# Effect of the Si/$SiO_2$ interface on self-diffusion of Si in semiconductor-grade $SiO_2$

Shigeto Fukatsu, Tomonori Takahashi, and Kohei M. Itoh[a)]
*Department of Applied Physics and Physico-Informatics and CREST-JST, Keio University, Yokohama 223-8522, Japan*

Masashi Uematsu, Akira Fujiwara, Hiroyuki Kageshima, and Yasuo Takahashi
*NTT Basic Research Laboratories, NTT Corporation, Atsugi 243-0198, Japan*

Kenji Shiraishi
*Institute of Physics, University of Tsukuba, Tsukuba 305-8571, Japan*

Ulrich Gösele
*Max Planck Institute of Microstructure Physics, D-06120 Halle, Germany*

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Self-diffusion of ion-implanted $^{30}Si$ in $SiO_2$ formed directly on Si substrates by thermal oxidation was studied as a function of the temperature and $SiO_2$ thickness (200, 300, and 650 nm). The diffusion coefficient increases by about an order of magnitude with decreasing $SiO_2$ thickness from 650 to 200 nm when silicon–nitride capping layers are placed on top of the $SiO_2$, i.e., the distance between the $^{30}Si$ diffusers and Si/$SiO_2$ interface has a strong influence. Because the stress on $SiO_2$ by nitride estimated for such a change in diffusivity is unrealistically large, Si species, most likely SiO, generated at the Si/$SiO_2$ interface and diffusing into $SiO_2$ must be affecting the self-diffusion of Si in $SiO_2$. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625775]

Despite the increasing importance of understanding the formation mechanism of thermal $SiO_2$ insulators for the coming age of nanoscale Si electronics, a series of self-diffusion studies of Si in $SiO_2$ has led to diffusivity values that differ by several orders of magnitude.[1–7] Without knowing the precise values of the Si self-diffusivity in $SiO_2$, it is not possible to formulate an accurate model of the thermal oxidation mechanism, which will be needed for the development of the next generation Si processes. The most recent studies based on direct probing of diffusion of stable Si isotopes have improved the situation significantly by placing the self-diffusivity ($D_{Si}^{SD}$) between $D_{Si}^{SD}=0.8\exp(-5.2$ eV/kT)[6] and $33.2\exp(-5.34$ eV/kT) $cm^2\,s^{-1}$.[7] However, there still exists more than one order of magnitude difference between the two sets of values, and the origin of this difference has been debated. The present work investigates the influence of the Si/$SiO_2$ interface on Si self-diffusion in $SiO_2$ and shows clearly that what appeared to be a discrepancy between Refs. 6 and 7 can be explained very well by the dependence of the diffusion constant on the distance between the diffusing Si species and Si/$SiO_2$ interface.

The samples were prepared as follows. Isotopically enriched $^{28}Si$ single crystal epilayers of 0.8 $\mu$m thickness, grown by chemical vapor deposition on 4 in. highly resistive Si wafers, were obtained from Isonics Corp., Colorado. The isotope composition of the $^{28}Si$ epilayer measured by secondary ion mass spectroscopy (SIMS) is $^{28}Si$ (99.924%), $^{29}Si$ (0.073%), and $^{30}Si$ (0.003%). The $^{28}Si$ surface of the epilayer was thermally oxidized in dry $O_2$ at 1100 °C to form $^{28}SiO_2$ of the thicknesses 200, 300, and 650 nm. The samples were implanted with $^{30}Si$ at 50 keV to a dose of $1\times10^{14}$ $cm^{-2}$ or $2\times10^{15}$ $cm^{-2}$. Half of the surface area of each implanted wafer was capped with a ~30-nm-thick silicon nitride layer by rf magnetron sputtering for protection of the $SiO_2$ layer from oxygen during annealing. The wafers having areas with and without silicon nitride were cut into $5\times5$ $mm^2$ pieces for the heat treatment. The final structures, i.e., the silicon–nitride-capped and uncapped samples, are shown in Fig. 1. Each piece was annealed in a resistively heated annealing furnace at temperatures between 1150 and 1250 °C. Semiconductor-processing-grade quartz tubes and gas sources (argon and oxygen) were employed to keep the samples as clean as possible. Annealing was conducted in flowing argon with 1% oxygen. The 1% oxygen is just enough to prevent $SiO_2$ decomposition. The depth profile of $^{30}Si$ was measured by SIMS using $O_2^+$ as a primary ion beam with acceleration energy of 5 keV. The depth profiles of $^{30}Si$ in the annealed samples were analyzed assuming a constant diffusion coefficient using the partial differential equation solver ZOMBIE.[8]

