Structural Change in the Near-Surface of a Silica Glass Block by Heat Treatment

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熱処理に伴うシリカガラス表面付近の構造変化

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The effect of annealing on the distribution of OH content and defect structures in a disk shaped block of fused silica containing approximately 1500 ppm of OH was investigated. Heating at 1160°C for 120 h reduced the OH content near surface by about 60 ppm, and absorption bands at 6.5, 5.8, 5.0 and 4.8 eV were induced near the side surface. The amount of the reduction of OH content near the top surface was about 45 ppm, and only the 6.5-eV band was induced.

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1. Introduction

Vitreous silica has high optical transmission in the ultraviolet (UV) region, and thermal expansion lower than that of multi-component optical glasses.¹⁾ Therefore this material is used in fine optical components with UV light sources such as lenses in step-and-repeat projectors (stepper) with KrF excimer laser as the light source. Projection optics in the KrF-laser-stepper require extremely high homogeneity; the range of refractive index distribution is $\leq 1 \times 10^{-6}$ over the whole optical component and maximum birefringence is ≈ 1 nm/cm.

The refractive index of the silica glass is controlled by OH and Cl contents, and fictive temperature, the temperature at which the equilibrium structure is frozen in.²⁾ To control the fictive temperature, a silica glass block is usually annealed above the annealing point, i.e., 1100–1200°C.¹⁾ However, strain may sometimes be newly introduced during the annealing process.³⁾ Yamagata^{4),5)} proposed a process to produce a silica glass block with high homogeneity, by which the refractive index distribution caused by the distribution of fictive temperature, OH and Cl contents distribution are balanced. However, he did not measure the fictive temperature directly and neglected the effect of strain induced by the annealing.

There are various kinds of vitreous silica.¹⁾ Of them, type-III fused silica synthesized directly by hydrogen-oxygen flame hydrolysis of SiCl_4 , is used in UV optical components. This type of silica contains 500–1500 ppm of OH. With increasing OH content, the silica glass network becomes softer and various properties are changed.⁶⁾ For example, the silica becomes excimer-laser resistive, i.e., intensity of excimer-laser-induced absorption becomes negligibly small. This may be because of the softness of the glass network; with increasing softness the probability of bond breakage by irradiating with excimer-laser should become lower. Even if a bond breaks, the bond could rebind immediately after stopping the irradiation.

The effect of $\equiv \text{SiOH}$ on the softness of the glass network is also supported by the fact that the Young's modulus was reduced by $\approx 4\%$ when the OH content increased from 40 ppm to 1200 ppm.⁷⁾ Additionally, viscosity at a high temperature decreases with increasing OH content.⁸⁾

These facts suggest that the structure of the glass network can be easily relaxed in materials containing higher OH concentrations. This is supported by the fact that in OH-free silica, the relaxation time for Raman bands at 606 and 495 cm^{-1} , caused by planar 3- and 4-fold rings, are about three orders longer than that of silica containing 1200 ppm of OH.⁹⁾ As shown above, with increasing OH content, the glass network becomes softer and structural relaxation time becomes shorter.

Due to the existence of many dangling bonds formed by breaking the Si-O bonds, the glass surface must be energetically unstable. Thus the structure would change to stabilize the surface. In fact, Agarwal, et al.¹⁰⁾ suggested that the Si-O-Si bond angles near the surface are easier to relax than those in the bulk by comparing an IR-band at 2260 cm^{-1} by absorption and a band at 1120 cm^{-1} by reflection spectra. In an annealed block of silica glass, the structural change near the surface must affect the optical homogeneity. To study the effect of annealing on the structural change near surface, we analyzed the OH content distribution and the internal absorption of a silica glass block.

2. Experimental procedure

We used a type-III fused silica¹⁾ synthesized directly by the hydrogen-oxygen flame hydrolysis of SiCl_4 . The OH content of the sample was 1400–1500 ppm (see Fig. 1). The sample was cut from the center portion of an ingot that was about 20 cm in diameter and 60 cm in length. The sample was 15 cm in diameter and 4.6 cm in thickness, with center axis of the sample being the same as that of the ingot. The surfaces of the sample were ground by diamond tools; with the side surface finished by a cylindrical grinder with a #80 diamond tool, and top and bottom faces are finished by a rotary grinder with a #150 diamond tool. To measure the radial distribution of OH content before annealing, we cut samples near the top surface.

