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Grazing-Exit X-Ray Spectrometry for Surface and Thin-Film Analyses

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Electron-probe x-ray micro analysis (EPMA) and particle-induced x-ray emission analysis (PIXE) were performed under grazing-exit conditions. To control the exit angle (take-off angle), a new sample holder having a stepping motor was developed for grazing-exit EPMA. A carefully polished surface of a stainless-steal sample was measured. The surface of stainless steel is normally covered with a thin native oxide layer. The intensity ratio of Cr K_α to Fe K_α increases significantly at the grazing angle, becoming about 5-times larger at 0.2˚ than at 40˚. This result indicates that grazing-exit EPMA is useful for surface analysis. In addition, a new PIXE equipment was developed for grazing-exit x-ray measurements. The sample is fixed and the x-ray detector is moved by applying a linear stage. Preliminary experimental results of grazing-exit PIXE are also shown.

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The measurement of characteristic x-rays at grazing-exit (small take-off) angles is called grazing-exit x-ray spectrometry (GE-XRS). GE-XRS has a potential for localized surface analysis. This means that localized analysis is possible by using an exciting beam of small diameter, and that surface analysis is also possible by applying a grazing-exit arrangement for x-ray measurements, as previously described.[1] A simple explanation for surface analysis by GE-XRS is that the observation depth is changed by a change in the exit angle. The observation depth decreases drastically below the critical angle for total reflection of the characteristic x-rays.

Up to now, the grazing-exit technique has been applied mainly to x-ray fluorescence (XRF);[2-4] however, it has rarely been applied to other x-ray analytical methods, such as electron probe microanalysis (EPMA) and particle-induced x-ray emission (PIXE). Compared with XRF, a micro beam can be easily used in EPMA. PIXE is also very promising for trace analysis, because the background intensity is quite low. EPMA and PIXE have unique characteristics that cannot be found in XRF. Therefore, fundamental research and an improvement in the experimental setup for grazing-exit EPMA (GE-EPMA) and grazing-exit PIXE (GE-PIXE) should be performed. In this paper, the status of grazing-exit EPMA and grazing-exit PIXE studies is described. Future work is also discussed.

GE-XRS

Comparison with grazing-incidence and grazing-exit arrangements in x-ray analysis

To understand the grazing-exit technique, it is most simple to compare it with the grazing-incidence mode, which has been applied in many XRS methods. When x-rays irradiate a flat solid surface at grazing-incidence angles of less than the critical angle for total reflection, they are totally reflected, as shown in Fig. 1(a). That is, the reflectivity becomes approximately unity; as a result, the penetration depth of the incident x-rays becomes quite small. Consequently, grazing-incidence x-ray spectrometry is useful for a surface-sensitive analysis. The grazing-incidence experimental geometry is applied in various x-ray analytical methods, such as XRF and x-ray photoelectron spectrometry (XPS). They are called total-reflection XRF (TXRF)[5,6] and total-reflection XPS (TRXPS).[7] The merit of TXRF is a high surface sensitivity with low background using an energy-dispersive x-ray detector (EDX).

The drawback of grazing-incidence is poor lateral resolution, because the incident x-rays irradiate the whole sample surface at small incident angles. A simple and rapid surface-analysis of a specified region is demanded in many practical cases. The grazing-exit arrangement shown in Fig. 1(b) enables one to perform surface analysis of small regions by using a small-diameter probe, because, similarly to grazing-incidence, the analyzing depth becomes several nanometers.[1,8] Another advantage of the grazing-exit arrangement may be that it needs only a small flat region that is analyzed with a small-diameter probe, while the whole sample area should be flat in the grazing-incidence geometry.

Experimental arrangement of GE-XRS

The difference between the conventional XRS and GE-XRS is in the detection angle for the x-ray measurement. In the case of GE-XRS, it should be controlled with an accuracy of about

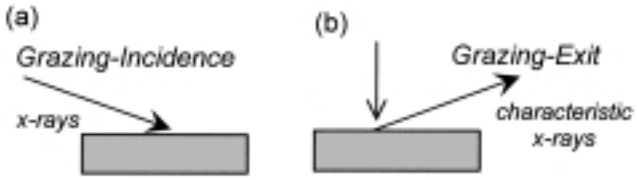

Fig. 1 (a) Grazing-incidence XRS. The x-rays irradiate the sample surface at grazing incident angles, and characteristic x-rays and photoelectrons are detected. (b) Grazing-exit XRS. Characteristic x-rays are detected at grazing-exit angles. X-rays, electrons and ions can be used as excitation probes.

