

The Effect of Partial Pressure of Oxygen on Self-Diffusion of Si in SiO₂

Shigeto FUKATSU, Tomonori TAKAHASHI, Kohei M. ITOH*, Masashi UEMATSU¹,
Akira FUJIWARA¹, Hiroyuki KAGESHIMA¹, Yasuo TAKAHASHI¹ and Kenji SHIRAIISHI²

Department of Applied Physics and Physico-Informatics and CREST-JST, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

¹NTT Basic Research Laboratories, NTT Corporation, 3-1 Wakamiya, Morinosato, Atsugi 243-0198, Japan

²Institute of Physics, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8577, Japan

(Received October 7, 2003; revised October 29, 2003; accepted October 30, 2003; published December 3, 2003)

The self-diffusion coefficient of Si in thermal oxides (SiO₂) formed on semiconductor silicon wafers has been determined with isotope heterostructures, ^{nat}SiO₂/²⁸SiO₂, as a function of the partial pressure of oxygen mixed into argon annealing ambient. The ^{nat}SiO₂ layers contain 3.1% of ³⁰Si stable isotopes while the ²⁸SiO₂ layers are depleted of ³⁰Si stable isotopes down to 0.003%, and the diffusion depth profiles of ³⁰Si isotopes from the ^{nat}SiO₂ to ²⁸SiO₂ layers after thermal annealing have been determined by secondary ion mass spectrometry (SIMS). The Si self-diffusivity is found not to depend on the partial pressure of oxygen within our experimental error of about ±33%. [DOI: 10.1143/JJAP.42.L1492]

KEYWORDS: silicon electronics, silicon dioxide, self-diffusion, gate insulator

Si self-diffusion in SiO₂ has been investigated extensively in the past decades,^{1–8)} because SiO₂ formed thermally on semiconductor Si wafers has been the most important gate material in the field of microelectronics. However, even among the most recent and reliable diffusion experiments using isotope heterostructures, the reported values of diffusivity are different by a couple orders of magnitude.^{6,7)} The present group reported on the silicon self-diffusivity $D_{\text{Si}}^{\text{SD}} = 0.8 \exp(-5.2 \text{ eV}/kT) \text{ cm}^2 \cdot \text{s}^{-16}$) in contrast to Mathiot *et al.*'s values $33.2 \exp(-5.34 \text{ eV}/kT) \text{ cm}^2 \cdot \text{s}^{-1}$.⁷⁾ More recently, we have shown very convincingly that $D_{\text{Si}}^{\text{SD}}$ in thermally grown SiO₂ depends strongly on the distance between the Si diffusers and Si/SiO₂ interface.⁸⁾ When such distance dependence is taken into account, Mathiot *et al.*'s $D_{\text{Si}}^{\text{SD}}$ (ref. 7) agrees very well with ours (ref. 6).⁸⁾ However, one question raised by Mathiot *et al.* remains. They suggested that our values of $D_{\text{Si}}^{\text{SD}} = 0.8 \exp(-5.2 \text{ eV}/kT)$ obtained in argon with 1% oxygen annealing atmosphere represented $D_{\text{Si}}^{\text{SD}}$ in an “oxidation ambient” and, therefore, were different from their $D_{\text{Si}}^{\text{SD}}$ obtained in the Si₃N₄ capped, “inert condition.” While our recent experiment has shown $D_{\text{Si}}^{\text{SD}} = 0.8 \exp(-5.2 \text{ eV}/kT)$ even for the Si₃N₄ capped SiO₂ film with the Si diffusers far enough from the Si/SiO₂ interface (Mathiot *et al.*'s $D_{\text{Si}}^{\text{SD}}$ obtained with thin SiO₂ was affected by the SiO defects arriving from the Si/SiO₂, i.e., it represented the non-intrinsic case), it is still important to determine whether Si self-diffusivity in SiO₂ depends on the oxygen partial pressure in the annealing ambient of argon gas.

