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Analysis of Glass Films Prepared from Alkoxides on Glass Substrates

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Synopsis. Sodium in 50 nm thick ZrO_2–SiO_2 glass films has been determined by secondary ion mass spectrometry. A remarkable sodium contamination from the Pyrex glass substrate has been confirmed.

The coating of glass surfaces with glass films of different kinds, prepared *in situ* by hydrolyzing mixtures of alkoxides, offers a new technique to improve the chemical and optical properties of glass surfaces.[1] By this technique, thin homogeneous glass films of various kinds, not obtainable by conventional techniques, may be prepared easily near the transition temperature of the glass.[2] To improve the chemical resistance of Pyrex glass ware, the present authors coated the glass surfaces with ultrathin films of 22 ZrO_2–78 SiO_2 mol% glass prepared from silicon tetraethoxide and zirconium tetrapropoxide. Contamination of sodium from the substrate during the preparation may occur and deteriorate the film. No information on this phenomenon is available to date and consequently the sodium in the films has been determined by secondary ion mass spectrometry (SIMS), which is the most suitable technique at present for the quantitative analysis of ultrathin films.

The glass films were transparent, homogeneous, and 50 ± 5 nm thick. Under the scanning electron microscope (2000X and 10000X), the surfaces of the films were found to be smooth and without pinholes and cracks. The films were not damaged by abrasive action with the fingers. Figure 1 shows the SIMS spectra of 22 ZrO_2–78 SiO_2 mol% glass films and Pyrex and silica glass substrates. In the film on the Pyrex glass substrate, sodium was found, but boron, aluminum, and potassium were found to be absent. The SIMS spectrum of the film on the silica glass substrate was identical with that of 22 ZrO_2–78 SiO_2 mol% glass flakes. The secondary ions originate from the region 10 nm from the surface.[3] The films were ion-etched only about 15 and 10 nm before and during the SIMS measurements, respectively, and therefore, the pure spectra of the films were obtained without interference from the substrate by this technique.

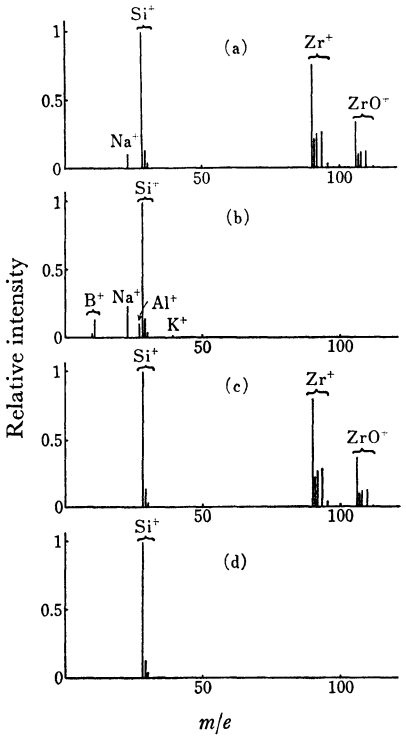

Fig. 1. SIMS spectra.
(a): ZrO_2–SiO_2 glass film on Pyrex glass, (b): Pyrex glass substrate, (c): ZrO_2–SiO_2 glass film on silica glass, (d): silica glass substrate.

Table 1. Sodium concentrations (Na_2O, mol %)

In glass flakes[a]	In glass films[b]	(Substrates)
0.0	1.4	(Pyrex)
0.0	0.0	(Silica)
0.29	0.31	(Silica)
2.5	2.5	(Silica)
5.2	5.5	(Silica)

a) Determined by flame photometry (maximum relative error ± 3%). b) Determined by SIMS (maximum relative error ± 10%).

In Table 1, the concentrations of sodium in the coating films have been compared with those in the corresponding glass flakes. Only the Pyrex glass substrate interacts with the glass film. The sodium concentrations in the films were constant between 20 and 35 nm from the surfaces. Additional heating at 450 °C for 5 h did not increase the sodium concentration. Therefore, the sodium contamination from the Pyrex substrate probably resulted from the presence of water in the film[2] between 200 and 400 °C during the preparation of the film.

Experimental

Preparation of Mixed Alkoxide Solutions. Into a 100 ml round-bottomed flask, silicon tetraethoxide (4 ml) (Nakarai Chemicals), zirconium tetrapropoxide (3 ml) (Ventron Corp.), sodium methoxide (0 to 0.6 ml) (Wako Pure Chemical Industries), and 1-butanol (13 ml) (dehydrated with Molecular Sieve 4A) were placed. A reflux condenser was attached to the flask, and the contents were well mixed with a magnetic stirrer for 3 h at 85 ± 5 °C in a stream of nitrogen (10 cm^3 min^{-1}, dried with calcium chloride). The mixture was cooled and stored in a glass stoppered bottle in a desiccator.

Coating. An 8×5 mm Pyrex or silica glass piece, 1 or 1.5 mm thick, was immersed in a 1:1 mixture of concentrated

nitric and sulfuric acids for 24 h, rinsed thoroughly with water, and dried over silica gel. The piece was immersed in a mixed alkoxide solution (100-ml beaker), and withdrawn vertically at a speed of 4 mm min^{-1} by a motor to form a film of uniform thickness. Hydrolysis was effected by placing the piece in a desiccator containing a saturated potassium sulfate solution (relative humidity 95%) at 50 °C for 60 min. The piece was heated at 150 °C for 60 min in an electric muffle furnace. Then the temperature was raised at a rate of 10 °C min^{-1}, kept at 550 °C for 30 min, and lowered to 350 °C at a rate of 1 to 2 °C min^{-1}. The piece was then cooled to room temperature.

Preparation and Analysis of Glass Flakes. A mixed alkoxide solution (1 ml) was placed in a 50 ml silica beaker, and allowed to stand for 24 h at ambient temperature (20—25 °C; relative humidity, 40—50%) to effect evaporation of the solvent and hydrolysis. The resulting flakes (*ca.* 3 mm × 3 mm × 50 μm) were heat-treated and annealed as described in the last paragraph, except that the heating time at 150 °C was increased to 2 h. The transparent glass flakes were used as standards in the SIMS determination of sodium in glass films on glass substrates. For standardization, the flakes were decomposed with hydrofluoric and hydrochloric acids, and sodium and zirconium were determined by flame photometry at 589.3 nm and inductively coupled plasma-optical emission spectrometry at 339.2 nm.

SIMS and Other Measurements. A Hitachi IMA-2 ion microanalyzer was operated under the following conditions: primary ions, argon; primary ion accelerating voltage, 5 kV; primary ion current, 0.1 μA; beam diameter, 250 μm; sample chamber pressure, 3×10^{-5} Pa; secondary ion accelerating voltage, 1.5 kV; electron-multiplier voltage; 2 kV. The electric charges accumulated on the glass surfaces were eliminated by the electron spray method. The SIMS spectra were recorded after ion etching 15 nm from the surface by rastering the primary beam (total number of scanning lines, 500; line frequency, 100 Hz) over a square area of 0.8 mm around the spot to be measured. For the determination of sodium in glass films, peak ratios of $^{23}Na^+$ to $^{28}Si^+$ were measured, and the sodium concentrations were obtained from a calibration curve. The curve (peak ratio *vs.* atom % Na) was prepared using glass flake standards [(22—21)ZrO_2–(78—74)SiO_2–(0—5)Na_2O mol % glasses] and was a straight line through the origin. The thickness of the glass films was measured with a Mizojiri Kogaku model II multiple beam interferometer (Hg 546.1 nm, magnification 40X), with a maximum error of ±3 nm.

References

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