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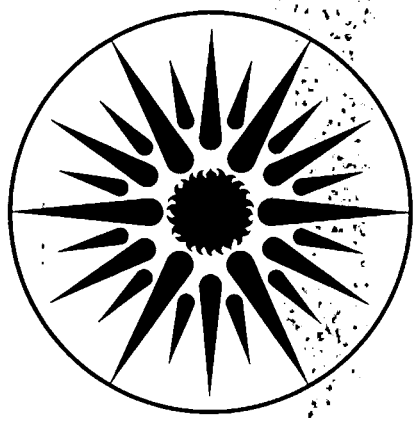
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San Diego, CA, August 19-24, 1984

HIGH-RESOLUTION ELECTRON MICROSCOPY STUDY OF  
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September 1984

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HIGH-RESOLUTION ELECTRON MICROSCOPY STUDY OF SILICA  
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# High resolution electron microscopy study of silica aerogel transparent insulation

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## Abstract

The structure of silica aerogel was studied by transmission electron microscopy. The aerogel network consists of particles about 10.0 nm in diameter. The chemical composition of these aggregates was found to be a pure stoichiometric  $\text{SiO}_2$  by both ESCA and Auger spectroscopy. These  $\text{SiO}_2$  groups appear to form a random network within each particle. The details of this arrangement have yet to be determined, because in this preliminary study, silica aerogel was found to transform after exposure to the intense electron beam.

## Introduction

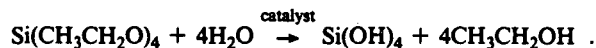
Silica aerogel is essentially a porous material consisting of particulate  $\text{SiO}_2$  arranged in a skeleton network. Prior work on silica aerogel has reported basic optical and thermal properties and laser light-scattering studies.<sup>1,2</sup> This material is highly transparent over the solar spectrum (transmittance  $T_S = 0.93$ ), with little scattering. The particle size and packing matrix determine the aerogel's light-scattering and transmission properties. In addition, the porous nature of silica aerogel determines its low thermal conductivity,  $0.019 \text{ Wm}^{-1}\text{K}^{-1}$ .<sup>3</sup>

The purpose of this work is to gain a better understanding of the microstructure of silica aerogel by its direct evaluation using transmission electron microscopy (TEM).

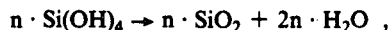
## Experimental procedures

### Preparation of silica aerogel

The silica aerogel is prepared in two steps. The first step involves obtaining monosilicic acid by hydrolysis of tetraethyl orthosilicate in ethanol, catalyzed by HCl and HF, as described by the following reaction:<sup>4,5</sup>



In the second step monosilicic acid condenses to produce colloidal silica in the reaction



after which ethanol is removed by supercritical drying at pressures above 110 bars and a temperature of 270°C. The porous material is formed because of the lack of surface tension, related to the disappearance of the vapor/liquid interface above the critical point of ethanol. (The surface tension would cause collapse of the pores.) The resulting aerogel has low density,  $\rho = 0.141 \text{ gcm}^{-3}$ , and high porosity (volume fraction of air),  $\epsilon = 0.937$ .

### Auger and ESCA analysis

Freshly cleaved specimens of silica aerogel were used to determine chemical composition and the possible presence of impurities. Both Auger and ESCA (x-ray photoelectron spectroscopy) were used to study the aerogel. The apparatus used was a PHI Model 590 scanning Auger microscope (SAM) integrated with a PHI ESCA spectrometer.

The samples were prepared differently for each technique. For Auger analysis the aerogel specimen was coated with a thin layer of gold 5 - 10 nm thick to reduce charging. Uncoated samples were attempted, but charging interfered adversely with the Auger signal. In the SAM an argon ion beam was used to lightly sputter away a small portion of the gold layer, exposing a 2-3  $\mu\text{m}$  diameter area of aerogel. The Auger signal was monitored during sputtering to verify that ion-induced chemical changes were not taking place during sputtering. For ESCA studies the specimen was not coated or treated in any way.

### Transmission electron microscopy

Specimens for TEM were prepared by crushing small pieces of silica aerogel between two glass slides. The particles of aerogel were then collected between a folding mesh grid. Thin regions of aerogel, transparent to electrons, were imaged in a JEM 200 CX transmission electron microscope. The microscope was equipped with the high resolution pole piece ( $C_S = 1.2 \text{ mm}$ ) and was operating at 200 kV, with a point-to-point resolution of about 0.26 nm. All high resolution images were obtained in axial illumination.

