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Structural Analysis of SiO_2 Gel Films by High Energy Electron Diffraction

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Abstract. The structure of SiO_2 gel-films prepared from acid and basic TEOS solutions is analyzed by high energy transmission electron diffraction method. The Si–O bond length of gel-films is 1.58 to 1.60 Å, which is shorter than that of vitreous silica (1.61 Å) but similar to that of 80 Å thick evaporated a-SiO_2 film. An atomic pair peak with 0.81 Å distance exists on the reduced radial distribution functions of the gel-films, which is believed to be O–H, but being smaller than that of H_2O (0.969 Å).

Keywords: SiO_2 gel, thin film, atomic structure, electron diffraction, O–H bond, Si–O bond

1. Introduction

Sol-gel process has a huge potential for producing functional materials through simple procedures. The gel-materials are generally not dense and need a thermal treatment for transformation to stable glasses and ceramics. The atomic network grows with the association of small clusters and the dehydration on the surface of the clusters during the thermal treatment. The structure of gel materials therefore affects the densification process.

In this study, the atomic structure of thin SiO_2 gel-films is analyzed by use of high energy transmission electron diffraction method.

2. Experimental

The sols were prepared from the standard solution being a mixture of 15 ml TEOS and 28 ml ethanol. Sols labeled A-1, A-2 and I were obtained from the standard solution by acidifying with aqueous HCl in order to be apparent pH (pH*) of 0.6, 1.6 and 2.6 (isoelectric point of SiO_2), respectively. Sol B with pH* of 10.5 was prepared by adding aqueous NH_4OH to the standard solution. The ratio TEOS : H_2O : ethanol is kept almost constant for all the sols (1 : 5.8 : 7.1 in mole ratio). The sols were aged for 5 days at room temperature without evaporation.

The gel-films were prepared by the following procedures. A mesh Cu grid with 0.24 mm diameter hole was immersed into a sol and withdrawn vertically. Thin films in the holes of mesh grid were self-supported by the surface tension and they were then dried in warm air at 40 to 50°C for 10 to 30 seconds.

An electron diffraction apparatus was operated at an electron energy of 55.8 keV. The electron-beam size was about 70 μm and the beam current was of the order of 10^{-9} A. The diffraction pattern of the gel-films was measured in the s-value range 0.3 to 34 $Å^{-1}$, $s = (4\pi/\lambda)\sin(\theta/2)$, θ is the angle between the incident and diffracted beam, and λ is the electron wavelength. The intensity of transmitted electron-beam through gel-films was measured by a Faraday cage with a aperture of 0.1 mm in diameter. The Faraday cage captured the electron-beam with diverging angle un-

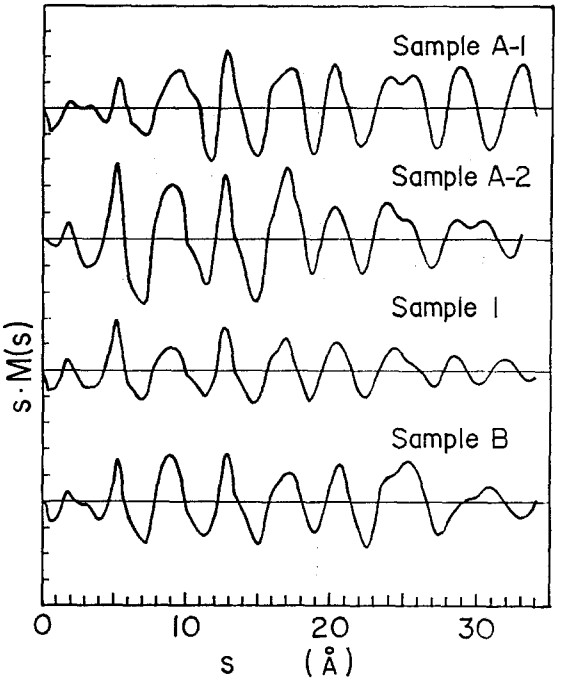

Fig. 1. Interference functions $sM(s)$ versus s for sample A-1, A-2, I and B.

til 0.016° corresponding to 0.03 $Å^{-1}$ of s-value. The film thickness of the gel-films was estimated from the electron-beam transmittance by comparison with the transmittances of evaporated of SiO_2 films. The transmittance for sample A-1, A-2, I and B were 9.7, 28.7, 18.2 and 5.4% and the estimated film thicknesses are about 210, 110, 150 and 260 Å, respectively.

