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Combination of high spatial resolution and low minimum detection limit using thinned specimens in cutting-edge electron probe microanalysis

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ABSTRACT

The effect of sample thickness on the spatial resolution and minimum detection limit (MDL) has been investigated for field-emission electron probe microanalysis with wavelength dispersive X-ray spectroscopy (FE-EPMA–WDX). Indium gallium phosphide samples thinned to thicknesses of about 100, 130, 210, 310, and 430 nm provided effective thin-sample FE-EPMA–WDX in the resolution range of 40–350 nm and MDL range of 13,000–600 ppm (mass). A comparison of the FE-EPMA results for thin and bulk samples demonstrated that thin-sample FE-EPMA can achieve both higher sensitivity and better spatial resolution than is possible using bulk samples. Most of the X-rays that determine the MDL are generated in a surface region of the sample with a depth of approximately 300 nm. The spatial resolution and MDL can be tuned by the sample thickness. Furthermore, analysis of small amounts of Cl in SiO_2 indicated that thin-sample FE-EPMA can realize a spatial resolution and MDL of 41 nm and 446 ppm at I_{prob}=50 nA, respectively, whereas bulk-sample FE-EPMA offers a resolution of only 348 nm and MDL of 426 ppm.

1. Introduction

Electron probe X-ray microanalysis (EPMA) has become an indispensable technique for trace element analysis of micro-areas in both the material science and industrial fields [1–3]. EPMA systems incorporated with wavelength dispersive X-ray spectroscopy (WDX) are useful analytical tools and are commercially available through JEOL Ltd., Cameca, and Shimadzu Corp. Systems combining energy dispersive X-ray spectroscopy (EDX) with field emission (FE) electron gun scanning electron microscopy (SEM) are also in use and are commercially available through Carl Zeiss, Hitachi, FEI, and JEOL Ltd.

EPMA–WDX offers a higher peak/background ratio and a higher energy resolution than FE-SEM–EDX [3–5]. These advantages allow elemental analysis with a lower minimum detection limit (MDL) and higher precision. FE-SEM–EDX, in contrast, allows multi-element analysis and a short measurement time. Hence, both EPMA–WDX and FE-SEM–EDX can be used for different types of analysis in accordance with their practical advantages. The spatial resolution of EPMA–WDX, available with W or LaB_6 electron guns, is only a few micrometers, while that for FE-EPMA–WDX is approximately 160 nm [6–10], allowing a spatial resolution of FE-SEM–EDX up to 31 nm [11]. However, this difference in spatial resolution between FE-EPMA–WDX and FE-SEM–EDX is considered to be mainly attributable to the difference in the measurement conditions used, that is, the acceleration voltage (V_{acc}) and the probe current (I_{prob}).

The recent miniaturization of materials and device structures has led to an increasing demand for high resolution and high sensitivity elemental analysis [12]. The resolution of an EPMA system is mainly determined by the sum of the diameter of the electron beam on the sample surface and the lateral width of the characteristic X-ray generation region in the sample [1]. For most FE-EPMA–WDX and FE-SEM–EDX systems, the X-ray generation region is much larger than the electron beam size [6,7,10]; therefore, high resolution analysis is generally performed at a lower V_{acc}, which limits the size of the detectable element due to the critical voltage and also degrades the MDL [1–4]. To achieve a better spatial resolution and overcome the critical voltage limitation and degradation of the MDL, the use of a thinner sample and a higher V_{acc} is a promising approach [13,14], as illustrated in Fig. 1.

Sample thinning to about 100 nm or less is generally performed for transmission electron microscopy (TEM) and scanning TEM (STEM) observations [5]. The MDL and spatial resolution of thin-sample TEM/STEM-EDX have been intensively studied [5,15–18]. Quantitative analysis methods for thin samples by EDX were

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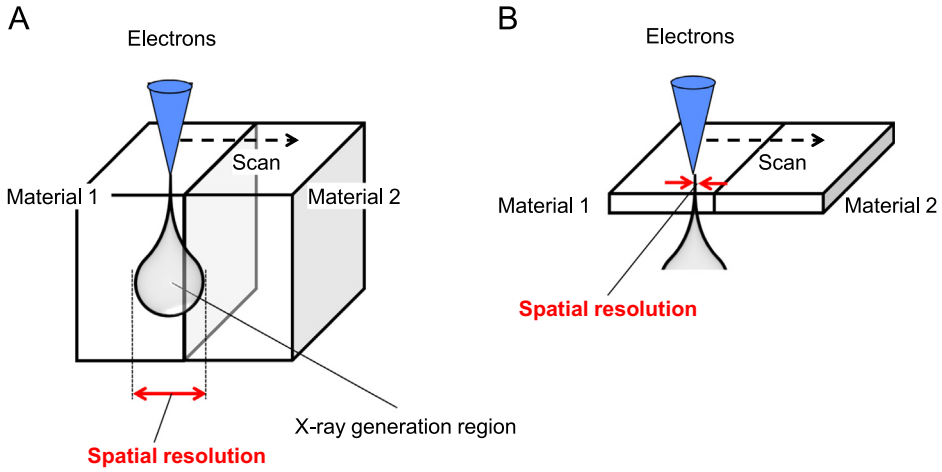

Fig. 1. Concept of spatial resolution improvement in FE-EPMA by sample thinning. A: Bulk-sample FE-EPMA. B: Thin-sample FE-EPMA. A comparison of diagrams A and B shows that sample thinning improves the spatial resolution and the detection sensitivity is worsened due to the reduction in sample volume.

extensively studied in the 1970s when there was an explosive increase in the use of EDX with TEM and SEM [19,20].