Samples employed in this study were prepared as follows. Isotopically enriched ²⁸Si single crystal epi-layers of 0.8 μm thickness grown by chemical vapor deposition (CVD) on 4-inch highly resistive Si wafers were provided by Isonics Corp., Colorado, USA. The isotope composition of the ²⁸Si epi-layer measured by secondary ion mass spectrometry (SIMS) was ²⁸Si (99.924%), ²⁹Si (0.073%), and ³⁰Si (0.003%). The ²⁸Si surface of the epi-layer was thermally oxidized in dry O₂ at 1100°C for 20 hours to form 650 nm thick ²⁸SiO₂. Subsequently, about 50 nm thick ^{nat}SiO₂ was deposited on top of the ²⁸SiO₂ film by low-pressure chemical vapor deposition (LPCVD) using tetraethoxysilane (TEOS) at 700°C. The isotopic composition of naturally available

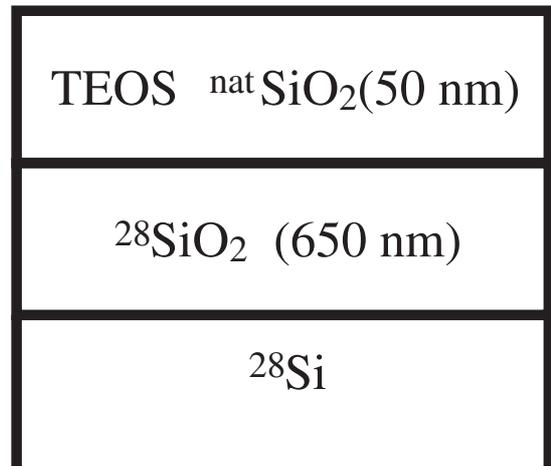


Fig. 1. Schematic of the samples employed in this study.

silicon (^{nat}Si) is ²⁸Si (92.2%), ²⁹Si(4.7%), and ³⁰Si(3.1%). The completed structures are shown in Fig. 1. These structures were cut into 5×5 mm² samples. An each piece was diffusion annealed in a resistively heated furnace. Semiconductors processing grade quartz tubes and gas sources (argon and oxygen premixed in the 49 liter gas cylinders) were employed for maintaining the sample as clean as possible. Diffusion annealings were conducted under flowing argon with 1, 10, 20, 50, and 100% oxygen fractions at temperatures 1200 and 1250°C. At least 1% of oxygen mixed into argon was necessary in order to prevent SiO₂ from decomposition, which tended to occur at higher temperatures and for lower oxygen partial pressures. This 1% was just enough to slowly oxidize the structure to counterbalance the decomposition, i.e., the total thickness of the oxide (^{nat}SiO₂ and ²⁸SiO₂) changed very little (<10%) before and after the diffusion annealing. SIMS using O₂⁺ for a primary ion beam with the acceleration energy 5 keV was used to determine the depth profile of ³⁰Si. An electron beam was irradiated during the measurement in order to prevent samples from charging up.

Figure 2 shows one of the ³⁰Si profiles of the heterostructures before and after annealing in 1–100% oxygen ambient. The SIMS profile of the as-grown, abrupt ^{nat}SiO₂/²⁸SiO₂ interface is broaden, though it should have ideally

