Surface Dissolution and Diffusion of Oxygen Molecules in SiO₂ GlassKoichi KAJIHARA,^{*} Taisuke MIURA,^{*,**} Hayato KAMIOKA,^{*} Masahiro HIRANO,^{*}
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KSP C-1232, 3-2-1, Sakado, Takatsu-ku, Kawasaki-shi 213-0012^{**}Solid-State Optical Science Research Unit, RIKEN, 2-1, Hirosawa, Wako-shi 351-0198^{***}Institute of Solid State Physics, University of Latvia, Kengaraga iela 8, LV1063 Riga, Latvia^{****}Materials and Structures Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama-shi 226-8503SiO₂ ガラスにおける酸素分子の表面溶解と拡散梶原浩一^{*}・三浦泰祐^{*,**}・上岡隼人^{*}・平野正浩^{*}・Linards Skuja^{*,***}・細野秀雄^{*,****}^{*,†}科学技術振興機構 ERATO 透明電子活性プロジェクト, 213-0012 川崎市高津区坂戸 3-2-1 KSP C-1232^{**}理化学研究所固体光学デバイス研究ユニット, 351-0198 和光市広沢 2-1^{***}ラトビア大学固体物理学研究所, Kengaraga iela 8, LV1063 Riga, Latvia^{****}東京工業大学応用セラミックス研究所, 226-8503 横浜市緑区長津田 4259

Surface dissolution and diffusion of oxygen molecules (O₂) in SiO₂ glass were studied by their photoluminescence at 1272 nm excited with a titanium sapphire laser oscillating at 765 nm. The dissolution of O₂ from ambient atmosphere at both surfaces was much faster than the following diffusion of O₂ into SiO₂ glass, indicating that the surface dissolution is not the rate-limiting step for the saturation of SiO₂ glass with O₂. The time- and temperature-dependent concentration changes of O₂ allow to evaluate the diffusion coefficient and the saturation solubility of O₂ in SiO₂ glass.

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1. Introduction

Diffusion of oxygen in oxides is closely related to various important phenomena in oxides such as oxidation and corrosion of metals, sintering, and transport of oxide ions in oxide electrolytes, and radiation-induced defect processes.^{(1),(2)} Several techniques have been developed to study the diffusion of oxygen in oxides. A straightforward way is the permeation method which measures amount of oxygen passed through thin plate or film samples.⁽³⁾ Isotopic labeling is very useful to trace the rearrangement of oxygen induced by the diffusion.⁽⁴⁾⁻⁽¹²⁾ Mobility of charged oxygen can be evaluated by electrochemical methods because the Nernst-Einstein equation relates the diffusion coefficient and the ionic conductivity. However, it is not generally easy to characterize separately transports of oxygens of different chemical forms and via different diffusion paths such as lattice interstitials, vacancies, and grain boundaries.

The oxygen molecule (O₂) is particularly interesting among possible mobile oxygen species since it is selectively probed by its infrared photoluminescence (PL) band at 1272 nm, attributed to the transition from the first singlet excited state ($a^1\Delta_g$) to the triplet ground state ($X^3\Sigma_g^-$). It was noted that this PL band is detectable even for a very low concentration of O₂ in SiO₂ glass ($\sim 10^{14}$ cm⁻³) by populating the second singlet excited state of O₂ ($b^1\Sigma_g^+$) at 765 nm with titanium sapphire laser light.⁽¹³⁾ These properties are quite useful to investigate the diffusion of O₂ in SiO₂ glass.⁽¹⁴⁾

Surface dissolution of O₂ into oxides has been little studied. Direct uptake of O₂ from ambient atmosphere may be

relatively fast because the chemical state of oxygen is largely preserved. In contrast, surface dissolution of oxygen into oxides sometimes involves activation processes which slow down the dissolution rate. For example, dissolution of oxygen in solid oxide electrolytes is considerably slow, because O₂ has to be converted into a pair of O²⁻.^{(15),(16)}

The purpose of the present study is to investigate the diffusion of O₂ in SiO₂ utilizing its PL with taking the rate of the surface dissolution into account.

