Grazing-Exit Electron Probe Microanalysis (GE-EPMA)

Kouichi Tsuji

Graduate School of Engineering, Osaka City University, PRESTO, JST

Introduction

Electron probe microanalysis (EPMA or SEM-EDS) is an indispensable analytical method for materials development or various inspections. The electron probe microanalyzer (EPMA), a general-purpose surface analyzer, allows observation of surface shapes of specimens using a finely focused electron beam. It can also perform qualitative and quantitative analysis of constituent elements in the specimen by detecting characteristic X-rays emitted from the specimen irradiated with the electron beam. The X-ray generation occurs in a region measuring several micrometers deep in many cases, as will be explained later. Since this can be regarded as a local region, the EPMA can offer micro-area element (qualitative) analysis. In addition, various correction methods have been devised for quantitative analysis through many studies so far, making it possible for the EPMA to provide highly accurate quantitative analysis. Furthermore, improvements in analytical software and the method of operating the EPMA have made it easy to use.

On the other hand, the EPMA has several demerits: a) the specimen is susceptible to damage due to electron-beam irradiation, b) the specimen has to be placed in vacuum, c) the analysis region is of the order of micrometers (not nanometers), d) it is difficult to analyze micro-volume specimens. To overcome demerits a) and b), the low-vacuum SEM and the environmental SEM have been developed, and with these developments, the application fields of the EPMA have broadened.

As shown in **Fig. 1 (a)**, since an electron beam is scattered by a solid specimen, even when the diameter of the electron beam irradiating the specimen surface is only several tens of nanometers, the characteristic X-rays emitted by the specimen come from a region several micrometers in depth within the specimen. As miniaturization of semiconductor devices and research on nano-science increasingly advance, analysis of a very minute region is increasingly required. Thus, although several-micrometer-order analysis may meet users' needs depending on the type of specimens, measures to support analysis of smaller regions are needed. Since the analysis depth depends on the accelerating voltage of the electron beam, the application of low accelerating voltages limits the characteristic-X-ray generation region to a minute region near the specimen surface. However, the energies of the X-rays are less than those of the accelerated electrons; this causes a new problem: the use of analytical X-ray lines is limited. This is particularly serious for SEM-EDS that has low energy resolution. The next section introduces the grazing-exit X-ray analysis method, which has the possibility for improving the analysis region and micro-volume analysis.

Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan
E-mail : tsuji@a-chem.eng.osaka-cu.ac.jp

Grazing-Exit X-ray Analysis

In many cases, conventional EPMA or SEM-EDS detects characteristic X-rays with a relatively large take-off angle of 30 to 45°. In particular, an EDS detector is placed as near as possible to the specimen so that the X-rays are measured with a larger solid angle. Thus, the analysis depth extends to the order of micrometers, as shown in **Fig. 1 (a)**. Let me repeat that many specimens afford such a micrometer-order deep analysis, making EPMA a useful method for localized analysis. However, if it is necessary to obtain information on the region from the surface to a depth of a few nanometers, conventional EPMA has difficulty in analyzing this limited region. A method to break through this obstacle is grazing-exit X-ray analysis, which measures X-rays at very small take-off (grazing-exit) angles from the specimen surface, as shown in **Fig. 1 (b)** [1-4]. To limit the solid angle, a slit is attached between the specimen and the detector, actually, on the top of the EDX detector. This instrument layout enables one to measure only characteristic X-rays emitted from the near-surface regions: that is, the X-rays emitted from the deep regions are not detected by the EDX detector due to strong X-ray absorption in the specimen and refraction effects at the specimen surface (**Fig. 2**). Compared to conventional EPMA, the intensity of the detected X-rays is lower; however, an important point for surface analysis is the ratio of the signal intensity from the surface to that from the bulk. The grazing-exit analysis (**Fig. 2**) greatly enhances surface sensitivity in X-ray measurement. For the instrument configuration needed for this grazing-exit analysis, refer to different papers [3, 5, 6].

