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Section 4. Transport properties

Spontaneous oxygen loading into SiO_2 glass by thermal anneal

Koichi Kajihara [a,*], Taisuke Miura [b], Hayato Kamioka [a], Masahiro Hirano [a], Linards Skuja [a,c], Hideo Hosono [a,d]

[a] *SORST, Japan Science and Technology Agency, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b] *Solid-State Optical Science Research Unit, RIKEN, Wako 351-0198, Japan*
[c] *Institute of Solid State Physics, University of Latvia, Riga LV1063, Latvia*
[d] *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

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Abstract

The interstitial oxygen molecules (O_2) in SiO_2 glass were detected down to $\sim 10^{15}\,cm^{-3}$ by photoluminescence of O_2 at 1272 nm excited at 765 nm by a continuous-wave titanium sapphire laser. It was evidenced that SiO_2 glass thermally annealed in air between 800 and 1100 °C spontaneously absorbs $\sim 10^{16}\,cm^{-3}$ of O_2 from the ambient atmosphere. The time-dependent concentration change of the interstitial O_2 allows the determination of both the diffusion coefficient and the solubility of the interstitial O_2.
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1. Introduction

A continuous three-dimensional network of corner-shared SiO_4 tetrahedra is a structural feature of SiO_2 glass (amorphous SiO_2). Since the structure does not permit a dense packing of the tetrahedra, relatively large interstitial spaces remaining in SiO_2 glass allow the dissolution and diffusion of small molecules. One of the most frequently found guests is the oxygen molecule (interstitial O_2). It has attracted attention as a chemical species which strongly affects ArF (193 nm or 6.4 eV) or F_2 (157 nm or 7.9 eV) laser toughness of SiO_2 glass because direct excitation of dissociative optical absorption band of the interstitial O_2 ($\lesssim$200 nm) yields the atomic oxygens, which are very reactive and proceed various defect processes [1–4].

The interstitial O_2 is commonly observed in SiO_2 glasses synthesized by the chemical vapor deposition in an oxygen plasma [5,6]. It is also formed together with the oxygen vacancy (Si–Si bond) as the intrinsic Frenkel-type defect pair in SiO_2 glass when the Si–O–Si bonds are decomposed by dense electronic excitations [7–10]. Further, the following observations suggest that O_2 in ambient atmosphere is another possible source of the interstitial O_2. First, thermally activated permeation of oxygen through a plate of SiO_2 glass has been confirmed by mass spectroscopy [11]. Second, preparation of insulating amorphous SiO_2 films by thermal oxidation of silicon utilizes oxygen transport through the oxide layer [12]. Third, thermal anneal in air annihilates the preexisting Si–Si bonds [13,14], and enhances the following radiation-induced formation of the peroxy radicals ($\equiv$SiOO$^\bullet$) from the silicon dangling bonds ($\equiv$Si$^\bullet$) [15]. However, oxygen uptake beyond the stoichiometric composition of SiO_2 has been largely overlooked in many studies, and the incorporated oxygens have not been directly observed.

* Corresponding author. Tel.: +81 44 850 9759; fax: +81 44 819 2205.
E-mail address: k-kajihara@net.ksp.or.jp (K. Kajihara).

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In the present study, we examined concentration change of O_2 in SiO_2 glass during thermal anneal in air. We observed that the thermal anneal spontaneously loads SiO_2 glass with O_2 from ambient atmosphere, and demonstrated that the time-dependent concentration change of the interstitial O_2 is useful to evaluate the diffusion coefficient (D) and the solubility (S) of the interstitial O_2 in SiO_2 glass.

