Shouldering in B diffusion profiles in Si: Role of di-boron diffusion

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The role of di-boron diffusion in evolution of B diffusion profiles has been investigated. We find that boron pair ($B_s - B_i$) diffusion can become as important as boron-interstitial pair ($B_s - Si_i$) diffusion when both boron concentration and annealing temperature are very high, leading to concentration-dependent B diffusion. Our simulated B diffusion profiles with dramatic shouldering are in excellent agreement with experimental ones reported by Schroer *et al.* [Appl. Phys. Lett. **74**, 3996 (1999)] for high-temperature ($\approx 1200\,°C$) postimplantion annealing of ultralow-energy (≈ 500 eV) implanted high-concentration ($>10^{19}$ cm^{-3}) boron in silicon. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1619219]

Boron doping is an essential ingredient in the fabrication of silicon-based semiconductor devices. As gate dimensions shrink to nanometer scales (≤ 100 nm), it becomes critical to gain precise control of doping profiles. Consequently, a great deal of effort is being devoted to understanding and controlling transient enhanced diffusion (TED) of boron during implantation and postimplantation annealing.

While it is understood that a mobile boron-silicon interstitial pair ($B - Si_i$) plays an important role in B TED,[1,2] still little is known about underlying reasons for the enhancement (or the retardation) of B diffusion at high concentrations of boron ($>10^{18}$ cm^{-3}) (or impurities, such as carbon or oxygen).

We were particularly intrigued by the diffusion profiles (Fig. 1) determined by Schroer *et al.*[3] using secondary ion mass spectroscopy (SIMS). Their results show clearly a concentration-dependent behavior; that is, B diffusion is enhanced as the B concentration increases. They implanted boron at energies ~500 eV with a dose of 10^{15} cm^{-2} into a *p*-type, epitaxially grown (epi) silicon layer on Si(001). Then, the substrate was annealed at 1200 °C. The concentrations of oxygen and carbon in the epi-Si layer are typically less than 10^{15} cm^{-3}. Hence, impurities are likely to play an insignificant role in determining the doping profiles in these experiments. In addition, high temperature annealing at 1200 °C results in fast dissolution of B clusters formed at the very early stages of annealing. Therefore, the density of *immobile* large boron clusters, if any, is too low to influence diffusion profile evolution. This suggests that only Si interstitials and *mobile* B species should be considered in explaining these experiments. In the absence of concentration-dependent and/or transient effects, single component diffusion should lead to a Gaussian distribution (once the diffusion profile is fully developed), but the experimental results[3] in Fig. 1 differ substantially from a simple Gaussian. B TED appears to be enhanced with increasing B concentration, leading to *shouldering* in the diffusion profiles. The

shouldering behavior is consistent with a previous experimental observation[4] that shows B diffusion enhancement at high B concentration; that is, ^{10}B diffusion increased at the presence of high concentrations ($\approx 10^{19}$ cm^{-3}) of background boron ^{11}B. In fact, the concentration-dependent B diffusion has been explained by the variation of charged defect concentrations under extrinsic conditions (i.e., Fermi level shift effect, *vide infra*).[10]

In this letter, we present the influence of di-boron diffusion and other possible factors including Fermi level shift on evolution of B diffusion profiles.

The kinetic model used here includes only the formation/dissolution of $B_s - Si_i$ and $B_s - B_i$ pairs; that is, $B_s + Si_i \leftrightarrow B_s - Si_i$ and $B_s + B_s - Si_i \leftrightarrow B_s + B_i \leftrightarrow B_s - B_i$. This neglects many details in the interactions between B and Si atoms. But the influence of larger *immobile* B clusters should be negligible due to their low concentrations as a result of fast dissolution at high temperature annealing. When clustering is insignificant, the equilibrium concentrations of $B_s - Si_i$ and $B_s - B_i$ are mainly determined by the total boron and interstitial concentrations. Hence, the simplified kinetics should provide a reasonable description in the overall physical picture.

Figure 2 shows a comparison between simulated diffusion profiles and SIMS profiles[3] (from Fig. 1). Our simulations start with the initial (as implanted) distribution while
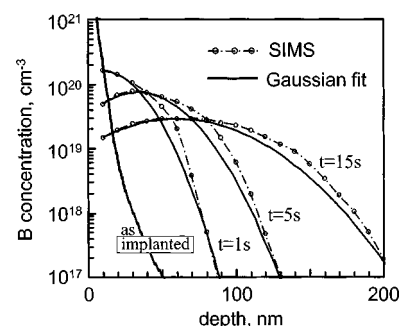

FIG. 1. The experimental (SIMS) profiles (Ref. 3) for three different annealing times, $t = 1$, 5, and 15 s. Fitting Gaussian functions to the early time evolutions leads to significant discrepancies for longer time, indicating that at least two components play a role.