However, sample thinning is seldom employed in present-day laboratories that conduct FE-EPMA–WDX and FE-SEM–EDX analysis. The generally accepted reason for this is that sample thinning is considered to significantly reduce both the X-ray signal intensity and degrade the detection sensitivity because the sample volume is reduced [5]. Joy et al. reported that the MDL for thin-sample TEM-EDX was 30,000 ppm (mass) [15], which is much worse than that for bulk-sample EPMA–WDX (100 ppm at best) [21].

We have previously demonstrated that thin-sample FE-EPMA is largely superior to STEM-EDX in terms of detection sensitivity, where an indium gallium phosphide (InGaP) semiconductor sample was thinned to about 100 nm [14]. In the present study, a more detailed investigation into the effect of sample thickness on the spatial resolution and MDL for FE-EPMA was conducted using InGaP semiconductor and SiO_2 glass samples. The spatial resolution and MDL for thin-sample FE-SEM were also determined using the semiconductor sample.

2. Materials and methods

2.1. Sample preparation

An epitaxial film of InGaP on a gallium arsenide (GaAs) substrate was used to determine the spatial resolution and MDL for FE-EPMA–WDX and FE-SEM–EDX. The InGaP layer was first epitaxially grown on a GaAs substrate using metal-organic vapor phase epitaxy. The Ga/In atomic ratio in the InGaP layer was confirmed to be approximately 1 using the ZAF correction method in FE-EPMA [22]. InGaP/GaAs samples were thinned perpendicular to the layer structure, as shown in Fig. 1B, using a Ga focused ion beam (FIB), to thicknesses of approximately 100, 130, 210, 310, and 430 nm, as confirmed by secondary electron images of the sample cross sections [14]. The accuracy of the length measurement using SEM images is $\pm 5\%$. The mounting method of the samples has been fully described in a previous report [14]. The cleaved cross section of a bulk InGaP/GaAs sample was also analyzed as a reference.

In addition, chlorine-doped silicon dioxide (Cl-SiO_2) glass was used to determine the MDL for FE-EPMA. The X-ray count associated with Cl was first measured using FE-EPMA for a cleaved SiO_2 bulk sample, and the Cl concentration was determined to be 1500 mass ppm, as confirmed using ion chromatography. The glass was then thinned to 140 nm using FIB. The methods used for conductive mounting of the thin Cl-SiO_2 sample were similar to those for the thin InGaP/GaAs sample.

2.2. FE-EPMA–WDX measurements

X-ray line profiles and energy dispersions were measured using an FE-EPMA–WDX system (JXA-8530F, JEOL Ltd.). For all measurements, the working distance was about 11 mm and the takeoff angle was 40°. The measured X-rays were In-Lα in InGaP/GaAs and Cl-Kα in the Cl-SiO_2 glass. For both types of X-rays, the radius of the Rowland circle was 100 mm (H-type spectrometers in JEOL microprobes) and the analyzing crystal used was pentaerythritol (PETH). The X-rays were collimated through a 0.5 mm wide slit and then detected using a sealed proportional counter filled with Xe. The FE-EPMA measurement conditions were I_{prob}=5, 20, 50, 100, or 200 nA, V_{acc}=30 kV (InGaP/GaAs thinned samples), 5.5, 10 kV (InGaP/GaAs bulk sample), or 30 kV (Cl-SiO_2 thinned sample), and a sampling time of 1 s per point. During the InGaP measurements, the electron beam was focused on the sample, whereas it was broadened to a diameter of 5 μm during the Cl-SiO_2 measurements to avoid sample damage by electron irradiation. It should be noted that the critical excitation voltages for In-Lα and Cl-Kα X-rays are 3.73 and 2.82 keV, respectively.

2.3. FE-SEM–EDX measurements

X-ray line profiles and energy dispersions were measured using an FE-SEM–EDX system (ULTRA 55, Carl Zeiss) with a silicon drift detector (QuanTax QX200, Bruker), instrumentation that is prevalent worldwide. The measured X-rays were In-Lα in InGaP/GaAs. For all measurements, the working distance was about 8.5 mm and the takeoff angle was 35°. FE-SEM–EDX was measured with a V_{acc} of 30 kV (InGaP/GaAs thinned samples), 5.5, 8, or 10 kV (InGaP/GaAs bulk sample). The I_{prob} were 0.73, 3.0, 10.4 nA (V_{acc}=30 kV), 0.35, 1.5, 5.4 nA (V_{acc}=5.5 kV), 0.41, 1.7, 6.2 nA (V_{acc}=8 kV), 0.45, 1.9, or 6.9 nA (V_{acc}=10 kV). The sampling time for the line profile measurements was 1 s per point and the data acquisition time for the energy dispersions measurements, except for the dead time, was 100 s.

2.4. Determination of spatial resolution for FE-EPMA–WDX and FE-SEM–EDX

To determine the spatial resolution for FE-EPMA–WDX and FE-SEM–EDX, an In-Lα line profile was measured across the InGaP/