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Correlated diffusion of silicon and boron in thermally grown SiO_2

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Si self-diffusion and B diffusion in SiO_2 were simultaneously investigated in thermally grown $^{28}SiO_2$ co-implanted with ^{30}Si and B. The B diffusivity increases with decreasing distance between the implanted B and Si/SiO_2 interface, in the same way as Si self-diffusivity. This result together with a numerical simulation shows that SiO molecules, which are generated at the Si/SiO_2 interface and diffusing into SiO_2, enhance not only Si self-diffusion, but also B diffusion. In addition, we found that the diffusivities of both Si and B increase with higher B concentration in SiO_2. The experimental results can be quantitatively explained by a numerical simulation assuming that the diffusivity of SiO, which enhances the diffusivities of Si and B, increases with higher B concentration. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1771811]

As the thickness of the SiO_2 layers for metal-oxide-semiconductor (MOS) devices decreases, atomic and molecular diffusion in SiO_2 becomes a fundamental issue. Concerning impurity diffusion, boron (B) penetration through the thin SiO_2 layer is still a serious problem in high-κ gate dielectrics because of the formation of an interfacial SiO_2 layer.[1] For Si self-diffusion, we have recently found, based on experimental and simulation results, that SiO molecules generated at the Si/SiO_2 interface and diffusing into SiO_2 enhance Si self-diffusion in SiO_2.[2,3] This suggests that the effect of the Si/SiO_2 interface must be taken into account in thermal processing involving ultrathin SiO_2 layers. In addition, diffusion of SiO is closely related to the viscosity of SiO_2, which is an important property of materials.[4] The present work investigates the correlation between Si self-diffusion and B diffusion in SiO_2, and their interaction with SiO arriving from the Si/SiO_2 interface.

An isotopically enriched ^{28}Si single-crystal epilayer was thermally oxidized in dry O_2 at 1100 °C to form $^{28}SiO_2$ of thicknesses of 200, 300, and 650 nm. The samples were implanted with ^{30}Si at 50 keV to a dose of 2×10^{15} cm^{-2} and capped with a 30-nm-thick silicon nitride layer by rf magnetron sputtering. These procedures lead to the sample structure in Fig. 1(b) of Ref. 2. Subsequently, the samples were implanted with ^{11}B at 25 keV to a dose of 5×10^{13} or 3×10^{15} cm^{-2}, which will be referred to as low-dose and high-dose samples, respectively. The implantation energy was chosen so that the peak position of implanted B would be close to that of ^{30}Si. The as-implanted profiles of ^{30}Si and B are shown in Fig. 1. Samples were pre-annealed at 1000 °C for 30 min to eliminate implantation damage and diffusion-annealed at temperatures between 1100 and 1250 °C in a resistively heated annealing furnace. The depth profiles of ^{30}Si and B were measured by secondary ion mass spectrometry (SIMS) using O_2^+ as a primary ion beam with acceleration energy of 5 keV.

Figure 1 shows the depth profiles of ^{30}Si and B in the high-dose 200-nm-thick sample after diffusion anneal of 6 h at 1250 °C. The as-implanted profiles before pre-annealing are shown as initial profiles in Fig. 1 because the profiles after the pre-annealing showed no observable diffusion within the accuracy of our SIMS measurements. The ^{30}Si depth profile of the annealed sample without B implantation is also shown. The profile of ^{30}Si in the high-dose samples shows larger diffusion than that without B. On the other hand, the ^{30}Si profile of the low-dose samples (not shown in

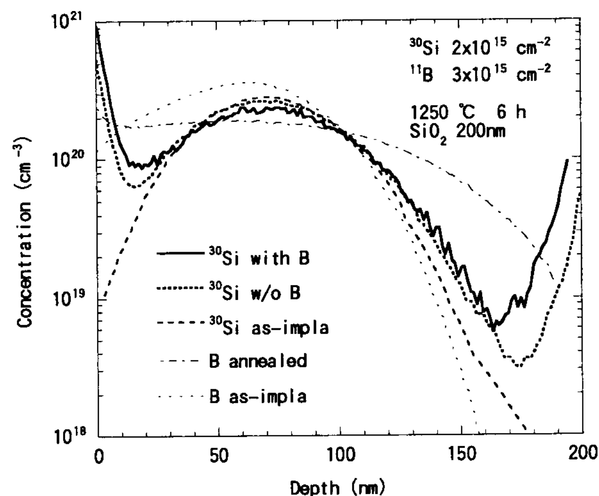

FIG. 1. Diffusion profiles of ^{30}Si and B in the 200-nm-thick sample implanted with B to a dose of 3×10^{15} cm^{-2} after diffusion anneal of 6 h at 1250 °C. The as-implanted profiles are shown as initial profiles. The ^{30}Si diffusion profile without B implantation is also shown. In the data, the increase of ^{30}Si concentration close to the surface (0~20 nm) is an artifact from silicon-nitride caps, and that deep in the bulk (>160 nm) is ^{30}Si that diffused from Si substrates with the natural isotopic abundance (800 nm below the ^{28}Si epilayer) during the thermal oxidation to prepare the sample.