The small transmittances of the gel-films indicate the occurrence of multiple scattering, and the total diffracted intensity, I_{tot} therefore is written as

$$I_{\mathrm{tot}}(s) = I_0 N\{J_{\mathrm{m}}(s) + J_{\mathrm{el}}(s) + J_{\mathrm{inel}}(s)\} + I_{\mathrm{mult}}(s) \quad (1)$$

where I_0 is incident beam intensity, N is the number of SiO_2 unit compositions in the volume irradiated by the electron-beam, $J_{\mathrm{m}}(s)$, $J_{\mathrm{el}}(s)$ and $J_{\mathrm{inel}}(s)$ are interatomic interference, elastic atomic and inelastic atomic scattering per unit composition, respectively, and $I_{\mathrm{mult}}(s)$ is multiple scattering intensity. A division of $J_{\mathrm{m}}(s)$ by $J_{\mathrm{el}}(s)$ gives the interference function $M(s)$ and a sine-Fourier transformation of interference function $sM(s)$ produces the differential radial distribution function (RDF),

$$4\pi r\{D(r) - D_0\} = \frac{2}{\pi}\int_0^{s_{\max}} sM(s)\exp(-\alpha^2 s^2)\sin(sr)\,ds \quad (2)$$

Table 1. Si–O bond lengths, O–O atomic distances and calculated O–Si–O angles for sample A-1, A-2, I and B.

Sample	$r_{\mathrm{Si-O}}$	$r_{\mathrm{O-O}}$	∠O–Si–O
A-1	1.58 Å	2.55 Å	107.6°
A-2	1.59	2.62	111.0
I	1.60	2.63	110.5
B	1.58	2.52	105.8

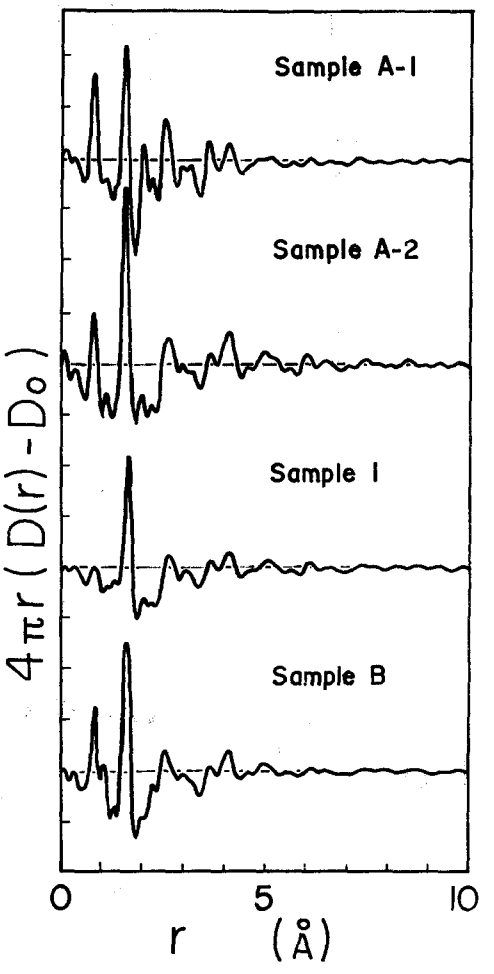

Fig. 2. Differential radial distribution functions for sample A-1, A-2, I and B.

where α is the artificial temperature factor used to reduce termination effects due to the finite measurement range (until $s_{\max}$) and taken equal to 0.0506 Å in this study.

$J_{\mathrm{m}}(s)$ is determined from the experimentally obtained $I_{\mathrm{tot}}(s)$ with the following consideration. $J_{\mathrm{el}}(s)$ and $J_{\mathrm{inel}}(s)$ are calculated theoretically by using the elastic and inelastic scattering factors for Si and O atoms [1]. Since $J_{\mathrm{m}}(s) = 0$ and assuming $I_{\mathrm{mult}}(s)$

Table 2. Si–O bond lengths, O–O atomic distances and calculated O–Si–O angles for evaporated amorphous SiO_2 films.