In this method, precise take-off (exit) angle control is of crucial importance. To put it simply, this is achieved by tilting the specimen stage in the direction of the X-ray detector [6]. Another way of doing this is to move the X-ray detector or the specimen stage up and down [5, 7]. For providing a slit, two pieces of metal are affixed on the top of the EDX detector, or an aperture is placed between the specimen and the detector. Therefore, a special device is not needed and one can perform grazing-exit X-ray analysis using a commercial EPMA or SEM-EDS.

Application Examples of Grazing-Exit X-ray Analysis to EPMA

Surface analysis

Figure 3 shows the dependence of the analysis depth on exit angle for characteristic X-rays (in this case, Si*Kα* from a silicon wafer) [1, 2]. It is shown that a certain critical angle exists, and that the analysis depth becomes as shallow as a few nanometers at angles below the critical angle. Thus, it is possible to perform surface analysis by setting the exit angle to this range of angles and by measuring the X-rays. Although it is not easy to precisely determine the critical angle, when X-ray measurement or mapping measurement is carried out while the specimen is tilted to decrease the exit angle, the intensity of characteristic X-rays changes at a certain angle, showing the transitional behavior from bulk analysis to surface analysis. **Figure 4** shows an example of observation of the contamination on a specimen surface using the grazing-exit X-ray analysis [8]. It is found that the contamination on the surface is well observed with high sensitivity at small exit angles, which was not realized at conventional large exit angles.

Reduction of background

An important point for observation and analysis of trace components is signal-to-background intensity ratio (S/B ratio), that is, the enhancement of the ratio of the signal intensity of characteristic X-rays to the background

Table 1 Analysis regions within the specimen estimated by Monte Carlo simulation of electron trajectories (unit: nm)
(The horizontal arrow in Fig. 1 indicates the size.)

		Electron acc. voltage (kV)		
		5	10	20
Si	Conv.	311	899	1415
	GE	68	122	171
Cu	Conv.	124	294	828
	GE	84	121	148
Au	Conv.	85	184	421
	GE	62	112	190

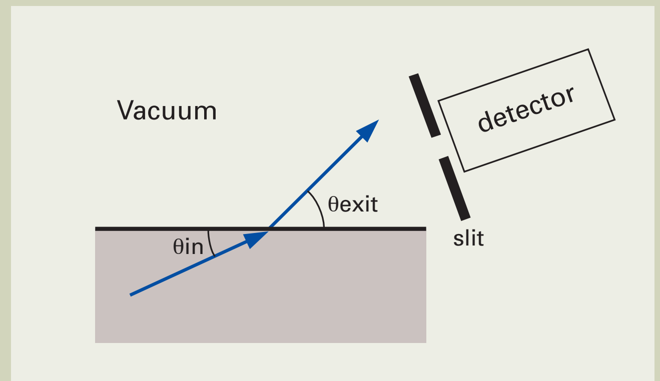

Fig. 2 Refraction effects of X-rays at the specimen surface.

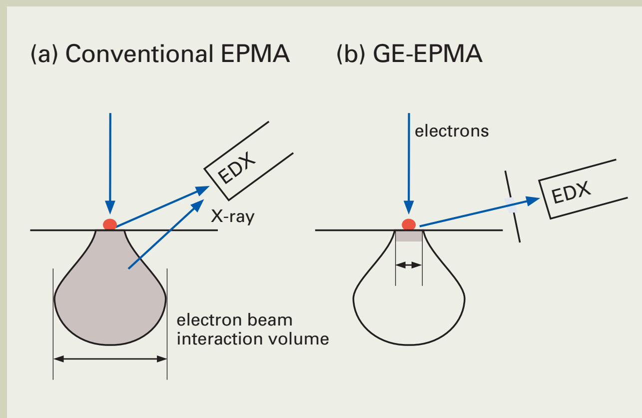

Fig. 1 Schematic of EPMA analysis by conventional EPMA and grazing-exit (GE) EPMA. The specimen is assumed to be a micro particle on a flat substrate.

