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The Depth Profiling of Glass Surfaces by Mass Spectrometry Using Neutral-particle Bombardment

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Glass surfaces are bombarded by energetic neutral argon atoms or oxygen molecules, and the resulting sputtered ions are mass-analyzed. This technique has a higher depth resolution than conventional secondary-ion mass spectrometry. Quantitative depth-concentration profiles of sodium and potassium in the top layer of the surface (within several tens of nanometers of the surface) of Pyrex glass are obtained by the proposed technique.

Depth profiles of glass components, especially of univalent ions, in the glass surface layer are quite useful in studies of the physical chemistry of glass surfaces and glass technology. Recently, secondary-ion mass spectrometry (SIMS),[1-3] Auger electron spectrometry (AES) using ion beams for etching,[4] and ion-beam-induced radiation[5] have been applied to the depth profiling of glass surfaces. In the top layer of the surface (within several tens of nanometers of the glass surface), however, discrepancies[3-5] have been found among the profiles of the alkali ions obtained by these techniques. These facts suggest that all the techniques using ion bombardment are still qualitative in the top layer of the surface.

By the energetic ion or electron bombardment of glass, the surfaces become charged, and the resulting electric field may cause a migration of the univalent ions in the glass. Additionally, preferential sputtering, knock-on effects, and primary-ion implantation may be caused by ion bombardment within the top layer of the surface. These phenomena may distort the original depth-concentration profiles in glass and may change the secondary-ion yields, thus resulting in the discrepancies described above. McCaughan and Kushner[6] investigated the migration of sodium in thin silicon dioxide films on silicon by the radioactive-tracer technique. Neutral-particle bombardment gave less sodium migration than ion bombardment by at least four orders of magnitude, and less migration than ion bombardment with electron flooding (spraying) by at least two orders of magnitude. These results suggest that the migration of univalent ions in glass may be disregarded if mass spectrometry using neutral-particle bombardment[7] is used for depth profiling. Although the effects of preferential sputtering, knock-on effects, and primary-particle implantation cannot be reduced, it is shown in the present work that mass spectrometry using neutral-particle bombardment is more useful than conventional SIMS for obtaining quantitative depth-concentration profiles of sodium and potassium ions in the top layer of the surface of borosilicate glass.

Experimental

Apparatus. A Hitachi IMA-2 ion microanalyzer was modified for neutral-particle bombardment, as is shown in Fig. 1. The neutral-particle beam was obtained by removing ions by electrostatic deflection electrodes (515—530 V)[8] from the primary beam consisting of ions and neutral atoms or molecules probably produced by ion-neutral particle reactions and recombination. The spot diameters of the neutral atom or molecule beam were adjusted by means of apertures of 0.3, 0.5, 1, and 3 mm. The operating conditions of the microanalyzer are listed in Table 1. The ion intensities of boron, sodium, aluminium, silicon, and potassium were measured intermittently by means of manual magnetic scanning. For SIMS, electron flooding was started 10 s before the ion bombardment to eliminate the charge accumulation.

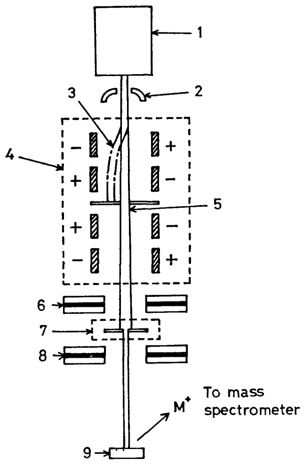

Fig. 1. Apparatus for mass spectrometry with neutral-particle bombardment. ⬚ indicates the parts attached to a Hitachi IMA-2 ion microanalyzer. 1: Primary-ion source, 2: accelerator electrode, 3: ion beam, 4: electrostatic deflection electrodes (4 pairs), 5: neutral-particle beam, 6: condenser lens, 7: aperture, 8: objective lens, 9: sample.

