B diffusion and clustering in ion implanted Si: The role of B cluster precursors

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A comprehensive model for B implantation, diffusion and clustering is presented. The model, implemented in a Monte Carlo atomistic simulator, successfully explains and predicts the behavior of B under a wide variety of implantation and annealing conditions by invoking the formation of immobile precursors of B clusters, prior to the onset of transient enhanced diffusion. The model also includes the usual mechanisms of Si self-interstitial diffusion and B kick-out. The immobile B cluster precursors, such as BI_2 (a B atom with two Si self-interstitials) form during implantation or in the very early stages of the annealing, when the Si interstitial supersaturation is very high. They then act as nucleation centers for the formation of B-rich clusters during annealing. The B-rich clusters constitute the electrically inactive B component, so that the clustering process greatly affects both junction depth and doping level in high-dose implants. © *1997 American Institute of Physics.* [S0003-6951(97)04117-X]

Recently much effort has been devoted to the understanding and control of the transient-enhanced diffusion (TED) of B in Si during implantation and annealing,[1–3] as the spreading of the B profile poses a real limitation for the formation of shallow junctions in submicron device structures. Another problem is the incomplete activation of the implanted B, even after the usual annealing period. The phenomenon of B TED is well understood in terms of the formation of a mobile B-Si interstitial pair by the excess population of Si interstitials caused by ion implantation.[4] There is, however, little understanding of the formation of the electrically inactive component, although it is thought that B forms clusters even at concentrations far below the solubility limit. In this letter we present a model of the formation of the immobile B clusters and TED; the model accurately describes the diffusion and clustering over wide ranges of annealing times, temperatures, B concentration, and implantation doses.

We use an atomistic simulator (BLAST) to help elucidate this complex problem.[5] A simulation based on the binary collision approximation (MARLOWE[6]) provides the coordinates of interstitials (I) and vacancies (V) generated during ion implantation. Those coordinates are transferred to a Monte Carlo diffusion simulator. Interstitials and vacancies are then given random jumps at a rate derived from their diffusivities. The model includes interaction between the particles leading to clustering and re-emission from clusters, trapping and de-trapping with native traps (e.g., carbon and oxygen). The rates of these processes are determined by specific binding energies derived from molecular dynamics, first principles calculations, and experiments.[5] Annihilation of point defects at the surface is assumed to be perfectly efficient.

The interaction between a B atom and a Si self-interstitial is described in terms of pairing and kick-out mechanisms, with the energies reported by Zhu *et al.* from a first-principles calculation.[7] The Si interstitial is bound to a substitutional B atom with an energy of 1 eV, but this pair configuration is a low mobility state. The B-I pair must surmount an energy barrier (also ≈1 eV) to reach a higher mobility state, the interstitial B configuration (B_i). The complex will make several transitions on average between the mobile and immobile states until the pair breaks up, leaving the B atom again in a substitutional position and releasing a Si interstitial. This model provides a good description of the TED of B for low B concentrations, when all of the B participates in TED. The case of high B concentration, where an immobile B component is observed, is a more complex problem. Only a few theoretical calculations on some specific configurations of B clusters have been performed[7,8] and no comprehensive explanation of the formation of B clusters has been presented yet.

We base our discussion on structures consisting of molecular beam epitaxy (MBE)-grown B marker layers implanted with Si ions, since the depth distributions of the mobile and immobile B components can be clearly distinguished. Figure 1 shows the secondary-ion-mass spectrometry (SIMS) measurements of a B profile of one such structure implanted with 40 keV Si and annealed for 10 min at 790 °C. Important properties of the process can be extracted directly from a detailed analysis of this experiment: (i) Immobile B regions are observed only to depths within 3000 Å of the surface. (The is the region that experiences a very high supersaturation of Si interstitials during implantation.) (ii) The clustered component of B shows no broadening from the as-grown profile. (iii) All of the spikes, even the deepest ones, experience TED. These facts impose severe constraints on the possible mechanisms for cluster nucleation.

We have tested several mechanisms for the nucleation of B clusters. First, we assumed a large binding energy between the B_i and a substitutional B (B_s). In this model, B_s-B_i initiated B clusters, which were observed in all of the spikes

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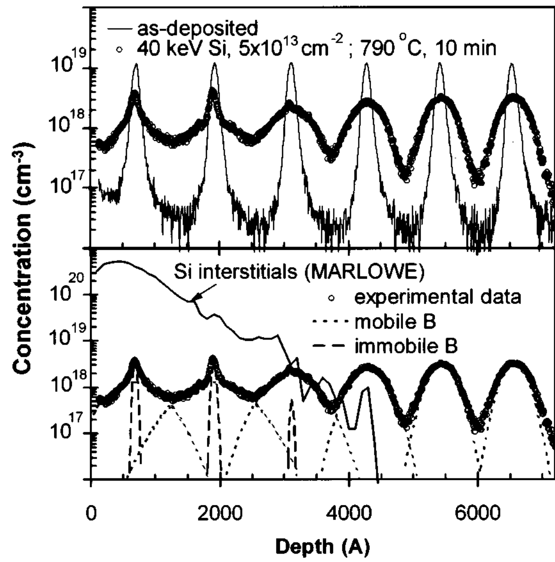

FIG. 1. (a) SIMS profiles in B-doped superlattice as-deposited and after 40 keV, 5×10^{13} cm^{-2} Si implantation and 10 min anneal at 790 °C. (b) Deconvolution of the doping markers into Gaussian diffusion profiles and an immobile fraction in the near-surface spikes, along with the MARLOWE calculation of the initial Si interstitial distribution after implantation.

