3Å], chromium[6Å] and titanium[18Å] are put at the surface and each interface respectively. Since incident X-ray energy was set at 8 keV, copper lines were not observed in Fig.3. Iron fluorescence was strong at a low angle, 6.2 mrad, but at 7.7 mrad, the chromium peak became stronger than iron. L-lines from the silver layer were also observed at this angle. At 9.2 mrad, titanium peaks, although weak, became visible, and chromium intensity weakened again. As shown in Fig. 4, the integrated intensity of each peak exhibits a different dependence. Each fluorescent signal peaks at a different angle, and this has distinct advantages when it comes to analyzing specific interfaces. The grazing incidence X-ray fluorescence technique is obviously surface sensitive at a low angle, but at 7.7 mrad, the 1st interface, not the surface, is significantly enhanced, and the 2nd interface is emphasized at 9.2 mrad. This indicates that the detection limit for trace elements at a particular interface can be improved by carefully tuning the glancing angle so as to get the maximum enhancement. Furthermore, when a certain interface is enhanced, the X-ray intensity at the neighboring interface is decreased. When the chromium peaks, iron becomes weak, and as the titanium peaks, chromium becomes weak.

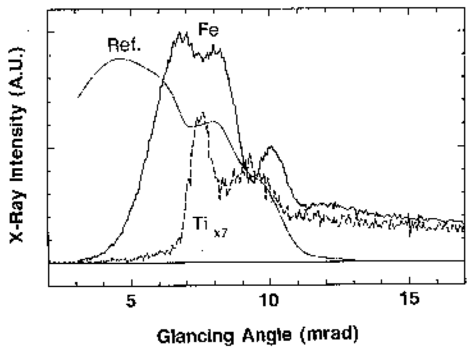

Figure 2. Angular dependence of reflectivity and fluorescence intensities of a Cu[235Å]/Au[500Å] thin film. Fe and Ti signals are emitted from the surface and interface, respectively. Incident X-ray energy is set at 8 keV.

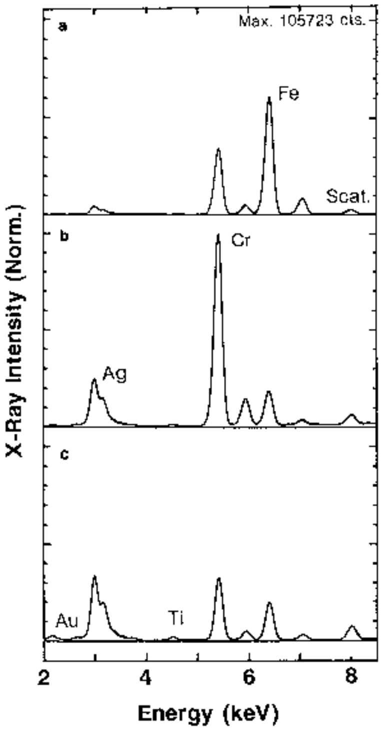

Figure 3. X-ray fluorescence spectra of a Cu[100Å]/Ag[230Å]/Au[500Å] thin film at variety of angles. (a) 6.2mrad, (b) 7.7 mrad, (c) 9.2 mrad.

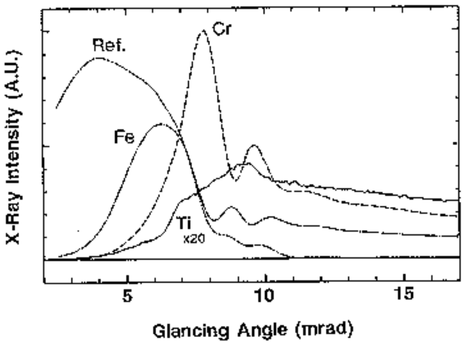

Figure 4. Angular plot of reflectivity and integrated fluorescence intensities of iron, chromium, and titanium from the surface and interfaces of a Cu/Ag/Au thin film.

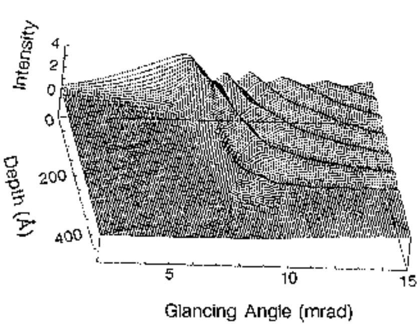

Figure 5. Calculated internal X-ray intensity distribution in a Cu/Ag/Au thin film. It is clearly seen that the intensity oscillates because of the interference effect.

ANALYSIS OF INTERFERENCE EFFECT

To quantify these experimental results, some calculations have been made. Figure 5 shows the calculated intensity distribution of the internal X-ray electric field for a Cu[100Å]/Ag[230Å]/Au[500Å]/Si, and is expressed as a function of both depth and glancing angle. It is essentially based on the Parratt's recursive formulation, considering the boundary condition of the incoming and reflecting electric field at the interface. Interference oscillation can be understood visually by this 3D image. It depends sharply on both depth and angle. As is more clearly shown in the other plot, Fig.6, the intensity at 7 mrad is highest at the surface and exponentially decreases. This angle is therefore still in the evanescent wave region because of shallow penetration. However, at 8 mrad, the distribution begins to change because of the interference effect. The oscillation of the wave becomes clear at 9 mrad and further changes at 10 mrad. One can see that the interference effect causes oscillation of intensity at the surface and interfaces as the angle increases, and each of them shows a different dependence. Such an angular change of electric fields has some similarity to that of the standing wave, but it is important to note that the interference effect is observed for thin films with no periodicity and cases where there are fewer layers.