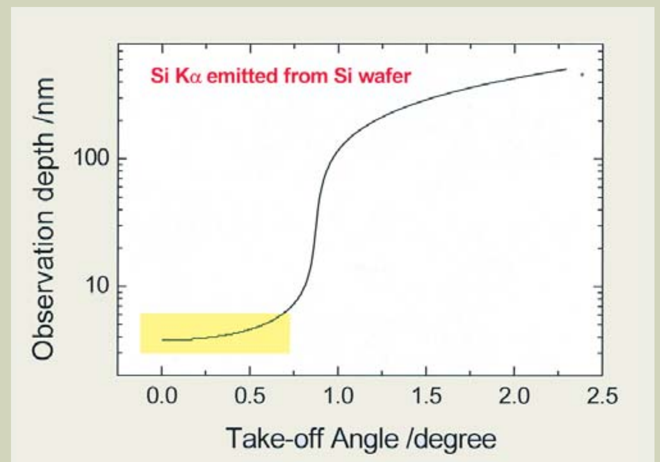

Fig. 3 Exit-angle dependence of analysis depth under grazing-exit conditions. This data is obtained by calculations of SiKα generated from a silicon wafer.

intensity. The reduction of this background enables one to perform micro-volume analysis and surface analysis. **Figure 5** shows the energy distribution of the continuous X-ray background from a silicon wafer at three different exit angles [9, 10]. Since the characteristic X-rays from Si are only observed at 1.74 keV and no characteristic X-rays appear in the energy region higher than this energy, the X-ray spectrum of Si is useful for measuring the continuous X-ray background. As indicated in **Fig. 5**, as the exit angle decreases, the continuous X-ray intensity also decreases. In particular, the decrease in continuous X-rays is noticeable in the low-energy region. This phenomenon seems to be related to the distribution of continuous X-ray generation in the depth direction; hence, it is possible to perform surface analysis at low exit angles (grazing-exit angles) with low background.

Thus, under grazing-exit conditions, the characteristic X-rays can be measured with high sensitivity even from the top surface of a thin film. For example, in the analysis of a Ti-Cr alloy film 4 nm thick formed on a Au film on a Si substrate, at an exit angle of 40°, the characteristic X-rays from Ti and Cr were not observed due to high continuous X-ray background; however, decreasing the exit angle resulted in clearly revealing Ti and Cr on the top surface due to the reduction of the background [11].

Improvement in lateral resolution in the specimen

As shown in **Fig. 1 (a)**, in conventional EPMA, even when a small electron probe with a diameter of 10 nm is used, the analysis region broadens due to the diffusion of electrons in the specimen. However, the broadening of the analysis region in the lateral direction is more noticeable in the deep regions than in the near-surface regions (although the difference in broadening is dependent on the specimen). That is, in the near-surface regions, the incident electrons do not broaden very much in the lateral direction.

This phenomenon can be estimated by Monte Carlo simulation of electron trajectories. A Monte Carlo simulation study was performed on the variation of the characteristic-X-ray generation region in the specimen with various accelerating voltages of the electron beam and constituent elements in the specimen. Especially, in order to evaluate the spatial resolution in the lateral direction for element analysis, the maximum diffusion width of the electron beam in the specimen was obtained under conventional EPMA conditions as shown in **Fig. 1 (a)**, then the diffusion width near the surface under the grazing-exit EPMA conditions (in **Fig. 1 (b)**) was estimated [12]. **Table 1** shows the estimated result. It was found that the grazing-exit EPMA drastically improves lateral resolution, more than ten times that with conventional EPMA. This improvement seems to be particularly noticeable for a matrix specimen of light elements. At present, an experimental study on the improvement in lateral resolution is in progress.

An application to the analysis of a micro particle specimen

It is well known that a trace amount of impurities on a semiconductor wafer greatly affects the performance of the semiconductor device. The increasing integration of semiconductor devices makes it necessary to address impurities at sizes smaller than a micrometer, requiring a method for analyzing such a micro particle. Other analysis methods such as Auger electron spectroscopy can be applied in some cases; however, the EPMA method is still effective considering the fact that it excels in quantification and that it can measure a particle of micrometer to sub-micrometer size.