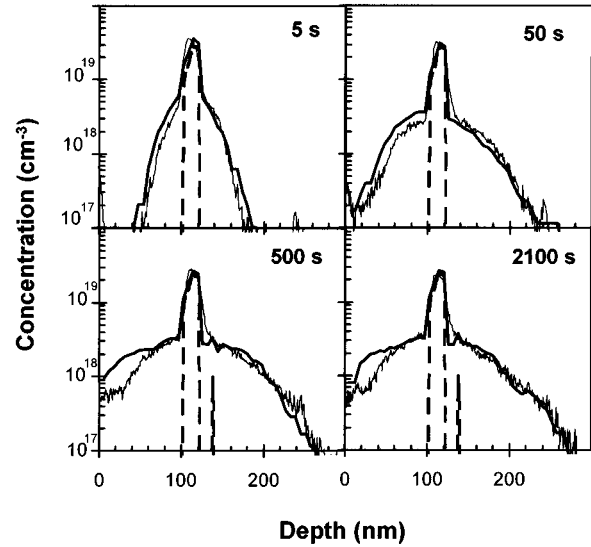

FIG. 2. Simulated and experimental profiles of a 4.5×10^{19} cm^{-3} B spike after 40 keV 9×10^{13} cm^{-2} Si implant and 5, 50, 500, and 2100 s anneal at 800 °C. Thin lines represent experimental data, thick solid lines the simulated B profile, and thick dashed lines the simulated B in clusters.

and also outside of the initial B spike (the mobile B_i encounters B_s atoms throughout the diffused region). The experimental fact that B clusters only appear in the region of the initial high Si interstitial concentration suggests a second model, which includes a large binding energy between two B_i leading to B_i-B_i pairs. However, the diffusion distance required for one B_i to be captured by another is large enough (4.6 nm in a 10^{19} B/cm^3 spike) to produce a significant broadening of the clustered component of the spike (10 nm wide), in contradiction with the experiment.

The absence of broadening of the clustered component implies that a fraction of the B atoms must be immobilized before any B diffusion occurs, i.e., during the room-temperature implantation or at a very early stage of the annealing. In addition, no significant number of new nucleation sites can be formed once B starts diffusing, otherwise clustering would also take place outside of the initial spike. We propose that an immobile configuration (the B cluster precursors) consisting of a B atom and several Si interstitials, for example BI_2, is formed during the initial stage. After that, very few new BI_2 are formed, since the concentration of free Si interstitials drops very soon as a result of recombination and clustering.

However, BI_2 cannot be the final configuration that is obtained after several minutes of high temperature annealing. If BI_2 is allowed to be stable during TED, many Si interstitials are prevented from taking part in TED, and the B displacements are much less than those observed in the experiment. Furthermore, if this were the case, an immobile B region should be seen for any B concentration as long as a high Si interstitial concentration were present. Experimental data[9] show that after implantation and annealing at 800 °C, clustering is not observed when the B concentration is lower than 10^{18} cm^{-3}. This fact also indicates that the binding energy for this precursor BI_2 must be 1.2 eV, i.e., it must be stable only during the time necessary for other B_i to join it (displacement of 10 nm for a 10^{18} cm^{-3} concentration) and form a more stable cluster. Therefore, we can conclude that a species such as BI_2 immobilizes the B atoms and acts as a nucleation center for the growth of B clusters.

In order to better analyze the evolution from these B cluster precursors into larger B clusters, we have used samples with a single B marker layer. A B spike of 20 nm width and a concentration of 4.5×10^{19} cm^{-3} was grown by MBE and this sample was implanted with 40 keV, 9×10^{13} cm^{-2} Si. Figure 2 shows the SIMS profiles in a sequence of anneal times at 800 °C, along with the simula-

TABLE I. Simulation parameters. D_I, D_V are the I and V diffusivities, respectively, $Et_{nB,nI}$ is the potential energy of B clusters, where n_B, n_I are the number of B atoms and Si interstitials, respectively.

