Self-diffusion of Si in thermally grown SiO_2 under equilibrium conditions

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Self-diffusion coefficients of Si in thermally grown SiO_2 on a semiconductor-grade silicon wafer have been determined at temperatures between 1150 and 1300 °C under equilibrium conditions using isotope heterostructures ($^{nat}SiO_2/^{28}SiO_2$). Si self-diffusion was induced by appropriate heat treatments, and the diffusion depth profiles of ^{30}Si isotope from $^{nat}SiO_2$ to $^{28}SiO_2$ layers were determined by secondary ion mass spectrometry (SIMS). The diffusion coefficients found in the present study for 1150–1300 °C are more than two orders of magnitude smaller than the values measured with semiconductor-grade SiO_2 in the presence of excess silicon, i.e., in nonequilibrium conditions, and agree very well with previously reported values of Si self-diffusion in fused silica under equilibrium conditions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1554487]

Thermal oxidation of silicon is the key step in the fabrication of gate insulators for metal-oxide-semiconductor field effect transistors (MOSFETs). Atomic-level understanding of the oxidation mechanism is becoming increasingly important with the reduction of the oxide thickness down to 2 nm. While the rate of oxygen arriving at the Si/SiO_2 interface primarily determines the speed of thermal oxidation when the SiO_2 thickness is much larger than 100 nm,[1] more recent oxidation models, mostly for much thinner cases, demonstrate the importance of silicon self-diffusion processes for the thermal formation of SiO_2.[2–7] Therefore, self-diffusion of Si in thermally grown SiO_2 is a fundamental physical phenomenon that must be understood in order to achieve a complete understanding of thermal oxidation processes.

There have been only two experimental investigations of Si self-diffusion performed with SiO_2 formed thermally on semiconductor silicon.[8,9] In one of them, ^{30}Si isotopes were ion implanted into isotopically enriched $^{28}SiO_2$ layers, and their diffusion profiles were measured by secondary ion mass spectrometry (SIMS) after appropriate annealing procedures.[8] Because ion implantation increases the silicon concentration in SiO_2 beyond its equilibrium value, the diffusion coefficient reported in Ref. 8 corresponds to nonequilibrium conditions. In the other experiment, self-diffusion was studied indirectly by monitoring the formation of defects that are believed to be triggered by self-diffusion of Si in SiO_2.[9] This experiment has also been performed under nonequilibrium conditions, since the diffused Si species were produced in excess by oxidation. The equilibrium self-diffusion properties of Si in SiO_2, on the other hand, have not been measured with thermal oxides on semiconductor silicon, but with other types of SiO_2 such as fused silica[10] and quartz.[11] The self-diffusion constants found in these studies, and their variation with temperature, are summarized in Fig. 1. What is clearly missing is an experiment performed under equilibrium conditions using thermal oxides grown directly on semiconductor-grade silicon wafers. The Si self-diffusion coefficients previously measured with semiconductor-grade thermally grown SiO_2[8,9] are 2 to 3 orders of magnitude higher than the values measured with fused silica[10] and quartz.[11] Whether this large difference in the diffusion coefficients is due to the nonequilibrium versus equilibrium conditions or to subtle differences in the structural properties of thermally grown SiO_2, fused silica, and quartz is not obvious.

To answer these questions, the present work reports on Si self-diffusion experiments in thermally grown SiO_2 under equilibrium conditions. The investigation has been performed using the isotope heterostructures ($^{nat}SiO_2/^{28}SiO_2/^{28}Si$) shown in Fig. 2. $^{nat}SiO_2$ and $^{28}SiO_2$ indicate SiO_2 composed of natural Si and isotopically enriched ^{28}Si, respectively. The silicon isotopic composition in $^{nat}SiO_2$ is ^{28}Si (92.2%), ^{29}Si (4.7%), and ^{30}Si (3.1%), while that in $^{28}SiO_2$ is ^{28}Si (99.9%), ^{29}Si (0.07%), and ^{30}Si (0.003%). Subsequent to heat treatments at the desired diffusion temperatures, SIMS measurements of the diffusion depth profile of the ^{30}Si isotope concentration across $^{nat}SiO_2$ and $^{28}SiO_2$ layers have allowed the accurate determination of Si self-diffusion coefficients under equilibrium conditions. Isotope heterostructures are clearly the ideal systems to study self-diffusion under equilibrium conditions because the concentrations of the constituents (Si and O) and the native defects remain at equilibrium values throughout the course of the experiments.

