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Diffusion of oxygen molecules in fluorine-doped amorphous SiO_2

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ABSTRACT

Effects of fluorine doping on the diffusion of interstitial oxygen molecules (O_2) in amorphous SiO_2 (*a*-SiO_2) were compared to those obtained from *a*-SiO_2 containing SiOH groups. Incorporation of moderate concentration ($\sim 10^{19}\,cm^{-3}$) of SiF groups gives rise to minor changes in diffusion parameters between 800 and 1100 °C: only a slight decrease in solubility and an increase in the activation energy for diffusion can be detected. Incorporation of SiOH groups has similar weak effects on the solubility and activation energy for diffusion. These minor changes are most likely due to the enhancement of the flexibility of local Si–O network as a result of the dissociation of the network by SiOH and SiF groups. However, in contrast to the SiF doping, SiOH doping leads to a notable decrease in the diffusion coefficient. The heat of solution changes by ~0.1–0.2 eV at ~1000 ° C and it is attributed to the glass transition of *a*-SiO_2.

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1. Introduction

Amorphous SiO_2 (*a*-SiO_2) is widely used as gate dielectric films for silicon microelectronic circuits, optical fibers for telecommunication, and optical components in excimer laser photolithography. Fluorine is one of the most important dopant for *a*-SiO_2 used as such devices, because moderate fluorine doping increases the radiation hardness of *a*-SiO_2[1–4], suppresses the electrical breakdown of the gate dielectric films, and improves the optical transmittance near the absorption edge of *a*-SiO_2 located at $h\nu \simeq 8$ eV [5]. These improvements are mainly due to the breaking up of Si–O network by Si–F bonds. It decreases the viscosity of *a*-SiO_2[3] and enhances the structural relaxation [6,7], facilitating the removal of "strained" Si–O–Si bonds, which are considered to be a major source of point defects in *a*-SiO_2[8–13]. Furthermore, Si–F bonds themselves are stronger than Si–O bonds that build the *a*-SiO_2 network and are hardly decomposed. Thus, radiation hardness of fluorine-doped *a*-SiO_2 is better than that of *a*-SiO_2 containing other network modifiers, such as SiOH and SiCl groups. Similarly to SiF groups they enhance the structural relaxation, however, they can be converted to point defects under radiation or electrical stress.

Oxygen molecules dissolved in interstices of Si–O network (interstitial O_2) are the main mobile oxygen species in *a*-SiO_2[14–16]. They play a key role in thermal oxidation of silicon [17] and radiation induced defect processes in *a*-SiO_2[18]. Interstitial O_2 in *a*-SiO_2 are sensitively detected by their characteristic infrared photoluminescence at ~1273 nm, attributed to the transition from the lower excited singlet state ($a^1\Delta_g$) to the ground state ($X^3\Sigma_g^-$) [19]. It is possible to detect as few as $\sim 10^{14}\,cm^{-3}$ interstitial O_2 when the upper excited singlet state ($b^1\Sigma_g^+$) is populated using a continuous-wave laser light at a wavelength of 765 nm [20]. The sensitivity is sufficient to detect interstitial O_2 incorporated during thermal annealing in air [21], offering an easy and straightforward way to quantitatively study the thermal diffusion of interstitial O_2 in *a*-SiO_2[22]. Furthermore, this PL method is precise enough to evaluate the variations of the solubility and diffusion coefficient of interstitial O_2 with the incorporation of $\sim 10^{20}\,cm^{-3}$ SiOH groups [23,18], which are the most common network modifiers in synthetic *a*-SiO_2.

The purpose of the present study is to examine the influence of the incorporation of SiF groups on the diffusion of interstitial O_2 in *a*-SiO_2 and to compare it with that of SiOH groups.

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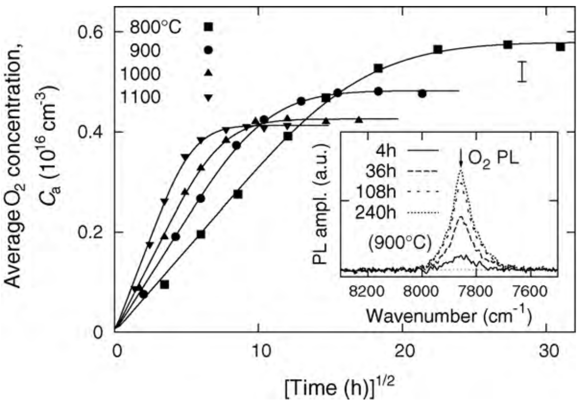

Fig. 1. Variation of the thickness average of interstitial O_2 concentration C_a with annealing time t for 1 mm-thick samples annealed in air at 800, 900, 1000, or 1100 °C. The error bar indicates the experimental uncertainty. The inset shows the PL band of interstitial O_2 for samples annealed at 900 °C.

2. Experimental procedure

Fluorine-doped synthetic SiO_2 glass containing $\sim 1.4 \times 10^{19}\,cm^{-3}$ of SiF groups and $\sim 1\text{–}2 \times 10^{18}\,cm^{-3}$ of SiOH groups was cut into specimens in the form of 7 mm × 10 mm × 1 mm, and the two largest faces were polished to an optical finish. They were thermally annealed in air at 800, 900, 1000, or 1100 ° C to incorporate interstitial O_2. The PL band of interstitial O_2 in the O_2-loaded samples was excited at 765 nm using an AlGaAs laser diode (~1.5 W at the sample position) and was measured using the detector part of a Fourier-transform Raman spectrometer (Model 960 Nicolet). The laser light was directed normal to the polished surface and the backscattered PL signal was recorded. The peak amplitude of the PL band is proportional to the thickness average of the concentration of interstitial O_2, C_a, and the proportionality factor was determined using a reference sample with a known O_2 concentration.

