Secondary Ion Mass Spectrometry for Diffusion Studies in Glass

Atsushi MIZUIKE and Akira IINO
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464
(Received December 24, 1976)

A procedure has been established for obtaining quantitative diffusion profiles by means of an ion microanalyzer in the narrow region within 1 μm of the glass surface. The interdiffusion of silver and sodium ions in Pyrex glass immersed in molten silver nitrate was studied as an example.

Diffusion kinetics during ion exchange in various glasses has been studied by many workers[1] from purely physicochemical points of view (*e.g.*, to get a better understanding of the basic mechanism of ionic transport in glass and the structure of glass) and in connection with industrial problems (*e.g.*, the strengthening of glass). The radioactive tracer technique and electron microprobe X-ray analysis have been employed extensively in these studies to obtain diffusion profiles (concentration *vs.* depth curves).

Secondary ion mass spectrometry (SIMS) offers a new means for obtaining profiles in the near-surface region (within 1 μm of the surface). In this technique, the sample surface is bombarded with a beam of high-energy primary ions, and the resulting ions from the sample are analyzed by means of a mass spectrometer. The successive removal by sputtering of the surface layers enables one to obtain the profiles by monitoring the ion intensity at the appropriate mass *vs.* sputtering time. This technique, however, is still semiquantitative,[2] because there remain three unresolved problems. First is the quantification of the SIMS intensities, *i.e.*, the conversion of the ion intensity at the appropriate mass into the concentration of the corresponding element. The large variations in the secondary ion yields and the matrix effects complicate the quantification. Although a theoretical correction procedure based on the local thermal equilibrium model has been proposed by Andersen and Hinthorne,[3] standard samples are still generally required for an accurate quantification. These standards have to shape both the chemical and physical nature of the sample as much as possible; therefore, their preparation is often very difficult. Second is the depth assignment, *i.e.*, the conversion of the sputtering time into depth. The rate of material removal depends on the sample matrix as well as the primary ion characteristics. Third, ion migration induced by ion bombardment may distort the diffusion profiles.[4]

The present work has been undertaken in order to resolve these problems and to establish a procedure for obtaining quantitative diffusion profiles in the near-surface region by SIMS. Experiments have been carried out on the interdiffusion of silver and sodium ions in Pyrex glass immersed in molten silver nitrate.

Experimental

Apparatus. A Hitachi IMA-2 ion microanalyzer was operated under the following conditions unless otherwise stated: primary ion-source gas, 99.99% argon; primary ion-accelerating voltage, 15 kV; primary beam current, 0.1 μA; spot diameter, 250 μm; sample chamber pressure, 3×10^{-5} Pa; secondary ion-accelerating voltage, 3 kV; electron-multiplier voltage, 2 kV. The electric charges accumulated on the glass surfaces were eliminated by means of the electron-spray method. The SIMS peak ratios—$^{109}Ag^+/^{30}Si^+$, $^{23}Na^+/^{28}Si^+$, and $^{39}K^+/^{28}Si^+$—were measured after rastering the primary beam (total number of scanning lines, 500; line frequency, 100 Hz) over an area 0.8 mm square around the spot to be measured. A Mizojiri Kogaku model II multiple-beam interferometer (Hg 546.1 nm, magnification 40X) was used to measure the depth of craters formed on glass surfaces by ion etching (ion sputtering) and the thickness of the chemically etched glass-surface layers. A Nippon Jarrell-Ash AA-1 MK II atomic-absorption flame-emission spectrophotometer with an SA-61 slit burner (acetylene 2 l/min, air 7 l/min) and a Hitachi model QPD53 recorder was employed for the atomic-absorption spectrophotometric determination of silver at 328.1 nm and the flame-photometric determination of sodium at 589.3 nm.

Material. Pyrex glass sheets (81% SiO_2, 13% B_2O_3, 4% Na_2O, 2% Al_2O_3, 0.5% or 0.04% K_2O; density, 2.2 g/cm^3) were annealed at 550 °C for 30 min and then cooled to room temperature at a rate of 1—2 °C/min. They were then washed with a detergent solution, followed by water, at room temperature, and subsequently dried.

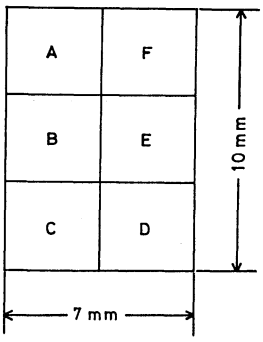

Fig. 1. Standard sample.

Preparation of Standard Sample. A 30-mm-square glass piece was immersed in molten silver nitrate at 335 °C for 90 min to effect the interdiffusion of silver and sodium ions into the glass. The piece was then withdrawn, cooled, washed in water, and dried. A 10×7 mm piece was cut from the above piece, and after covering Part A of the piece (see Fig. 1) with paraffin wax, we immersed it in 5% hydrofluoric acid at 19 °C for 15 min, withdrew it, washed it in water, and dried it. Parts B to E of the piece were successively covered with paraffin wax, and the above chemical etching was repeated. Finally, all the paraffin was removed with benzene. The piece thereafter served as a standard sample with 6 different surface concentrations of silver and sodium.