The samples employed in this study were prepared as follows. Isotopically enriched ^{28}Si single crystal epilayers of 0.8 μm thickness grown by chemical vapor deposition (CVD) on 4-in. highly resistive Si wafers were provided by

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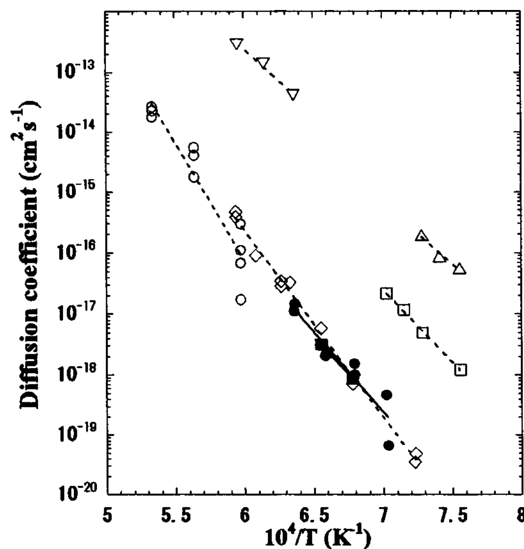

FIG. 1. Comparison with the temperature dependencies of Si self-diffusion coefficients D reported previously: (●) and (■) represent the results of the present study conducted in equilibrium conditions under 1% and 20% oxygen in argon, respectively. The results of Si self-diffusion in thermally grown SiO_2 under nonequilibrium conditions using ^{30}Si as markers (□) (Ref. 8), defect evolutions as markers (△) (Ref. 9), and in CVD SiO_2 using thermally migrated impurities as markers (▽) (Ref. 14). The results of Si self-diffusion under equilibrium conditions in fused silica (◇) (Ref. 10) and quartz (○) (Ref. 11) are also shown.

Isonics Corp., Colorado, USA. The isotope composition of the ^{28}Si epilayer measured by SIMS is ^{28}Si (99.9%), ^{29}Si (0.07%), and ^{30}Si (0.003%). The ^{28}Si surface of the epilayer has been thermally oxidized in dry O_2 at 1100 °C for 20 h to form 650 nm thick $^{28}SiO_2$. Subsequently, about 50 nm thick $^{nat}SiO_2$ has been deposited on top of the $^{28}SiO_2$ film by low-pressure chemical vapor deposition (LPCVD) using tetraethoxysilane (TEOS) at 700 °C. The completed structure is shown in Fig. 2.

The heterostructures grown on the 4 in. wafer were cut into 6×6 mm^2 samples. Each piece was annealed in a resistance furnace at temperatures between 1150 and 1300 °C. Semiconductors processing grade quartz tubes and gas sources (argon and oxygen) were employed to keep the sample as clean as possible. A well-calibrated thermocouple covered by a clean quartz tube was placed right next to the sample. The temperature was monitored and recorded automatically by a computer throughout the course of annealing. The fluctuation of temperature was found to be less than 0.5%. Annealing was conducted under flowing argon with 1% oxygen. The oxygen was added to the argon in order to

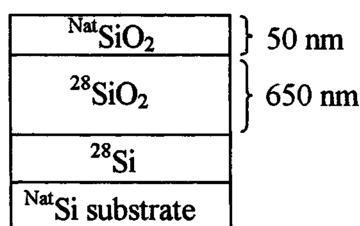

FIG. 2. Schematic of $^{nat}SiO_2/^{28}SiO_2$ isotope heterostructures employed in this study.

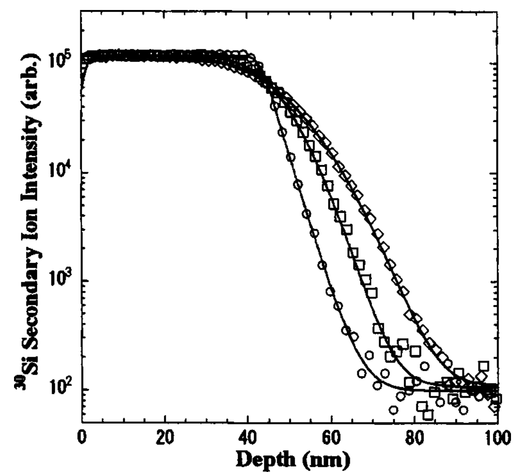

FIG. 3. SIMS depth profiles of ^{30}Si before (○) and after annealing at 1200 °C for 72 h (□) and at 1300 °C for 16 h (◇). Solid curves of annealed samples are the best fits of Eq. (1) with correction of SIMS broadening effect by the deconvolution technique described in Ref. 13. Solid curve of the as-grown sample is convoluted profile assuming that the actual profile at the interface is a complete step function.

prevent SiO_2 from decomposing, which tends to occur at higher temperatures and with lower oxygen partial pressures. This oxygen not only prevents decomposition but also oxidizes ^{28}Si at the $^{28}SiO_2/^{28}Si$ interface and forms thicker $^{28}SiO_2$. In order to keep the oxidation rate as small as possible, the least amount of oxygen needed to maintain the SiO_2 intact at 1300 °C was chosen, which turned out to be 1%.[12] The thickest $^{28}SiO_2$ of all heat procedures in this experiment was formed by annealing at 1150 °C for 540 h, during which the thickness of the $^{28}SiO_2$ increased from 650 to 780 nm. However, this oxidation takes place more than 650 nm away from the $^{nat}SiO_2/^{28}SiO_2$ interface where ^{30}Si self-diffusion takes place, i.e., the two regions are sufficiently well separated so they do not affect each other. It is also possible that the excess oxygen atoms introduced into the SiO_2 heterostructure from the surface might affect the self-diffusion of Si. Some of our samples were annealed in an atmosphere of 20% oxygen in argon in order to check for such possibilities. The duration of annealing (diffusion time) was chosen such that it leads to diffusion lengths of $2(Dt)^{1/2}=10-20$ nm. The samples were annealed for at least two different durations at each given temperature in order to check for reproducibility. The depth profile of ^{30}Si was measured by SIMS using O_2^+ as the primary ion beam with acceleration energy 5 keV. An electron beam was applied during the measurement in order to prevent samples from charging up. A typical size for a sputtered crater was 300 ×420 μm^2 and secondary ions were detected from the central 90×130 μm^2 region of the crater. Crater depths were measured with a surface profilometer (Talystep of Taylor-Hobson) with an accuracy within 10%. Figure 3 shows typical depth profiles of ^{30}Si before and after thermal treatment. The $^{nat}SiO_2/^{28}SiO_2$ interface of the as-grown sample, that should be a sharp step function, is broadened. This broadening is inherent in SIMS measurements and is caused by ion mixing and surface roughening due to ion sputtering. The solid curve in Fig. 3 for the as-grown sample represents the