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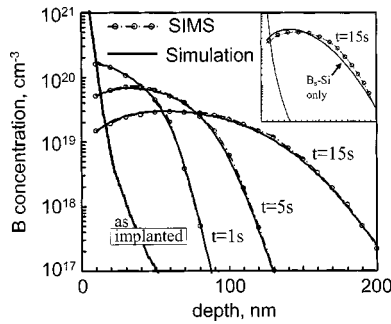[b)Author to whom correspondence should be addressed; electronic mail: wag@wag.caltech.edu

FIG. 2. A comparison between the experimental (SIMS) profiles (Ref. 3) and the profiles from simulations. The simulations, which include both B_s-B_i and B_s-Si_i diffusion, are in quantitative agreement with experiment providing strong support for the role of the B dimer diffusion at high temperatures. The inset shows a comparison between SIMS and simulated profile with B_s-Si_i diffusion only.

controlling precipitation (and/or evaporation) at the surface to match the integrated amount of B in the substrate to be same as experiments. When both B_s-Si_i and B_s-B_i diffusion are included, as shown in Fig. 2, we see that there is excellent agreement between the simulated and experimental results. Suppose that only B_s-Si_i diffusion is important and the Fermi level effect is insignificant, then substantial B clustering would lead to capture of mobile B_s-Si_i species by a second B complex to form a stable multiboron cluster. Such clustering would impede B TED, leading to a "tailing" behavior (i.e., the displacement of diffusion profiles becomes larger as the B concentration decreases) opposite to what is observed (see the inset in Fig. 2).

In the absence of the Fermi level shift effect, essential to the success in accurate modeling these experiments was including diffusion of the boron dimer (B_s-B_i). Recently, Hwang and Goddard[5] used first principles quantum mechanics (DFT/GGA) to follow the details of boron dimer diffusion. They found a pathway leading to an energy barrier of only 1.81 eV for the dimer diffusion. Although far larger than the activation energy for B_s-Si_i diffusion (~ 0.68 eV),[1] the larger binding energy for B_s-B_i[6,7] leads to a B_s-B_i contribution to diffusion comparable with the B_s-Si_i when both B concentration and annealing temperature are very high.[5]

Since clustering is insignificant at 1200 °C, the shape of the diffusion profile is dominated by the ratio of the mean diffusion length between B_s-B_i and B_s-Si_i pairs, $\lambda(B_s-B_i)/\lambda(B_s-Si_i)$.[8] Based on literature values of the diffusivities and binding energies

$$[D_e(Si_i) = 5\exp(-1/k_BT) \text{ cm}^2/\text{s},[9]$$

$$D_e(B_s-Si_i) = 1\times10^{-3}\exp(-0.68/k_BT) \text{ cm}^2/\text{s},[3]$$

$$E_b(B_s-Si_i) = 0.5 \text{ eV},[7]$$

and $E_b(B_s-B_i) = 1.5$ eV],[7] we deduce that the ratio of the mean diffusion length between B_s-B_i and B_s-Si_i pairs is[8] $\lambda(B_s-B_i)/\lambda(B_s-Si_i) \approx 56.46$. The results in Fig. 2, used a value of $\lambda(B_s-B_i)/\lambda(B_s-Si_i) = 55$, well within the uncertainty. (Since the density of free Si interstitials does not affect the mean diffusion length, these simulations simply assume the free interstitial concentration of 10^{14} cm^{-3}.)[3]

The importance of di-boron diffusion is determined mainly by the total concentration of nonclustered (free) bo-

ron. We define γ as the relative contribution of B_s-B_i and B_s-Si_i to B TED in terms of the equilibrium concentrations (C_{eq}) and the diffusivities (D_e):

$$\gamma = 2D_e(B_s-B_i)C_{eq}(B_s-B_i)/D_e(B_s-Si_i)C_{eq}(B_s-Si_i).$$

Here the factor of 2 arises because two boron atoms are transported in B_s-B_i diffusion. Our kinetic simulation shows that, as the total boron concentration is increased, the B_s-B_i concentration increases almost *quadratically*, but in contrast the B_s-Si_i concentration increases *sublinearly* at a high B concentration region ($>10^{18}$ cm^{-3}) due to suppression by B_s-B_i cluster formation.[5] As a result, at 10^{20} cm^{-3}, the equilibrium concentration of B_s-B_i becomes four orders of magnitude larger than the B_s-Si_i one.[5] We calculate that $\gamma \approx 1.4$ when $C_B = 10^{20}$ cm^{-3} (it increases linearly with C_B) using the diffusivities and the binding energies listed before. Here, the prefactor of B_s-B_i and B_s-Si_i dissociation rates is estimated based on the Debye frequency ($=10^{13}$ s^{-1}).

This study suggests that the B_s-B_i component may become as important as the B_s-Si_i component in determining diffusion profiles when both B concentration and annealing temperature are very high. For low temperature annealing (<900 °C), however, the boron clustering at high concentrations ($>10^{18}$ cm^{-3}) makes di-boron diffusion unimportant.