The surface concentrations were determined as follows. Another 10×7 mm piece was cut from the 30-mm-square

piece, and after its edges had been covered with paraffin wax, immersed in 5% hydrofluoric acid at 19 °C for 15 min, withdrawn, washed in water, and dried. The hydrofluoric acid and the washings were analyzed for silver and sodium by atomic absorption spectrometry and flame photometry. The above procedure was then repeated. The means of the concentrations of silver (or sodium) in two adjacent etched layers correspond to the surface concentrations of the standard sample.

Results and Discussion

Construction of Concentration Calibration Curves. A standard sample was prepared by the interdiffusion of silver and sodium ions in Pyrex glass, followed by chemical etching as has been described above. The corresponding diffusion profiles, obtained by chemical etching and chemical analysis, are shown in Fig. 2. The potassium profile was measured by SIMS, the details of which will be published elsewhere. The sum of the atomic concentrations of silver and sodium, as well as the potassium concentration, remained nearly constant over the whole range. Figure 3 illustrates the concentration calibration curves constructed by the use of the standard sample. Before each SIMS measurement, the surface layer (about 30 nm) of the standard sample was removed by ion etching (0.1 μA, 7-min rastering). The SIMS peak ratios were proportional to the atomic concentrations of the corresponding ions, with maximum deviations of about ±10%. There was no day-to-day variation in the calibration curves.

Depth Resolution and Depth Scale Assignment. When the primary beam was continuously focused on a spot on the glass surface, a conical crater was produced by ion sputtering and the signal from the crater walls deteriorated the depth resolution. To overcome this difficulty, the primary beam (0.3 μA) was rastered over an area 0.8 mm square in order to produce a flat-bottomed crater; then the beam (0.1 μA) was focused for 1 min on the center of the area for SIMS measurements. A fresh spot on the glass surface was used for each measurement. Thus, a depth resolution of the order of 10 nm was achieved.

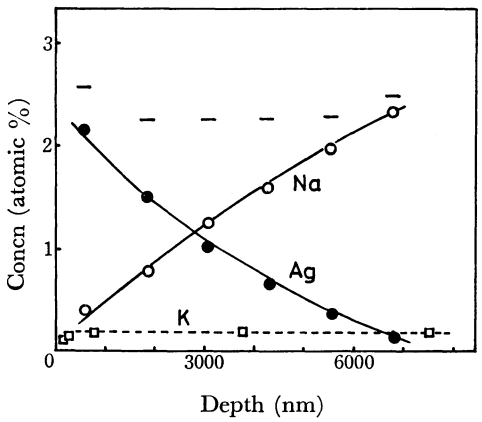

Fig. 2. Diffusion profiles. Pyrex (0.5% K_2O). 335 °C, 90 min. —: Sum of Ag and Na.

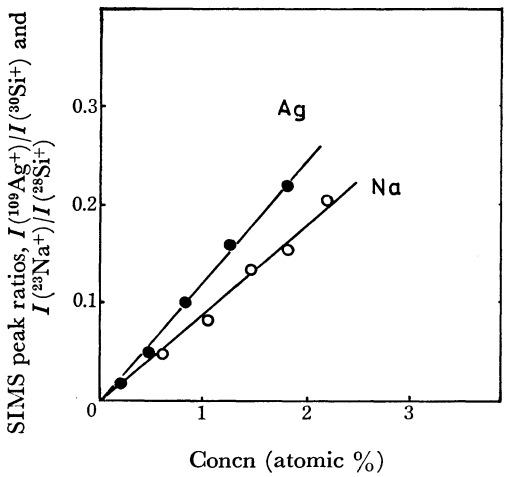

Fig. 3. Concentration calibration curves. Pyrex (0.5% K_2O).

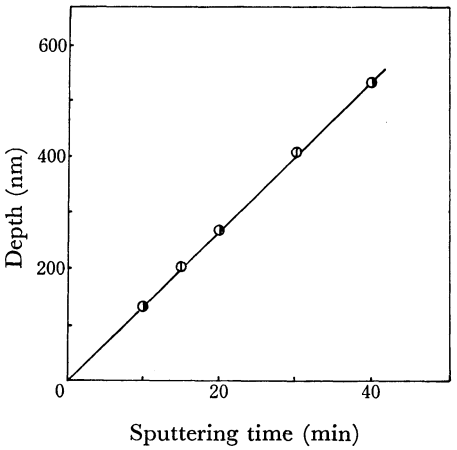

Fig. 4. Plots of crater depth *vs.* sputtering time. ⦶: Pyrex (0.5% K_2O), ◑: Pyrex (0.5% K_2O) in which Na is nearly completely replaced by Ag.