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convoluted profile of a presumably sharp interface (step function), from which characteristic parameters needed for the correction of the instrumental broadening are determined.[13] The depth profiles of ^{30}Si in the annealed samples were modeled by:

$$C(x)=C_{28}+\frac{C_{nat}-C_{28}}{2}\left[\mathrm{erf}\left(\frac{x+h}{2\sqrt{Dt}}\right)-\mathrm{erf}\left(\frac{x-h}{2\sqrt{Dt}}\right)\right], \tag{1}$$

where $x=0$ is the surface of the samples. C_{nat} and C_{28} are the initial concentrations of ^{30}Si in $^{nat}SiO_2$ and $^{28}SiO_2$, respectively. The constant h is the thickness of the $^{nat}SiO_2$ layer, D is the Si self-diffusion coefficient, and t is the annealing time. The thickness of the $^{28}SiO_2$ layer is regarded as infinite because no ^{30}Si reaches the $^{28}SiO_2/^{28}Si$ interface in the present annealing process. The same set of characteristic parameters for correction of the SIMS broadening obtained with the as-grown sample is used throughout this study so that the self-diffusion coefficient D in Eq. (1) is the only fitting parameter in our diffusion analysis. The diffusion coefficients determined in this manner are typically 10%–20% smaller than those obtained without the instrumental correction.

The self-diffusion coefficients D for the temperature range 1150–1300 °C obtained in the present study are shown in Fig. 1. (filled circle and filled square for 1% and 20% oxygen mixtures, respectively.) D for 1% oxygen can be described by an Arrhenius equation:

$$D=0.8\exp\left(\frac{-5.2\ \mathrm{eV}}{kT}\right)\mathrm{cm}^2\ \mathrm{s}^{-1}. \tag{2}$$

The error of the activation energy 5.2 eV was ±0.8 eV. The results for 20% oxygen also fall on essentially the same curve, i.e., the values of the self-diffusion constants do not depend on the oxygen partial pressure of the ambient atmosphere in the investigated temperature range. One may point out that the diffusion constants measured across the CVD-grown $^{nat}SiO_2$ and the thermally formed $^{28}SiO_2$ do not represent the intrinsic values of the Si self-diffusion constants in thermally formed oxides. Such concern is legitimate in principle, but the excellent fit of Eq. (1) to the experimentally measured profiles shown in Fig. 3 and to the results of all the other combinations of annealing durations and temperatures indicates that the diffusivity remains unchanged across the CVD and the thermally grown oxides. Therefore, our data represent very well the intrinsic values of Si self-diffusion constants in thermally formed SiO_2 grown directly on semiconductor-grade Si wafers.

The self-diffusion coefficients determined in this study agree well with those determined with fused silica under equilibrium conditions.[10] Thermally formed SiO_2 on Si and fused silica are both amorphous silicon dioxide and share many properties in common. Obtaining the same self-diffusion constants is therefore understandable, although this was not obvious prior to this study. The diffusion coefficients found in the present work are two orders of magnitude lower than the diffusion coefficients determined by Tsoukalas *et al.* under nonequilibrium conditions in the presence of excess Si concentrations.[8] Therefore, it is of great interest for future studies to investigate quantitatively the influence of the excess silicon on the Si self-diffusion coefficients. As shown in Fig. 1, there is another group of data that lies four orders of magnitude higher than the values determined by our work. Tsoukalas *et al.* have estimated the Si self-diffusion coefficients in thermally grown SiO_2 via the observation of defect formation.[9] Celler *et al.*'s estimation is based on the thermomigration of impurities in SiO_2 made by CVD.[14] Both of these studies, in our view, are too indirect to determine the self-diffusion coefficients of Si in SiO_2 though they propose a very interesting model in which the diffusion species in SiO_2 are SiO instead of Si.

In conclusion, we have reported on the direct measurement of Si self-diffusion in thermally grown SiO_2 under equilibrium conditions using isotope heterostructures ($^{nat}SiO_2/^{28}SiO_2$). The diffusion coefficients determined agree very well with those of fused silica and are lower than values measured under nonequilibrium conditions.

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