Point defect formation and annihilation in silica glass by heat-treatment: Role of water and stress


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Abstract

It was discovered that $E'$ centers were created by heat-treatment when silica glass contains water and has residual stress. Silica glass samples were heat-treated at 1000 °C for various lengths of time in 355 torr (47000 Pa) water vapor pressure and dry nitrogen gas atmospheres. The electron paramagnetic resonance (EPR) signal of $E'$ centers increased initially with heat-treatment time in both atmospheres but then decreased afterwards in the wet atmosphere. It is known that water molecules eliminate paramagnetic defects, such as $E'$ centers and non-bridging oxygen hole centers (NBOHCs) by reacting with these defects in the glass, transforming them to non-paramagnetic species such as $\equiv$Si–OH or $\equiv$Si–H. The present study indicates that water molecules are also capable of initially creating paramagnetic defects in the glass structure by breaking the silica network structure in the presence of stress. The present observation may be relevant to mechanical strength reduction of silica glasses, which is commonly observed in the presence of water and stress.

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1. Introduction

Silica glass has been widely used in many fields due to its superb properties. It is found in optical waveguides and in the gate layers of silicon-based semiconductor device. It is well recognized that impurity in silica glasses and thermal history are important parameters that greatly influence properties of silica glasses. Chemical impurities in silica glasses have been greatly reduced by synthetic silica glass deposition techniques. However, even in the absence of impurities, a variety of structural defects [1,2] can be introduced in silica glass during its fabrication process [3] or post-treatment [4] and play important roles by affecting various properties of silica glass, such as optical absorption and luminescence bands [5,6], refractive index [7] and density [8] of silica glasses.

Water is one of the most important impurities in glasses, having a disproportionately large influences on various glass properties. For example, a trace amount of water can reduce the viscosity and the glass transition temperature measurably [9,10]. It can also reduce chemical durability [11] and density of the glass [12], increase thermal expansion coefficient [12], crystallization rate [13], structural relaxation rate and resistance to radiation damage [14–16]. Even when water is not contained in a glass, it can enter into the glass surface through diffusion, thereby affecting the chemical and mechanical properties of glass. Water in the surrounding atmosphere shortens the static fatigue life of silica glass [17,18]. Furthermore, water can interact with the defects in glasses. It is important, therefore, to understand the structure and behavior of water in glass, especially in relation to the interaction with point defects. It is the objective of the present research to investigate the formation and annihilation of structural defects in silica glass by heat-treatment in the presence of water and residual stress.

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2. Experimental procedure

High purity type I [19] fused silica glass tube, with outer diameter (OD) 4 mm and inner diameter (ID) 3 mm, made by General Electric Co. was primarily used in the present research. As-formed silica tubes normally contain residual stress due to their fabrication process. The presence of residual stress in silica tubes can be confirmed by measuring dimensional changes after axial slotting of the silica tubes [20,21]. If the ends of slot move outwards and the tube diameter expands, net residual tensile forces were present. If, on the other hand, the ends of the slot move inward and the tube diameter contracts, net residual compressive surface forces were present. We compared the dimensional changes after slotting of the silica tubes before and after annealing at 1100 °C for 8 h. The lengths of the silica tubes for the slotting test were ∼5 cm, and the lengths of axial slots were ∼2.5 cm. A diameter increase of approximately 0.007 mm was observed for the as-received silica tubes after slotting, indicating a net surface residual tensile force on the tube. No dimensional change was detected for the annealed silica tubes. The diameter increase is due to the bending of the two prongs, moving symmetrically. The bending moment \( M_r \) of the prong was calculated using the equation [21]

\[
M_r = \frac{EI}{L^2} \cdot 2\delta,
\]

where \( E \) is Young’s modulus of silica glass, \( I \) is the moment of inertia of the prong, \( L \) is the length of the slot and \( 2\delta \) is the diameter change after slotting. The moment of inertia of the prong, \( I \), was estimated to be \( 5.3 \times 10^{-12} \text{ m}^4 \). Using Young’s modulus of silica glass, 73 GPa, the value of moment \( M_r \) was obtained as \( 4.33 \times 10^4 \text{ Nm} \). The corresponding surface tensile stress can be estimated using the relation, \( \sigma = M_r/cI \), where \( c \) is the maximum stress on the surface of a bent bar with thickness \( 2c \). The residual stress in the as-received silica tube was estimated to be approximately 1 MPa.

