JOURNAL OF MATERIALS SCIENCE 27 (1992) 2857–2862

Fabrication of high-purity silica glass through the WSPA–sol–gel process

M. TOKI*, T. TAKEUCHI, S. MIYASITA, S. KANBE
Seiko Epson Corporation, Research and Development Division, 3-3-5, Ouwa, Suwasi, Naganoken, Japan

High-purity and large-size silica glass was prepared by a wet process silica and pH adjustment (WSPA)–sol–gel process which involved the following steps: (1) colloidal silica synthesis through the hydrolysis reaction of TEOS catalysed by ammonia solution; (2) sol preparation through the hydrolysis reaction of TEOS by hydrochloric acid; (3) mixing the colloidal silica and sol solution; (4) adjusting the pH values of the mixed solution to 4–6; (5) gelling; (6) drying to a dry gel; (7) heat treatment of the gel to collapse the pores, finally to become a silica glass. The purity of the derived silica glass was examined in relation to the metallic impurities and –OH impurities. The relation between ultraviolet absorption of silica glass and metallic impurities was investigated. Ti addition to the silica glass gave a strong absorption at 200 µm, for which the ultraviolet absorption coefficient, ε, was found to be $1.57 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. The effects of the properties of colloidal silica on the –OH concentration and also the relations between the sintering conditions and residual –OH concentration in silica glass were examined. Using colloidal silica with a large particle size and heat treatment in vacuum resulted in a silica glass with a low concentration of residual –OH.

1. Introduction

Recently, silica glass has become an important material in the IC fabrication process, for example IC photo-mask substrate, furnace tube, and lens material for excimer stepper equipment, because of its high purity and high transparency in the ultraviolet (UV) and visual (vis) region, and low thermal expansion coefficient. Silica glass optical fibre is a typical instance of a new glass which is a key material in various industries [1]. In spite of many such merits, however, the application of silica glass has been restricted in high technology industry because of its high fabrication cost.

A new fabrication process was desired to prepare the silica glass at low cost. One of the candidates for the low-cost fabrication process is the so-called sol–gel process. This process has the advantage that the high-purity glass can be prepared at low sintering temperature. However, large size silica glass could not be obtained by the sol–gel process, because of the occurrence of cracking during the drying and sintering of the gel, and to bloating on heat treatment. Therefore, much effort has been made to overcome these disadvantages. Drying control chemical additives (DCCAs) [2], and super-critical drying [3], are the powerful methods to avoid cracking and bloating, as can be seen in Fig. 1, which indicates the classification of the sol–gel process. However, silica glass made by these sol–gel processes are not yet available on the market, because of such defects as poisonous additives in DCCAs, and the complexity of the autoclave in the supercritical drying. Consequently, easier, safer and more feasible sol–gel processes are industrially desired.

A new sol–gel process was proposed by Toki *et al.* [4–6], which involved the following characteristic steps: (1) addition of silica particles to the hydrolysed solution of TEOS; (2) pH adjustment of the sol to 4–6 from 1–2 by the addition of ammonia solution, later called the quick-set process [7]. The process, including the addition of colloidal silica which was prepared from the hydrolysis of TEOS by basic catalysts as the silica particles above-mentioned, is named the WSPA–sol–gel process [6]. The objects of this communication are to show the possibility of fabrication

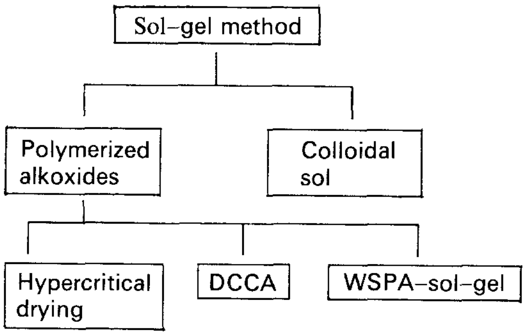

Figure 1 The classification of the sol–gel process.