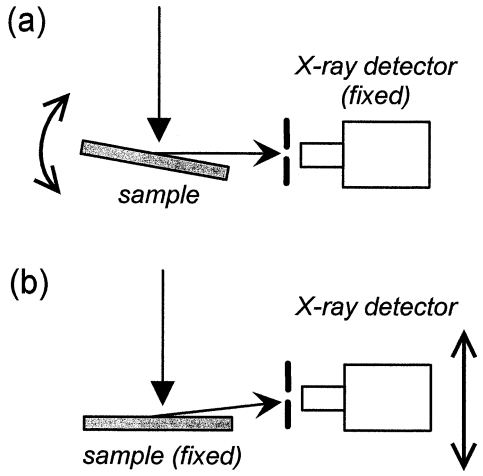

Fig. 2 Experimental arrangements to control the exit angle in GE-XRS measurements. (a) X-ray detector is fixed and the sample is rotating. (b) The x-ray detector is moved and the sample is fixed.

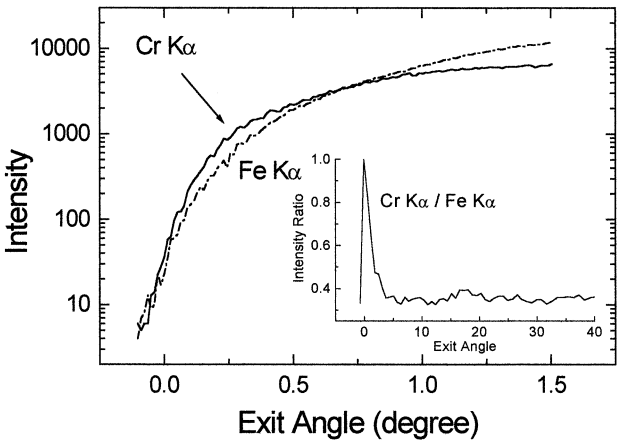

Fig. 4 Intensity variation of characteristic x-rays emitted from a stainless-steel sample as a function of the exit angle, which was changed with a step angle of 0.018˚. The intensity ratio of Cr K_α to Fe K_α is also shown. The GE-EPMA apparatus shown in Fig. 3 was used.

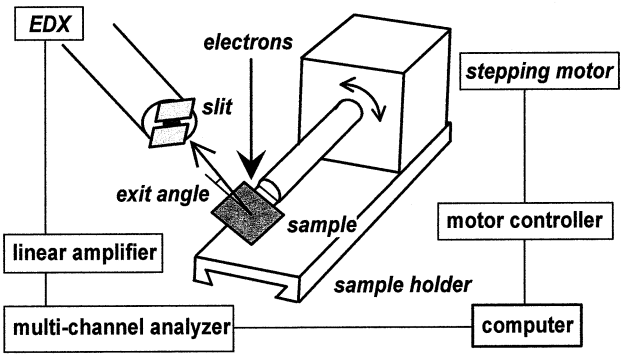

Fig. 3 Experimental setup for GE-EPMA. A sample is attached at the center of the rotation of a stepping motor, which is controlled by a computer. The exit angle is changed by rotating the sample. A slit of 0.5-mm is attached in front of EDX at a distance of about 100 mm from the sample.

0.01˚. To change the exit angle, we can use two types of the experimental setups for GE-XRS. As shown in Fig. 2(a), the exit angle can be changed by tilting the sample. Since the electron (or ion) source and the x-ray detector are fixed in many commercial apparatus, this method is an easy way to change the exit angle. The problem of this method is that the analyzed position probably changes when the sample is tilted, because it is difficult to make the sample surface to be placed exactly at the center of rotation for tilting. This is a serious problem, especially for a localized analysis. Another method to change the exit angle is to move the x-ray detector with a slit by using a linear translation stage, as shown in Fig. 2(b). In principle, this method is the best way to control the exit angle; however, the design of the experimental apparatus must be changed. Since EPMA and PIXE are normally measured under a high vacuum, it may be troublesome to move the detector while keeping the vacuum.