To determine the hydroxyl water content, a fundamental OH stretching band at 3673 cm\(^{-1}\) in infrared absorption was obtained using a Nicolet Magna 560 Fourier transform infrared (FTIR) spectrophotometer. The OH content can be determined from IR absorbance using an extinction coefficient of \( 77.5 \pm 1.5 \text{l g}_{\text{glass}}/\text{molOH cm}_{\text{glass}} \) [22]. The calculated OH concentration in the as-received silica glass tube was ∼20 ppm. For comparison, various different silica glass samples without residual stress, containing different hydroxyl contents were also investigated. They were TO8 (Heraeus Amersil product, type II, ∼180 ppm of OH), Suprasil II (Heraeus Amersil product, type III, 1200 ppm of OH), Infrasil (Heraeus Amersil product, type I, ∼9 ppm of OH), Furukawa (Furukawa Electric product, CVD, <0.1 ppm of OH).

These silica glass samples were heat-treated in a tube furnace at 1000 °C in either wet or dry atmosphere. For the wet atmosphere, 355 torr (47000 Pa) water vapor pressure was maintained by bubbling air through an 80 °C water bath and directing it into the furnace during heat-treatment. For the dry atmosphere, dry N\(_2\) gas was passed into the furnace. The water vapor pressure, in this case, is estimated to be ∼0.3 torr (∼40 Pa) [23] from the hydroxyl uptake in a dry silica glass. Specimens were periodically removed from the furnace, and their EPR and UV spectra were measured.

The electron paramagnetic resonance (EPR) spectra measurements were made at room temperature using a Bruker spectrometer operating at X-band and at 100 kHz magnetic field modulation frequency. The magnetic field was in the range of 3475–3485 G. The EPR signal intensity of each sample was calibrated with a reference sample and the error range was determined by taking a total 10 measurements of sample. The UV spectra were obtained using a Varian Cary 1000 spectrometer scan in the 190–300 nm wavelength region.

3. Results

Fig. 1 shows the EPR signal of the as-received silica glass tube sample, which indicates the presence of \( E' \) centers (≡Si\(_2\)). The \( E' \) center consists of unpaired electron in a tetrahedral sp\(^3\) hybrid orbital of silicon atom bonded with three separate oxygens (in this paper the ‘’ represents the unpaired electron and the ‘≡’ denotes bonding with three separate oxygen atoms, respectively). Fig. 2 shows the UV absorption spectrum of as-received silica glass. A 248 nm absorption band, corresponding to oxygen deficient centers (ODCs) [1,5] was observed. From these data, it is clear that the as-received silica glass tube samples used for the present research are oxygen deficient and contain a finite concentration of \( E' \) centers.

Fig. 3 shows the EPR signal of the silica glass tube sample, (a) before the heat-treatment, (b) after heat-treatment for 1 h at 1000 °C, under 355 torr (47000 Pa) water vapor pressure and (c) after heat-treatment for 80 h at 1000 °C, under 355 torr (47000 Pa) water vapor pressure. The EPR signal intensity was calibrated with a reference sample for each measurement and the relative magnitude of the signal intensities in Fig. 3(a)–(c) can be directly compare...
pared. The $E'$ EPR signal intensity corresponds to the concentration of $E'$ centers and was found to increase after a 1 h treatment in the wet atmosphere. However, after 80 h heat-treatment in the wet atmosphere, the $E'$ signal intensity was observed to decrease markedly.

Fig. 4 shows the variation of the 248 nm absorption band resulting from the heat-treatment at 1000 °C under 355 torr (47000 Pa) water vapor pressure. The 248 nm absorption band decreased following the heat-treatment. The simple tangential lines, as shown in Fig. 4, were used as background base lines. The absorbance value of a 10 h heat-treated sample after background subtraction is about 40% of that for the as-received sample. The decrease of the 248 nm absorption band indicates a decrease of ODCs concentration. The ODCs, such as oxygen vacancies, are considered as possible precursors of $E'$ centers. When $E'$ centers are created from ODCs the concentration of ODCs will decrease. Also, the ODCs annihilation in silica by water diffusion has been reported [24]. Therefore, the 248 nm absorption band decrease is to be expected by heat-treatment in wet atmosphere. In contrast, we could not see a clear decrease of 248 nm absorption band in silica glass when it was heat-treated in dry atmosphere.

