Problems in Impurity Analysis of an Insulating Powder Sample by SIMS

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This paper describes the source of variation in the SIMS determination of impurities in an insulating powder sample mixed together with graphite powders for electrical conductivity. The predominant factors were the local charge buildup on the sample surface and the local distribution of impurities originally present in the graphite powders. The local charge buildup due to the inhomogeneity of the tablet sample resulted in obvious changes of the secondary ion energy distributions. The local distribution of impurities in the graphite powders caused the occasionally anomalous high values in the determination.

1. Introduction

Secondary ion mass spectrometry (SIMS) has the advantage of being able to characterize directly a solid sample with excellent sensitivity. It has been widely used for the analysis of many kinds of materials in various fields of industry and science.¹⁾ Unfortunately, many of the useful and/or interesting materials are insulators or semi-conductors, hence charge buildup effect may be encountered. In order to minimize the effect, various methods have been designed with regard to sample pre-treatments and instrumental characteristics.^{2), 3)}

As far as insulating powder samples are concerned, they have typically been analyzed in a tablet form pressed together with conducting fine powders. Although some kinds of powders can be used, graphite powders are often used due to the high purity and a small contribution to the spectral interferences.^{4)~7)} Nevertheless, the influence of graphite mixing on

secondary ions intensities has not been investigated. We have felt that this mixing technique results in poorer reproducibility than that obtained with conductive or semi-conductive samples having mirror-finished surfaces.^{4)~9)} In our laboratory, a reciprocal analysis for the same position of a sample prepared by the technique has revealed to give better reproducibility than that for the different positions of the sample. What is the reason for this position to position variation on the same sample? A SEM observation revealed that the graphite was piling up in flakes of several tens microns in size and coarsely dispersed here and there in the admixture. The coarse dispersion of graphite powders may locally bring the sample surface some impurities originally present in themselves and may also give the admixture imperfect conductivity different from the case of forming a uniform phase like an alloy.

The aim of this paper is to clarify factors affecting the reproducibility in the

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analysis of insulating powders mixed together with graphite powders. We will discuss the mixing ratio of graphite to insulating powders, the changes of secondary ion energy distributions (SEDs) caused by locally restricted charge buildup due to inhomogeneous mixing and the anomalous distribution of some impurities in graphite powders.

2. Experimental

2.1 Reagents

Zirconium oxide powders (>99.99% pure, Dai-Ichi Kigenso Kagaku Co.) were used as an insulating sample. They were converted into solution by acid-pressure decomposition¹⁰⁾ and then diluted with distilled water to obtain the Zr stock solution (3.7 %w/v Zr in 4.5 mol/l H_2SO_4). The stock solutions of Al, Mg, Fe, and Ti were prepared from Titorisols (Merck) to make up Al, Mg, Fe, and Ti doped-zirconium oxide powders as described sample preparation section below. That of Y was prepared from yttrium oxide (99.999% pure, Shin-Etsu Chemical). Yttrium oxide of 1.2699 g was dissolved in 22 ml of HNO_3 (1 + 3) and then diluted with distilled water to 50 ml (2 %w/v Y in 2 mol/l HNO_3). Spectroscopic graphite powders (SP-1, National Carbon Co.) were used to prevent charge buildup on the sample surface.

2.2 Sample preparation

Aluminium, Mg, Fe, Ti, and Y doped-zirconium oxide powders were prepared as follows: the appropriate portions of the stock solutions of each element were added to 8.1 ml of Zr stock solution in a porcelain crucible (10 ml). After thorough mixing, the solution was heated to dryness on the hot plate. The dried products were transferred to an alumina crucible

(>99.9% pure, 30 ml) and kept at 1200°C for 20 min in the furnace to convert completely all the elements into their oxides. The powder briquette obtained was crashed in an agate mortar with an agate pestle and mixed well in a plastic container with a plastic ball by the mixer/mill.

Then, the powders were mixed with the graphite powders, followed by pressing to form a tablet of 1 cm diameter and 1 mm thickness. A sheet of PTFE (1 mm thickness) was placed between the sample powder and the platen to prevent contact of the powder with the platens. As will be discussed in the next section, the doped impurities seemed to be homogeneously distributed in the zirconium oxide powders by comparing secondary ion intensities obtained from several different analysis areas. A further study to ensure the homogeneity was not conducted.