*E-mail address: kitoh@appi.keio.ac.jp

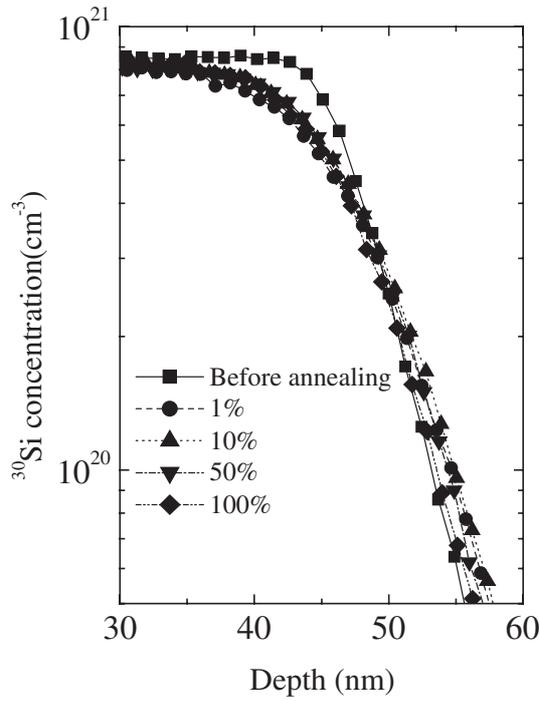


Fig. 2. Comparison of the diffusion profiles of ^{30}Si from the $^{\text{nat}}\text{SiO}_2$ to $^{28}\text{SiO}_2$ layers before and after 48 h diffusion annealings at 1200°C with oxygen fractions 1, 10, 50, and 100% in the argon ambient.

exhibited a step profile. Unavoidable atomic mixing due to collisional cascades and the surface roughening due to statistical sputter emission processes that are inherent of the SIMS measurements cause this so-called “SIMS broadening.” In the first step of our analysis, the effect of SIMS broadening has been subtracted based on the method developed by Hoffman.⁹⁾ Then the diffusion profiles of ^{30}Si are fitted by the following equation;

$$C(x) = C_{28} + \frac{C_{\text{nat}} - C_{28}}{2} \times \left[\text{erf}\left(\frac{x+h}{2\sqrt{D_{\text{SD}}t}}\right) - \text{erf}\left(\frac{x-h}{2\sqrt{D_{\text{SD}}t}}\right) \right] \quad (1)$$

where $x = 0$ is taken at the surface of samples. C_{nat} and C_{28} are the initial concentrations of ^{30}Si in $^{\text{nat}}\text{SiO}_2$ and $^{28}\text{SiO}_2$, respectively. The constant h is the thickness of the $^{\text{nat}}\text{SiO}_2$ layer, D_{SD} is the Si self-diffusion coefficient, and t is the annealing time. The thickness of the $^{28}\text{SiO}_2$ layer is regarded as infinite because no ^{30}Si reaches the interface $^{28}\text{SiO}_2/^{28}\text{Si}$ by the present annealing process. The only fitting parameter D_{SD} in eq. (1) is the silicon self-diffusion coefficient. The diffusion coefficients determined with the SIMS broadening corrections are 10–20% smaller than those obtained without the correction.

D_{SD} for various oxygen concentrations in the ambient is shown in Fig. 3. Our earlier data⁶⁾ that correspond to the values for 1% oxygen are also shown for the comparison. D_{SD} depends very little on the oxygen concentration in the ambient and agrees nicely with our earlier data with 1% oxygen. The error in the broadening correction procedure is estimated to be about $\pm 2\%$. This error is much smaller than about $\pm 30\%$ error arising from the SIMS mass separation and depth measurements. Also fitting with eq. (1) leads to an error of a couple percent. By adding these three major