**Present address*: KRI International Inc., Kyoto Research Park, 17, Chudoji-Minamimachi, Shimogyo-ku, Kyoto 600, Japan.

0022-2461

of the high-purity silica glass and the large size silica glass by this WSPA–sol–gel process, and also to clarify the fabrication conditions for preparing the highly pure silica glass.

2. Experimental procedure

2.1. WSPA–sol–gel process to produce silica glass

Colloidal silica was prepared by the hydrolysis reaction of the TEOS (commercial) with ammonia solution as basic catalyst. The components of the reaction mixture were in following molar ratio: $[Si(OC_2H_5)_4]$:$[NH_4OH]$:$[H_2O]$:$[C_2H_5OH]$ = 1:0.07:4.5:6. The reaction mixture stood overnight to yield colloidal silica with 0.3 μm particles. The derived colloidal silica was concentrated by evaporating the solvent, and colloidal silica containing 30 wt % silica particles was obtained. The pH of the colloidal silica was adjusted to 3 by the addition of 0.1 N HCl solution.

TEOS was hydrolysed using hydrochloric acid. The reaction was performed in following ratio to yield silica sol: $[Si(OC_2H_5)_4]$:$[HCl]$:$[H_2O]$ = 1:0.0016:4.5.

The colloidal silica and silica sol obtained as above were mixed, and the pH of the mixed solution was adjusted to 4.5 from 2, by the addition of ammonia solution. Gelation occurred after 1 h, and the gel was allowed to stand for 3 days at 30 °C to age in order to make the gel network stiffer.

A dry gel was obtained by drying the gel in a polypropylene container covered with a pinholed lid for 10 days at 60 °C. The dry gel derived is shown in Fig. 2. The dry gel was heated at 800 °C in air, and at 1300 °C in vacuum to collapse the pores. A typical heat-treatment schedule is shown in Fig. 3. The large size (15 cm × 15 cm × 0.5 cm), highly transparent silica glass was then obtained as shown in Fig. 2.

2.2. Measurements of optical property and purity of silica glass

The impurity concentration of the silica glass was determined by the inductively coupled plasma (ICP) method. Samples for ICP measurements were prepared by the following treatment: (1) dissolving the silica glass in HF solution; (2) evaporating the HF solution with SiF by heat treatment; (3) the residual material, which was the impurities in the silica glass, was diluted in hydrochloric acid. The impurities in hydrochloric solution were inserted into the plasma flame of the ICP equipment.

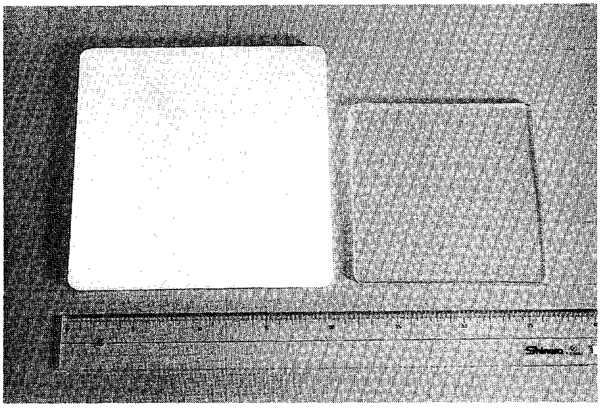

Figure 2 Gel and sintered silica glass derived from the WSPA–sol–gel process.

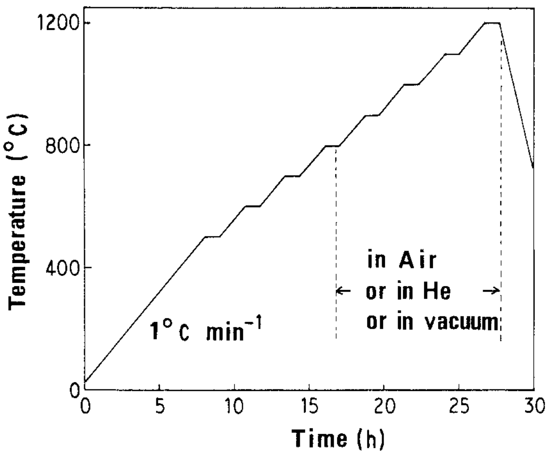

Figure 3 Typical heat-treatment schedule of the gel.