2. Experimental procedure

Synthetic SiO₂ glass containing $\sim 2 \times 10^{18}$ cm⁻³ of SiOH groups was used as samples. First, the samples were thermally annealed in vacuum at 800, 900, 1000, or 1100°C to relax the sample structure at the annealing temperature. It was followed by a thermal anneal in air at the same temperature as that of the vacuum anneal to incorporate O₂ from ambient atmosphere. Then the concentrations of O₂ were measured at ambient temperature by detecting its PL band at 1272 nm using a Fourier-transfer Raman spectrometer (Model 960, Nicolet) with a spectral resolution of 8 cm⁻¹. The PL band was excited at 765 nm with a home-made continuous-wave titanium sapphire laser offering good stabilities of output wavelength ($\sim \pm 0.3$ nm) and power ($\sim \pm 1\%$ rms). Thereby the fluctuation of PL intensity was minimized. The concentrations of O₂ were determined from the ratios of PL intensities between the samples and a reference SiO₂ glass with a known O₂ content following the procedure described in Ref. 14) in detail.

3. Mathematics for data analysis

In this section, formula used to analyze the observed data will be presented.^{(17),(2)} Assuming that there is a gradient of concentration only along the x -axis, concentration of diffus-

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ing substance at time t and position x , $C(x, t)$, may follow the one-dimensional Fick's second law,

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2}. \quad (1)$$

The diffusion coefficient D can be taken as a constant when the concentration of diffusing substance is much less than the number of solubility sites per unit volume. Diffusion in a plane sheet whose thickness is L and surfaces are at $x = \pm L/2$ can be described by boundary conditions of $C(\pm L/2, t) = C$ and $C(|x| < L/2, 0) = 0$, where C denotes the saturated concentration, i.e., the concentration in equilibrium with the partial pressure of the diffusing substance in the gas phase, $C = \lim_{t \rightarrow \infty} C(x, t)$. The former condition postulates that the surface is always saturated with the diffusing substance because of its rapid dissolution. The solution of Eq. (1) under these conditions is

$$\frac{C(x, t)}{C} = 1 + \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{2n-1} \exp \left\{ -\frac{D(2n-1)^2 \pi^2 t}{L^2} \right\} \times \cos \frac{(2n-1)\pi x}{L}. \quad (2)$$

Integration of Eq. (2) between $x = \pm L/2$ yields the average concentration at t ,

$$\frac{C_a(t)}{C} = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp \{ -D(2n-1)^2 \pi^2 t / L^2 \}}{(2n-1)^2}. \quad (3)$$

However, the surface dissolution may be measurably slow if it involves significant activation processes. There are at least two different models to formulate such situation.^{17,2)} The first model assumes that the flux across the surface is proportional to $C - C(\pm L/2, t)$, the difference between the surface concentrations at $t \rightarrow \infty$ and t . Thus $C(\pm L/2, t)$ is no longer a constant but satisfies the differential equation

$$-D \frac{\partial C(x, t)}{\partial x} \bigg|_{x=\pm L/2} = \alpha \{ C - C(\pm L/2, t) \}, \quad (4)$$

where α is a coefficient representing the dissolution rate. Here, the solution of Eq. (1) becomes

$$\frac{C(x, t)}{C} = 1 - \sum_{n=1}^{\infty} \frac{2K \cos(2\beta_n x/L) \exp(-4\beta_n^2 D t/L^2)}{(\beta_n^2 + K^2 + K) \cos \beta_n}, \quad (5)$$

where $K \equiv L\alpha/2D$ and β_n denote the positive roots of $\beta \tan \beta = K$ satisfying $(n-1)\pi < \beta_n < (n-1/2)\pi$. The average concentration at t is expressed by

$$\frac{C_a(t)}{C} = 1 - \sum_{n=1}^{\infty} \frac{2K^2 \exp(-4\beta_n^2 D t/L^2)}{\beta_n^2 (\beta_n^2 + K^2 + K)}. \quad (6)$$

In the second model, $C(\pm L/2, t)$ is given as a root of a equation on exchange of diffusing substance between the surface and gas phase as

$$-\frac{\partial C(\pm L/2, t)}{\partial t} = k_1 C_g - k_2 C(\pm L/2, t), \quad (7)$$

where C_g is the concentration of diffusing substance in the gas phase and k_1 and k_2 are the rate constants. Integration of Eq. (7) yields

$$C(\pm L/2, t) = C \{ 1 - \exp(-\beta t) \}, \quad (8)$$

where relationships $C = k_1 C_g / k_2$ and $\beta = k_2$ hold. The solution of Eq. (1) under Eq. (8) is given by

$$\begin{aligned} \frac{C(x, t)}{C} = & 1 - \exp(-\beta t) \frac{\cos(2xK^{1/2}/L)}{\cos K^{1/2}} \\ & + \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n \exp \{ D(2n-1)^2 \pi^2 t / L^2 \}}{2n-1} \frac{1 - (2n-1)^2 \pi^2 / (4K)}{1 - (2n-1)^2 \pi^2 / (4K)} \\ & \times \cos \frac{(2n-1)\pi x}{L}, \end{aligned} \quad (9)$$

where $K \equiv L^2 \beta / 4D$, and the average concentration is

$$\begin{aligned} \frac{C_a(t)}{C} = & 1 - \exp(-\beta t) K^{-1/2} \tan K^{1/2} - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \\ & \times \frac{\exp \{ -D(2n-1)^2 \pi^2 t / L^2 \}}{1 - (2n-1)^2 \pi^2 / (4K)}. \end{aligned} \quad (10)$$