3. Results

Fig. 1 shows the variation of C_a with annealing time t at 800, 900, 1000, or 1100 °C. C_a was proportional to $t^{1/2}$ at small t, and saturated at a constant value at large t. This observation indicates that the dissolution of O_2 from air is much faster than the following O_2 diffusion in a-SiO_2[22] and is consistent with previous results [22,23]. Thus, the observed variation of C_a with t was simulated well by an equation describing the simplest one-dimensional diffusion in a parallel sheet of a thickness L [24],

$$\frac{C_a(t)}{C_0} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp[-D(2n-1)^2\pi^2 t/L^2]}{(2n-1)^2}, \qquad (1)$$

using the diffusion coefficient D and the saturation concentration C_0 as adjustable parameters. The best-fit theoretical curves are shown as solid lines in Fig. 1. The solubility S was calculated from the relation $S = C_0/p_{O_2}$, where p_{O_2} is the partial pressure of O_2 in air at atmospheric pressure ($p_{O_2} = 0.209$ atm), provided that C_0 is proportional to p_{O_2} at this pressure range [15,23].

The D and S values derived from the data shown in Fig. 1 are plotted in Fig. 2 and are referred to as "F-doped". Both $\log D$ and $\log S$ were almost proportional to the reciprocal of the absolute temperature T, with slight deviations starting to appear above ~1000 ° C in the S plot. Apart from the point at 1100 ° C in the S plot, these data were fitted to the simple Arrhenius-type relations

$$D = D_0 \exp(-\Delta E_a/kT), \qquad (2)$$

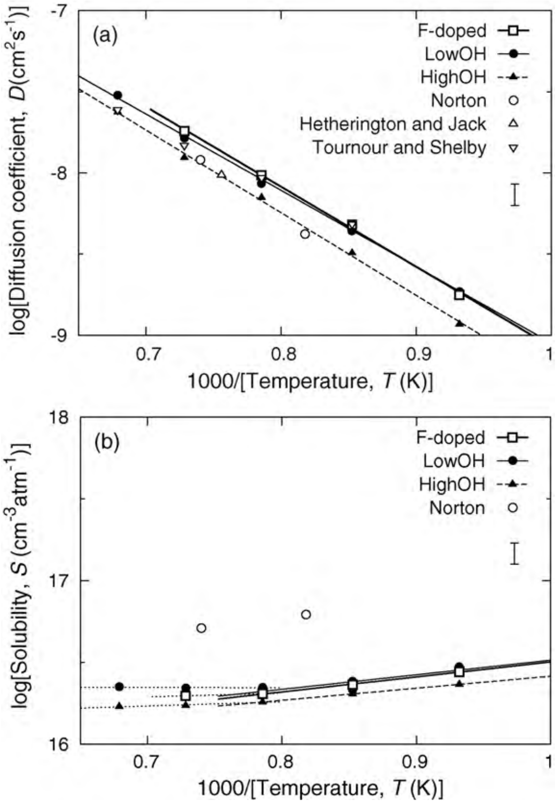

Fig. 2. Arrhenius plots of the diffusion coefficient (a) and solubility (b) of interstitial O_2. Data taken from Refs. [15,35,23,36] are also shown. The error bars indicate the experimental uncertainty for data obtained by our group (F-doped, LowOH, and HighOH). The dotted lines at $T \geqq 1000$ ° C in panel (b) correspond to linear fits drawn to guide the eye.

$$S = S_0 \exp(-\Delta H/kT), \qquad (3)$$

to evaluate the activation energy for diffusion ΔE_a, the heat of solution ΔH, and the preexponential factors D_0 and S_0. k in Eqs. (2) and (3) denotes the Boltzmann constant. The calculated parameters are listed in Table 1. The experimental uncertainties of ΔE_a and D_0 were larger for the F-doped sample than for the LowOH and HighOH samples reported previously [23,18], because the temperature range used for the fitting of the F-doped sample data was narrower.

4. Discussion

Fig. 2 also shows D and S values of interstitial O_2 reported to date. The obtained ΔE_a, ΔH, D_0, and S_0 values are listed in Table 1, along with the measurement method, sample type, and abbreviated name. Agreements among data are good for D, ΔE_a, and ΔH. However, our S data are ~2.5 times smaller than those reported in Ref. [15].

The LowOH sample is fluorine-free and contains SiOH groups in concentration comparable with that in the F-doped sample. In these two samples the behavior of diffusion of interstitial O_2 is very similar, except for a subtly higher ΔE_a and smaller S in the F-doped sample. This observation indicates that incorporation of $\sim 10^{19}\,cm^{-3}$ SiF groups does not significantly modify the diffusion of interstitial O_2.

The diffusion of molecular species in solids has been studied well for amorphous organic polymers, and these results may provide insight into the diffusion of molecular species in a-SiO_2. In amorphous organic polymers, ΔH above the glass transition temperature (T_g) is generally larger (i.e., smaller by absolute value since

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