Ultraviolet absorption spectra of the silica glass whose both sides were polished were measured using an Hitachi 340 type spectroscope. Silica glass samples including a small quantity of one kind of the metal impurity for ultraviolet measurement, were prepared by the addition of the metal nitride to the above-mentioned sol solution which was the precursor of the silica glass.

The residual –OH concentration of the derived silica glass was determined from the infrared absorption spectrum. Samples for infrared measurements were silica glass polished on both sides. Calculation of –OH concentration (C wt %) was performed using the following Lambert–Beer equation

$$C = 1/\varepsilon t \times \log I/I' \times M/10d \qquad (1)$$

where ε is the infrared absorption coefficient which was 86 [8], t (cm) is the thickness of the polished silica glass, I is the transparency at 2.6 μm and I' is the transparency at 2.72 μm, M is the molecular weight of –OH which was 17, and d is the specific gravity of the silica glass, which was 2.2.

3. Results and discussion

3.1. Residual –OH concentration in silica glass

The residual –OH concentration was measured from the infrared spectrum of silica glass derived by the WSPA–sol–gel process. A typical infrared spectra is shown in Fig. 4. The concentration of –OH in silica glass is thought to depend on the conditions of the fabrication process [9], therefore in the WSPA–sol–gel process, the relationship between the concentration of –OH and the processing conditions was investigated.

It is well known that the particle size of colloidal silica can be varied by changing the pH of the reaction mixture which includes TEOS, H_2O and NH_4OH [10]. By changing the pH of the reaction mixture to 10.0, 10.5, 11.0, 11.5, four sizes of colloidal silica, 0.1,

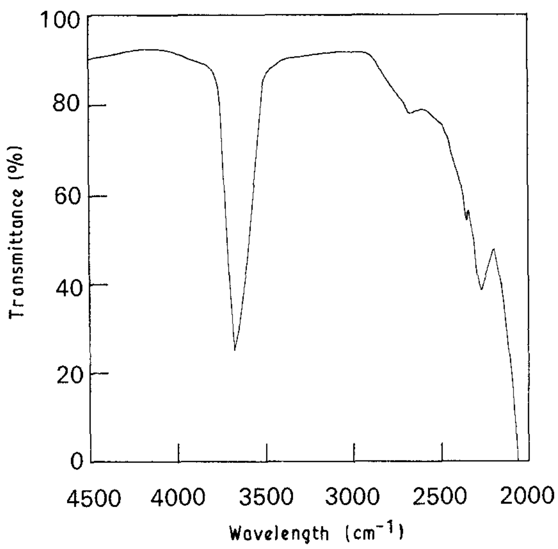

Figure 4 Infrared spectra of WSPA-derived silica glass.

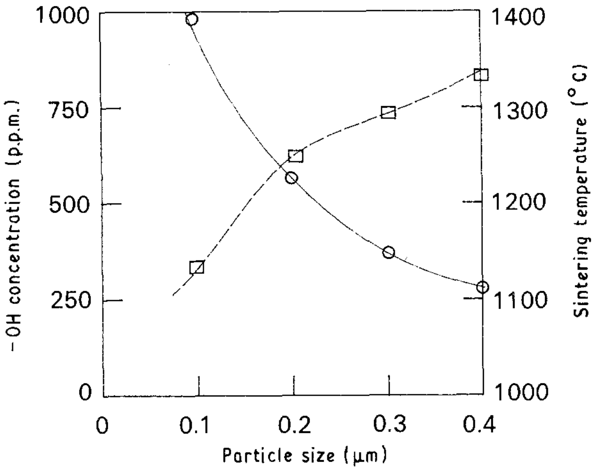

Figure 5 Correlation between -OH concentration of the silica glass and particle size of the colloidal silica. (○) -OH concentration, (□) temperature.