Table 1. Operating conditions

Bombarding particles and their energies		Bombarding-beam spot diameter	Sputtering rate
	keV	mm	nm h^{-1}
Ar^0	4	1	5
	7	1	20
Ar^+	4	0.3	73
	7	0.3	160
O_2^0	7	1	12
O_2^+	7	0.3	110

Other conditions: source gas, 99.99% argon or 99.7% oxygen; primary-ion current, 50 nA; sample-chamber pressure, 3×10^{-5} Pa; secondary-ion accelerating voltage, 3 kV; electron-multiplier voltage, 2.5 kV.

The depth of the craters formed on glass surfaces by sputtering was measured with a Mizojiri Kogaku Model II multiple-beam interferometer (Hg 546.1 nm, magnification

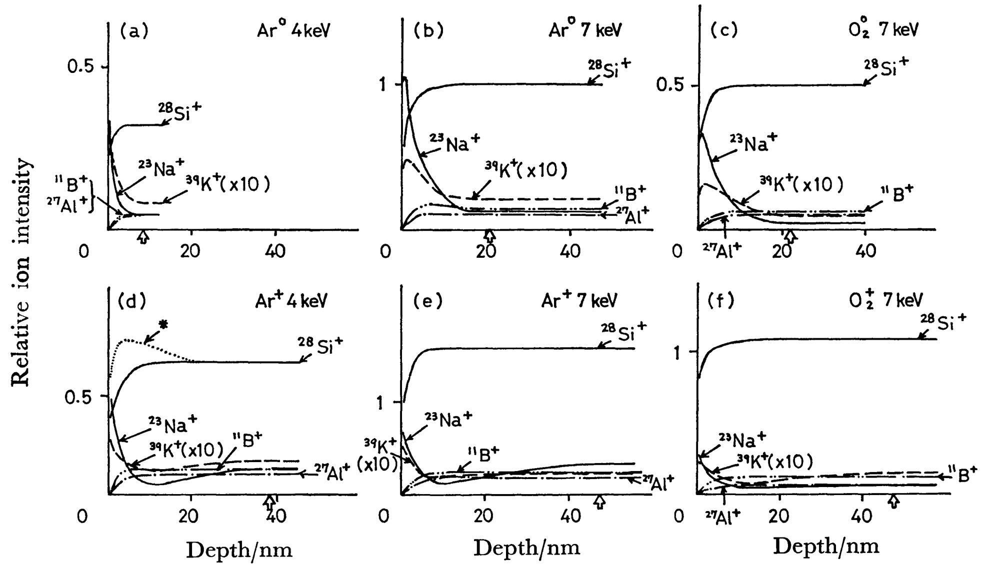

Fig. 2. Depth profiles of fracture-exposed surfaces of borosilicate glass R501.
*: A maximum peak sometimes appears. ⇧: Depth where the ion intensities reach steady values.

40X), with a maximum error of ±3 nm. An Olympus Model MF microscope (magnification 100—400X) with a Model MF-NIC Nomarski interference contrast attachment, and a Hitachi-Akashi Model MSM-2 scanning electron microscope (magnification 2000—10000X) were used for the observation of the glass surfaces.

Materials. Japanese standard-reference-material borosilicate glass R501 rods (79.9 SiO_2, 13.2 B_2O_3, 3.88 Na_2O, 2.17 Al_2O_3, 0.30 K_2O wt%, 6 mmϕ × 100 mm) were cut into *ca.* 8-mm lengths. The fracture-exposed surfaces were smooth under optical and electron microscopes. Pyrex glass sheets (81 SiO_2, 13 B_2O_3, 3.9 Na_2O, 2.2 Al_2O_3, 0.5 K_2O wt%, thickness; 1 mm) were annealed, etched *ca.* 1 μm with 1.4 M hydrofluoric acid-1.3 M sulfuric acid at 20±3 °C for 15 min, washed with water, and dried in a silica-gel desiccator.

Interdiffusion of Potassium and Sodium Ions. In a 50-ml silica glass beaker, 17.8 g of potassium nitrate and 6.4 g of sodium nitrate (70 KNO_3–30 $NaNO_3$ mol%) were melted and thoroughly mixed at 270±1 °C. A 30-mm-square piece of a Pyrex glass sheet was immersed in the molten salt to effect the interdiffusion of potassium and sodium ions in the glass. The piece was then withdrawn, cooled, washed in water, and dried in a silica-gel desiccator. After the interdiffusion no change was observed on the glass surfaces under optical and electron microscopes.