2. Experimental procedure

High-purity SiO_2 glass containing $\sim 2\times10^{18}\,cm^{-3}$ of the SiOH groups was used, and it was cut into $10\times6.5\times1\,mm^3$ sample plates. The interstitial O_2 was measured at the center of the $10\times6.5\,mm^2$ face by detecting PL band at 1272 nm ($a^1\Delta_g \rightarrow X^3\Sigma_g^-$, full-width at half-maximum (FWHM): $\sim 86\,cm^{-1}$) [8,16] using a Fourier-transform infrared (IR) Raman spectrometer (Model 960, Nicolet) with a spectral resolution of $8\,cm^{-1}$. The PL band was excited at 765 nm ($X^3\Sigma_g^- \rightarrow b^1\Sigma_g^+$) [17]. Since FWHM of this transition band is as narrow as ~5 nm, the PL intensity is sensitive to power and wavelength fluctuations of the excitation source [17]. To stabilize the PL output, a continuous wave $Ti{:}Al_2O_3$ laser, of which stabilities of output power and wavelength were ~±1% rms and ~±0.3 nm, respectively, was newly developed. The integral PL intensity was obtained with a relative error of ±5% by fitting the PL spectrum to a Lorentzian function. To calculate the absolute concentration of the interstitial O_2, the PL intensity was normalized to that of a plate of reference SiO_2 glass (O_2-rich and SiOH-free SiO_2 glass, an analog of commercial Suprasil W). Concentration of the interstitial O_2 in the reference ($\sim 1.2\pm0.5\times10^{18}\,cm^{-3}$) was determined using a reported ratio of integral intensities between the O_2 PL band and the fundamental Raman bands of SiO_2 glass at 1000–1300 cm^{-1}, simultaneously recorded under a Nd:YAG laser excitation [16]. The PL quantum yield (Φ) of the interstitial O_2 may not be same among the sample and the reference SiO_2 glasses since the glass compositions are different. To improve the linearity between the concentration of the interstitial O_2 and the PL intensity, variation of Φ was evaluated by

$$\Phi = \frac{k_r}{k_r + k_{nr}} = k_r\tau, \qquad (1)$$

where k_r and k_{nr}, respectively denote the radiative and non-radiative transition rates, and k_r was assumed to be constant. The decay constant of PL (τ) was determined from PL decay curves recorded by an IR photodiode (G5832-05, Hamamatsu) connected to an oscilloscope. A mechanical shutter was used to periodically cut the excitation light. This procedure allowed to evaluate the absolute concentration of the interstitial O_2 down to $\sim 10^{15}\,cm^{-3}$ with an accuracy of ±50%.

3. Results

First, the samples were thermally annealed in vacuum for 450 h at 800 °C, 120 h at 900 °C, 20 h at 1000 °C, or 5 h at 1100 °C to equilibrate the glass structure with that at the anneal temperatures. Then each sample was thermally annealed in air at the same temperature as that of the vacuum anneal to incorporate O_2 from ambient atmosphere.

The PL decay of the interstitial O_2 was well fitted with a single exponential. The observed τ values for the samples were 0.84 ± 0.03 s, while that for the reference was 0.85 ± 0.03 s. Thus the Φ ratio of the sample to the reference is estimated to be ~0.99 from Eq. (1).

Fig. 1 shows the concentration change of the interstitial O_2 with duration of thermal anneal in air at 800 °C. The inset of Fig. 1 shows PL spectra for the samples before and after the air anneal for 720 h at 800 °C. The PL band due to the interstitial O_2 was detected at 1272 nm only after the air anneal: it was neither found before the vacuum anneal nor after the vacuum annealed but before the air anneal. Thus it is evident that the interstitial O_2 was supplied from ambient atmosphere. Fig. 2 summarizes the concentration changes of the interstitial O_2 with duration of the thermal anneals in air at 800, 900, 1000, and 1100 °C. The abscissa is plotted in the square root of time. The concentration of the interstitial O_2 was saturated more quickly at higher temperature, while the saturated concentration was generally smaller.

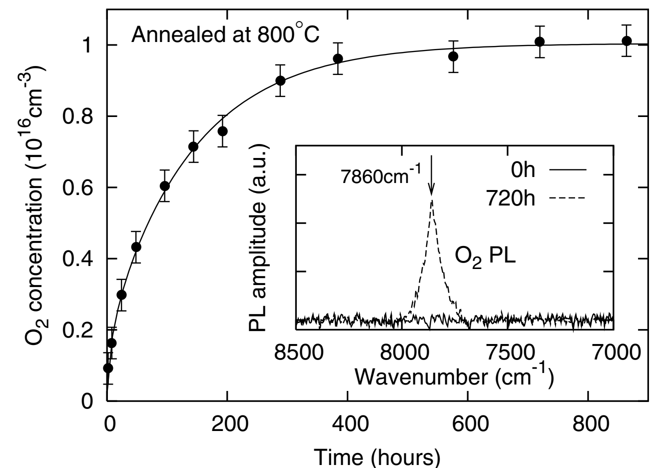


Fig. 1. Growth of the concentration of the interstitial O_2 in samples of SiO_2 glass plates with a thickness of 1 mm during thermal anneal in air at 800 °C. The solid line denotes a least-squares fit of the experimental points with Eq. (2). The inset shows PL spectra of the interstitial O_2 of the samples before and after thermal anneal in air for 720 h at 800 °C.