0.2, 0.3, 0.4 µm diameter particle sizes were prepared, respectively. By using these colloidal silicas in the WSPA-sol-gel process, four silica glasses were obtained, whose infrared spectra were measured to determine the -OH concentration, after polishing on both sides. The calculated -OH concentrations for each silica glass are plotted in Fig. 5. The residual -OH concentration decreased with increasing diameter of the colloidal silica particles, as can be seen in Fig. 5.

On the other hand, the pore-collapse temperature was increased with increasing diameter of the colloidal silica. The reduction of -OH concentration with larger particle size is attributed to the increase in pore-collapse temperature and to the maintenance of a porous state of the gel up to high temperatures during heat treatment. Therefore, in order to achieve low -OH concentrations in silica glass, a larger colloidal silica particle size is needed.

The relation of -OH concentration or collapse temperature with the silica molar ratio of colloidal silica to TEOS in the starting sol components of the WSPA-sol-gel process were investigated. Silica glasses were prepared by changing the ratio of colloidal silica to TEOS, and the derived silica glasses were polished on both sides to measure their infrared spectra and to calculate the residual -OH concentrations of the silica glass. In Fig. 6, the dependence of the calculated -OH concentration and the consolidating temperature on the colloidal silica content is shown. The residual -OH concentration decreased with increasing ratio of colloidal silica to TEOS; the consolidating temperature also increased with increasing ratio. These phenomena can be explained by the porous state of the gel during heat treatment. The state of the porous gel was maintained up to a higher temperature due to the larger colloidal silica contents in the sol, and then the -OH concentration would be decreased.

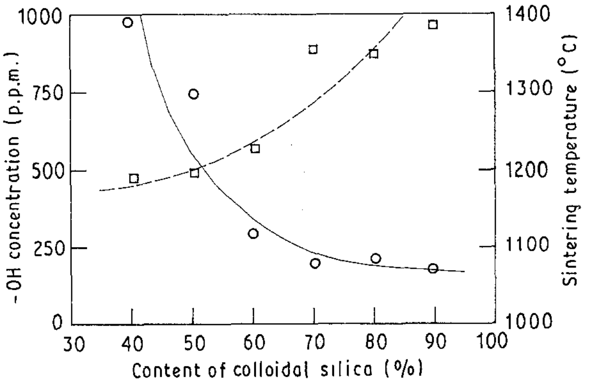

Figure 6 Correlation between -OH concentration of the silica glass and the colloidal silica content in the sol composition. (□) Temperature, (○) -OH concentration.

In order to achieve low -OH concentration of silica glass, a larger colloidal silica content in the sol solution is required.

3.2. -OH distribution in bulk silica glass

The distribution of -OH concentration in the bulk silica glass derived from the WSPA-sol-gel process was investigated by measuring the infrared spectra of silica glass at several points in the thickness and width directions. Six sides of a 60 mm sized cubic silica glass were optically polished, the infrared spectra were measured at several points, and the -OH concentrations were calculated. The results of all data obtained by this measurement are plotted in Fig. 7.

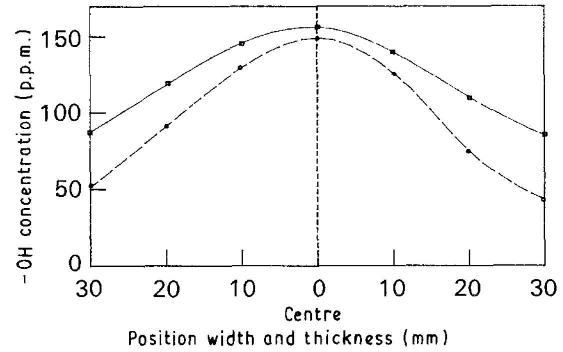

Figure 7 Distribution of the residual -OH concentration in the silica glass derived from the WSPA-sol-gel process. (—□—) Width, (-- ● --) thickness.