The rate of material removal by ion sputtering under the above conditions was independent of the possible variation in composition of the glass under study, as is shown in Fig. 4. In addition, the day-to-day instrumental fluctuation was negligible. Therefore, the sputtering time can be readily converted to the depth.

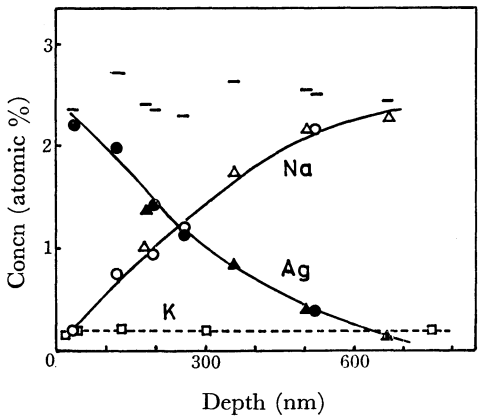

Fig. 5. Diffusion profiles. Pyrex (0.5% K_2O). 335 °C, 1 min. ●○: Ion etching, ▲△: chemical etching. —: Sum of Ag and Na.

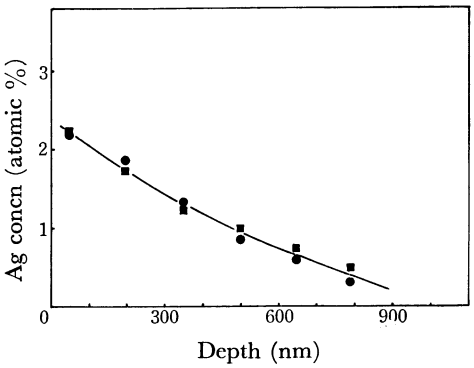

Fig. 6. Diffusion profile. Pyrex (0.04% K_2O). 335 °C, 1 min. ●■: Data on two separately prepared samples.

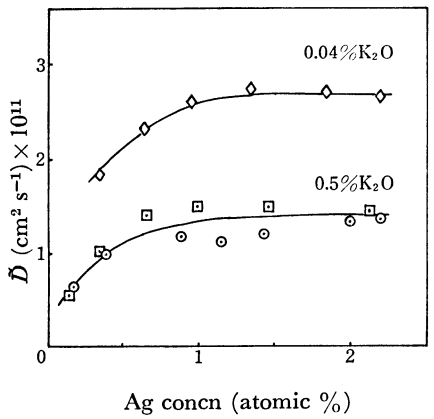

Fig. 7. Interdiffusion coefficients $\tilde{D}$ *vs.* silver concentration. Data from Fig. 2 (⊡), Fig. 5 (⊙), and Fig. 6 (◇).

Diffusion Profiles in the Near-Surface Region. The interdiffusion of silver and sodium ions was effected at 335 °C for 1 min, after which the diffusion profiles were obtained by SIMS. The results are shown in Figs. 5 and 6. The distortion of the diffusion profiles due to ion migration during the ion etching is negligible, because there is no appreciable difference from the profiles obtained by chemical etching with 0.8% hydrofluoric acid instead of ion etching prior to SIMS measurements.

Interdiffusion Coefficients. The interdiffusion coefficients at 335 °C were obtained from the profiles shown in Figs. 2, 5, and 6 by the Boltzmann-Matano method.[5] The results are illustrated in Fig. 7. The interdiffusion coefficients (between 1 and 2.4 atomic% Ag) are 1.4×10^{-11} cm^2 s^{-1} for Pyrex glass containing 0.5% K_2O and 2.7×10^{-11} cm^2 s^{-1} for Pyrex glass containing 0.04% K_2O, showing the mixed alkali effect.[6] The latter value is in reasonable agreement with the values obtained for Pyrex glass containing a negligible amount of potassium by Sjöblom and Andersson (2.6×10^{-11} cm^2 s^{-1})[7] and by Doremus (3.0×10^{-11} cm^2 s^{-1}).[8]

References

1) R. H. Doremus, "Ion Exchange," Vol. 2, ed by J. A. Marinsky, Marcel Dekker, New York (1969), p. 1.
2) P. Heyndryckx, *Glastechn. Ber.*, **44**, 543 (1971).
3) C. A. Andersen and J. R. Hinthorne, *Anal. Chem.*, **45**, 1421 (1973).
4) 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), p. 627.
5) J. Crank, "The Mathematics of Diffusion," 2nd ed, Clarendon Press, Oxford (1975), p. 230.
6) D. E. Day, *J. Non-Cryst. Solids*, **21**, 343 (1976).
7) C. A. Sjöblom and J. Andersson, *Z. Naturforsch., Teil A*, **21**, 274 (1966).
8) R. H. Doremus, *Phys. Chem. Glasses*, **9**, 128 (1968).