QUANTITATIVE ANALYSIS OF SMALL PARTICLES BY SUBMICRON SECONDARY ION MASS SPECTROMETRY

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Abstract - Relative sensitivity factors (RSFs) of thirteen elements in oxide glass matrix were determined for a secondary ion mass spectrometry (SIMS) with gallium focused ion beam (FIB). Reproducibility of RSFs was good, sample-to-sample scattering of RSF values was relatively small, and dependence of RSFs on the first ionization potential is reasonable. To check validity of the RSFs, coal fly ash particles and glass fiber sample were analyzed. The results were in reasonable agreement with the data obtained by the bulk chemical analysis.

Key words secondary ion mass spectrometry, focused ion beam, gallium, relative sensitivity factor

Recently a gallium FIB began to be used as a primary beam of high spatial resolution SIMS. However, basic data for quantitative analysis for FIB-SIMS, has been little accumulated. The authors constructed a submicron SIMS using a gallium focused ion beam and multichannel parallel detection system.[1] In this paper, relative sensitivity factors of thirteen elements in glass matrices for a gallium primary beam are reported and discussed.

EXPERIMENTAL

Apparatus The detail of the apparatus was described in Ref. 1. Field-emitted Ga^+ ions are accelerated to 35kV and focused on the sample. Secondary ions (SI) are accelerated by a sample bias (5-10kV) and transferred to the mass spectrometer. The Mattauch-Herzog type mass analyzer features plane focusing with the dispersion proportional to $(m/e)^{1/2}$ along the focal plane. Therefore, this type of mass analyzer is suitable for multichannel detection by using a position sensitive detector. A multichannel parallel detection is placed on the focal plane, and covers 1:2 mass range with 120 independent channels. Therefore, all ions whose m/e are within 1:2 mass range (e.g., $m/e=10-20$, $20-40$) are detected simultaneously.

Shave-Off Mode[2] In this study, fine particle samples were used for measurement of RSF. Generally, secondary ion yield largely depends upon the incident angle of a primary ion beam to the sample surface. When a sample is not a flat plate, this fact introduces a different topographic effect. In order to circumvent the topographic effect which is typically observed as edge enhancement, the authors developed a new kind of scanning mode -- shave-off mode. In shave-off mode, the fast horizontal sweep is combined with a very slow vertical sweep. The most important point of this scanning mode is that the speed of the vertical sweep is slow enough to "shave-off" the sample from one edge to the other edge. The entire volume of the sample is sputtered after only a single frame scan. In this mode, the primary ion beam shaves the sample, and the incident condition of primary ion beam to the sample is held constant during measurement. By using shave-off mode, every part of a single small particle equally contributes to measured signal intensity.

Samples Samples were nine NBS Standard Reference Materials of glass. The composition of the reference sample is given in Table 1. K961 is spherical beads, 91 and 89 are glass powder, and other samples are glass blocks. There are two advantages in the use of glass samples. First, uniform materials of wide range of element concentration are available. Second, matrix effects are minimized because of stable oxide.

Experimental Procedure Glass powders of the standard sample were used for the measurement in order to analyze in shave-off mode. A block sample was ground down to micrometer particles in a boron nitride mortar. After that, aerodynamic size fractionation was carried out for each sample in order to separate particles whose diameter were 2-4 μm . Powder particles were dispersed on an indium plate. Several particles per each sample were analyzed by shave-off mode. RSFs were calculated from integrated intensity of secondary ions during a shave-off mode scanning, the isotopic abundance and the atomic concentration for each particle.

RESULTS

Relative Sensitivity Factor for 13 Elements in Glass Matrix Table 2 shows the analytical results of NBS Standard Reference Material 1412 (Multicomponent Glass) glass particles. Measured species were single-charged atomic positive ions of largest natural abundance. From the certificated composition of the sample, atomic concentration of each species was calculated. For this sample, five particles were analyzed. The number of detected ions are shown at the left side of the colon. From these values and concentration, RSF was calculated, and listed at rightmost of the columns. These values of standard deviation tell that values of RSF of each element is considerably uniform among five particles analyzed.

Table 3 shows the RSFs obtained from nine kinds of samples. The number in the parentheses after sample identification indicates the number of particles analyzed for each sample. Mean RSF and percent standard deviation values were 10-20 percent. It is considered from the results of K411 that the particle-to-particle repeatability of less than 5 percent can be achieved in microparticle analysis by submicron SIMS.