Thickness	r_{Si-O}	r_{O-O}	∠O–Si–O
4 Å	1.54 Å	2.48 Å	107.2°
10 Å	1.54	2.51	109.8
20 Å	1.57	2.56	119.6
40 Å	1.57	2.58	110.3
80 Å	1.58	2.58	109.3

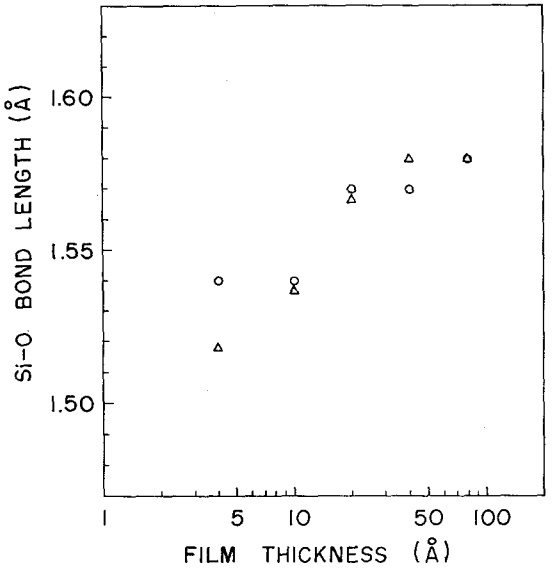

Fig. 3. Si–O bond length versus films thickness of ev. a-SiO_2. o represents the directly obtained length and Δ represents the length calculated from O–O distance assuming SiO_4-tetrahedron.

is nearly zero, the extrapolation of $I_{tot}(s)$ for $s = 0$ allows the determination of the tentative normalization constant for intensity $I_0N = I_{tot}(0)/\{J_{el}(0) + J_{inel}(0)\}$. $I_{mult}(s)$ was obtained by using of the fact that $J_m(s)$ is a smooth function oscillating around zero. The determined $I_{mult}(s)$ increases monotonously with s-value and consequently the determined I_0N is the best obtainable value.

The shortening of observed O–H bond length was studied by calculating the ab initio self-consistent field molecular orbitals of silicon-oxide clusters terminated by hydrogen atoms using a STO-3G basis and the computer program GAUSSIAN-80 [2].

3. Results and Discussion

The obtained interference functions $sM(s)$ for gel-films are shown in Fig. 1: the differential RDF's for them are presented in Fig. 2. From the analogy of the

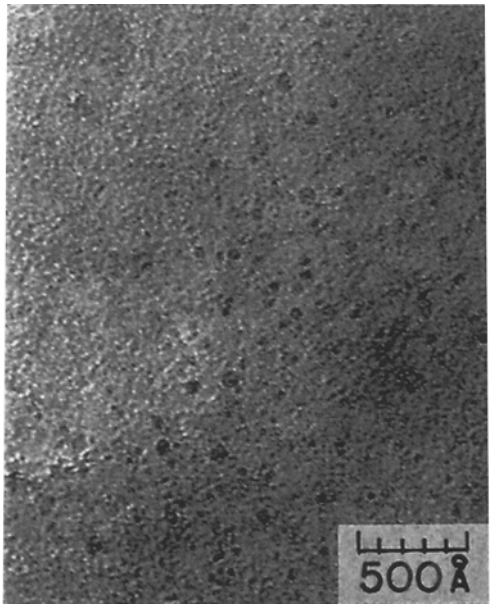

Fig. 4. Micrograph of sample A-2 with the 200 kV transmission electron microscope.

atomic distances for vitreous silica [3, 4], the peaks around 1.6 and 2.6 Å on the differential RDF curves can be assigned to Si–O bonded pairs and O–O atomic pairs of O–Si–O structure, respectively, and the Si–O bond lengths, O–O atomic distances and O–Si–O angles calculated from these two distances are given in Table 1. The calculated O–Si–O angles are close to that of SiO_4-tetrahedron (110°). All the gel-films are therefore considered to be constructed from SiO_4-tetrahedrons. The Si–O bond length of the gel films is smaller than that of bulk vitreous silica (1.61 Å). Bond shortening of Si–O bond length has been observed in the extremely thin films of evaporated amorphous SiO_2 (ev. a-SiO_2): the Si–O bond lengths, O–O atomic distances and calculated O–Si–O angles for the films are listed in Table 2 [5, 6]. Since the O–Si–O angles are nearly equal to 110°, the ev. a-SiO_2 films are considered to be constructed from the SiO_4-tetrahedrons. The shortening of Si–O bond length shown in Fig. 3 indicates that the SiO_4-tetrahedrons shrink with the decrease of ev. a-SiO_2 film thickness. Considering the short Si–O bond lengths of gel-films with these results, the gel-films are believed to be made up of loose bound grains. This is supported by 200 kV transmission electron micrograph of sample A-2 presented in Fig. 4.