Apparently, the –OH concentration at the centre of the silica glass was larger than that towards the outside of the silica glass. This phenomenon may be explained by H_2O from the polymerization reaction at outer region of the gel by heat-treatment being easily volatilized, whereas H_2O from the centre region of silica glass cannot easily drift to the outer regions of the silica glass and thus is not easily volatilized.

3.3. Relation between –OH concentration and sintering atmosphere

The relation between residual –OH concentration of silica glass and the atmospheric conditions of sintering the gel to become silica glass, was also investigated using the WSPA–sol–gel process.

After heating the dry gel in air to 1000 °C, the heated gel was sintered in air or in a reduced pressure at 1000–1300 °C to produce silica glass, in order to clarify the effects of sintering atmosphere on –OH concentration. The –OH concentration of the derived silica glass on sintering under various conditions is plotted in Fig. 8. As can be seen the –OH concentration of silica glass derived in air was larger than that derived under reduced pressure, and in each case, longer heat treatments of the gel resulted in low –OH concentrations. These phenomena may be explained by the difference in H_2O mobility in the gel during heat treatment in air or in reduced pressure, and also by the difference in H_2O drift mobility over short or long sintering times.

3.4. Metal impurities

The purity of silica glass obtained from the WSPA–sol–gel process was investigated, and a comparison between WSPA in this work or in a previous sol–gel process [5] using Aerosil 0X-50 as colloidal silica, and silica glass on the market, was performed.

The purity of silica glass was investigated using ICP equipment. These data are given in Table I. It is indicated that the most pure silica glasses were synthetic silica glass and WSPA-derived silica glass, and WSPA-derived silica glass was purer than silica glass from the previous sol–gel process which used Aerosil 0X-50. This is ascribed to the metal inclusion existing in Aerosil 0X-50, whereas in the WSPA process the starting material did not include any metallic impurities. Therefore, very pure silica glass was obtained by the WSPA–sol–gel process.

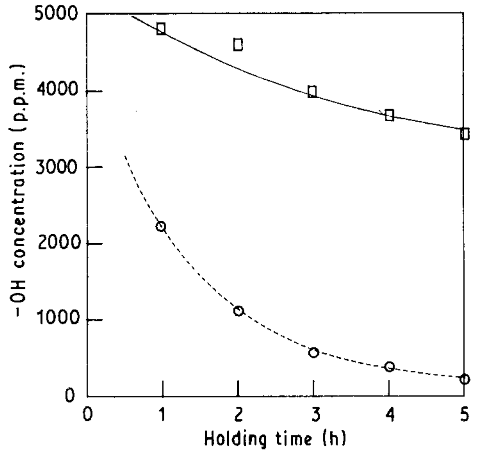

Figure 8 Correlation between residual –OH concentration of the silica glass and conditions of sintering. (□) 1 atm, (○) 0.05 mm Hg.

On the other hand, natural silica glass includes metallic impurities, especially large amounts of Al ions. Natural silica glass also includes transition metals such as Ti, Fe, Cr, Ni, which were also found in silica glass from the previous sol–gel process. Metallic impurities originated in the starting material of the silica glass which is natural quartz sand or quartz crystal.

3.5. Ultraviolet spectrum of silica glass

Highly ultraviolet-transparent silica glass is required in the field of IC fabrication or optical material for the deep ultraviolet region. Therefore the investigation of the ultraviolet absorption of silica glass obtained from the WSPA–sol–gel process, is important when considering the application. In Fig. 9, the ultraviolet absorption spectra of silica glass derived from the WSPA–sol–gel process in this work, and that of a silica glass derived from a previous sol–gel process, are shown. The thickness of the ultraviolet sample of silica glass was 2.3 mm. Obviously, WSPA silica glass exhibited no ultraviolet absorption at near 200 μm, whereas silica glass from the previous work had an apparent peak at 200 μm. This ultraviolet absorption could be attributed to the metallic impurities of silica glass.