However, as shown in **Fig. 1 (a)**, when the particle size becomes smaller, the electron beam can easily penetrate the particles and enter the wafer, generating high-intensity X-rays from the wafer. Therefore, if the particle contains the same element (Si, in a case of silicon wafer) present in the wafer, conventional EPMA measurement cannot distinguish between the Si X-rays that emerge from the

wafer and those from the micro particle. Moreover, as mentioned above, because the continuous X-ray background increases, it becomes difficult to analyze the trace elements in the micro particle. Consequently, we studied whether single-particle analysis is possible or not using the grazing-exit X-ray analysis method [13].

Figure 6 shows an X-ray spectrum obtained by an EDS measurement for a particle of Fe_2O_3 (particle diameter: about 1 μ m) on an Au thin film on a silicon wafer. **Figure 6 (a)** shows an X-ray spectrum measured under conventional EPMA conditions, namely a large take-off angle; the characteristic X-rays from the Au and Si under the micro particles appear with high intensities. On the other hand, **Fig. 6 (b)** shows an X-ray spectrum measured at a grazing-exit angle. The characteristic X-rays from Au and Si completely disappear, and only the characteristic X-rays from the Fe_2O_3 micro particles are observed. This shows that single-particle analysis is possible. Other than this analysis, there is a report on an application of the grazing-exit EPMA method to element analysis for an inclusion in a metal specimen [14]. This report shows that it is possible to analyze the inclusion by completely separating it from the matrix after exposing the inclusion in the metal specimen on the surface.

In addition, when this method is applied to a micro particle specimen, the electron beam should be set to the same size as the micro particle or smaller. This is because, if the electron beam size is larger than the particle as shown in **Fig. 7**, the characteristic X-rays generated from places other than the particle make it difficult to analyze the specimen. However, if the grazing-exit EPMA method is applied, restriction on the electron beam size gives no problems; because, even if the electron beam irradiates places other than the micro particle (for example, a substrate beneath the micro particle) and generates X-rays, the grazing-exit condition can prevent detection of these X-rays. **Figure 7** shows X-ray spectra measured under conventional EPMA conditions and grazing-exit conditions [11].

Summary

In the present article, we introduced the grazing-exit EPMA method and presented examples of applications that make use of its merit. On the other hand, a disadvantage of the grazing-exit EPMA method is that the charac-