GE-EPMA

Experimental setup

In previous studies,[11-14] the exit angle was changed by manually tilting the sample holder. The minimum step angle was about 0.5˚ and the reproducibility was also not very good. Therefore, a rotating stepping motor was attached to a sample holder,[15] as shown in Fig. 3. This motor was rotated with a minimum step angle of 0.018˚. A slit of 0.5 mm width was fixed in front of a Si(Li) EDX detector. This detector was installed in the EPMA equipment (Superprobe 8621, JEOL) at a direction of 40˚ to the horizontal plane. Thus, the sample was tilted, as shown in Fig. 3. A computer controlled both the stepping motor and the multi-channel analyzer (MCA) to automatically measure the exit angle dependence of the characteristic x-ray intensity. The accelerating voltage was 20 kV and the electron-beam current was 6.0 nA. The exit angle was calibrated by fitting the angle dependence of Si K_α from a Si wafer with the calculated curve.[2]

Results

GE-EPMA was applied for the surface analysis of a stainless-steel sample,[15] whose surface was carefully polished to be a mirror surface. Figure 4 shows the exit-angle dependence of Fe K_α and Cr K_α. The exit angle was changed at 0.018˚ intervals, and the x-rays intensity was measured for 60 s at each angle. Although these x-ray intensities were almost constant at exit angles above 10˚, and Fe K_α intensity was larger than Cr K_α, the Cr K_α intensity was dominant at angles of less than 0.5˚. The intensity ratio of Cr K_α to Fe K_α increases significantly at the grazing exit angle, becoming about 5-times larger at 0.2˚ than at 40˚, as shown in the inset of Fig. 4. Since the surface sensitivity increases at the grazing angle, this result indicates that Cr is enriched at the surface of the stainless steel. This agrees well with the fact that the surface of stainless steel is covered with a chemically stable chromium oxide layer.

An ultra-thin Co film (5 nm) on an Si wafer was also measured by GE-EPMA.[15] The Si K_α intensity decreased dramatically with decreasing the exit angle, while the x-ray intensity of Co K_α decreased monotonically. As a result, the Co K_α line was dominant at grazing angles of less than 0.5˚, indicating that the GE-EPMA method has a possibility for the analysis of thin films having a thickness of 5 nm, or even less.

Figure 5 shows the GE-EPMA result of a layered sample of Ni (10 nm)-Mn (20 nm)-Au (100 nm)-Si wafer. The Ni K_α x-rays emitted from the top layer are dominant at exit angles of

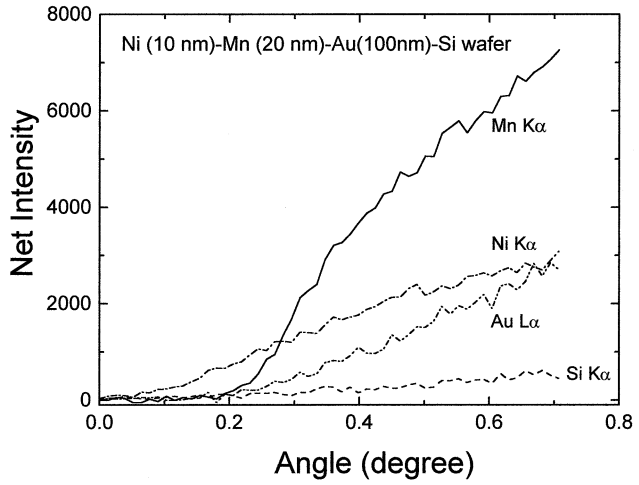

Fig. 5 Intensity variation of characteristic x-rays emitted from the layered material of Ni(10 nm)-Mn(20 nm)-Au(100 nm) on an Si wafer as a function of the exit angle, which was changed with a step angle of 0.018˚. The GE-EPMA apparatus shown in Fig. 3 was used.