Figure 2 shows the $^{30}Si$ depth profiles of samples before and after diffusion anneals of 24 h at 1250 °C. The diffusion

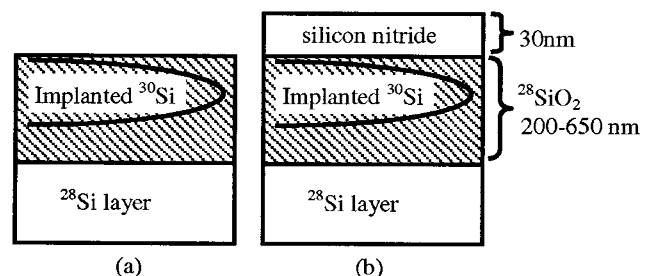


FIG. 1. The sample structures employed in this study: (a) uncapped and (b) silicon–nitride capped layers.

[a)]Electronic mail: kitoh@appi.keio.ac.jp

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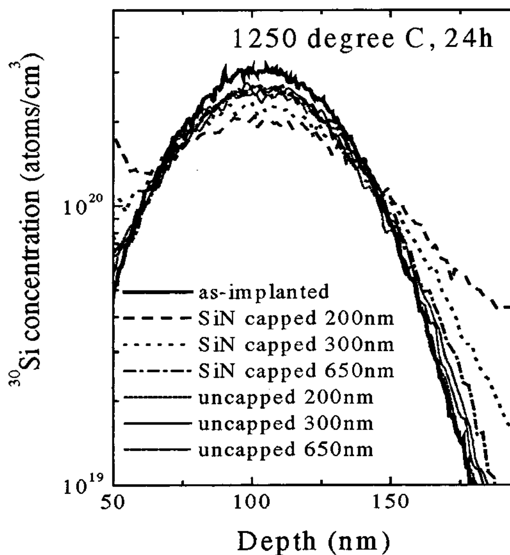


FIG. 2. Diffusion profiles of $^{30}$Si in the isotopically enriched structure after 24 h anneals at 1250 °C. The as-implanted profile is also shown as a reference.

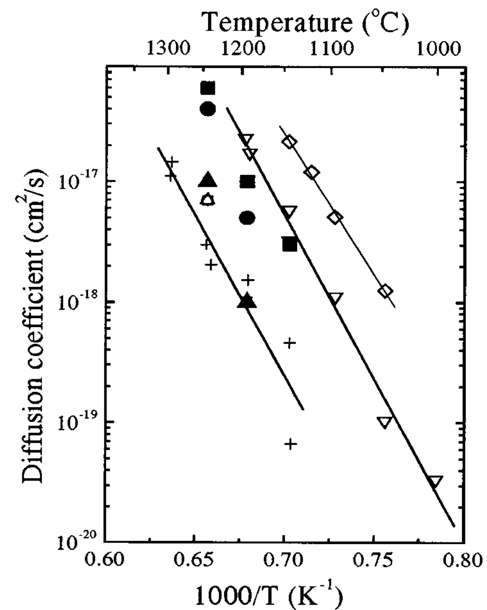


FIG. 3. Comparison of the temperature dependencies of the Si self-diffusion coefficients $D_{Si}^{SD}$ found in this study with those reported previously in the literature. Filled squares (■), filled circles (●), and filled triangles (▲) represent the present results for the silicon–nitride-capped samples with 200-, 300-, and 650-nm-thick $^{28}SiO_2$ layers, respectively. Open squares (□), open circles (○), and open triangles (△) represent the present results for the uncapped samples with 200-, 300-, and 650-nm-thick $^{28}SiO_2$ layers, respectively. The previously reported values are for Si self-diffusion in 170-nm-thick $^{28}SiO_2$ using implanted $^{30}$Si as markers (◇) (see Ref. 5), isotope heterostructures with 650-nm-thick $^{28}SiO_2$ (+) (see Ref. 6), and isotope heterostructures with 200-nm-thick $^{28}SiO_2$ (▽) (see Ref. 7).

