ELECTRON DIFFRACTION ANALYSIS OF THE STRUCTURE OF SiO_2 GEL-FILM

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ABSTRACT

The structure of self-supported SiO_2 gel-films prepared from acid and basic TEOS solutions is analysed by high energy transmission electron diffraction method. The reduced radial distribution function (RDF) curves show that all the films are already well dense despite the low drying temperature (≲50° C) and short drying time (≲30 s). The Si-O bond length of the gel-films prepared from highly acid and basic solutions is about 1.58 Å; it is smaller than that of bulk vitreous silica (1.61 Å) but similar to that of 80 Å thick evaporated a-SiO_2 film.

INTRODUCTION

Sol-gel process has a huge potential for producing functional materials using simple procedures. The gel materials are generally porous and a thermal treatment is necessary to transform them into dense glasses and/or ceramics. The microscopic and atomic structures of gel materials are therefore important parameters for the densification process.

In this study, the atomic network of thin SiO_2 gel-films is analysed for the first time by using electron diffraction method.

EXPERIMENTAL

The sols were prepared by mixing 15 ml TEOS and 28 ml ethanol. Sols labelled A-1, A-2 and I have been acidified by addition of aqueous HCl in order to get apparent pH (pH*) of 0.6, 1.6 and 2.6 (isoelectric point of SiO_2), respectively, while the pH* of sample B has been adjusted to 10.5 by adding aqueous NH_4OH. 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 without any evaporation.

The gel-films were prepared by the following procedures. A #100 mesh Cu grid with 0.24 mm diameter hole size was immersed into a sol and withdrawn vertically. Thin films of sol retained in the holes of the mesh grid were self-supported by the surface tension and they were then dried in warm air at 40 - 50° C for 10 - 30 s.

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 range of the scattering angle corresponds to $s_{min}=0.3$ Å^{-1} and $s_{max}=34$ Å^{-1}, where $s=(4\pi/\lambda)\sin(\theta/2)$, θ is the angle between the incident and diffracted beam, and λ is the electron wavelength. The intensity of transmitted electron-beam was measured by a Faraday cage with an aparture of 0.1 mm in diameter; the Faraday cage captured the electron-beam with diverging angle until 0.016° (s=0.03 Å^{-1}). The transmittance for sample A-1, A-2, I and B were 9.4, 9.2, 18 and 5.4 % and the film thicknesses estimated from these values

are about 500, 500, 400 and 600 Å, respectively.

The small values of transmittance indicate the occurence of multiple scattering so that the total diffracted intensity, Itot(s) can be written as

$$Itot(s) = Io \cdot N \{Jm(s) + Jel(s) + Jinel(s)\} + Imult(s) \quad (1)$$

where Io is incident beam intensity, N is the number of SiO_2 unit compositions in the volume irradiated by the electron-beam, Jm(s), Jel(s) and Jinel(s) are interatomic interference, elastic atomic and inelastic atomic scatterings per unit composition, respectively, and Imult(s) is multiple scattering intensity. A division of Jm(s) by the Jel(s) gives the interference function M(s) and a sine-Fourier transformation of s·M(s) produces the differential RDF,

$$4\pi r\{D(r) - Do\} = \frac{2}{\pi} \int_0^{S_{max}} s \cdot M(s) \exp(-a^2 \cdot s^2) \sin(sr)\, ds \quad (2)$$

where a is the artificial temperature factor used to reduce termination effects due to the finite measurement range and taken equal to 0.0506 Å in this study.

Jm(s) is determined from the experimentally obtained Itot(s) and the following considerations. Jel(s) and Jinel(s) are calculated by using the elastic and inelastic scattering factors for Si and O atoms [1]. Since Jm(0)=0 and assuming that Imult(0) is nearly zero, the extrapolation of Itot(s) for s=0 allows the determination of the tentative normalization constant Io·N = Itot(0)/{Jel(0) + Jinel(0)}. Imult(s) was obtained by using the fact that Jm(s) is a smooth function oscillating around zero. The determined Imult(s) increases monotonically with s-value and consequently the determined Io·N is the best obtainable value.