The sample was annealed using a Naber Therm N300/14 muffle furnace with the inner muffle dimensions 50 cm in width, 70 cm in height, and 60 cm in length. The sample was set in the center of the muffle. The temperature profile across the muffle is uniform to within $\pm 2^\circ\text{C}$. The sample

Fig. 1. Distribution of OH content before and after annealing as a functions of distance from surface in (a) the radial and (b) the axial directions.

was heated at a rate of 30°C/h up to 1160°C, and held at this temperature for 120h. The sample was then cooled to 600°C at a rate of 6°C/h, and then cooled to room temperature uncontrolled. A sample with size of 1.5 cm in width and 1 cm in thickness was cut from the middle of the block along the radial direction.

Two opposite surfaces of the sample were polished and the OH content and internal absorption measured about every 2 mm along the samples radial direction. Another sample was cut along the center axis (referred to as the axial direction). OH content and absorption spectra were measured by a Shimadzu UV3101-PC spectrophotometer, which can measure the absorption at the wavelengths in 190–3200 nm. OH content was calculated from an absorption peak at 2.2 μm ,^{11,12} the extinction coefficient of which 1.72 l/mol cm is obtained by comparing the absorption intensities of 0.7-mm thick samples at 2.7 μm (extinction coefficient being 77.5 l/mol·cm¹¹) and those of 10-mm thick samples at 2.2 μm for various OH amount. Using the internal absorption in the center of the before annealing sample as a reference, internal absorption after annealing was measured. Obtained spectra were analyzed by Gaussian peak decomposition described elsewhere.¹²

3. Results

Figure 1 shows OH content distribution before and after annealing as a function of the distance from the surface in the radial direction (Fig 1(a)) and the axial direction (Fig. 1(b)). In the radial direction, OH content has a range of ≈ 100 ppm. Although there was no direct measurement of the axial OH content before annealing, OH content can be

Fig. 2. Distribution of absorption bands produced by the annealing.

assumed as constant because the sample had been cut from the center portion of ingot with almost constant diameter.

In the radial direction, reduction of OH content was observed within ≈ 6 cm from the surface, and the amount of the reduction is ≤ 60 ppm. In the axial direction, the apparent change of OH content by annealing was observed only within ≈ 0.3 cm from the surface, and magnitude of the change in the surface is ≤ 45 ppm. The OH concentration of center of the sample before annealing is shown by horizontal solid line in the figure; this value is the OH content at the center axis. A small variation of OH content, ≈ 10 ppm, is observed within ≈ 0.3 cm from the surface in the axial direction. This variation may not be significant but just the error of the observation.

In the previous papers, one of the present authors and coworkers showed the X-ray,¹² ArF excimer laser,^{6,13} and γ -ray¹⁴ induced absorption can be fitted by the Gaussian absorption bands peaking at 6.5, 5.8, 5.4, 5.0 and 4.8 eV. Absorption bands produced by annealing can also be fitted by the same set of the absorption bands with the same peak positions and full width at half maxima (FWHM's). Figure 2 shows the distribution of absorption components using the same peak positions and FWHM's as in Ref. 12. Differences between the radial and the axial distributions are also observed as in the case of the OH content distribution. In the radial direction, absorption bands at 6.5, 5.8, 5.0 and 4.8 eV were observed. In the axial direction, however, only the 6.5-eV band was observed, its intensity is weaker than the 6.5-eV band of the radial direction. The absorption intensity is strongest at the surface and observed within ≈ 0.5 cm from the surface except the 6.5-eV band, which was induced further in from the surface.

4. Discussion

Reduction of OH content near surface should mainly caused by,

In a previous paper,¹¹ one of the present authors and coworkers proposed that the existence of $\equiv\text{Si}-\text{H} \quad \text{HO}-\text{Si}\equiv$ structures in type-III fused silica synthesized under reducing conditions. From this structure, OH content can be reduced as,

The origin of the 6.5-eV band is not known, but it could be related to metallic impurities.

The 5.8-eV band is ascribed to the E' center ($\equiv\text{Si}\cdot$). The 5.0-eV band is $B_2\alpha$ band¹⁵ ascribed to oxygen deficient center (ODC; $\equiv\text{Si}\cdots\text{Si}\equiv$). The ODC must be produced by

breaking Si-O-Si bond by the stress produced by the shrinkage of the glass network accompanied with the reduction of water as described by Eq. (1). Part of the ODC might changed into the E' center.¹⁵⁾ In fact OH- and Cl-free synthetic fused silica have a weak 5.8-eV band accompanied with the 5.0-eV band.⁶⁾ There is another type of 5.0-eV band called the $B_2\beta$ band.¹⁵⁾ Although these two types of bands can be distinguished by their emission spectra, luminescence caused by impurity contamination during the annealing could interfere with the distinction.