profiles of the uncapped samples show very little dependence on the $^{28}SiO_2$ thickness, while the silicon nitride capped samples demonstrate a strong dependence on the thickness of the $^{28}SiO_2$ layer. In the silicon nitride capped samples, the 200-nm-thick $^{28}SiO_2$ layer leads to the broadest diffusion profile. Consequently the thinner the $^{28}SiO_2$ layer is, the broader the diffusion profile becomes. In other words, the shorter the distance from the $Si/SiO_2$ interface, the higher the diffusivity in the silicon nitride capped sample. This tendency was observed consistently for other temperatures probed in this study.

The temperature dependence of the Si self-diffusion constants for each sample as determined by ZOMBIE is shown in Fig. 3. It is shown that the diffusivity values of the uncapped samples are lower than that of silicon–nitride-capped samples with no thickness dependence and that they agree with the $D_{Si}^{SD}=0.8\exp(-5.2\text{ eV/kT})$ of Takahashi *et al.*, which was determined using $^{nat}SiO_2/^{28}SiO_2$ structures having $^{28}SiO_2$ thickness (i.e., the distance between diffusing $^{30}$Si and $Si/^{28}SiO_2$) equal to 650 nm.[6] ($^{nat}$Si refers to Si with the natural isotopic abundance.) This observation eliminates concerns related to diffusion under a nonstoichiometric condition (excess Si in $SiO_2$) and to implanted damage associated with $^{30}$Si implantation into the $^{28}SiO_2$ employed in this study. In order to further assure our equilibrium condition, we studied samples with two implanted doses, $1\times10^{14}\text{ cm}^{-2}$ and $2\times10^{15}\text{ cm}^{-2}$, and confirmed that $D_{Si}^{SD}$ remains unchanged.

On the other hand, $D_{Si}^{SD}$ in the capped samples changes with the distance of Si diffusers from the $Si/SiO_2$ interface. As expected, $D_{Si}^{SD}$ in the capped samples with the 650 nm $SiO_2$ agrees with that of Takahashi *et al.*'s samples with no capping layer because theirs is the true equilibrium value of $D_{Si}^{SD}$ in semiconductor-grade $SiO_2$ as we claimed earlier.[6] Mathiot *et al.*'s argument[7] that the $D_{Si}^{SD}=0.8\exp(-5.2\text{ eV/kT})$ of Takahashi *et al.*[6] represents diffusion in an oxygen-rich condition, not the true equilibrium condition, fails since $D_{Si}^{SD}$ obtained with 650 nm thickness agrees regardless of the presence of silicon-nitride capping and the partial pressure of $O_2$ in Ar atmospheres.[9] In addition, our data for the capped 200-nm-thick sample, the same thickness investigated by Mathiot *et al.*,[7] are very close to their values $33.2\exp(-5.34\text{ eV/kT})\text{ cm}^2\text{ s}^{-1}$. Mathiot *et al.* did not take into account the $SiO_2$ thickness dependence of $D_{Si}^{SD}$, and this led them to their earlier argument. Figure 3 also shows the data of Tsoukalas *et al.*,[5] which was obtained for a capped 170-nm-thick $SiO_2$ layer. Their $D_{Si}^{SD}$ is larger than our $D_{Si}^{SD}$ obtained for the capped 200 nm sample because the distance to the $Si/SiO_2$ is smaller by 30 nm compared to the 200-nm-thick one.