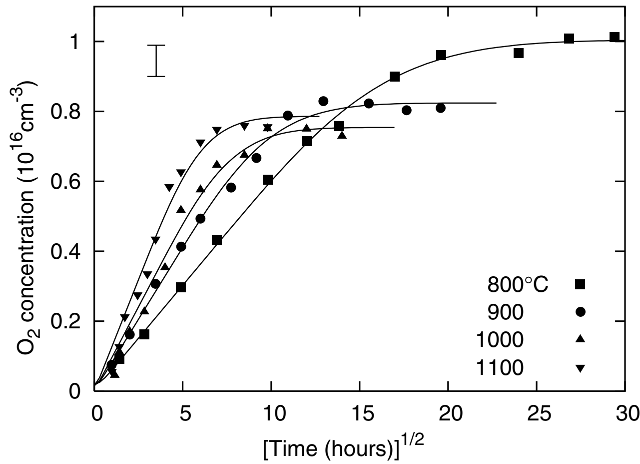


Fig. 2. Growth of the concentration of the interstitial O_2 during thermal anneals in air at 800, 900, 1000, and 1100 °C. The unit of abscissa is the square root of time. The solid lines denote least-squares fits of the experimental points with Eq. (2). The bar in the figure shows the relative error.

4. Discussion

To evaluate D and S, time-dependent concentration change of the interstitial O_2 was analyzed assuming an one-dimensional diffusion in a parallel plate with a thickness L [18],

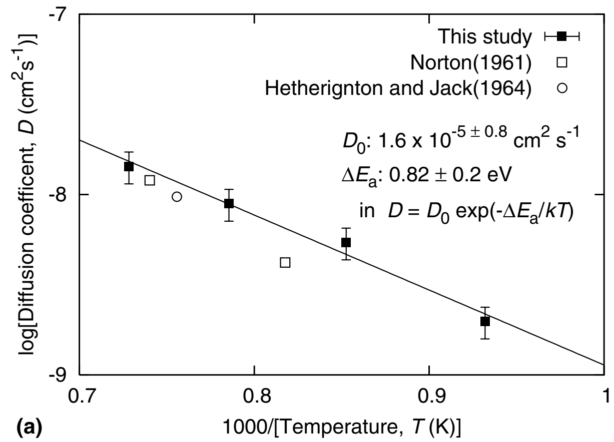
$$\frac{C(t)}{C} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp\{-D(2n-1)^2\pi^2 t/L^2\}}{(2n-1)^2}, \quad (2)$$

where $C(t)$ denotes the concentration of the interstitial O_2 averaged over the thickness at time t. At a large t, $C(t)$ equals C. At a small t, on the other hand, Eq. (2) is approximated [18] as

$$\frac{C(t)}{C} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}, \quad (3)$$

indicating that the slope of an $C(t) - t^{1/2}$ plot is proportional to $D^{1/2}$. As shown in Fig. 2, D increased while C decreased with an increase in the anneal temperature, in accordance with the common dissolution behavior of gaseous species in SiO_2 glass [19,20]. However, the decrease in C was likely to be saturated at 1100 °C.

Solid lines in Figs. 1 and 2 denote least-squares fits of the experimental data to Eq. (2), where C and D were treated as fitting parameters. The resultant D and S values are plotted in Fig. 3(a) and (b), respectively. Here, the S values are defined as the C values under the ambient partial pressure of O_2 of 1 atm providing that C is proportional to the partial pressure of O_2 [11]. Assuming simple Arrhenius-type relationships for the diffusion and dissolution processes, temperature dependences of D between 800 and 1100 °C and S between 800 and 1000 °C can be expressed as