Fig. 5 shows the $E'$ EPR signal intensity variation with heat-treatment time at 1000 °C under 355 torr (47000 Pa) water vapor pressure and dry N$_2$ atmospheres. In the wet atmosphere, the $E'$ EPR signal intensity initially increases rapidly and then decreases with further heat-treatment time. This experiment was repeated several times and the $E'$ EPR intensity variation described was reproducible. In the dry N$_2$ gas atmosphere, the $E'$ EPR signal intensity also initially increased rapidly in the same manner as in the wet condition. However the $E'$ signal intensity did not decrease much after the initial rise, exhibiting only a small change after 80 h of heat-treatment.

In contrast, no $E'$ center signal was observed in any of the as-received annealed silica glasses investigated.
regardless of the different water contents or the presence or absence of oxygen deficient centers (ODCs). No E’ center signal was generated in these samples upon the heat-treatment at 1000 °C in both dry and wet atmospheres.

4. Discussion

The as-received silica glass tube contained E’ centers and ODCs. Those defects were presumably introduced in the silica glass during the fabrication process. The fused silica glass tube samples used in this study were made by an electrical fusion process. The natural quartz powder was melted in a crucible which was heated by an electric heater and finally drawn as tube. During the fabrication process of the tube, tensile stress was applied and this applied stress could have caused the defect formation and also strained bonds in the silica glass structure, which are possible defect precursors. This defect and precursor generation by this processing here is similar to that produced by the fiber drawing process [3].

The variation of E’ center concentration with heat-treatment time as shown in the Fig. 5 will now be analyzed. The concentration of E’ center in silica glass increased during the first 1 h of heat-treatment at 1000 °C, under 355 torr (47000 Pa) water vapor pressure, but then decreased by further treatment. From the results, we can assume that there are two factors affecting E’ center concentration, S₁, by an isothermal treatment in wet atmosphere. The first factor is E’ center creation from its precursors with a rate constant, τ(c), and the second factor is their subsequent annihilation with a rate constant, τ(a). A fitting function, including the amount of the E’ center existing in the as-received sample, S₁,

\[
S₁ = \{S₁ + S₂(1 - \exp[-t/τ(c)])\} \exp[-t/τ(a)]
\]

was used to simulate the time variation of the E’ signal intensity. The first part of fitting function (2) involving τ(c) corresponds to the E’ center creation from its precursors and the second part involving τ(a) corresponds to E’ center annihilation. The best fitting curves are indicated by the solid and dotted lines for heat-treatment under wet and dry N₂ atmosphere conditions, respectively, in Fig. 5. The estimated fitting parameters, including their errors, are summarized in Table 1. In the wet atmosphere, the rate constant for E’ center creation is much faster that the rate constant for annihilation, thus giving rise to the initial sharp increase of EPR signal intensity followed by the gradual decrease. In the dry N₂ gas atmosphere, due to the fast rate constant for E’ center creation, the E’ EPR signal intensity also initially increased rapidly in the same manner as in the wet condition. However the E’ signal intensity decrease was not detectable until 30 h heat-treatment. Only a small decrease was observed even after 80 h of heat-treatment. This decrease may due to the original water content (∼20 ppm of OH) in silica tube sample or small amount (∼0.3 torr (∼40 Pa)) of moisture in N₂ gas.

The defect center annihilation by water diffusion is a well known phenomenon and was reported by our group

![Figure 5](image-url)
previously. Kokura et al. [25] reported that the defects created by mechanical crushing of bulk silica were annihilated by the subsequent heat-treatment in a wet atmosphere. In Fig. 5, we can compare the $E'$ center annihilation by heat-treatment in wet or dry atmospheres. In the wet atmosphere, the annihilation of $E'$ centers is taking place during the heat-treatment, while in the dry atmosphere, there is little annihilation taking place even after 80 h of treatment. From these results, it can be concluded that the $E'$ annihilation by heat-treatment is mainly due to the water diffusion from outside and subsequent reaction with $E'$ center, to produce $\equiv\text{Si-O}\equiv$ or $\equiv\text{Si-H}$ centers, which are not observable by EPR:

$$2\equiv\text{Si} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-O}\equiv + \equiv\text{Si-H}.$$  