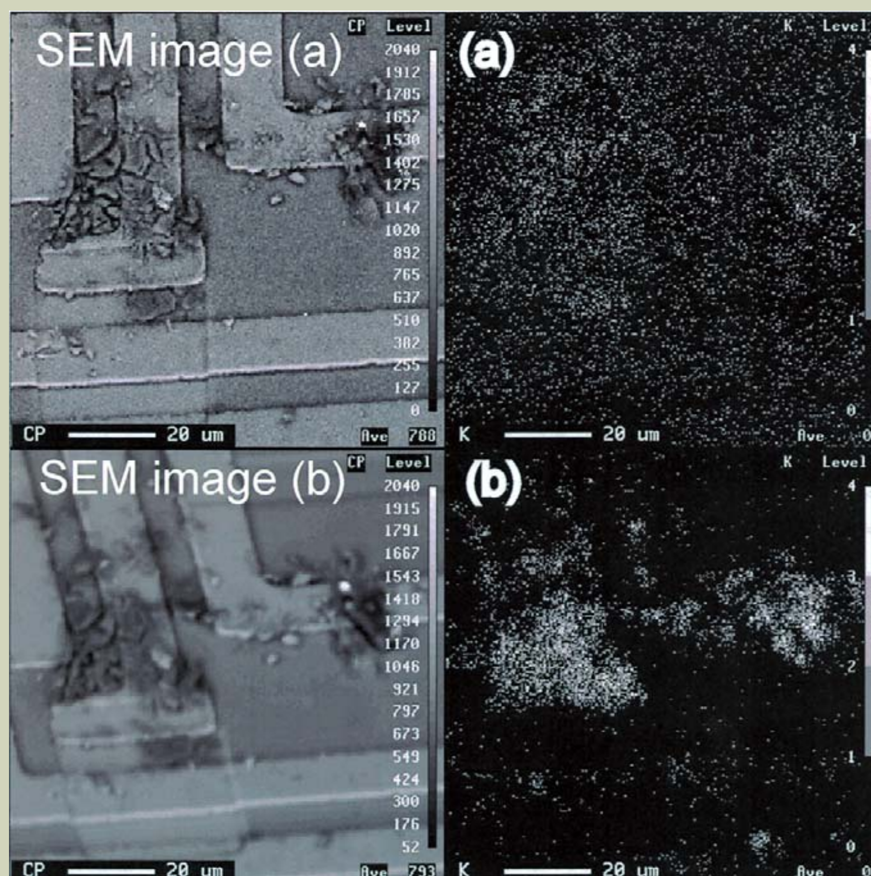

Fig. 4 Element mapping of K from contaminants on the specimen surface. (a) An element map obtained using conventional EPMA. (b) That obtained using grazing-exit EPMA.

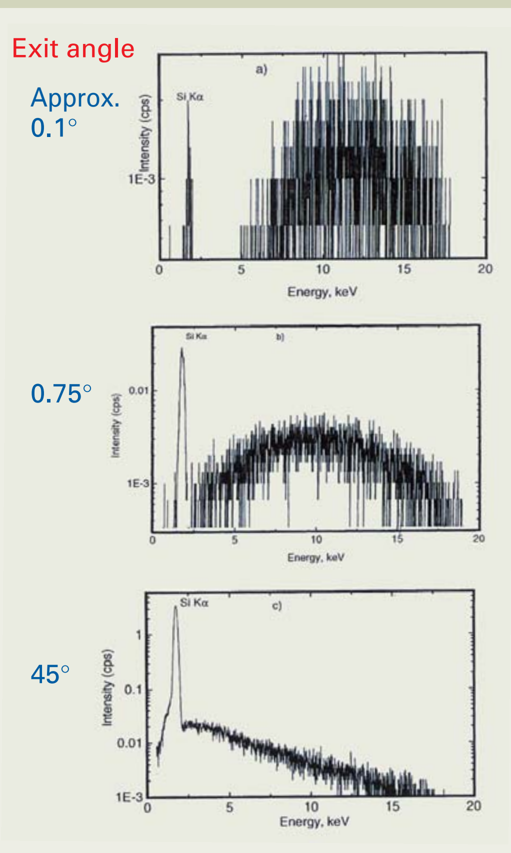

Fig. 5 X-ray spectra of a silicon wafer taken at various exit angles. The difference in energy distribution of the continuous X-ray background is clearly seen.

teristic X-ray intensity is weak. Of course, as mentioned above, the matters of importance are S/B ratio and surface sensitivity; it is wrong to state that the grazing-exit EPMA method has a disadvantage simply because its analysis-line intensity is weak. However, it is necessary to improve measurement efficiency; one method of doing so is to arrange multiple detectors around the specimen. Although the characteristic X-rays emerge in all directions, at present only a portion of them is measured. Therefore, it may be possible to drastically improve the measurement efficiency by using multiple detectors or a ring-shaped detector [2].

Furthermore, as the grazing-exit method has a connection with the total reflection X-ray fluorescence method, the specimen surface in principle must be flat. However, when the specimen consists of micro particles or has an uneven shape, one can also perform the EPMA measurement while keeping the advantages of the grazing-exit X-ray measurement as well as in the flat specimen. Consequently, the requirement of the grazing-exit method for the flatness of specimen is not as severe as that of the total reflection X-ray fluorescence method; from the practical point of view, this grazing-exit method may be applied to many kinds of specimens.