RESULTS AND DISCUSSION

The differential RDF curves for the four samples are shown in Fig.1. The peaks on the curves inside r = 1 Å are apparently due to noise because no atomic pair with bond length less than 1 Å can exist. From the analogy of the atomic distances for vitreous silica and crystalline SiO_2, the peaks around 1.6 and 2.6 Å can be assigned to Si-O bonded pairs and O-Si-O atomic pairs, respectively. The slope of the internal part of the differential RDF reflects the bulk density of the sample; the straight dashed lines correspond to 4πrDo in eq.(2) calculated by using the density of vitreous silica (2.2 g/cm^3). The slope is proportional to the experimentally obtained Jm(s), which is inversely proportional to the determined normalizing constant Io·N because the oscillating term Io·N·Jm(s) should be determined independently on the other terms in eq.(1). The determined normalizing constants are the maximum possible values because the values were obtained on the assumption of Imult(0)=0. Thus, the slope matched to the differential RDF curve should be equal to or smaller than the true slope. The reduced RDF, 4πrD(r), curves are shown in Fig.2. While the slopes have a large error (~20 %) due to the uncertainty on the drawing of the dashed line, the normal feature of the internal part of RDF's shows that the slopes do not differ too greatly from the true ones. This fact

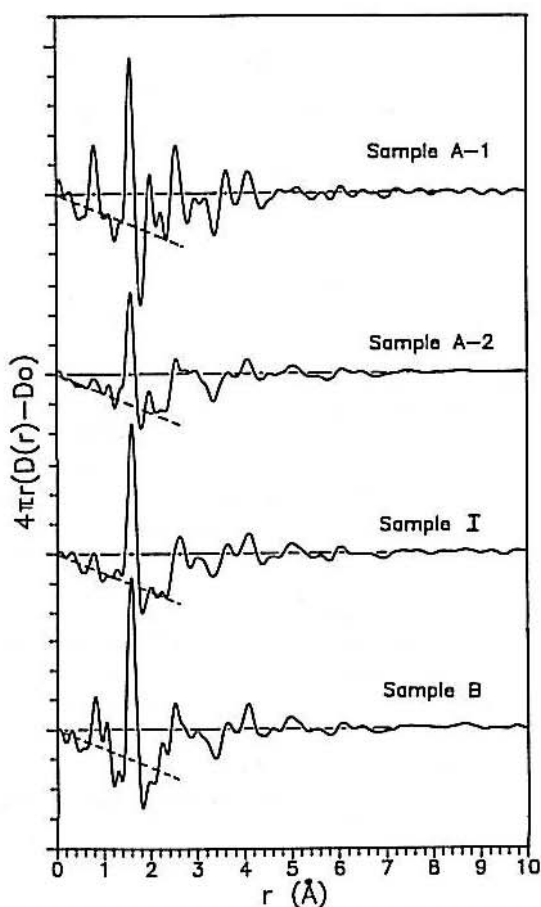

Fig.1 Differential RDF's for sample A-1, A-2, I and B.

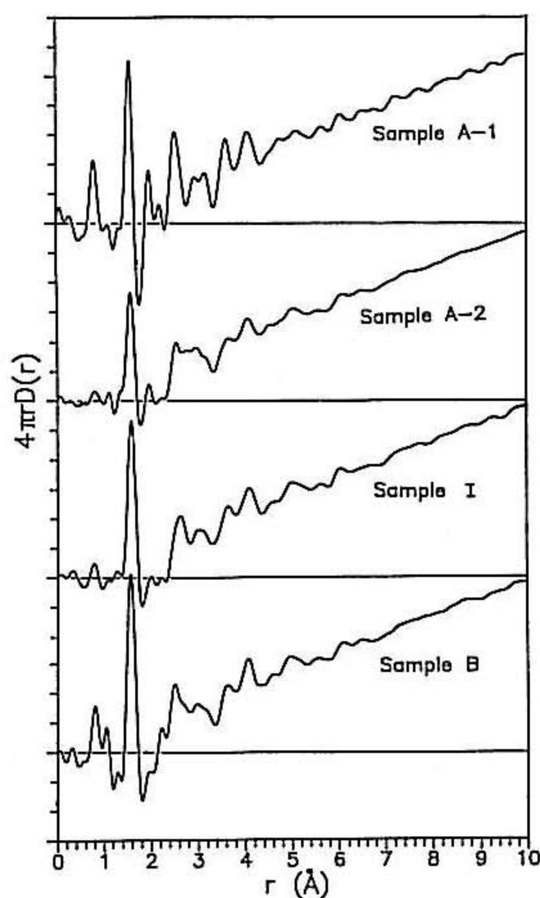

Fig.2 RDF's for sample A-1, A-2, I and B.

shows that the gel-films are well dense in spite of the low heating temperature (≲50° C) and the short heating time (≲30 s). It is well known that bulk SiO_2 gels are porous and have less density than that of vitreous silica. Then, the dense gel-films are supposed to be produced with easy displacement of atoms and molecules during the drying, which should be derived from the absence of substrate and/or their small thicknesses.