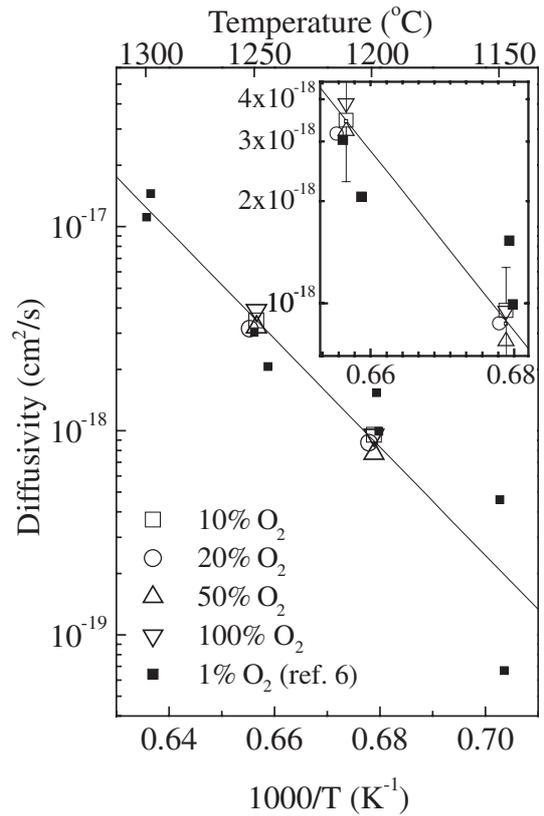


Fig. 3. Temperature dependence of the Si self-diffusion coefficient in SiO_2 with the oxygen fraction 1, 10, 20, 50, and 100% in the argon atmosphere. Solid line corresponds to the values for 1% oxygen in argon reported in our earlier study.⁶⁾ An inset shows the zoom-up of the temperature range $1200\text{--}1250^\circ\text{C}$.

sources of errors, we arrive at our total error bar of about $\pm 33\%$. It is clear in Fig. 3 that D_{SD} does not depend on the oxygen concentration within our experimental error of $\pm 33\%$.

Let us discuss why the oxygen partial pressure in the annealing ambient does not influence the Si self-diffusion in SiO_2 significantly. The diffusion coefficient of oxygen in SiO_2 is at least four orders of magnitude larger than the self-diffusion coefficient of Si for the temperatures 1200 and 1250°C .^{10,11)} Therefore, a fraction of oxygen atoms in the annealing ambient enters SiO_2 from the front surface and diffuse across the thickness of the SiO_2 film to reach the Si/ SiO_2 interface and forms additional SiO_2 bonds by reacting with the Si substrate.¹²⁾ There are some Si species going up from the Si/ SiO_2 interface to SiO_2 as was confirmed in ref. 8. However, ^{30}Si diffusers (the $^{\text{nat}}\text{SiO}_2/^{28}\text{SiO}_2$ interface) in our experiment situate so far away (650 nm) from the Si/ SiO_2 interface that practically no Si species emitted from the Si/ SiO_2 interface reaches the region where ^{30}Si diffusion is taking place. Consequently, we need to focus on the effect of oxygen species going through in the direction from the top surface to the Si/ SiO_2 interface on the diffusion of ^{30}Si . Theory predicts that the majority of oxygen in SiO_2 diffuses in the form of O_2 molecules and the minority in the form of atomic oxygen.^{13–16)} None of these theories of oxygen diffusion in SiO_2 predicts strong interaction of diffusing oxygen with silicon atoms forming the SiO_2 network. The average flux of oxygen in SiO_2 during our diffusion

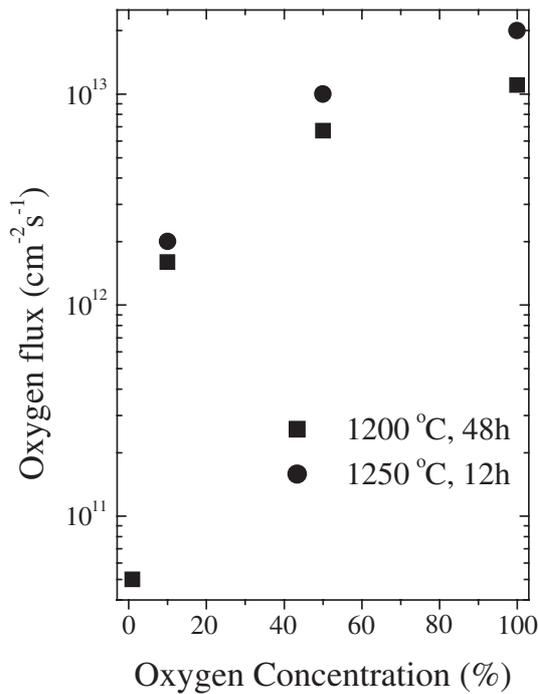


Fig. 4. Average oxygen flux in SiO₂ as a function of the oxygen concentration in the annealing ambient.

