significantly stronger than the unreduced glass. The strengthening is clearly confined to the surface and is confirmed by the apparent lack of strengthening in the abraded canes. (Abrasion penetrated the strengthened layer). Because of the possibility of the existence of flaws deeper than the strengthened layer, even in the unabraded canes, the standard deviation of the strength for the unabraded, reduced glass is larger than that for the unabraded, unreduced glass. Fractographs confirm the presence of a surface layer  $\approx 5 \ \mu m$  thick where fracture traveled comparatively slowly. That this slow velocity was perhaps not a consequence of a surface compression layer was indicated by polarized light microscopy. Using a stress optical coefficient of +2.2 Brewsters,<sup>3</sup> it was estimated that  $\approx$ 40  $\mu$ m of the surface was under  $\approx 0.5$  MPa tension. The slight tension could be a result of an increased thermal contraction coefficient of the surface layer after reduction. However, high-lead glasses are known to have near-zero or even negative stress optical coefficient.<sup>3</sup> Hence, the

apparent failure to detect surface compression could have been an artifact of the polarized light procedure. Because of the inaccuracies involved, estimates of surface compression, if any, could not be inferred from the measurements of the fractographic mirror radii.

Negative ion SIMS analysis showed a significant reduction in surface oxygen. Positive SIMS showed an increase in Si<sup>+</sup> and SiOH<sup>+</sup> concentration, indicating that many of the Si-O-Si bonds have been broken by H<sub>2</sub> to form Si<sup>+</sup> and SiOH<sup>+</sup> ending units in the network. (Because of the large atomic size, a quantitative analysis of Pb enrichment, if any, could not be performed using SIMS.) It may be concluded that reduction with H<sub>2</sub> alters the glass network in the surface layers. It is possible that this defect structure impedes the growth velocity of subcritical flaws (surface compression need not be present). This behavior suggests a structure which is quite different from that produced in aqueous media where the OH groups generally accelerate the crack velocity.

To resolve the question of strengthening resulting from surface compression versus strengthening from a significantly changed glass structure, we plan to conduct careful experiments to determine surface stresses and to examine the possibility that strengthening of this type can be achieved in glasses containing other heavy metal ions that can be reduced.

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### J. Am. Ceram. Soc., 70 [4] C-77-C-78 (1987)

# Transmission Electron Microscopic Observations of $\alpha$ -Cristobalite in Fused Silica

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Distinct crystalline phases in some commercial fused silicas were shown by transmission electron microscopy. They were identified to be  $\alpha$ -cristobalite by selectedarea electron diffraction. Their origin and the effect on the glass matrix are discussed.

COMMERCIAL fused silica is prepared by fusing pulverized quartz crystals or by hydrolysis and/or oxidation of SiCl<sub>4</sub> through flame fusion. The former process is still much less expensive and more widely used. However, because of the high viscosity of silica at the fusion temperature,

homogenization of the melt is inevitably incomplete, and inhomogeneities are observed routinely as an undulation of re-fractive index by pinhole shadowgraphs.<sup>1,2</sup> Inhomogeneities at few tens of nanometers scale, observed earlier by the electron microscope,<sup>3-5</sup> were once considered to reveal the structure of vitreous silica, but a later study noted no structure down to a resolution of  $\approx 2$  nm on different vitreous silicas.<sup>6</sup> It is also known that, when fused silica is formed by melting crystalline  $SiO_2$ , it is very difficult to remove all the structural features of the initial crystalline phase completely. For example, quartz samples heated to 200°C above their melting point for extended periods showed adsorption bands characteristic of quartz." The presence of submicroscopic crystals has been postulated as one explanation for these structural vestiges and/or inhomogeneities, but little direct evidence has been produced to confirm their presence. This paper reveals by transmission electron microscopy (TEM) the presence of distinct crystalline phases in several commercial high-purity fused silica wafers.

EXPERIMENTAL PROCEDURE

Two types of commercial fused silica glasses were examined in the present work: one manufactured from natural quartz by either electrical or flame fusion<sup> $\dagger$ </sup> (type 1) and the other manufactured by hydrolysis of  $SiCl_4^{\ddagger}$  (type 2). Sample glasses were pulverized with a mullite mortar and pestle, and the resultant powders, containing glass particles ranging from a few to several hundred nanometers in size (as seen in the electron microscope) were dispersed ultrasonically in water to obtain uniform suspensions. A drop of the suspension was then dried on a carbon film, which was formed on an electron microscope grid. The effects of electrostatic charging, characteristics of glass specimens, were avoided by carefully dispersing the glass particles on the grids and, when necessary, by evaporating a small amount of amorphous carbon onto the glass-containing microscope grids.