The Si-O bond lengths, O-O atomic distances of O-Si-O structure and O-Si-O angles calculated from these two distances are given in Table 1. Since the calculated O-Si-O angles are close to that of SiO_4-tetrahedron (110°), the gel-films are considered to be built up from SiO_4-tetrahedron units. The Si-O bond length of sample A-1, A-2 and B is 1.58 Å, and is smaller

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_{Si-O}	r_{O-O}	∠O-Si-O
A-1	1.58 Å	2.55 Å	107.6°
A-2	1.58	2.55	107.6
I	1.60	2.63	110.5
B	1.58	2.52	105.8

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

Thickness	r_{Si-O}	r_{O-O}	∠O-Si-O
4 Å	1.54 Å	2.48 Å	107.2°
10	1.54	2.51	109.8
20	1.57	2.56	109.6
40	1.57	2.58	110.3
80	1.58	2.58	109.3

than that of bulk vitreous silica (1.61 Å). Bond shortening has already been observed in the very thin films of evaporated amorphous SiO_2 (ev.a-SiO_2) [2]. The differential RDF curves for ev.a-SiO_2 films with 4, 20 and 80 Å thicknesses are shown in Fig.3. The peak heights of atomic pairs with large distances decrease remarkably with a decrease of film thickness. This result is explained by the fact that the number of atomic pairs with large atomic distance of thinner film is smaller than that of thicker film, and therefore indicates the consistency between the RDF curves. The Si-O bond lengths, O-Si-O atomic distances and calculated O-Si-O angles of ev.a-SiO_2 films are listed in Table 2. Since the O-Si-O angles are nearly equal to 110°, the ev.SiO_2 films are considered to be constructed from the SiO_4-tetrahedron units also. These results shows that the SiO_4-tetrahedrons shrink with the decrease of film thickness. Because of their short Si-O length (1.58 Å), sample A-1, A-2 and B are believed to be made up of loose bound grains. On the contrary, sample I which has 1.60 Å Si-O bond length has a well extended atomic network; the better quality of its atomic network may arise either from the paticular pH of the sol (isoelectric point of SiO_2) or the small film thickness (400 Å).

Since the extraneous scattering is not removed, it is difficult to assign the observed peaks around the Si-O-Si atomic peak (~3.0 Å) or to decide them the noises. Thus, the exact nature of the tetrahedra arrangement in the films and the presence of other structural units still remain open questions.

CONCLUSION

The first results of electron diffraction analysis of self-supported SiO_2 films prepared by sol-gel method show that the films are already well dense. The films produced from highly acid and basic sols have a 1.58 Å Si-O bond length smaller than that of bulk vitreous silica (1.61 Å) but similar to that of 80 Å thick ev. a-SiO_2 film. The film produced from sol at pH*=2.6 (isoelectric point of SiO_2) has a 1.60 Å Si-O bond length and is believed to have a well extended atomic network. The variety of Si-O bond length of gel-films suggests the different degrees of atomic network, and make plausible the presence of possible ways to get high quality glass materials only by sol-gel process.

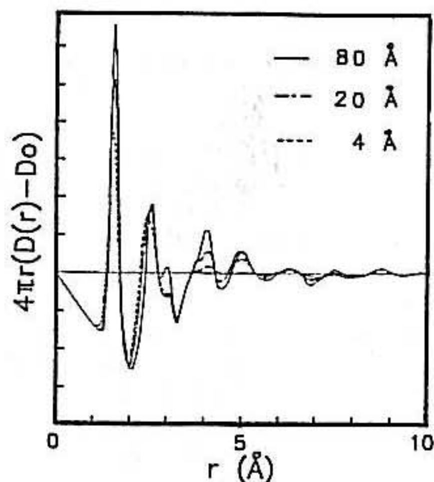

Fig.3 Differential RDF's for ev.a-SiO_2 films with 4, 20 and 80 Å thicknesses.

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