## Experimental results and discussion

### Chemical analysis

An Auger spectrum of silica aerogel is shown in Figure 1. The conditions used were an electron beam energy level of 5 kV and a current of  $0.7 \times 10^{-6}$  A. The principle Auger peaks for silicon LMM transition occur at 59, 63, and 76 eV, and KLL transition occurs at 1547, 1562, 1582, and 1606 eV. The oxygen KLL transitions occur at 503, 486, and 483 eV. These experimental results match well with reported transitions for  $\text{SiO}_2$ .<sup>6</sup>

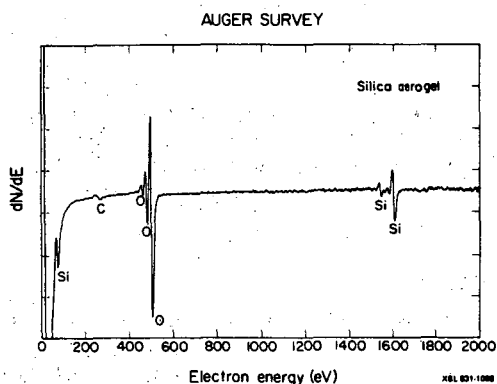


Figure 1. Auger electron spectroscopy showing the typical chemical composition of silica aerogel.

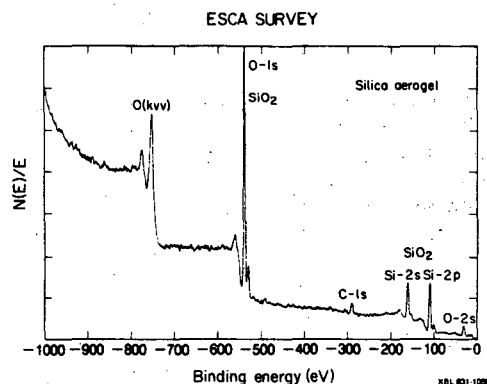


Figure 2. X-ray photospectroscopy of silica aerogel indicating that the material has the stoichiometry of  $\text{SiO}_2$ . The carbon is from surface contamination.

The ESCA results were obtained using  $\text{Mg K}_\alpha$  x-ray radiation with an energy level of 12 keV and a current of  $5 \times 10^{-2}$  A. An ESCA spectrum in Figure 2 shows the O-1s, C-1s, and Si-2p transitions. There is a uniform 3.8 eV shift in the spectrum to higher energies due to charging of the specimen, as determined by the C-1s transition observed at  $-288.4$  eV, compared to the theoretical value of  $-284.6$  eV. (The small carbon peak is due to atmospheric contamination of the surface.) The O-1s transition was measured at  $-533.2$  eV and compares to data for high purity  $\text{SiO}_2$  at  $-533$  eV.<sup>7</sup> The Si-2p transition was measured at  $-104$  eV, compared to reported values for high purity  $\text{SiO}_2$  at  $-103.9$  eV<sup>8</sup> (although a range of values for Si-2p in  $\text{SiO}_2$  exists from about  $-103$  to  $104$  eV). For comparison, the Si-2p transition in Si is at  $-99.15$  eV. From these data we conclude that this silica aerogel is composed of high purity  $\text{SiO}_2$  with no detectable impurities other than surface contamination by atmospheric carbon.

### Transmission electron microscopy of silica aerogel

A low magnification TEM image of an aerogel specimen is shown in Figure 3. Regions marked A and B represent edges of a larger aerogel particle; these edges are transparent to the electron beam. Small clusters, approximately 10 nm in diameter, form a network of aerogel. This morphology can be seen better in the higher magnification micrograph shown in Figure 4. The imaged area corresponds to the region marked A in Figure 3. A corresponding selected area diffraction pattern shown in Figure 5 consists of uniform rings. This suggests that the clusters are probably amorphous. However, similar rings could be formed by very fine randomly distributed crystalline particles.<sup>9</sup> In order to distinguish between these two cases, high resolution electron microscopy (HREM) was performed. A HREM image of area A in Figure 3 is shown in Figure 6. Different aggregates of silica have a nominal diameter range of 20–50 nm. The mottled contrast observed within these silica clusters is typical of amorphous material.<sup>10</sup>

The analysis can be extended to the three-dimensional distribution of the clusters. A particle to the left in Figure 7 is at the defocus value giving minimum contrast, while particles with dark Fresnel fringes around their edges correspond to particles located further from the objective lens (overfocus condition) than particles at minimum contrast. A white Fresnel fringe at the edge corresponds to underfocus conditions; therefore, these particles are closer to the objective lens than are the particles at minimum contrast. In both cases the particles are separated by a few hundred angstroms in the beam direction. This is consistent with the observed average size of particles. Different aggregates are connected by necks similar in appearance to those observed during an early stage of the sintering process. Thus observed aerogel morphology in high resolution images is to some extent induced by an electron-beam heating effect. This effect can be observed in Figure 8, in which area A was transformed under the electron beam while area B did not change. The aerogel particles appear to be stable after transformation.