Let us now discuss why there is a thickness dependence of $D_{Si}^{SD}$ for the capped samples but no such dependence for uncapped layers. We obtained the same $D_{Si}^{SD}$ for implanted $^{30}$Si and stoichiometric $^{nat}SiO_2/^{28}SiO_2$ heterostructures, which, as mentioned earlier, eliminated the possibility of nonstoichiometry (excess Si due to implantation). We have also eliminated the possibility of implantation damage for the same reason. On the other hand, it is possible that the stress on $SiO_2$ layers changes depending on the presence of the silicon–nitride capping layers. The diffusivity $D_{Si}'^{SD}$ under stress can be described by $D_{Si}'^{SD}=D_{Si}^{SD}\exp(-PV_d/kT)$, where $P$ is the stress and $V_d$ is the activation volume for diffusion in $SiO_2$ which has been estimated to be a few tens of Å$^3$ for oxygen diffusion.[10–12] At 1250 °C, we have observed a factor of 6 enhancement of $D_{Si}'^{SD}$ for 200 nm with respect to $D_{Si}^{SD}$ for 650 nm, and $P\sim10^{10}\text{ dyn/cm}^2$ of stress is required in order to obtain such enhancement. This required stress of $P\sim10^{10}\text{ dyn/cm}^2$ is unrealistically large for just having a 30 nm silicon–nitride layer on top; the typical stress

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expected for such a case is much less than $10^{10}$ dyn/cm$^2$. For example, the stress of $\sim 10^{10}$ dyn/cm$^2$ has been reported in the oxidation of Si nanopillers, where a nanosilicon rod is surrounded completely by $SiO_2$.[13] Such a large stress cannot result from capping with a silicon–nitride film of only ~30 nm thickness. We therefore conclude that the stress cannot account for the thickness dependence of $D_{Si}^{SD}$ observed for the capped samples.

The only remaining possibility is the effect of Si species emitted at the Si/$SiO_2$ interface that diffuse into the $SiO_2$ layer to enhance the $^{30}$Si self-diffusivity in $SiO_2$. In the case of the uncapped sample, oxygen species incorporated into the $SiO_2$ from the oxygen containing atmosphere diffuse across the thickness of the $SiO_2$. When oxygen atoms arrive at the Si/$SiO_2$ interface region, they recombine with the Si species emitted from the Si/$SiO_2$ to form additional $SiO_2$. Therefore, Si species emitted at the Si/$SiO_2$ interface never have an opportunity to reach the region where $^{30}$Si diffusion is taking place. Therefore, there is no enhancement of $D_{Si}^{SD}$ when $SiO_2$ is not capped with the nitride. On the other hand, for the case of the nitride-capped sample, the cappings act as perfect barriers against oxygen incorporation from the annealing atmosphere, i.e., there is no oxygen species coming into the $SiO_2$. Therefore, Si species emitted from the Si/$SiO_2$ have no extra oxygen species to recombine with to form additional $SiO_2$ and diffuse freely into the region where $^{30}$Si diffusion is taking place. Our belief is that these extra Si species coming from the Si/$SiO_2$ interface are the source of the enhanced $D_{Si}^{SD}$ for thin $SiO_2$ samples. Indeed, there have been a number of suggestions based on experimental speculations and theoretical predictions for emission of Si species from the Si/$SiO_2$ interface to $SiO_2$.[2,14–18] In our view, SiO generated at the Si/$SiO_2$ interface via the reaction $Si+SiO_2 \rightarrow 2SiO$[2,14] is the most likely candidate as the dominant Si species arriving from the interface. In this context, the present work should be regarded as the experimental evidence of Si species emission from the Si/$SiO_2$ interface to $SiO_2$ to enhance Si self-diffusion. We are in the process of developing a quantitative self-diffusion model that accounts for the enhancement of $D_{Si}^{SD}$ by emitted and diffusing Si species in order to justify our claim.

In summary, we have investigated the self-diffusivity of Si in semiconductor grade $SiO_2$ with and without silicon nitride capping layers. In the presence of the capping layers, the diffusivity shows a strong dependence on the $SiO_2$ thickness. The Si species emitted at the Si/$SiO_2$ interface and diffusing into $SiO_2$ have a strong influence on the self-diffusivity of Si in $SiO_2$.

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