The 4.8-eV band is an oxygen related center and a number of models, such as nonbridging oxygen hole center (NBOHC; $\equiv\text{Si}-\text{O}\cdot$), peroxyradicals (PR; $\equiv\text{Si}-\text{OO}\cdot$) and O_3 , are proposed.¹⁵⁾ NBOHCs are produced by breaking Si-O-Si bonds as,

Oxygen atoms will be produced by,

which can form O_2 and/or O_3 molecules by reacting with each other. By reacting oxygen atoms with E' centers, NBOHCs will be formed as,

and by reacting oxygen molecules with E' centers, PR's will be formed as

Another probable origin of the 4.8-eV band is H_2O molecules bound to $\equiv\text{SiOH}$ by hydrogen bond which could cause the 4.8-eV band accompanied with the 5.8-eV band.¹⁶⁾

The change in OH content and creation of absorption bands show that the damage in the radial direction is stronger than that in the axial direction. A probable origin of this difference is that the difference in curvatures between the side and the top surfaces; the manner to stabilize the surface structures could be strongly dependent on the surface curvature. Another probable origin is the difference in the finishing conditions; the top surface was finished with a rotary grinder with a #150 diamond tool and the side surface was finished with a cylindrical grinder with a #80 diamond tool. From the present data, however, we cannot determine which is main the factor to produce the changes to OH content and the absorption bands.

5. Conclusions

We have investigated the effect of the annealing on the structure near surface of a silica glass block. By monitoring the OH content distribution and induced absorption, it was found that the OH content is reduced near the surface and absorption bands at 6.5, 5.8, 5.0 and 4.8 eV are induced. In

the view point of developing a high homogeneity optical material, we have to monitor the change of refractive index distribution and birefringence in addition to the OH content distribution and induced absorption. We need further studies on this aspect.

Silica glass is constructed of a network of connected SiO_4 tetrahedra by covalent bonds. Since many defect structures formed by the breaking of Si-O bonds should exist on the surface, surface free energy should be higher than that of multicomponent glasses in which modifier ions would stabilize the surface. During annealing of a fused silica block, the surface structure would be changed to reduce the surface free energy of the silica glass.

Since the silica glass is an amorphous material, direct comprehension of this structure is difficult. Studies on the change of the near-surface structure would be fruitful not only to understanding engineering problems such as cutting, grinding and polishing, but also scientific interest that could be clarify the silica glass structure.

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References

- 1) N. Kuzuu, "Sekiei Garasu no Sekai (Introduction to Silica Glass Science and Technology)," Kogyo Chosakai (1995) pp. 103-39 (in Japanese).
- 2) R. Brückner, *J. Non-Cryst. Solids*, 5, 123-75 (1970).
- 3) W. Primak, *Phys. Chem. Glasses*, 24, 8-18 (1983).
- 4) S. Yamagata, *J. Ceram. Soc. Japan*, 100, 337-41 (1992).
- 5) S. Yamagata, *Mineral. J.*, 16, 1-15 (1992).
- 6) N. Kuzuu, T. Taga and N. Kamisugi, *J. Appl. Phys.*, 81, 8011-17 (1997).
- 7) H. Kobayashi, T. Kosugi and Y. Kogure, *Physica B*, 219 & 220, 276-79 (1996).
- 8) Y. Kikuchi, H. Sudo and N. Kuzuu, *J. Ceram. Soc. Japan*, 105, 645-49 (1997).
- 9) F. J. Galeener, *J. Non-Cryst. Solids*, 71, 373-86 (1985).
- 10) A. Agarwal, K. M. Davis and M. Tomozawa, *J. Non-Cryst. Solids*, 185, 191-98 (1995).
- 11) N. Kuzuu, Y. Komatsu and M. Murahara, *Phys. Rev. B*, 44, 9265-70 (1991).
- 12) N. Kuzuu, *J. Non-Cryst. Solids*, 179, 170-78 (1994).
- 13) N. Kuzuu and M. Murahara, *Phys. Rev. B*, 52, 3241-47 (1995).
- 14) Y. Kawaguchi and N. Kuzuu, *J. Appl. Phys.*, 80, 5633-38 (1996).
- 15) D. L. Griscom, *J. Ceram. Soc. Japan*, 99, 923-42 (1991).
- 16) N. Kuzuu, Y. Komatsu and M. Murahara, *Phys. Rev. B*, 45, 2050-54 (1992).