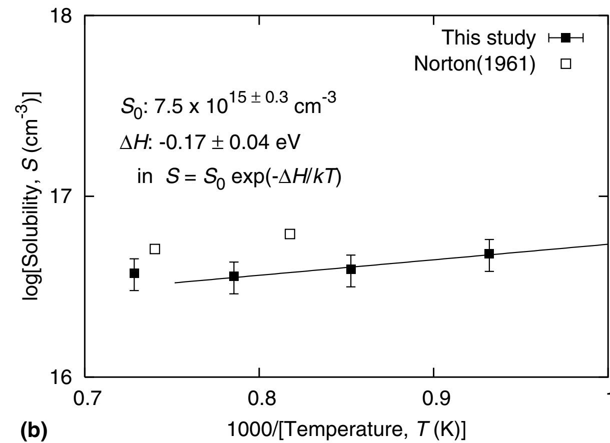


Fig. 3. Arrhenius plots of (a) the diffusion coefficient and (b) the solubility of the interstitial O_2. Data taken from Refs. [11,13] are shown for comparison.

$$D = 1.6 \times 10^{-5\pm0.8}\ \mathrm{cm^2\,s^{-1}} \exp\left(\frac{-0.82 \pm 0.2\ \mathrm{eV}}{kT}\right) \quad (4)$$

and

$$S = 7.5 \times 10^{15\pm0.3}\ \mathrm{cm^{-3}} \exp\left(\frac{0.17 \pm 0.04\ \mathrm{eV}}{kT}\right), \quad (5)$$

respectively, where k denotes the Boltzmann constant. These values agree well with the reported values [11,13], which have been used to describe the observed kinetics of the thermal oxidation of silicon [12]. This good agreement indicates that the interstitial O_2 is the dominant mobile oxygens in amorphous SiO_2 films during their growth on silicon substrates.

5. Conclusion

SiO_2 glass thermally annealed in air becomes oxygen-rich by absorbing $\sim10^{16}\,\mathrm{cm^{-3}}$ of O_2 from ambient atmosphere. This phenomenon has to be taken into account when studying optical properties and defect processes in SiO_2 glass. Both the diffusion coefficient and the

solubility of the interstitial O_2 were determined from the time-dependent concentration changes of the interstitial O_2. They agreed well with the reported diffusion parameters of mobile oxygens controlling the thermal oxidation of silicon, indicating that the interstitial O_2 is the primary mobile species.

References

[1] K. Awazu, H. Kawazoe, J. Appl. Phys. 68 (1990) 3584.
[2] L. Skuja, M. Hirano, H. Hosono, Phys. Rev. Lett. 84 (2000) 302.
[3] L. Skuja, K. Kajihara, T. Kinoshita, M. Hirano, H. Hosono, Nucl. Instr. Meth. Phys. Res. B 191 (2002) 127.
[4] K. Kajihara, L. Skuja, M. Hirano, H. Hosono, Phys. Rev. Lett. 92 (2004) 015504.
[5] D.L. Griscom, J. Ceram. Soc. Jpn. 99 (1991) 923.
[6] Y. Morimoto, T. Igarashi, H. Sugahara, S. Nasu, J. Non-Cryst. Solids 139 (1992) 35.
[7] T.E. Tsai, D.L. Griscom, Phys. Rev. Lett. 67 (1991) 2517.
[8] L. Skuja, B. Güttler, Phys. Rev. Lett. 77 (1996) 2093.
[9] H. Hosono, H. Kawazoe, N. Matsunami, Phys. Rev. Lett. 80 (1998) 317.
[10] M.A. Stevens-Kalceff, Phys. Rev. Lett. 84 (2000) 3137.
[11] F.J. Norton, Nature 191 (1961) 701.
[12] B.E. Deal, A.S. Grove, J. Appl. Phys. 36 (1965) 3770.
[13] G. Hetherington, K.H. Jack, Phys. Chem. Glasses 5 (1964) 147.
[14] H. Imagawa, T. Arai, H. Hosono, H. Imai, K. Arai, J. Non-Cryst. Solids 179 (1994) 70.
[15] R.L. Pfeffer, The Physics and Technology of Amorphous SiO_2, Plenum Press, New York, 1988, p. 181.
[16] L. Skuja, B. Güttler, D. Schiel, A.R. Silin, J. Appl. Phys. 83 (1998) 6106.
[17] L. Skuja, B. Güttler, D. Schiel, A.R. Silin, Phys. Rev. B 58 (1998) 14296.
[18] J. Crank, The Mathematics of Diffusion, 2nd Ed., Oxford University, Oxford, 1975 (Chapter 4).
[19] D.E. Swets, R.W. Lee, R.C. Frank, J. Chem. Phys. 34 (1961) 17.
[20] R.C. Frank, D.E. Swets, R.W. Lee, J. Chem. Phys. 35 (1961) 1451.