2.3 Apparatus

A Cameca IMS-3F secondary ion mass spectrometer was used in this work. Oxygen negative ions generated in a duoplasmatron ion source were accelerated to 15.0 keV relative to the sample holder at 4.5 kV. The spot size of the primary ion beam was *ca.* 50 μm . Positive secondary ions were detected by an electron multiplier in pulse-counting mode. The apertures and slits located in the secondary column, *i.e.*, contrast aperture, entrance slit, field aperture, energy slit and exit slit, were kept fully open to obtain a maximum sensitivity. Secondary ion images on a channel plate/fluorescent screen were acquired with a CCD camera (TM-540, PULNiX Inc.) and processed by a personal computer (PC-9801F, NEC Co.). A Corning PC-100 hot plate, a Spex 8000 mixer/mill and a SUPER-

Table 1. Results of Reciprocal Analysis of the Secondary Ion Intensity Ratios on the Same Position of the Zirconium Oxide Powders Mixed together with Graphite Powders (1 : 1 in weight) for Four-days Run

Run	n	C/ ⁹⁶ Zr	O/ ⁹⁶ Zr	Al/ ⁹⁶ Zr	Fe/ ⁹⁶ Zr	¹⁷⁶ Hf/ ⁹⁶ Zr
1	7	0.448±0.005*	0.278±0.001	0.316±0.016	0.0329±0.0004	0.00468±0.00010
2	7	0.467±0.003	0.276±0.003	0.348±0.006	0.0303±0.0005	0.00490±0.00004
3	7	0.465±0.002	0.275±0.002	0.326±0.004	0.0292±0.0004	0.00493±0.00002
4	5	0.464±0.005	0.275±0.004	0.322±0.002	0.0290±0.0008	0.00495±0.00004
1~4	26	0.461±0.009**	0.276±0.002	0.328±0.014	0.0304±0.0018	0.00487±0.00012

Count time: ¹⁷⁶Hf, 5 s; others, 1 s.

* Mean±standard deviation.

** Mean±standard deviation of the four data sets.

Fig. 1. Secondary ion distributions of Zr for various mixing ratios of zirconium oxide (ZrO₂) and graphite (C).

BURN SBL-2025 electric furnace (Motoyama Co.) were used for sample preparation. A JEOL JSM-7M scanning electron microscope was used for sample surface observation.

3. Results and Discussion

3.1 Reproducibility of secondary ion intensities

The reciprocal analysis was conducted for the same position on the sample (mixed with graphite powders 1 : 1 in weight) containing *ca.* 1,000 $\mu\text{g} \cdot \text{g}^{-1}$ of some impurities and 21.7 $\text{mg} \cdot \text{g}^{-1}$ of Hf under the identical working conditions. The conditions of ion gun, both primary and secondary ion accelerating energy, and detection system were kept as con-

stant as possible; nevertheless a slight change of the analytical position arising from very little fluctuation of these conditions may occur. Table 1 contains the results of the secondary ion intensity ratios normalized to ⁹⁶Zr collected for four-days run. These variations must involve some inhomogeneity of the sample revealed during sputter etching (40 min for each analysis). Most of the daily variations falling within 3% encouraged us to carry out quantitative analysis with good precision.

In the case of position to position analysis, however, the variation increased to several times. We expect that this can be clarified from the evaluations of secondary ion energetic factors and contamination caused by the mixing between the sample powders and graphite powders.

3.2 Mixing ratio of graphite powder

The charge buildup of the sample is expected to decrease with increasing the mixing ratio of graphite powder to zirconium oxide powder. As well known, SEDs change according to the charge state of the sample surface. Figure 1 shows the changes of SED of Zr as a function of the mixing ratios of graphite (graphite/zirconium oxide in weight). The SED curves were measured by scanning the sample

Fig. 2. Secondary ion images of the sample tablet (zirconium oxide:graphite=1:1 in weight).

bias with an energy window of 10 eV. One may see that the lower the mixing ratios, the more negative charge buildup on the sample occurs associated with peak broadening. At the ratio of 1:0.05, the SED (Curve A in Fig. 1) shows severely negative shift and much reduction in its intensity. This shift is out of the energy window and cannot be compensated under conventional working conditions of our instrument. As will be discussed in the next section, the SEDs change from position to position even on the same sample surface. Since the slighter change is expected with the higher mixing ratio, it is concluded that the mixing ratio of 1:1 is advisable to hold the change at a minimum.