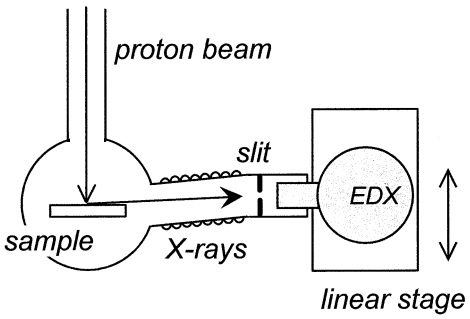

Fig. 6 Experimental setup for GE-PIXE. The proton beam (1 MeV, 300 nA) irradiated the sample surface at the normal angle. The characteristic x-rays were detected by an EDX, which was attached on a linear stage. A slit of 50-μm was fixed in front of the EDX at a distance of 62 mm from the sample.

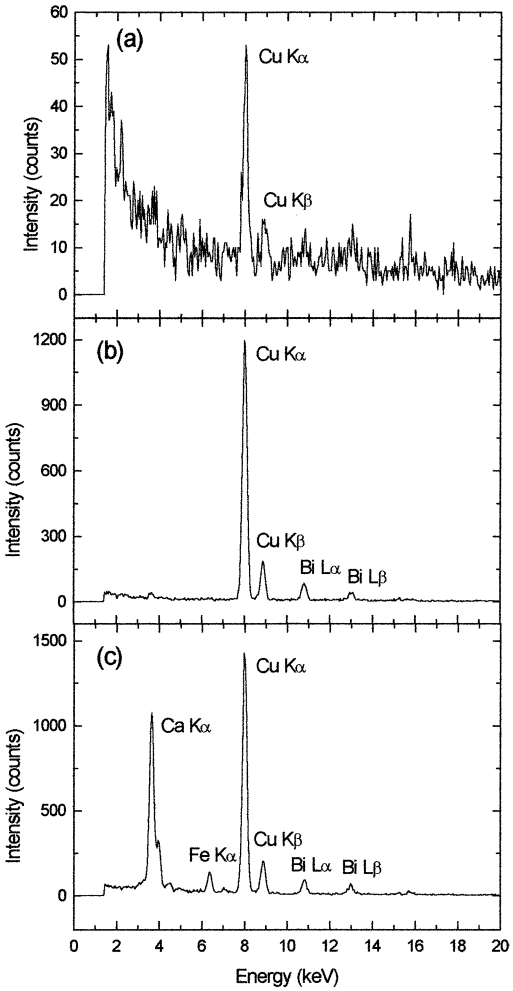

Fig. 7 GE-PIXE spectra taken for a layered sample of Cu(10 nm)-Bi(6 nm) on a glass substrate at the different exit angles of 0.4˚ (a), 1.0˚ (b) and 4.4˚ (c).[16]

less than 0.25˚. Similarly to the GE-XRF analysis, it would be possible to estimate the thickness and density of each thin film by fitting the experimental curves to the theoretical curves.

Future

The experimental arrangement shown in Fig. 2(a) is an easy way to change the exit angle; however, it is almost not possible to set the sample in such a way that the sample position does not change during tilting. Therefore, we intend to construct another experimental setup, shown in Fig. 2(b). In this arrangement, the exit angle is changed by moving an x-ray detector, and the sample is fixed during the measurements; hence, the analyzing position is stable. This is a good experimental condition, especially for small-particle analysis. Therefore, more precise measurements will be possible.

GE-PIXE

Experimental setup

The first GE-PIXE measurement was performed at Amsterdam Free University.[16] The obtained results were very promising for surface and thin-film analyses. The exit angle was controlled by rotating the sample holder. At Tohoku University, GE-PIXE equipment having another experimental arrangement (Fig. 2(b)) was installed in the summer of year 2000. The experimental setup is shown in Fig. 6. A proton beam (1 MeV, about 300 nA) irradiated the sample at the normal angle, and the proton-induced characteristic x-rays were measured at a direction of 90˚ by the EDX. After the measurement, it was confirmed that the sample surface was not damaged by the proton beam under these experimental conditions. In front of the EDX, a slit of 50-μm was attached at a distance of 620 mm from the sample position. The sample vacuum chamber and the EDX were connected by a flexible tube; therefore, the EDX could be moved by using a stepping-motor controlled linear stage. The beam current was also monitored, and the measured x-ray intensity was normalized with this current. The exit angle was calibrated by fitting the angle dependence of Si K_α from an Si wafer with the calculated curve.[2]