Next, we discuss the influence of the following factors on doping profile evolution:

(i)   Fermi level shift;
(ii) density distribution of neutral interstitials;
(iii) impurities such as oxygen and carbon; and
(iv) stresses caused by surfaces and extended defects.

Fermi level shift. In *p*-doped Si, interstitials may charge positively or remain neutral. Under extrinsic conditions, the concentration of the charged interstitials is a function of the Fermi level (that depends on the dopant concentration)[10,11] while the concentration of neutral interstitials remains unchanged. Therefore, the total interstitial concentration changes with the boron concentration if a substantial fraction of interstitials were charged, which may in turn result in a concentration-dependent behavior[10] as boron diffusion is mainly mediated by interstitials. Thus, an accurate estimation of the relative density of interstitials at a different charge state is essential.

The relative populations for positively charged interstitials under intrinsic conditions are determined by the donor levels, the Fermi level, and the substrate temperature.[12,13] For the first donor level $\approx E_c - 1.2$ eV,[6] the second donor level $\approx E_c - 0.4$ eV,[6] the intrinsic Fermi level ≈ 0.6 eV (where E_c is conduction band minimum), for instance, the estimated relative concentrations of 0, 1+, and 2+ charged interstitials are 1, 7.5×10^{-3}, and 0.038 at 1200 °C, respectively. With the intrinsic carrier concentration (n_i) of $\approx 2\times10^{19}$ cm^{-3} at 1200 °C, for $p = 10^{20}$ cm^{-3} (i.e., $p/n_i = 5$) the relative populations of 1+, 2+ charged interstitials increase to 3.75 $\times10^{-2}$ and 0.95, respectively. This indicates that the total interstitial concentration may increases substantially in the extrinsic region.

In addition to the interstitial concentration variation, the dissociation and diffusion rates of boron-interstitial complexes are likely to be strongly influenced by the Fermi-level

position.[1,2,6,7] However, the energies of the different charge states of boron-interstitial pairs and interstitials are poorly known, thus it is difficult to quantify the Fermi level effect.

Density distribution of neutral interstitials. The interstitials are usually generated by high-energy ion bombardment and remain in the form of small clusters during implantation. At the onset of annealing, most of the interstitial clusters (including interstitial-boron complexes) may exist near the surface. At the nonequilibrium stage where these clusters serve as a main source for excess interstitials through dissolution, a sizable gradient in the interstitial density may develop along the depth. However, high temperature annealing ($\approx 1200\,°C$) results in rapid dissolution of the clusters. According to a recent measurement,[9] {311} defects decay exponentially with annealing temperature; the characteristic decay time ranges from ~ 40 s at $815\,°C$ to ~ 4 h at $670\,°C$. Extrapolating to $1200\,°C$ leads to a decay time of $< 10^{-3}$ s. Given that smaller clusters dissolve much faster than the extended {311} complexes, this estimate suggests that most of interstitial clusters formed during implantation and/or the early stages of annealing evaporate within 10^{-3} s at $1200\,°C$. If so then the diffusion profile evolution will be barely influenced by the interstitial density gradient.

Even if the dissolution rate is far slower than 10^{-3} s, the resulting density gradient of interstitials will be insignificant in a short length scale (<100 nm) due to their high mobility $[D_e(\text{Si}) \approx 1.5 \times 10^{-3}$ cm^2/s at $1200\,°C]$.[14] In the end, the free interstitials may be equilibrated with interstitial-containing clusters. Once the equilibrium is established, the number of free interstitials decreases with the density of traps (such as interstitial clusters and boron-interstitial complexes). Thus, the observed shouldering phenomenon for B is quite unlikely to involve density gradient of free Si interstitials.

Impurities. Interactions with oxygen and carbon may affect the boron diffusion by forming B_iC_s (interstitial boron-substitutional carbon) or/and B_iO_i (interstitial boron-interstitial oxygen) complexes.[15] However, the concentrations of oxygen and carbon in the epi-Si layer are typically less than 10^{15} cm^{-3}. Hence, we believe that such impurities play an insignificant role in determining doping profiles in the high B concentration regime ($>10^{17}$ cm^{-3}).

Stresses. Stresses have been proposed as a factor that may influence boron diffusion, albeit there is a controversy over whether they enhance or retard B diffusion.[16] Very large stresses are usually built up in the silicon area near the edge of thin gate layers due to lattice mismatch. In addition, extended defects such as dislocation loops may create a stress field around them. However, the Schroer experiments[3] involve a planar free surface, which imposes only a small stress on the substrate. Thus, the induced stresses cannot be important. At high temperatures ($>1000\,°C$), extended defects (if any) would be dissolved too fast to have significant influence.[17]

In summary, we show di-boron diffusion can be important and lead to shouldering in B diffusion profiles for high temperature ($\approx 1200\,°C$) annealing with high B concentrations ($>10^{19}$ cm^{-3}). This study suggests that di-boron diffusion and Fermi-level shift would result in a similar concentration-dependent behavior of B diffusion, but their relative contributions are hard to be quantified as the relevant energetics is still poorly known.

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