Rightmost column in Table 3 shows the mean RSF over all standard samples. The number in parentheses indicates percent standard deviation. Sample-to-sample standard deviations are, in most cases, larger than particle-to-particle within-sample standard deviation values. Generally, sensitivity of elements in SIMS analysis largely depends on the sample matrix, and ten times or more difference is usual. In these results, difference was within a factor of two or three except sodium and potassium. Because all standard samples are oxide matrix, rather small divergence was observed. Figure 1 shows the logarithmic plot of mean RSF values obtained from nine standard samples as a function of the first ionization potential of each element. Electropositive elements such as alkali and alkali-earth metals gave large values of RSF. As the first ionization potential increases, RSF decreases logarithmically. In this plot, the slope is approximately 0.5 decade/eV. Novak et al.[3] categorized such slopes into three [matrix/primary beam] systems on the data obtained from ion-implanted samples. In their paper, the slopes of $[\text{SiO}_2/\text{O}]$, $[\text{Si}/\text{O}]$ and $[\text{Si}/\text{Ar}]$ were 0.35, 0.70 and 1.05 decade/eV, respectively. They interpreted this tendency on relation to the surface oxygen concentration. In $[\text{oxide glass}/\text{Ga}]$ system was considered to be between $[\text{SiO}_2/\text{O}]$ and $[\text{Si}/\text{O}]$ systems. The slope in this case is consistent with the tendency shown by Novak et al.

Analytical Results of Coal Fly Ash and Glass Fiber In order to check validity of RSF obtained above, the authors analyzed coal fly ash particles and glass fiber.

Coal fly ash is suspended particulate matter in the exhaust of coal burning furnace, and its component is similar to common minerals. Six particles of coal fly ash were analyzed with shave-off mode. From secondary ion intensity and relative sensitivity factors obtained above, relative atomic content of eight species were calculated, and shown in Table 4. A fraction of the same collection batch was analyzed with inductively coupled plasma atomic emission spectrometry. Second line in the Table 4 shows relative atomic content calculated from such bulk analysis data. Because coal fly ash is not a uniform material, strict comparison has not a large significance between individual particle analysis data and bulk chemical analysis data. However, rough estimation of validity of RSF is interesting. From this standpoint, two sets of analytical results are in remarkable agreement. Table 5 shows analytical results of glass fiber by using RSF obtained above and the con-

stituent of the glass fiber. About 1 μm long of 5 μm thick glass fiber was analyzed by shave-off mode, and relative atomic content of 4 species were calculated. The analytical results agree to the constituent of the sample. From those analytical data, RSFs determined in this study are thought to be reliable and practically useful for the analysis of oxide matrix particles. Bulk chemical analysis is not applicable for individual micro particles or analysis for specific microstructure, so the individual particle analysis by microbeam analysis is very important. Therefore, submicron SIMS together with RSFs determined above is a very useful tool for quantitative analysis of individual particle and microstructure sample.

CONCLUSION

Relative sensitivity factors of thirteen elements in oxide glass matrix for a gallium primary beam were determined. The RSFs were measured for main components in glass matrices. The reproducibility of RSF values within a sample was good, and the values of RSF among nine kinds of samples showed small dispersion. The relationship between RSF and the first ionization potential of elements was reasonable and the tendency of this relationship is similar to other data when positive ions are detected. By using these RSFs obtained in this study, quantitative analysis of oxide small particles and fibers by submicron SIMS was performed, and results were in reasonable agreement with bulk chemical analysis. The submicron SIMS can analyze individual microparticles and specific part of microstructure by utilizing its high spatial resolution. Therefore, these basic data made analysis of fine particles possible, which has not be able to be analyzed by means of bulk chemical analysis.

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TABLE 1 Composition of standard glass samples
(NBS Standard Reference Materials)

Major Constituent	Weight percent oxide							
	1412	1411	K961	K412	K411	93a	91	89
Li ₂ O	4.50	--	--	--	--	--	--	--
B ₂ O ₃	4.53	10.94	--	--	--	12.56	--	--
Na ₂ O	4.69	10.14	4.0	--	--	3.98	8.47	5.70
MgO	4.69	0.33	5.0	19.33	14.67	--	--	14.39
Al ₂ O ₃	7.52	5.68	11.0	9.27	--	2.28	6.01	3.69
SiO ₂	42.38	58.04	64.0	45.35	54.30	80.8	67.5	1.80
K ₂ O	4.14	2.97	3.0	--	--	--	--	72.08
CaO	4.53	2.18	5.0	15.25	15.47	--	10.49	0.41
TiO ₂	--	0.02	2.0	--	--	--	--	7.11
Fe ₂ O ₃	0.031	0.050	5.0	9.96(FeO)	14.42(FeO)	--	--	--
SrO	4.55	0.09	--	--	--	--	--	--
BaO	4.67	5.00	--	--	--	--	--	1.40
PbO	4.40	--	--	--	--	--	--	17.50