Results

Figure 7 is a typical result of a GE-PIXE analysis to demonstrate its potential for thin-film analysis.[16] The PIXE spectra were measured for Cu(10 nm)-Bi(6 nm) layers on a glass substrate at exit angles of 0.4˚, 1.0˚ and 4.4˚, respectively. These spectra were taken at the Amsterdam Free University by

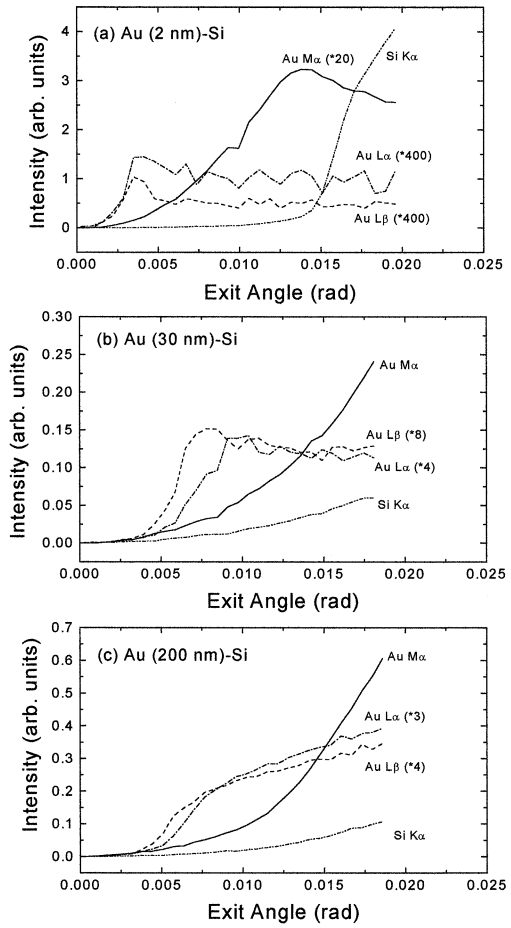

Fig. 8 Intensity variations of characteristic x-rays emitted from thin films of Au (2 nm) (a), Au (30 nm) (b) and Au (200 nm) (c) on Si wafers as a function of the exit angle. The GE-PIXE apparatus shown in Fig. 3 was used.

tilting the sample (see Fig. 2(a)). At an exit angle of 0.4˚ (Fig. 7(a)), only the Cu K_α x-ray peak emitted from the top Cu layer could be observed. In Fig. 7(b), the Bi L lines from the second layer begin to be observed. Finally, in Fig. 7(c), Ca K_α x-rays from the glass substrate appear. By changing the exit angle, depth profiling for layered materials can be non-destructively performed.

The GE-PIXE method was also applied to an analysis of aerosols deposited on a sample carrier.[16] At an exit angle of 4.4˚, it was difficult to recognize the characteristic x-rays of Ca K_α, Ti K_α and Zn K_α, emitted from aerosols, due to a large continuous x-ray background. In contrast, these x-ray peaks were clearly observed with a low background in the PIXE spectrum taken at 0.4˚. It was found that the detection limit for Ca K_α can be improved by a factor of 7 under the grazing-exit conditions.

Au thin films of 2, 30 and 200 nm on Si wafers were measured by the new GE-PIXE equipment shown in Fig. 6. The angle dependences of the characteristic x-rays for these samples are shown in Fig. 8. Au samples are useful to check the performance of this new GE-PIXE system, because they have been well investigated by other GE-XRS methods. When the Au thickness is very thin, less than 5 nm, the exit-angle dependent curve has a peak at an angle of about 3 mrad, which corresponds to the critical angle for total reflection of the Au characteristic L lines on an Si substrate. As the Au thickness increases, the position of the maximum shifts to a large angle, because the critical angles for the Au lines on Au substrate are larger. The preliminary experimental results shown in Fig. 8 agree well with this theoretical consideration.

Future

The results shown in Fig. 8 were not obtained by a completely automatic method. To obtain good repeatability, reproducibility, and accurate results, an automatic measurement system is indispensable. An analytical system to control MCA, a stepping motor of the linear stage and a monitor of the beam current will be created in the near future. Then, the analytical performance of GE-PIXE method will be checked using standard materials. The advantage of PIXE is extremely low background. Utilizing this merit, ultra-thin films, biological samples and small particles will be analyzed by GE-PIXE.

Acknowledgements

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