The clear peak at $r = 0.81$ Å on the differential RDF curves exists commonly for all the gel-films. Since no atomic pairs related to carbon bonding (expected Si–C

Table 3. Optimized and experimentally obtained O–H bond lengths of H_2O, OH molecule and $[OH]^-$ and $[OH]^+$ ions.

	Calculation			Experimental
		Ionicity		
Species	O–H bond length (Å)	O	H	O–H bond length (Å)
H_2O	0.9893	−0.331	+0.165	0.969
OH	1.0541	−0.320	+0.320	0.970
$[OH]^-$	1.0680	−0.742	−0.258	0.984
$[OH]^+$	2.1461	+0.008	+0.992	1.028

Table 4. Optimized structural parameters of SiO_4H_4 clusters. The value with superscript (*) indicates that the corresponding structural parameter was fixed during the optimization process.

			Ionicity			
	r_{Si-O} (Å)	r_{O-H} (Å)	Si	O	H	Energy (Hartree)
Cluster 1	1.8000*	0.9911	+1.062	−0.418	+0.158	−583.328
Cluster 2	1.6646*	0.9853	+1.281	−0.481	+0.161	−583.371
Cluster 3	1.5800*	0.9751	+1.471	−0.544	+0.177	−583.358
Cluster 4	1.6482	0.8100*	+1.342	−0.585	+0.250	−583.168

and C–C bond lengths being 1.9 and 1.5 Å, respectively) are observed, the peak is believed to be O–H bonded atomic pair. This O–H atomic distance is smaller than that in H_2O (0.969 Å), in OH (0.970 Å), in $[OH]^+$ (1.028 Å) or $[OH]^-$ (0.984 Å). In order to obtain information concerning the relationship between O–H bond length and ionicities of Si and O atoms, we made ab initio molecular orbital calculations using STO-3G basis set. Since STO-3G basis is simple, obtained bond lengths are not accurate but can be used for qualitative discussion. As given in Table 3, the order of the optimized O–H bond lengths of H_2O and OH's is same as the order of experimentally obtained bond lengths.

SiO_4H_4 cluster is assumed to be SiO_4-tetrahedron with four H atoms terminating O atoms equivalently and the optimized structural parameters are listed in Table 4. It is found that the clusters with more ionic O and H ions have shorter optimized O–H bond length, and ab initio calculations on clusters including 2 and 3 Si atoms shows the same tendency. Since the clear O–H peak with very short atomic distance is observed on the differential RDF's, the grains constructing gel-film are considered to be covered by O–H having strong ionicity.

Comparing the four analyzed gel films on Table 1 and Fig. 2, the two structural features, Si–O length bond and amount of O–H bonds are found to be strongly related to each other. The gel film prepared from the sol with isoelectric pH* for SiO_2 has the largest Si–O bond length and contains the smallest amount of O–H bonds. With pH* more deviating from the isoelectric point, the Si–O bond length and the O–H amount decrease. These facts are understood on the view point of atomic network of gel films: the well-networked gel which is constructed from larger grains and therefore has larger Si–O bond length, includes less O–H bonds because of less grain boundaries. In other words, the pH* is an important factor on the atomic network construction during sol-gel transition, and the isoelectric pH* for SiO_2 is the best environment for promoting the network construction.

4. Conclusions

The SiO_2 gel-films have shorter Si–O bond length than that of bulk vitreous silica but the length is similar to that of 80 Å thick ev. a-SiO_2 film. The short Si–O bond length suggests that the gel-films are constructed from loose bound grains. The atomic peak at 0.81 Å on differential RDF's are believed to be O–H bonded atomic peak, and the results of molecular orbital calculation suggest that its short O–H bond length is due to high ionicity of O and H ions.

The pH^* is found to be important on the atomic network construction during the sol-gel transition, and the sol with isoelectric pH^* for SiO_2 produces well-networked gel films.

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