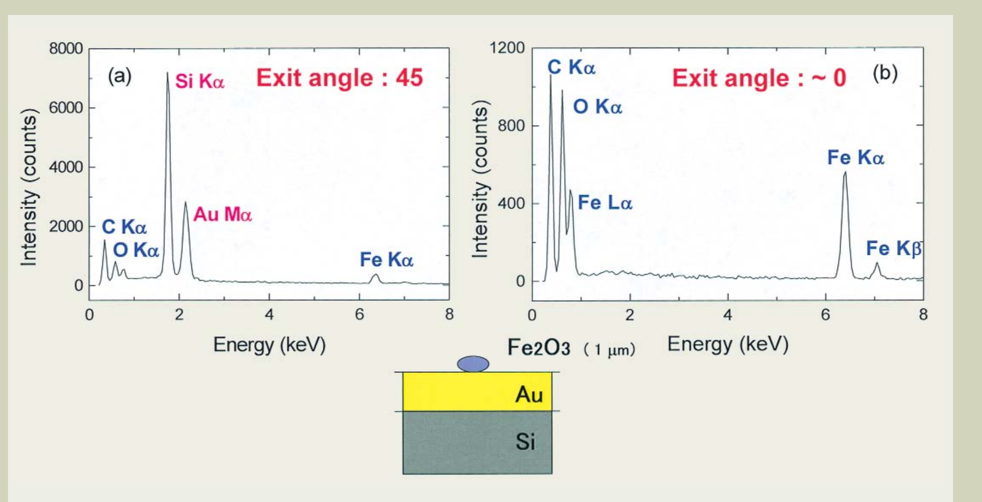

Fig. 6 Example of a single-particle analysis. The specimen is an Fe_2O_3 particle (size: about 1 μ m in diameter) captured on an Au thin film on a Si wafer. (a) X-ray spectrum measured at a take-off angle of 45°. (b) X-ray spectrum measured at an exit angle of nearly 0°.

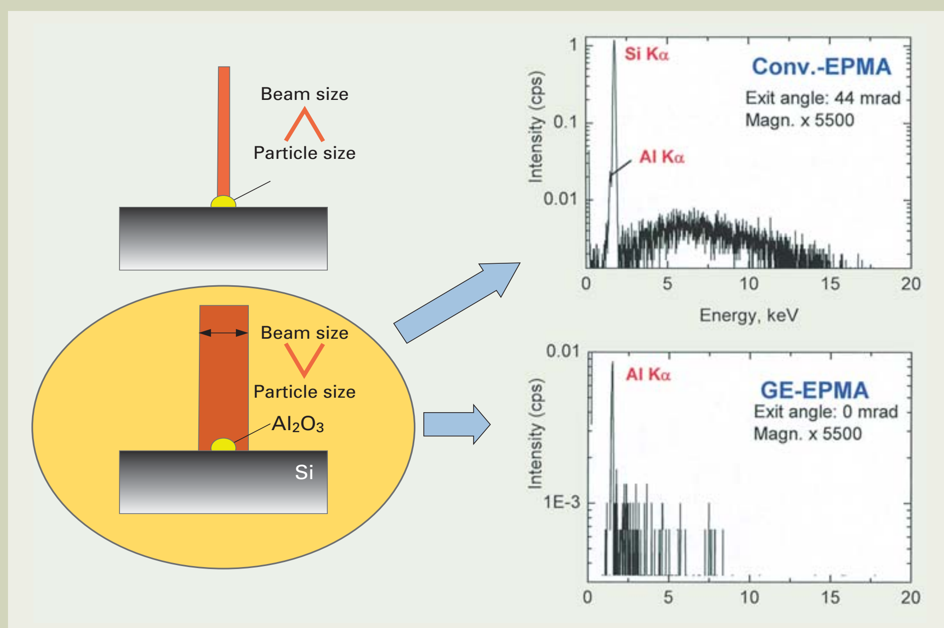

Fig. 7 Relationship between the electron beam size and particle size. An example of measurement is shown on the right when the electron beam size (actually, the region that electron beam scanned) is larger than the micro particle. An X-ray spectrum obtained at a take-off angle of 44 mrad is shown at the upper right. The spectrum shown at the lower right is measured at an exit angle of nearly 0°.

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