TABLE 2. Analytical results of NBS SRM 1412: Multicomponent Glass

Analyzed species	Atomic percent	Detected ion counts : Relative Sensitivity Factor(Si=1)					Mean RSF	Percent standard deviation
		Particle 1	Particle 2	Particle 3	Particle 4	Particle 5		
⁷ Li ⁺	6.35	14877 : 11.8	10048 : 11.9	5929 : 11.3	7143 : 15.1	6618 : 16.8	13.4	16
¹¹ B ⁺	2.37	375 : 0.79	287 : 0.91	153 : 0.79	124 : 0.70	118 : 0.80	0.80	8
²³ Na ⁺	3.45	14024 : 20.3	7786 : 17.0	3679 : 13.0	4366 : 16.9	3832 : 17.8	17.0	14
²⁴ Mg ⁺	2.08	1725 : 4.2	1299 : 4.7	599 : 3.5	584 : 3.8	457 : 3.6	4.0	11
²⁷ Al ⁺	3.35	4544 : 6.8	3171 : 7.1	1710 : 6.2	1760 : 7.1	1514 : 7.3	6.9	6
²⁸ Si ⁺	14.8	2961 : 1.	1963 : 1.	1216 : 1.	1106 : 1.	922 : 1.	1.	
³⁹ K ⁺	1.87	11399 : 30.5	7448 : 30.0	5440 : 35.4	7437 : 53.2	6422 : 55.1	40.1	28
⁴⁰ Ca ⁺	1.79	8272 : 23.1	5822 : 26.5	2688 : 19.0	3422 : 25.6	2240 : 20.0	22.8	13
⁸⁶ Sr ⁺	0.83	2479 : 14.9	1692 : 15.3	902 : 13.2	1014 : 16.3	812 : 15.7	15.1	7
¹³⁸ Ba ⁺	0.49	2399 : 24.5	1285 : 19.4	753 : 18.7	862 : 23.5	749 : 24.5	22.1	11

TABLE 3. Relative sensitivity factors for oxide glass matrix elements by gallium primary ion beam

Species	Sample (NBS Standard Reference Materials)								Average of nine samples
	1412(5)*	1411(10)	K861(8)	K412(9)	K411(10)	93a(10)	91(4)	89(7)	620(9)
⁷ Li	13.4 (16)*	—	—	—	—	—	—	—	13.4
¹¹ B	0.80 (8)	0.65 (9)	—	—	—	0.81 (3)	—	—	0.75(10)*
²³ Na	17.0 (14)	25.4 (14)	38.0 (32)	—	—	11.2 (8)	—	7.3 (37)	22.0 (51)
²⁴ Mg	4.0 (11)	11.9 (41)	4.3 (15)	9.6 (19)	5.8 (4)	—	—	—	6.8 (43)
²⁷ Al	6.9 (6)	8.0 (11)	10.0 (17)	15.1 (6)	—	5.8 (7)	9.8 (44)	—	9.4 (30)
²⁸ Si	1.	1.	1.	1.	1.	1.	1.	1.	1.
³⁹ K	40.1 (28)	102. (12)	190. (32)	—	—	—	55.4 (39)	27.9 (15)	135. (18)
⁴⁰ Ca	22.8 (13)	21.5 (13)	24.4 (15)	45.5 (16)	22.9 (3)	—	15.3 (45)	—	23.5 (11)
⁴⁰ Ti	—	—	6.2 (21)	—	—	—	—	—	6.2
⁵⁶ Fe	—	—	3.0 (24)	7.6 (18)	2.7 (5)	—	—	—	4.4 (51)
⁸⁸ Sr	15.1 (7)	—	—	—	—	—	—	—	15.1
¹³⁸ Ba	22.1 (11)	18.8 (11)	—	—	—	—	—	18.8 (15)	19.8 (8)
²⁰⁸ Pb	—	—	—	—	—	—	—	0.69(16)	0.69

* Number in parentheses after sample identification indicates the number of particles analyzed for each sample.

* Number in parentheses after relative sensitivity factors in each sample column indicates percent relative standard deviation over analyzed particles of each sample.

* Number in parentheses after relative sensitivity factors in average column indicates percent relative standard deviation over analyzed samples.

TABLE 4. Analytical results of coal fly ash particles

Method	Relative atomic content (Si=1)							
	²³ Na	²⁴ Mg	²⁷ Al	²⁸ Si	³⁹ K	⁴⁰ Ca	⁴⁰ Ti	⁵⁶ Fe
Submicron SIMS*	.080	.027	.652	1.	.066	.073	.013	.047
ICP-AES*	.017	.025	.427	1.	.031	.072	.008	.082

Average of results from analysis of six particles.

Inductively coupled plasma atomic emission spectrometry. Calculated from data by K. Nagashima *et al.*: Extended Abstract of 43rd Symposium on Analytical Chemistry Japan, 1982, p.3.

TABLE 5. Analytical results of glass fiber

	SiO ₂	Al ₂ O ₃	TiO ₂	CaO (wt.%)
Constituent	99	0.3	0.5	0.04
Analytical Data	98.37	0.20	1.39	0.05

Fig. 1 Relationship between relative sensitivity factor for a gallium primary ion beam and first ionization potentials of elements