The TEM observations were conducted with 300 keV. The condenser lens current was kept in such a way that no radiation damage to the specimens was detected during the TEM analysis. The use of higher voltages is known to reduce the damage to this kind of sample since the cross section for electrons decreases as the acceleration voltage increases. In addition, the obviously higher penetration power makes it possible to visualize thicker

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Vitreosil, Thermal American Fused Quartz Co., Montville, NJ.

Spectrosil, Thermal American Fused Quartz Co.



Fig. 1. TEM photograph of an embedded crystallite in fused silica (bar=0.05  $\mu$ m).



Fig. 2. TEM photograph of fused silica sample in higher magnification. Ordered structures in multiple orientations can be seen (bar=4 nm).

particles. A 100- $\mu$ m objective aperture allowed us to include higher-order reflections to form the fine images. The diffraction data were obtained using standard selectedarea diffraction (SAD).

# RESULTS

Of the two types of glasses prepared for TEM work, small crystalline regions, typically in the 70- to 80-nm range, were found in all the type 1 samples but never in the type 2 specimens. Careful diffraction analysis showed no evidence of microcrystallinity in the latter samples. Figure 1 shows a low-magnification micrograph of a type 1 specimen typically demonstrating the presence of such crystallites embedded



Selected area diffraction pattern of the Fig. 3. ordered structures observed by TEM.

Table I.	Comparison	of	Diffraction
Lines			

JCPDS	hkl	Observed
4.05	101	4.05
3.135	111	3.149
2.841	102	2.872
2.485	200	
2.465	112	2.462
2.340	201	2.344
2.118	211	
2.019	202	2.028
1.929	113	
1.870	212	1.812
1.757	220	
1.730	004	
1.690	203	1.667
1.634	104	
1.612	301	
1.600	213	

in the amorphous matrix. Figure 2 shows, on the other hand, a high-magnification micrograph of a type 1 specimen in which lattice fringes of the crystalline structure in multiple orientations can be seen clearly.

Selected-area electron diffraction was performed on all the samples that revealed the embedded crystallites, using a small SAD aperture to assure that the recorded diffracted beams correspond only to the small crystallites. All the electron diffraction patterns obtained were the same, as shown in Fig. 3, and identified as  $\alpha$ -cristobalite.<sup>8</sup> Evaporated gold was used as an external standard. Table I shows a comparison of the observed diffraction lines and those in the JCPDS file. All the observed d values match with the corresponding standard values within a few percent. Some of the lattice fringes observed in Fig. 2 correspond to the smallest Si-Si distances in the tetragonal  $\alpha$ -cristobalite structure.

## DISCUSSION

Crystallization of fused silica upon heating commonly has been observed as

devitrification from the surface by the formation of cristobalite layers.9 Occasionally however, internally nucleated crystallization has been reported.9.10 Since we confirmed the existence of crystallites of cristobalite in commercial fused silica, we now believe that these crystallites act as nucleation sites of internal crystallization, perhaps by epitaxial growth.<sup>11</sup> Although the crystalline phase observed in this study was identified as  $\alpha$ -cristobalite instead of the high-temperature  $\beta$ -form, this is probably caused by our sample preparation procedure. As described in the Experimental Procedure section, our sample glasses were pulverized for TEM observation. By heat treatment of a fused silica test piece at 1483°C for 70 h, on the other hand, Wagstaff<sup>10</sup> formed  $\beta$ -cristobalite crystals of >100  $\mu$ m in size, which could be retained in the fused silica at room temperature, as long as the strain energy which was holding the cristobalite in the  $\beta$ -form metastably was not released. The thermal expansion coefficient of  $\beta$ -cristobalite in the range 300° to 600°C is  $5.7 \times 10^{-6}$ /°C, greater than that of fused silica by  $5 \times 10^{-6}$ /°C. In contrast, the average of the thermal expansion of  $\alpha$ -cristobalite plus the transition expansion of  $\alpha$ - to  $\beta$ -form is  $50 \times 10^{-6}$ /°C in the range 20° to 300°C,<sup>12</sup> almost 1 order greater than that of  $\beta$ cristobalite. Probably such a large difference in thermal expansion could induce strain energy large enough to retain  $\beta$ -form metastably at room temperature, if it is not released by crushing as in our case, or by forming numerous fissures by itself as observed more commonly in the devitrification of fused silica.

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