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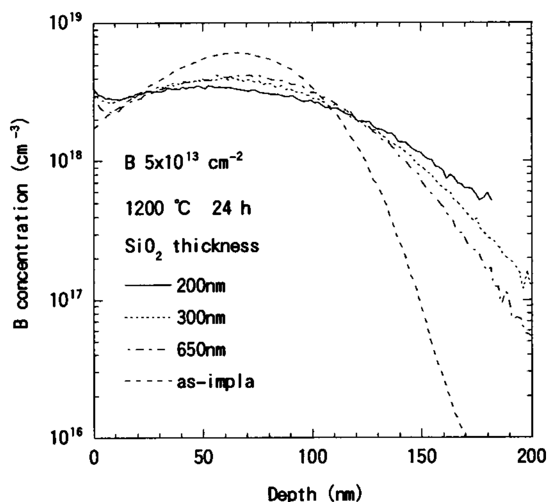

FIG. 2. Diffusion profiles of B in SiO_2 with various thicknesses. Samples were implanted with B to a dose of 5×10^{13} cm^{-2} and annealed at 1200 °C for 24 h.

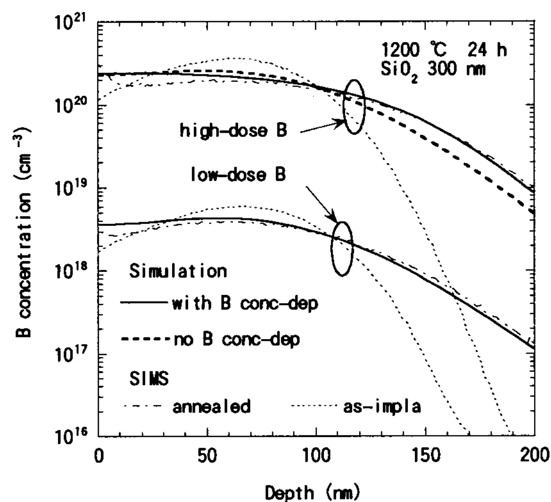

FIG. 3. Experimental and simulated B profiles in the 300-nm-thick sample with high- and low-B doses after annealing of 24 h at 1200 °C. The calculation result without B concentration dependence for the high-dose case is also shown (thick dotted line).

Fig. 1) showed no significant difference from that without B. In addition, for the high-dose sample, a significant decrease in the ^{30}Si concentration at its peak region was observed, where B concentration is high. In contrast, the tail region of ^{30}Si showed less significant diffusion, where B concentration is low. The same tendency was consistently observed for $^{28}SiO_2$ samples with other thicknesses and for different annealing conditions; for example, after 24 h at 1200 °C.

Before we present a consistent numerical simulation of these experimental results to support our correlated diffusion model, we address the possible concern that the implantation damage and strain in SiO_2 may play a role in the diffusion of Si and B. We believe that the implantation damage is of no concern because the self-diffusivity of implanted Si in thick SiO_2 agrees with that obtained from damage-free chemical vapor deposition SiO_2,[5] and remains unchanged for the doses between 1×10^{14} and 2×10^{15} cm^{-2}, as described in Ref. 2. In addition, we performed pre-annealing prior to the diffusion anneals. The strain in thin samples is also of no concern because the Si self-diffusion, which increases with time due to increasing amounts of SiO arriving from the Si/SiO_2 interface,[3] would decrease with time if the diffusion were affected by the strain (or by damage), which should be gradually relieved (reduced) by the anneals.

Figure 2 shows the B profiles in low-dose samples after annealing at 1200 °C for 24 h. As we revealed for Si self-diffusion,[2,3] the B profile demonstrates a clear dependence on the thickness of the $^{28}SiO_2$ layer; the shorter the distance from the Si/SiO_2 interface, the higher the B diffusivity in SiO_2. This tendency was observed consistently for the high-dose samples and other temperatures employed in this study. This dependence of B diffusivity on the distance indicates that Si self-diffusion and B diffusion as well are enhanced by SiO molecules, which are generated at the Si/SiO_2 interface and diffusing into SiO_2. The experimental signature of the B diffusivity enhancement with decreasing SiO_2 thickness is also found in Refs. 6 and 7, where highly B doped poly-Si in MOS structures was used as the source of diffusing B.