$D_I=5\ \exp(-1/kT)$ cm^2/s	$E_{binding}(n_I)=2.7-2.65[n_I^{1/2}-(n_I-1)^{1/2}]$ eV
$D_V=10^{-3}\exp(-0.4/kT)$ cm^2/s	$E_{binding}(n_V)=3.6-4.9[n_v^{2/3}-(n_V-1)^{2/3}]$ eV
$E_{binding}(C-I)=2.6$ eV	$E_{binding}(O-V)=3.0$ eV
$D_{Bi}=10^{-3}\exp(-0.3/kT)$ cm^2/s	$E_{binding}(B-I)=1$ eV $E_{binding}(BI_2)=1.2$ eV
$Et_{2,0}=0.0$ eV $Et_{2,1}=-2.1$, $E_{barrier}=0.5$ eV	$Et_{2,2}=-4.8$ eV
$Et_{3,0}=0.8$ eV $Et_{3,1}=-4.0$ eV	$Et_{3,2}=-5.5$ eV $Et_{3,3}=-6.8$ eV
$Et_{4,0}=-1.2$ eV $Et_{4,1}=-5.0$ eV	$Et_{4,2}=-6.4$ eV $Et_{4,3}=-7.4$ eV $Et_{4,4}=-8.5$ eV
$Et_{nB,NI}=-0.2n_B-2.0n_I$ eV, $n_B\geq5$; $E_{barrier}=1$ eV, $n_B=5$	

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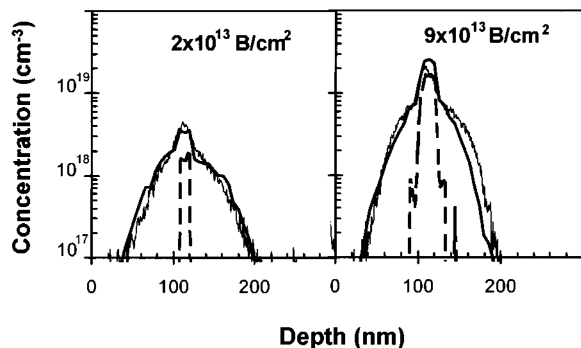

FIG. 3. Simulated and experimental profiles of a 2×10^{13} cm^{-2} and 9×10^{13} cm^{-2} B spike after 40 keV 2×10^{13} cm^{-2} Si implant and 35 min anneal at 800 °C. Thin lines represent experimental data, thick solid lines the simulated B profile, and thick dashed lines the simulated B in clusters.

tion results obtained with the B clustering mechanism described here, using the parameters listed in Table I (Ref. 10). Notice the excellent agreement between the model and the experiment over the entire run. The predicted electrically-inactive or clustered B distribution also agrees with spreading resistance profilometry (SRP) data (not plotted in the figure). Figure 2 shows that at 5 s about 50% of the B atoms are in clusters and some B diffusion has already occurred. During subsequent annealing, there is additional TED, but no increase of the immobile B fraction is observed.

The B clusters are formed as a result of the capture of additional B_i by BI_2. If the binding energy of the B atoms to the cluster were assumed to increase with cluster size as expected, for example, for a spherical precipitate, the B clusters would grow to large sizes, and this would cause the fraction of B in clusters to increase during TED by adding more B_i to the existing B clusters. The experimental data shows no increase of the clustered B fraction during TED, but a slight reduction. This indicates that larger B clusters are unstable or that an energy barrier prevents their formation. We assume an energy barrier corresponding to clusters larger than 5 B atoms, blocking further growth. The emission of a small number of B_i from the B clusters produces the non-Gaussian shape of the diffused profiles beyond 500 s.

In order to check the number of Si interstitials retained in the B clusters, a Si implant of 2×10^{13} cm^{-2} was performed on two samples containing B spikes of 20 nm width and a concentration of 10^{19} and 4.5×10^{19} cm^{-3}, respectively; i.e., with a ratio implanted Si ions to B atoms of 1:1 and 1:4.5, respectively. The SIMS profiles after 2100 s anneal at 800 °C are shown in Fig. 3. Notice again the excellent prediction of the model using the same parameters from Table I. Both model and experiment show about 30% of B in clusters and comparable diffusion distances. This is not the case if the ratio Si interstitial to B atoms in the B clusters is 1:1 or even 1:2, since the diffusion length is then much smaller than that observed experimentally, especially in the case where the number of implanted Si ions is much less than the B atoms. This indicates that some Si interstitials are released from the B clusters as the Si interstitials population decreases. Some Si interstitials are trapped in the B clusters, since more TED is observed during the complete dissolution of the B clusters, which takes several hours.[3] Trapped Si interstitials are also indicated by a reduction in the density of {311} defects at large B concentrations.[11] The model predicts that after a 35 min anneal at 800 °C, the B clusters have a variety of compositions, mainly B_3I and B_4I. This result also agrees with other experimental data in which several precipitates (B_xI, $x=2.89-4$) have been identified.[12]

In conclusion, we have developed a physically-based model that successfully explains and predicts the behavior of B during implantation and annealing. The nucleation takes place by the formation of immobile precursors (BI_2) during implantation or the early states of annealing. Other possible precursor configurations cannot be ruled out provided that (i) they are formed in the region of initial high Si interstitial and vacancy concentrations, (ii) they immobilize a fraction of B atoms prior to the onset of B diffusion, and (iii) their rate of formation diminishes once B diffusion begins. The B clusters are of small size, of the order of 3 or 4 B atoms, and they contain approximately one Si interstitial. This model provides parameters and simplified mechanisms which can be implemented in continuum process simulators, such as SUPREM-IV or PROPHET.

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