In both models, the dimensionless parameter K represents the normalized rate of the surface dissolution. At $K < 100$, the delay of the surface dissolution becomes appreciable.

4. Results

To demonstrate the effects of rate of the surface dissolution, cross-sectional concentration profiles were simulated. **Figures 1(a), (b), and (c)** show $C(x, t)$ curves calculated from Eqs. (2), (5) and (9), respectively. The time-dependent saturation behaviors of the surface concentration are clearly different between profiles for slow surface dissolutions (Figs. 1(b) and (c)) and those of rapid dissolution (Fig. 1(a)). Thus the cross-sectional profile is useful to evaluate the rate of the surface dissolution.

The cross-sectional profiles were measured as follows. Samples with an initial dimension of $20 \times 20 \times 5$ mm³ were loaded with O₂. The concentration profile at the center of the sample was measured using a $20 \times 5 \times 2$ mm³ parallelepiped quarried from the middle of the sample. The spatial resolution, determined by the positioning accuracy and the diameter of the

Fig. 1. Simulated cross-sectional concentration profiles calculated from (a) Eq. (2), (b) Eq. (5), and (c) Eq. (9). Parameters used for the calculations are shown in the figures.

Fig. 2. Experimental and simulated cross-sectional concentration profiles of the interstitial O_2 in SiO_2 glass. The solid curves are drawn by fitting the experimental data points with Eq. (2). The inset shows the PL spectrum taken at -0.20 cm for the sample thermally annealed for 840 h.

focused excitation laser beam, was $\sim \pm 0.1$ mm. **Figure 2** shows the results after thermal annealings for 120 and 840 h at 900°C and a typical PL spectrum. The data points were fitted with Eqs. (2), (5), or (9) using common fitting parameters for both curves. The obtained parameters were $D = 4.4 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ and $C = 5.1 \times 10^{15} \text{ cm}^{-3}$ for Eq. (2); $D = 4.4 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$, $C = 5.1 \times 10^{15} \text{ cm}^{-3}$, and $\alpha = 4.1 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ for Eq. (5); and $D = 4.5 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$, $C = 5.1 \times 10^{15} \text{ cm}^{-3}$, and $\beta = 3.1 \times 10^{-5} \text{ s}^{-1}$ for Eq. (9). Notably, these fittings yielded nearly the same D and C values and the simulated curves are almost identical with each other. Thus Fig. 2 only shows the curves calculated by Eq. (2). Further, the K values were calculated to be ~ 230 for Eq. (5) and ~ 430 for Eq. (9), indicating that the dissolution of O_2 at both surfaces is much faster than the diffusion of O_2 in SiO_2 glass. These analyses indicate that Eqs. (2) and (3) are accurate enough to describe the diffusion of the interstitial O_2 in SiO_2 glass.

An alternative way to evaluate the D and C values is to measure the average concentration $C_a(t)$. This method is more convenient because it does not need the sample cutting after the O_2 loading. The size of the samples was $10 \times 6.5 \times 1 \text{ mm}^3$ and the PL spectra were measured at the center of the $10 \times 6.5 \text{ mm}^2$ face. **Figure 3** shows the $C_a(t)$ data taken at 900°C . Fitting of the result with Eq. (3) yielded $C = 5.8 \times 10^{15} \text{ cm}^{-3}$ and $D = 4.7 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$, showing a good agreement with the D and C values derived from Fig. 2. These values at other temperatures were evaluated in a similar way. However, they can also be derived by analyzing the curve separately before and after the characteristic time defined as $t_c \equiv \pi(L/4)^2/D$: the height of the plateau at $t \gg t_c$ equals C as $C = C_a(t \rightarrow \infty)$ while the slope of the $C_a(t) - t^{1/2}$ curve at $t \ll t_c$, is proportional to $D^{1/2}$ as $4C(D/\pi)^{1/2}/L$.