Results and Discussion

Bombardment by Neutral Atoms and Molecules. The fracture-exposed surfaces of borosilicate glass R501 were bombarded by the neutral atom (Ar^0), the neutral molecule (O_2^0), or the ion (Ar^+, O_2^+) beam, and the resulting sputtered ions were mass-analyzed. Figure 2 shows the depth profiles thus obtained. The concentrations of boron, sodium, aluminium, silicon, and potassium in the top layer of the fracture-exposed surfaces can be assumed to be constant.[9] The ion intensities of these elements, however, change with the increase in the depth in the top layer of the surface. The depth where the ion intensities reach steady values is smaller in the neutral-atom or -molecule bombardment than in SIMS. This suggests a higher depth resolution in the former technique. In SIMS, primary ions with energies as low as 3 keV produced insufficient secondary ions for mass spectrometry, and lower primary-ion densities on the sample surface did not improve the depth resolution. Bombardment with neutral argon atoms is mainly used in the present work, because there is little difference in depth resolution between the argon-atom and the oxygen-molecule bombardment and because the sputtering rate is larger in the former.

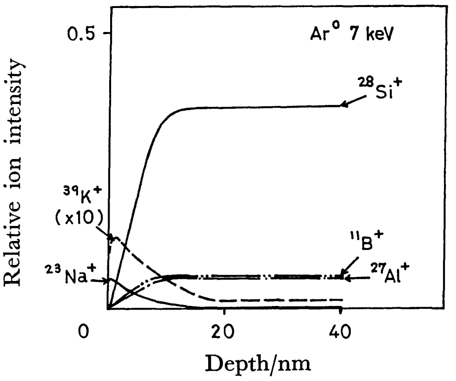

Fig. 3. Depth profiles of fracture-exposed surface of borosilicate glass R501 after electron flooding (1.5 keV, 25 μA) for 5 min.

In SIMS, in addition to ion bombardment, electron flooding may distort the depth profiles. The latter effects are shown in Fig. 3. Compared with Fig. 2(b), the ion intensities of sodium and potassium relative to silicon remarkably decreased upon electron flooding.

Calibration Graphs. To obtain quantitative depth-concentration profiles from the observed depth profiles in the top layer of the surface, calibration graphs were constructed by the use of the borosilicate

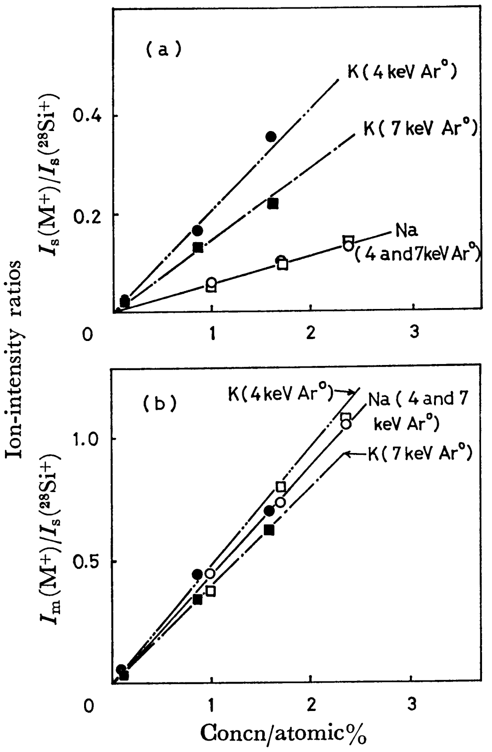

Fig. 4. Calibration graphs.
(a) For sodium and potassium concentrations at 10 nm (4 keV Ar^0) and 20—30 nm (7 keV Ar^0) from surfaces. (b) For surface sodium and potassium concentrations.