Experiments in progress are attempting to reduce the transformation rate of the aerogel and will allow analysis of the structure before transformation.

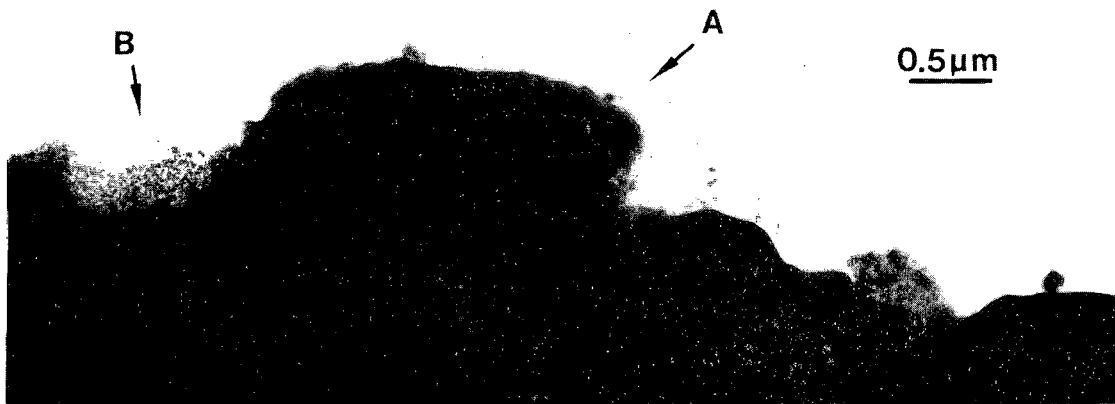


Figure 3. Low magnification bright-field TEM image of the silica aerogel. A and B indicate regions transparent to electrons. (XBB 847-5465)

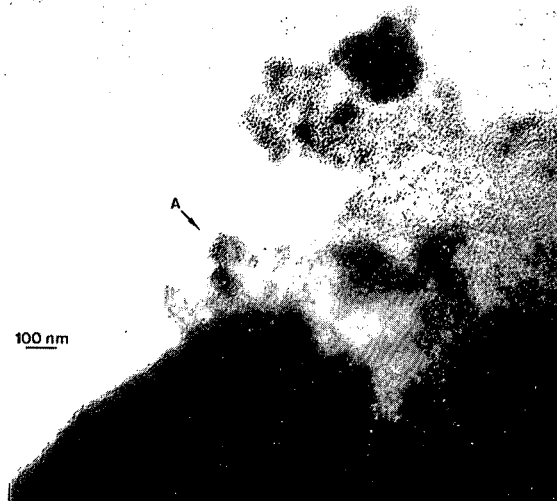


Figure 4. Higher magnification bright-field image of the area A in Figure 3. (XBB 847-5466)



Figure 5. Selected-area diffraction pattern of the area A in Figure 3. (XBB 847-5471)



Figure 6. High resolution image of the silica aerogel (area A in Figure 3). (XBB 847-5481)



Figure 7. High resolution image of the silica aerogel. A particle to the left is at minimum contrast. Particles with a dark Fresnel fringe around the edge correspond to particles located further from the lens (over-focus condition). Particles with a white Fresnel fringe around the edge are closer to the objective lens than the particles at minimum contrast. (XBB 847-5475)





Figure 8. Low magnification image of the specimen after exposure to an intense electron beam during high resolution imaging (area A). Notice the difference between areas A and B. (XBB 847-5468a)

### Conclusions

This study of the chemistry and structure of silica aerogel demonstrates that:

1. Silica aerogel consists of a network of amorphous stoichiometric silica clusters with an average size about 10 nm.
2. The aerogel transforms readily under an intense electron beam. The sizes of the particles increase to 20–50 nm and appear to be stable with time after the transformation. The structure of the transformed clusters is amorphous, as determined by high resolution electron microscopy.
3. High resolution electron microscopy also allowed us to determine the distribution of the aerogel particles in the direction of the beam.

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