(3)

If we approximate the silica tube (OD 4 mm, ID 3 mm, wall thickness $d$ is 0.5 mm) as a plate sample, and if we consider the heat-treatment time range where only annihilation is taking place, the apparent diffusion coefficient, $D$, can be evaluated using the following relation [26],

$$
(S_t - S_0) / (S_\infty - S_0) = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n + 1)^2 \pi^2} \exp[-D(2n + 1)^2 \pi^2 t / d^2],
$$

(4)

where $S_t$, $S_0$ and $S_\infty$ are the amounts of a given species, e.g. $E'$ centers, at the time $t$, zero and infinity, respectively and $d$ is the specimen thickness. In the present experiment, $S_\infty$ is zero for the $E'$ center annihilation. Fig. 6 shows the relationship between $(S_t - S_0) / (S_\infty - S_0)$ vs $t$. Here we took the highest value of the $E'$ signal intensity (at 1 h heat-treatment of time) in Fig. 5 as $S_\infty$, and 1 h of heat-treatment time as $t = 0$. The satisfactory fitting of the annihilation of $E'$ center by the diffusion equation strongly suggests that $E'$ centers formed are uniformly distributed in the glass tube sample.

The fitting of the experimental data with Eq. (4) shown in Fig. 6 yielded the apparent diffusion coefficient associated with $E'$ annihilation, $D_{E'}$, as $6.5 \pm 0.5 \times 10^{-9}$ cm$^2$/s. The accepted literature value of the measured hydroxyl water diffusion coefficient, $D_{\text{OH}}$, at 1000 $^\circ$C is $\sim 5.5 \times 10^{-10}$ cm$^2$/s [24, 27]. From the values it can be seen that the water diffusion coefficient for $E'$ center annihilation, $D_{E'}$, is higher than the usually accepted hydroxyl water diffusion coefficient, $D_{\text{OH}}$ by one order of magnitude. This discrepancy we believe is not due to experimental error. In fact, we have previously reported similar observations of faster-than-expected diffusion during oxygen vacancy annihilation [24] as well as during surface structural relaxation [27]. We assert here again that, even at high temperature, there exists a small amount of molecular water which is not restricted by equilibrium, and which can diffuse farther than the conventionally expected diffusion front of hydroxyl water.

From the change of absorption band at 248 nm shown in Fig. 4, it is possible to estimate an amount of OCDs annihilated by the heat-treatment. Approximately 60% of the OCDs concentration was annihilated by the 10 h of heat-treatment, which is higher than the amount of annihilated $E'$ centers, which is about 40% by the same heat-treatment. This difference may be due to the transformation of OCDs to $E'$ centers, which was observed to increase in the first stage as shown in Fig. 5.

It is considered that the initial $E'$ center creation by the heat-treatments shown in Fig. 5 is also related to water. Nishikawa et al. [28] found that water in glass is one of the main factors for $E'$ center creation. They showed that the $E'$ center creation rate of high-OH containing silica glass by Excimer laser irradiation is higher than that of low-OH containing glass. The $E'$ center creation rate, shown in our result, is certainly too fast to consider that this is due to the water diffusion form outside. Also, the $E'$ center creation by the heat-treatment here in dry atmosphere was almost the same as that in the wet atmosphere. Therefore, we believe that the water, existing in the as-received silica glass itself, is one of the main factors for the creation of $E'$ centers from their precursors such as strained bonds or oxygen vacancies which are also introduced during the fabrication process. Water diffusion from outside during the heat-treatment may also create some $E'$ centers, but this effect is overwhelmed by the effect of the water initially present in the bulk.

Stress is also one of the main factors involved in the creation of defect centers. Munekuni et al. [29] showed that the creation rate of $E'$ center in silica glass by $\gamma$-ray radiation was increased by mechanical stress. They found that a much larger concentration of $E'$ centers was created by $\gamma$-ray radiation in crushed silica glass than in the annealed silica glass. The reason claimed for this phenomenon is that the applied stress provides abundant defect precursors, such as strained bonds. Therefore, the rate of defect creation in silica glass with residual stress is expected to be higher than the rate of defect creation in annealed silica glass. In the present research, $E'$ center creation could not be observed in several types of annealed silica glass that
were heat-treated in the same manner. Therefore, we also conclude that the stress is one of main factors of \(E^*\) center creation in our research.