The results in Fig. 2 indicate that B in SiO_2 diffuses via two independent mechanisms: one does not involve SiO (hereafter referred to as thermal B diffusion) and the other involves SiO. Evidence for the existence of two mechanisms is that very few SiO molecules arrive from the interface in the 650-nm-thick sample. B diffusion via SiO can be described as $B(s)+SiO(i)\Leftrightarrow Si(s)+B(i)$, assuming that it is similar to B diffusion in Si via the kick-out mechanism. Here, B atoms substituted in the Si sites of SiO_2 [denoted as (s)] diffuse via the kick-out reaction with diffusing SiO molecules in interstitial sites [denoted as (i)], and B(i) may correspond to BO according to the first-principles calculation of B diffusion in SiO_2.[8] By replacing ^{30}Si with B in Eq. (1) of Ref. 3, B diffusion in SiO_2 can be simulated in a manner similar to our recent simulation of Si self-diffusion in SiO_2. Likewise, $D^{SD}_{Si(th)}$ (thermal Si self-diffusivity) should be replaced with $D^{eff}_{B(th)}$ (the effective diffusivity of thermal B diffusion), and D^{SD}_{SiO} (Si self-diffusivity via SiO) with D^{eff}_{i} (the effective diffusivity of B diffusion via the kick-out mechanism with SiO), which corresponds to D^{eff}_{i} for B diffusion in Si.[9,10] The total effective B diffusivity is expressed by $D^{eff}_{B}=D^{eff}_{B(th)}+D^{eff}_{i}C_{SiO}/C^{0}_{SiO}$, where C^{0}_{SiO} denotes the maximum concentration of SiO interstitials in SiO_2.[3] The experimentally obtained B diffusivity in thick (>1 μm) SiO_2, $D^{eff}_{B(th)}=3.12\times10^{-3}\exp(-3.93\text{ eV}/kT)$ cm^2/s,[11] which corresponds to the effective thermal B diffusivity, is used in our simulation. Consequently, the only parameter needed to fit the experimental B profiles in Fig. 2 is D^{eff}_{i}, and we consistently obtained $D^{eff}_{i}=6.4\times10^{-2}\exp(-4.1\text{ eV}/kT)$ cm^2/s for all samples. For the simulation, diffusion equations derived for B diffusion were solved numerically by the partial differential equation solver ZOMBIE.[12]

Figure 3 compares the experimental and simulated B profiles in the 300-nm-thick sample with high and low-B doses after annealing at 1200 °C for 24 h. With the D^{eff}_{i} given earlier, the B diffusion profiles of low-dose samples were well reproduced by the simulation. However, the same simulation of the B diffusion for high-dose samples underestimated the results, as shown by the thick dotted line in Fig. 3. Strong enhancement of the boron diffusion in SiO_2 for the boron concentration above 10^{20} cm^{-3} has been reported previously,[13] and we should take into account such an effect in our simulation. In order to reproduce the experimentally

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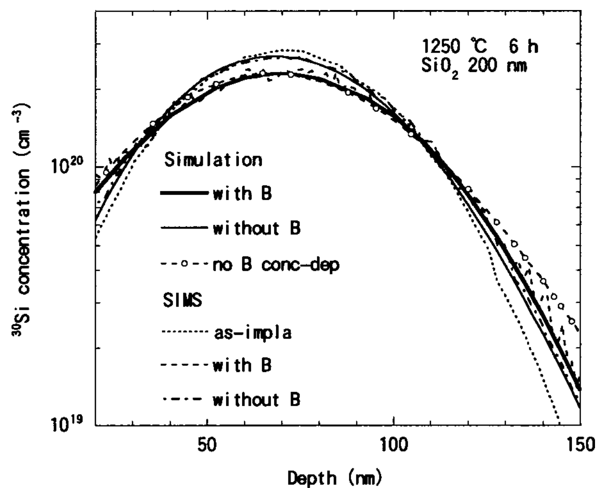

FIG. 4. Simulated ^{30}Si profiles with high-dose B implantation and without B after annealing at 1250 °C for 6 h. The SIMS profiles are those of ^{30}Si in Fig. 1. The calculation result without B concentration dependence is also shown for the high-dose case (thick dotted line with open circles).

obtained enhancement of the B diffusion in the high-dose sample, we introduced a B concentration dependence of $D_{B(th)}^{eff}$ for thermal B diffusion and of D_i^{eff} and D_{SiO}^{SD} for B diffusion via SiO by multiplying a factor of $\exp(C_B/C_B^{cri})$ to imitate the strong dependence on B concentration, where C_B^{cri} denotes the critical B concentration above which the high-concentration effect occurs. Consequently, the factor $\exp(C_B/C_B^{cri})$ is applied to D_B^{eff}, which represents the sum of the two contributions to B diffusion (thermal diffusion and diffusion via SiO). Using $C_B^{cri}=2\times10^{20}$ cm^{-3}, high-B-dose B profiles were fitted by the same set of diffusion parameters as that for low-dose profiles, as shown in Fig. 3.