All the D and C values determined in this study are summarized in **Fig. 4**. The dissolution of O_2 in SiO_2 glass follows the Henry's law, $C = Sp(O_2)$ when the partial pressure of O_2 in the gas phase, $p(O_2)$, is below several atm.³⁾ Thus we will define the solubility S as C under $p(O_2) = 1 \text{ atm}$ and use it here instead of C . Least-squares fittings of all D values and S values at $\leq 1000^\circ\text{C}$ yielded

$$D = 3.6 \times 10^{-5 \pm 0.4} \text{ cm}^2 \cdot \text{s}^{-1} \exp \left(\frac{-0.91 \pm 0.1 \text{ eV}}{kT} \right), \quad (11)$$

Fig. 3. Experimental and simulated changes of average concentration of the interstitial O_2 in SiO_2 glass. The experimental data points are fitted with Eq. (3) to evaluate D and C values. The other curves indicating the effect of slow surface dissolution are drawn by Eqs. (6) and (10) using parameters shown in the figure.

Fig. 4. Arrhenius plot of the (a) D and (b) S values obtained in this study. Data taken from Refs. 3) and 19) are shown too.

and,

$$S = 4.8 \times 10^{15 \pm 0.2} \text{ cm}^{-3} \text{ atm}^{-1} \exp \left(\frac{0.18 \pm 0.03 \text{ eV}}{kT} \right), \quad (12)$$

respectively.

The effect of slow surface dissolution was examined by

Fig. 5. Schematic illustration of the interstitial O₂ (dark spheres) in SiO₂ glass. Silicon and oxygen atoms are shown as small and large spheres, respectively.

simulating $C_a(t)$ curves at $K=2.5$ from Eqs. (6) and (10) as shown in Fig. 2. These curves did not fit the experimental data well because of their slow initial growth and fast saturation, supporting the conclusion shown in Fig. 2. However, the shape of the $C_a(t)$ curves varies less distinctly with K than that of the $C(x, t)$ curves shown in Fig. 1. Thus K values were not evaluated here.

5. Discussion

The diffusion of oxygen in SiO₂ glass measured so far can be classified into fast and slow ones.¹⁸⁾ The D values reported in Refs. 3) and 19) are more than 5 orders of magnitude larger than those reported in other papers.^{4)–12)} The slow diffusion has been attributed to the movement of oxygen involving the hopping of oxygen atoms belonging to the SiO₂ lattice. It is similar to the common mechanism of oxygen diffusion in oxides: diffusion via vacancy and interstitial sites.¹⁾ On the other hand, compared to other oxides, structure of SiO₂ glass is relatively sparse, allowing the incorporation of O₂ as schematically shown in Fig. 5. Thus the fast diffusion has been suggested to be due to the transport of O₂ without a significant interaction with the SiO₂ lattice.^{2),18)} This mechanism is supported by the following observations. In a permeation experiment in which the amount of gaseous species through thin SiO₂ glass plates was measured, the permeation rate of species with a molecular mass 32 has found to be proportional to the partial pressure of O₂ applied to the other surface.³⁾ This is an indication that the Henry's law holds for the dissolution of O₂, further suggesting that O₂ does not dissociate at the surfaces. The D and S values determined in Ref. 3) have been the standard parameters to predict the growth of insulating amorphous SiO₂ films by thermal oxidation of silicon.²⁰⁾ However, direct detection of the mobile species dominating the fast oxygen diffusion has not been reported.

In this study, diffusion of oxygen was measured by monitoring the concentration change of O₂ in SiO₂ glass. Analyses shown in Figs. 2 and 3 indicate that the incorpora-

tion of O₂ at the surface of SiO₂ glass is much faster than its diffusion in SiO₂ glass. Further, the observed D and S values agree well with those reported by Refs. 3) and 19). Thus we clearly demonstrate that the dissolution of O₂ into SiO₂ glass does not involve significant activation processes, and the subsequent diffusion of O₂ through the interstitial spaces in SiO₂ glass is responsible for the fast oxygen transport in SiO₂ glass contributing to the thermal oxidation of silicon.

6. Conclusions

Surface dissolution and diffusion of O₂ in SiO₂ glass were studied by monitoring spatially resolved laser-induced photoluminescence of O₂. The time- and positional-dependences of O₂ concentration were theoretically analyzed by considering both the rates of dissolution at the surfaces and diffusion in the medium. This procedure verified that the interstitial O₂ dominates long-range oxygen transport in SiO₂ glass and its incorporation at the glass surfaces is not the rate-limiting process.

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