In order to clarify the effects of metal ions on the ultraviolet absorption of silica glass, silica glass doped with various metals was prepared, and measurements of the ultraviolet spectrum of these doped silica glasses were performed. The various metal-doped silica glasses were prepared by the following steps: (1) metal

TABLE I Purity of the various silica glasses

Sample	Impurity concentration (p.p.m.)							
	Na	Li	Ca	Al	Ti	Fe	Cr	Ni
WSPA–sol–gel process	0.1	ND	0.1	0.05	ND	0.07	ND	0.01
Previous sol–gel (Aerosil 0X-50)	0.5	ND	0.1	1.0	0.5	0.2	0.1	0.07
Synthetic silica glass	0.1	ND	ND	0.03	0.04	ND	0.02	ND
Natural silica glass	0.5	5.0	0.2	30.5	0.03	0.2	0.3	0.01

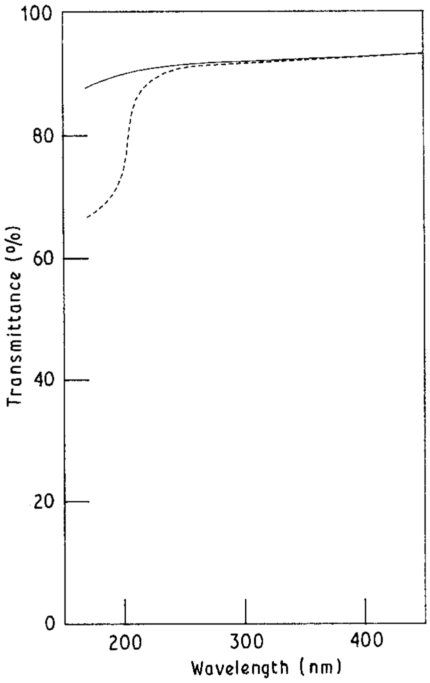

Figure 9 Ultraviolet absorption spectra of silica glass from (——) WSPA–sol–gel process and that (– – –) of the previous sol–gel process, using Aerosil 0X-50 as colloidal silica.

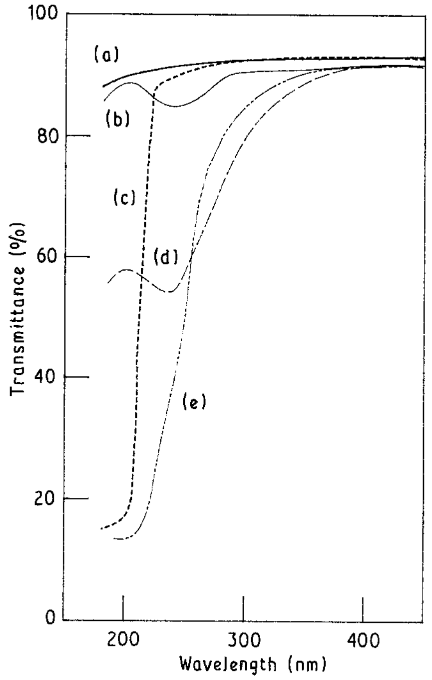

Figure 10 Ultraviolet absorption spectra of silica glass doped with various metal ions. (a) 10 p.p.m. Al, (b) 0.8 p.p.m. Ni, (c) 4.0 p.p.m. Ti, (d) 4.3 p.p.m. Fe, (e) 3.4 p.p.m. Cr.

nitride was added to WSPA sol solution which included TEOS hydrolysed sol and colloidal silica from TEOS hydrolysation by ammonia catalyst: (2) pH adjustment of the mixed sol; (3) gellation; (4) drying to a dry-gel; (5) heat treatment to sinter the gel to produce metal-doped silica glass.