Finally, we show the simulation result for the increase of Si self-diffusivity with higher B concentration. In order to model the ^{30}Si diffusion with the B concentration dependence taken into account by multiplying D_{SiO}^{SD} by a factor of $\exp(C_B/C_B^{cri})$, the diffusion mechanism of Si self-diffusion developed in our previous paper[3] and that of B diffusion discussed earlier are combined to explain the simultaneous enhancement of the ^{30}Si and B diffusion by ^{28}SiO(i) arriving from the Si/SiO_2 interface. Figure 4 shows the simulated ^{30}Si profiles after annealing at 1250 °C for 6 h, which reproduce the experimental profiles for both high-dose and unimplanted (also low-dose) samples by using the same single set of parameters obtained from the B profiles discussed above. Inclusion of the B concentration dependence $[\times\exp(C_B/C_B^{cri})]$ of $D_{Si(th)}^{SD}$ in addition to that of D_{SiO}^{SD} is essential to explain the ^{30}Si self-diffusion enhancement in the 650-nm-thick sample {Then, the factor $\exp(C_B/C_B^{cri})$ is applied to D_{Si}^{SD} [Eq. (7) in Ref. 3], which represents the sum of the two contributions to Si self-diffusion}. In this sample, very few SiO molecules arrive from the interface and the B concentration enhancement of Si self-diffusion therefore takes place almost totally via thermal Si diffusion, not via the kick-out by SiO. The ^{30}Si profile in the high-dose sample calculated without taking into account the B concentration dependence is also shown in Fig. 4. Fitting the ^{30}Si peak leads to an overestimation of the tail part, which confirms that the ^{30}Si diffusion at its peak region is enhanced by the existence of high-concentration B. The present result indicates that Si and B atoms in SiO_2 diffuse correlatively via SiO; namely, the enhanced SiO diffusion by the existence of B enhances B diffusion and Si self-diffusion. This correlation is consistent with the theoretical result that SiO molecules diffuse predominantly through interstitial sites with frequent atomic exchange interactions with substitutional atoms.[8] Furthermore, because viscosity is inversely proportional to diffusivity[14] and the viscosity of SiO_2 strongly depends on the impurity content,[15] the increase of SiO diffusivity may be closely related to decreasing SiO_2 viscosity with higher B doping.

In summary, Si self-diffusion and B diffusion in SiO_2 were simultaneously observed in $^{28}SiO_2$ samples co-implanted with ^{30}Si and B. Both Si self-diffusivity and B diffusivity increase with decreasing distance from the Si/SiO_2 interface. This indicates that SiO molecules govern not only Si self-diffusion but also B diffusion. In addition, both Si self-diffusivity and B diffusivity increase as B concentration increases, indicating faster SiO diffusion with higher B concentration in SiO_2. We have developed a numerical simulation that takes into account the correlated diffusion indicated in the experiments.

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[1]G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[2]S. Fukatsu, T. Takahashi, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi, K. Shiraishi, and U. Gösele, Appl. Phys. Lett. **83**, 3897 (2003).
[3]M. Uematsu, H. Kageshima, Y. Takahashi, S. Fukatsu, K. M. Itoh, K. Shiraishi, and U. Gösele, Appl. Phys. Lett. **84**, 876 (2004).
[4]R. H. Doremus, J. Appl. Phys. **92**, 7619 (2002).
[5]T. Takahashi, S. Fukatsu, K. M. Itoh, M. Uematsu, A. Fujiwara, H. Kageshima, Y. Takahashi, and K. Shiraishi, J. Appl. Phys. **93**, 3674 (2003).
[6]R. B. Fair, IEEE Electron Device Lett. **17**, 242 (1996).
[7]R. B. Fair, J. Electrochem. Soc. **144**, 708 (1997).
[8]M. Otani, K. Shiraishi, and A. Oshiyama, Phys. Rev. B **68**, 184112 (2003).
[9]M. Uematsu, J. Appl. Phys. **82**, 2228 (1997).
[10]M. Uematsu, Jpn. J. Appl. Phys., Part 2 **36**, L982 (1997).
[11]T. Aoyama, H. Tashiro, and K. Suzuki, J. Electrochem. Soc. **146**, 1879 (1999).
[12]W. Jüngling, P. Pichler, S. Selberherr, E. Guerrero, and H. W. Pötzl, IEEE Trans. Electron Devices **32**, 156 (1985).
[13]T. Aoyama, H. Arimoto, and K. Horiuchi, Jpn. J. Appl. Phys., Part 1 **40**, 2685 (2001).
[14]H. Eyring, J. Chem. Phys. **4**, 283 (1936).
[15]A. J. Ikushima, T. Fujiwara, and K. Saito, J. Appl. Phys. **88**, 1201 (2000).

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