Mechanical strength of glasses decreases in the presence of water and mechanical stress. The phenomenon is usually explained in terms of stress-corrosion, or water-glass chemical reaction, accelerated by stress, although the details of the mechanism are not clear. For the explanation of this stress-corrosion by water, Michalske et al. [17] invoked a model of the reaction between a single water molecule and a strained Si–O–Si bond at a crack tip as follows:

\[ \text{H}_2\text{O} + \text{Si–O–Si}^\equiv \rightarrow \equiv\text{Si}–\text{OH} + \text{OH}–\text{Si}^\equiv. \]  

(5)

However, this explanation does not describe the \(E^*\) center creation shown in our results. Del Bene et al. [30] suggested that the interaction of Si–O bond with a water dimer, that is two molecule of water, is most favorable. Bakos et al. [31] suggested that the water dimer in silica could form \(\text{OH}^-\) and a hydronium ion, which is proton linked with a water molecule, as follows:

\[ 2\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_3\text{O}^+ \quad (\text{H}^+ + \text{H}_2\text{O}). \]  

(6)

We propose that these hydronium ions or protons are highly reactive with unstable bonds, such as un-relaxed oxygen vacancies or ordinary strained bonds, to create \(E^*\) centers. The creation mechanisms of \(E^*\) centers by the reaction between precursors and hydronium ions or protons are not clearly understood. We propose the following possible reactions:

(I) \[ \equiv\text{Si}^i–\text{Si}^\equiv + \text{H}_2\text{O}^+ \rightarrow \equiv\text{Si}^i + \text{H}_2\text{O}^+ + \text{H}^+ + \text{H}_2\text{O} \rightarrow \equiv\text{Si} + \text{Si}^\equiv + \text{H}^0 + \text{H}_2\text{O} \]  

(7)

or

(II) \[ \equiv\text{Si}^+–\text{Si}^\equiv + \text{H}_2\text{O}^+ + \text{e}^- \rightarrow \equiv\text{Si}^i + \text{H}_2\text{O}^+ + \text{e}^- + \text{O}–\text{Si}^\equiv + \text{H}_2\text{O} \rightarrow \equiv\text{Si} + \text{HO}–\text{Si}^\equiv + \text{H}_2\text{O}. \]  

(8)

Here the symbol of ‘\(^i\)’ denotes a strained and un-relaxed bond. The first proposed mechanism (I) is similar to the Fiegl–Fowler–Yip model [32] for \(E^*_f\) center formation in \(\alpha\)-quartz or \(E^*_f\) center formation in amorphous silica by a hole trapping in ODC, except that we consider that the stress and water are involved in the reaction. The generated electron can then react with the proton to produce a hydrogen atom, or become trapped in non-bridging oxygen site to make hydroxyl species as shown in Eq. (8). These bond breakages and \(E^*\) center formation may be the important steps of the stress-corrosion reaction. In fact, mechanical fracture is known to be accompanied by \(E^*\) center formation, as has been observed in the crushing of silica glass [25].

The creation and annihilation of \(E^*\) centers by heat-treatment in a wet atmosphere can take place simultaneously. However, the large number of precursors and the consequent higher \(E^*\) center creation rate than its annihilation rate by water offer a reasonable explanation of increasing concentration of \(E^*\) center in the first stage of treatment. However, the amount of precursors is finite in the silica glass, and the precursors will be depleted eventually. Then the annihilation rate will become dominant, leading to the eventual decrease of the EPR signal.

5. Conclusions

The concentration of \(E^*\) center was found in some silica glass tubes to increase initially and then to decrease with the heat-treatment time at 1000 °C in a wet atmosphere of 355 torr (47000 Pa) water vapor pressure. In a dry atmosphere, a similar increase was observed but thereafter only a slight decrease took place. It is proposed that the creation of \(E^*\) centers in the initial stage is due to the existing water in the glass reacting with the silica structure, enhanced by the residual stress introduced during the glass tube fabrication process. It is proposed that the annihilation of \(E^*\) centers during further treatment is due to water diffusion and reaction with \(E^*\) centers, producing non-paramagnetic species such as Si–OH or Si–H. The initial increase of \(E^*\) center due to water and stress may be involved in the stress-corrosion reaction of glasses.

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