3.3 Local charge buildup

Figure 2 shows the secondary ion images of Zr and C on the sample surface with the mixing ratio of 1:1. Considering a narrow dynamic range of the images, the dark parts of images do not always mean the absence of each element. However, it has to be noticed that both of the powders are not homogeneously mixed in the sample. One can observe less intense region of Zr intensity on the sample sur-

face. This region can be caused by surface topographical effect, true deficiency of zirconium oxide powders at the region, and decrease of secondary ion intensity due to the development of charge buildup. Poor correspondence between the Zr and C images in Fig. 2 suggests that the surface topographical effect is not noticeable. Indeed, the SED of Zr in the region showed more negative shift of peak maximum and broader peak width than that in more intense region of Zr intensity. This supports that the contrast of the Zr ion image dominantly reflects the change of secondary ion intensity due to charge buildup. So, it is deduced that graphite is poorly present at the less intense region of Zr intensity. Different charge buildups may occur on the same sample surface depending on whatever the analyzed area more or less contains graphite. Assuming that the variation of SEDs is dependent on only the intensity ratio (C/Zr) at the bombarded region, it is expected that the two SEDs of any point on the sample surface showing the same C/Zr are identical. However, this does not appear to be true. This local variation of SED occurring on localized section on the one sample arises from local charge buildup.¹¹⁾ Thus the local charge buildup is influenced by the complicated charge situations on the inhomogeneous sample surface and results in the obvious changes of SEDs.

In SIMS analysis, secondary ions are usually detected through a fixed energy window which is sensitive to a change of SEDs. Since each element has intrinsic differences in the SEDs, the secondary ion intensity ratios vary according to the shift and broadening of the SEDs. This variation as well as matrix effects is one of the serious factors affecting the preci-

sion in quantitative analysis of multi-elemental specimens.

3.4 Impurities in graphite powder

The following results were obtained with the graphite powders pressed to form a tablet. Though the graphite powders used were of spectroscopic pure grade, the powders unexpectedly contained many impurities (Fig. 3). Since no great difference was found in the results

Fig. 3. Mass spectrum of graphite.

of the bulk analysis of the graphite by ICP-AES whether in the tablet-form or in the powder-form, the impurities were not introduced by sample processing but must have been originally present in the graphite powders. The acid-leaching of the powders (HF-HNO_3) was unsuccessful in removing the impurities. Figure 4 shows the secondary ion images of some impurities on the graphite tablet. Comparing the carbon secondary ion image with the others, no obvious surface topographical effects on the samples were observed. The impurities were locally distributed in lumps of several tens of microns in size.

Figure 5 shows secondary ion intensities of six elements taken from ten different positions on the same sample mixed together with graphite in 1 : 1. The intensities of Hf and Y were in good proportion to that of Zr because of their absence in the graphite powders. This indicates that Hf and Y were homogeneously distributed in the zirconium oxide powders. On the other hand, Al and Fe were

Fig. 4. Secondary ion images of impurities in graphite.

Fig. 5. Secondary ion intensities of ten different positions on the same sample. Each of numbers corresponds to each position measured. Each set of intensities for an element is represented in arbitrary units.

distributed with anomalously high concentrations at the position 6 (Fig. 5). It was impossible to distinguish whether they are located in the graphite or zirconium oxide by either the ion intensities or images. However, the behavior of Al and Fe except for position 6 suggests that Al and Fe are also homogeneously distributed in zirconium oxide (Fig. 2). Thus, the occasionally anomalous results must be attributed to impurities introduced by the graphite powders. According to Morrison's sampling constant concept,¹²⁾ larger area analysis is desirable for the quantitative analysis of inhomogeneously distributed elements in the NIST iron alloy sample. In this study, however, the use of larger analysis areas on the sample tablet always brought worse reproducibility. Assuming that some lumps of impurities distributed in the graphite powders may remain unbroken after mixing, one can understand how the use of smaller analysis areas could give better

reproducibility. There is a smaller probability of encountering these impurity lumps, resulting in better reproducibility, when the analysis area is kept small.

4. Conclusion

We studied the source of variation in the analysis of the tablet-formed samples of insulating powders (zirconium oxide) mixed together with graphite powders. It has been shown that the predominant factors affecting the variation are the local charge buildup occurring by the inhomogeneous mixing of two types of powders and the local distribution of the impurities present in the graphite powders mixed for electrical conductivity.

The local charge buildup on a sample will be compensated by the shift of sample bias according to the estimation of the SED curves in every analysis position on the sample. The probability of encountering the impurities introduced by graphite is expected to be minimized by

the use of purer graphite powders and more advanced image processing system applicable to more smaller area and concentration. The analysis of Al and Fe by the present method (mixing the powder sample together with conducting powders) requires utmost care under the present situation.

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Keywords

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