The derived doped silica glass was polished in order to measure the ultraviolet spectrum. In Fig. 10, ultraviolet spectra of metal-doped silica glasses are shown. Transition metals such as Ti, Ni, Cr, Fe in silica glass showed significantly strong peaks whereas Al in silica glass indicated no ultraviolet absorption. Ti, in particular, in silica glass strongly affected the ultraviolet absorption. The concentration of Ti in silica glass was then verified and the ultraviolet measurements of these samples were performed to calculate the optical absorption coefficient, ε. Fig. 11 shows the correlation between ultraviolet absorption at 200 μm and the concentration of Ti doped in silica glass. From the results of Fig. 11, ε was found to be 1.57×10^4 $1\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$. By using this ε value, the concentration of Ti in the silica glass could be obtained easily.

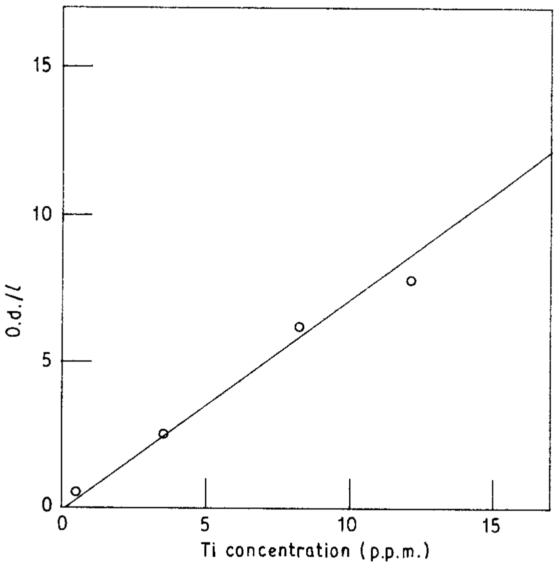

Figure 11 Correlation between ultraviolet absorption at 200 μm and the concentration of Ti doped in silica glass.

4. Conclusions

High-purity and large-size silica glass was prepared by the WSPA–sol–gel process which included a colloidal silica addition process and sol pH adjustment. The relation between processing conditions and properties of the derived silica glass was investigated with respect to the residual –OH concentration and impurities in the silica glass.

The optimum conditions for obtaining the silica glass with low –OH concentration by the WSPA–sol–gel process were:

(1) use of a colloidal silica with large particle size;
(2) a large content of colloidal silica in the silica sol;
(3) sintering in vacuum.

The purity of the silica glass was investigated using ICP equipment and ultraviolet spectroscopy. WSPA–sol–gel process-derived silica glass was the purest, compared with the silica glass derived by other methods, such as the previous sol–gel process and natural silica glass. In the previous sol–gel process which used Aerosil 0X-50 as colloidal silica, the derived silica glass included metallic impurities such as transition metals Ti, Cr, Ni, Fe, and metal impurity Al, originating from the Aerosil 0X-50. This previously obtained silica glass showed a significantly strong ultraviolet absorption at 200 μm. Ti ions, in particular, in silica glass indicated a strong ultraviolet absorption around 200 μm. The optical absorption coefficient was calculated and ε was found to be $1.57 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$.

References

1. S. SAKKA, *Polyfile* **4** (1987) 2.
2. L. L. HENCH and G. ORCEL, *J. Non-Crystalline Solids* **82** (1986) 1.
3. J. ZARZYCKI *et al.*, *J. Mater. Sci.* **17** (1982) 3371.
4. M. TOKI *et al.*, American Ceramic Society, 89th Annual Meeting, Abstracts (1987) p. 247.
5. M. TOKI *et al.*, *J. Non-Crystalline Solids* **100** (1988) 479.
6. M. TOKI and T. TAKEUCHI, Ceramic Society of Japan, Autumn Symposium, Abstracts (1988) p. 551.
7. W. M. JONES and D. B. FISCHBACH, *J. Non-Crystalline Solids* **101** (1988) 123.
8. J. P. WILLIAMS *et al.*, *Amer. Ceram. Soc. Bull.* **55** (1976) 524.
9. G. ORCEL, J. PHALIPPOU and L. HENCH, *J. Non-Crystalline Solids* **104** (1988) 170.
10. W. STOBER *et al.*, *J. Colloid. Interface Sci.* **26** (1968) 62.

Received 26 March
and accepted 20 December 1990