Figure 7 shows the calculated surface and interface intensity. This corresponds quite closely with the experimental fluorescence data shown in Fig.4 . Some differences between calculation and experiment, for example, the split peaks of the 1st interface intensity and a steep threshold of the 2nd interface, might be qualitatively explained by the effect of interface roughness, or chemical diffusion in the sample used in the present experiment. It is confirmed that each curve peaks at a different angle, and interface intensity then weakens at the neighboring interface peak. This means that the distinction of neighboring interfaces is possible. Where impurities are segregated at the interface due to diffusion or something similar, as is often the case of thin films in practice, this technique would tell us at which interface the element exists, and whether it is either at the top or bottom of the layer.

GRAZING EXIT CASE

The grazing exit fluorescence technique is complementary with grazing incidence technique. Becker et al. reported on reciprocal theorem for X-ray experiments, and showed essentially that surface information could be obtained by extremely shallow take off angle

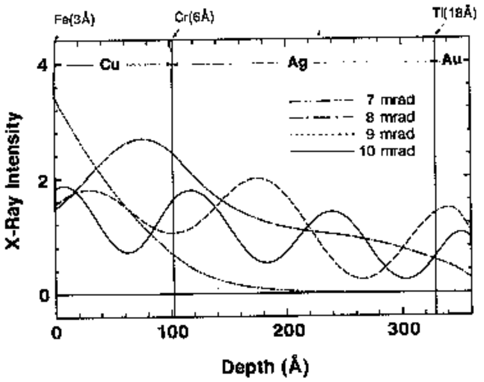

Figure 6. Another plot of calculated internal X-ray intensity distribution as a function of depth. The intensity at the surface and the interfaces sharply depend on the glancing angle.

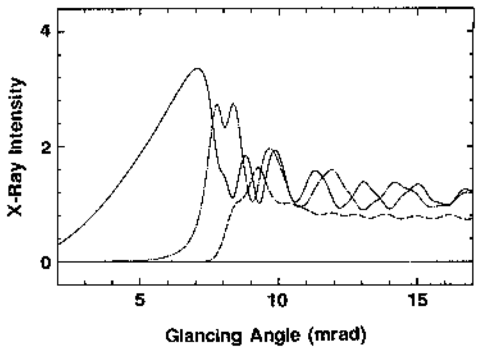

Figure 7. Calculated angular dependence of X-ray intensity at surface (solid line), 1st (broken and dotted line) and 2nd interfaces (dashed line).

arrangement.[16] In fact, the interference effect of fluorescent X-rays has been observed in the same way as the grazing incidence measurements. One of the advantages of a grazing exit arrangement is spatial resolution.[17] If we use a synchrotron micro beam, the spatial resolution is around 1 micron,[18] while that of grazing incidence experiments is around 1 cm. This means that one can get an elemental map of each interface by applying the present enhanced interface detection to the grazing exit measurements.

We tried to combine K-B mirror optics and grazing exit experiments; however, it was found that the intensity was not sufficient to get a signal from trace components in the sample. In the present study, beam size was adjusted to 1mm × 1mm, and a pair of Si/W multilayers was employed as a monochromator to get strong incident X-rays. A Si(Li) detector was used with a narrow slit to detect fluorescent X-rays with good angular resolution. Figure 8 shows the angular plot of the surface (iron) and interface (chromium) signals from a Cu[100Å]/Ag[230Å]/Au[500Å] thin film. The intensity was still weak, and we could not measure titanium fluorescence from the Ag/Au interface. However, it can be clearly seen that

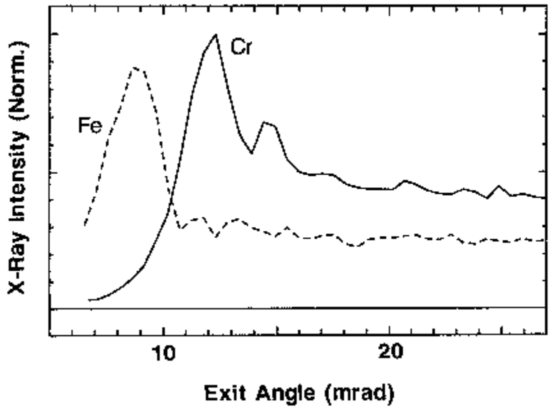

Figure 8. Angular plot for the grazing exit measurements of a Cu/Ag/Au thin film.

the iron and chromium signals show a very similar dependence compared with the grazing incidence results shown in Fig.4. Though there are some small changes because of differences in X-ray energy, this essentially indicates that interface analysis is possible using the grazing exit technique as well.

SUMMARY & ACKNOWLEDGMENTS

In conclusion, the interference effect observed in grazing incidence and exit fluorescence experiments can be used for interface analysis. It is possible to obtain X-ray fluorescence spectra emphasizing a certain interface. One can determine at which interface the element of interest is localized. When a grazing exit arrangement is employed, interface analysis with good spatial resolution is possible. The 3rd generation synchrotron19) will facilitate such measurements.

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