glass R501 and standard samples reported previously.[2) For obtaining sodium and potassium concentrations, at 10 and 20—30 nm from the surfaces, for 4 and 7 keV Ar^0 bombardments respectively, the steady values of the ion-intensity ratios, $I_s(^{23}\mathrm{Na}^+)/I_s(^{28}\mathrm{Si}^+)$ and $I_s(^{39}\mathrm{K}^+)/I_s(^{28}\mathrm{Si}^+)$, were plotted against the sodium and potassium concentrations {Fig. 4(a)}. For obtaining the sodium and potassium concentrations at the surfaces, the ratios of the maximum ion intensities of sodium and potassium to the steady values of the silicon-ion intensity, $I_m(^{23}\mathrm{Na}^+)/I_s(^{28}\mathrm{Si}^+)$ and $I_m(^{39}\mathrm{K}^+)/I_s(^{28}\mathrm{Si}^+)$, were plotted against the sodium and potassium concentrations {Fig. 4(b)}. All the calibration graphs were straight lines passing through the origin; the scattering of the points was less than ±10%. Also, no day-to-day variation in the calibration graphs was observed.

Depth-concentration Profiles. Figure 5 shows the quantitative depth-concentration profiles in the top layer of the surface of potassium-treated Pyrex glass sheets. The profiles obtained by the proposed technique (solid lines) are in good agreement with the calculated profiles (broken lines). The latter were calculated by using the interdiffusion coefficients reported previously[2) and the equilibrium surface concentrations of sodium and potassium as measured with a glass sheet immersed in a molten 70 $\mathrm{KNO_3}$–30 $\mathrm{NaNO_3}$ mol% bath at 270 °C for 1200 min.

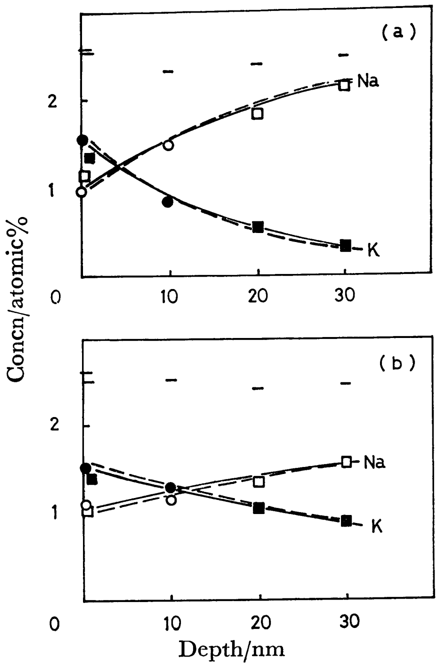

Fig. 5. Depth-concentration profiles after interdiffusion of potassium and sodium in Pyrex glass at 270 °C for (a) 1 min and (b) 7 min.
□■: 7 keV Ar^0, ○●: 4 keV Ar^0. Solid line: measured. Dashed line: calculated. —: Sum of K and Na (measured).

References

1) A. Mizuike and A. Iino, *Bull. Chem. Soc. Jpn.*, **50**, 1469 (1977).

2) A. Iino, H. Nakamura, and A. Mizuike, *Nippon Kagaku Kaishi*, **1977**, 1324.

3) R. G. Gossink, H. A. M. de Grefte, and H. W. Werner, *J. Am. Ceram. Soc.*, **62**, 4 (1979).

4) C. G. Pantano, Jr., D. B. Dove, and G. Y. Onoda, Jr., *J. Vac. Sci. Technol.*, **13**, 414 (1976).

5) H. Bach, *Radiat. Eff.*, **28**, 215 (1976).

6) D. V. McCaughan and R. A. Kushner, "Characterization of Solid Surfaces," ed by P. F. Kane and G. B. Larrabee, Plenum Press, New York (1974), Chap. 22.

7) S. Scherrer and F. Naudin, "Proc. The XIth Intern. Cong. Glass," Prague, July (1977), Vol. III, p. 301.

8) H. Kobayashi, K. Suzuki, Y. Yanagisawa, and K. Yukawa, *Shitsuryo Bunseki*, **25**, 315 (1977).

9) J. H. Escard and D. J. Brion, *J. Am. Ceram. Soc.*, **58**, 296 (1975).