annealings can be estimated simply from the total annealing time and the change of the oxide thickness before and after the annealing. The thickness change was measured accurately using an optical interferometer. As shown in Fig. 4, the average flux of oxygen going through the SiO₂ changes by an order of magnitude between 1 and 100% oxygen fractions in Ar. However, the oxygen flux as large as 10¹³ cm⁻²·s⁻¹ for 100% oxygen annealing was not significant enough to change D_{SD} by the amount larger than our experimental error of 33%. This observation is in accordance with the above-mentioned theories which predict little interaction between the diffusing oxygen and silicon forming the network. It should be also pointed out that our recent experiment⁸⁾ has indicated that SiO molecules diffuse much faster than substitutional Si atoms in SiO₂, because SiO molecules diffuse predominantly through interstitial sites with frequent atomic exchange interactions with the substitutional Si atoms as implied by the recent first-principle calculation of boron diffusion in SiO₂.¹⁷⁾ Our numerical

simulation of Si self-diffusion via SiO kick-out mechanism estimates that it requires formation of at least 10¹⁹ cm⁻³ SiO molecules in order to observe the enhancement of the Si self-diffusion larger than our experimental error of 33%. Because of the small interaction between diffusing oxygen and silicon forming the network, such a number of SiO was not formed to enhance the Si self-diffusion in the present experiment.

In summary, the effect of oxygen annealing ambient on Si self-diffusion in SiO₂ has been investigated. The Si self-diffusivity in SiO₂ does not depend on the partial pressure of oxygen within our experimental error of ±33%. Such observation is consistent with the picture that diffusing oxygen in SiO₂ interact little with substitutional Si atoms forming the oxide network.

We thank A. Takano for the SIMS measurements. The work at Keio was supported in part by a Grant-in-Aid for Scientific Research in Priority Areas "Semiconductor Nanospintronics (# 14076215)".

- 1) D. Tsoukalas, C. Tsamis and P. Normand: *J. Appl. Phys.* **89** (2001) 7809.
- 2) D. Tsoukalas, C. Tsamis and J. Stoemenos: *Appl. Phys. Lett.* **63** (1993) 3167.
- 3) G. Brebec, R. Seguin, C. Sella, J. Bevenot and J. C. Martin: *Acta Metall.* **28** (1980) 327.
- 4) G. K. Celler and L. E. Trimble: *Appl. Phys. Lett.* **54** (1989) 1427.
- 5) O. Jaoul, F. Bejina, F. Elie and F. Abel: *Phys. Rev. Lett.* **74** (1995) 2038.
- 6) T. Takahashi, S. Fukatsu, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi and K. Shiraishi: *J. Appl. Phys.* **93** (2003) 3674.
- 7) D. Mathiot, J. P. Schunck, M. Perego, M. Fanciulli, P. Normand, C. Tsamis and D. Tsoukalas: *J. Appl. Phys.* **94** (2003) 2136.
- 8) S. Fukatsu, T. Takahashi, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi and K. Shiraishi: *Appl. Phys. Lett.* **83** (2003) 3897.
- 9) S. Hofmann: *Surf. & Interface Anal.* **21** (1994) 673.
- 10) M. Uematsu, H. Kageshima and K. Shiraishi: *Jpn. J. Appl. Phys.* **39** (2000) L699.
- 11) E. L. Williams: *J. Am. Ceram. Soc.* **48** (1965) 190.
- 12) R. Jaccodine: *Mater. Res. Soc. Symp. Proc.* **716** (2002) 59.
- 13) W. Orellana, A. J. R. da Silva and A. Fazzio: *Phys. Rev. Lett.* **87** (2001) 155901.
- 14) Y.-G. Jin and K. J. Chang: *Phys. Rev. Lett.* **86** (2001) 1793.
- 15) D. R. Hamann: *Phys. Rev. Lett.* **81** (1998) 3447.
- 16) A. M. Stoneham, M. A. Szymanski and A. L. Shluger: *Phys. Rev. B* **63** (2001) 241304.
- 17) M. Otani, K. Shiraishi and A. Oshiyama: to be published in *Phys. Rev. B*.