B cluster formation and dissolution in Si: A scenario based on atomistic modeling

Lourdes Pelaz,[a] G. H. Gilmer, H.-J. Gossmann, and C. S. Rafferty
Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

M. Jaraiz and J. Barbolla
University of Valladolid, Campus Miguel Delibes s/n, 47011 Valladolid, Spain

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A comprehensive model of the nucleation, growth, and dissolution of B clusters in Si is presented. We analyze the activation of B in implanted Si on the basis of detailed interactions between B and defects in Si. In the model, the nucleation of B clusters requires a high interstitial supersaturation, which occurs in the damaged region during implantation and at the early stages of the postimplant anneal. B clusters grow by adding interstitial B to preexisting B clusters, resulting in B complexes with a high interstitial content. As the annealing proceeds and the Si interstitial supersaturation decreases, the B clusters emit Si interstitials, leaving small stable B complexes with low interstitial content. The total dissolution of B clusters involves thermally generated Si interstitials, and it is only achieved at very high temperatures or long anneal times. © *1999 American Institute of Physics.* [S0003-6951(99)00524-0]

Ion implantation has become a standard technique to introduce dopants in Si. However, energetic ions damage the lattice and generate a large concentration of defects in Si. These defects deteriorate the device performance and have to be annealed out, at the same time that the implanted ions are electrically activated by the anneal. Two important and undesired effects appear in the B profiles as a consequence of ion implantation and a postimplant anneal. First, B undergoes transient enhanced diffusion (TED) during the time in which a large concentration of intrinsic defects is present.[1] Second, in the presence of defects, B precipitates and becomes electrically inactive at concentrations much lower than the equilibrium solid solubility.[2] A significant amount of research in this field has provided a good understanding of TED.[1–4] The modeling of the inmobile and inactive fraction of B is a much more complex problem. Earlier attempts[5–8] have contributed to the understanding of the mechanisms that control the formation of B clusters, but many questions still remain open.

Theoretical studies using *ab initio*[3,7] or tight-binding[9] calculations have provided useful information about the stability of some B clusters ($B_{n\mathrm{B}}I_{nI}$, with nB the number of B atoms and nI the number of interstitials). Using these energies,[3,7] several groups have implemented B clusters in Monte Carlo diffusion codes[7] or continuum process simulators.[6,8] This approach has the advantage of the absence of free parameters. However, in practice, the calculated energy of these clusters is strongly dependent on the starting structure which has to be preset in the simulation, and as Luo *et al.* pointed out, there is no guarantee that the global minimum for the system has been located.[9] The calculated configuration energy depends as well on the simulation cell size and the charge state. A different set of parameters was extracted in Ref. 5, based on diffusion experiments. It was shown that the precursor of B clusters (BI_2) was an important ingredient in the understanding of B clustering formation.

The aim of this letter is to provide an understanding and physically based model of the mechanisms associated with the formation and dissolution of B clusters in Si. Experiments on ion implantation and oxidation are used both to extract information about the mechanisms involved in the process and to test the model. The combination of these experiments provides unambiguous information about the path of formation and dissolution of B clusters. The model reproduces a large body of experimental data with a single set of model parameters.

We have carried out atomistic simulations to follow the evolution of defects and B clusters in Si. We use MARLOWE[10] to generate the implantation cascades. The coordinates of the implanted ion and Si self-interstitials and vacancies generated in each cascade are transferred to the Monte Carlo diffusion code DADOS.[11] Diffusion and interactions between Si self-interstitials (I), vacancies (V), and dopants have been implemented as described elsewhere.[5,11] The oxidation process is simulated by assigning a supersaturation of Si interstitials at the surface. The energies of the B clusters are given in the schematic of Fig. 1. Entropy changes due to differences in the atomic vibrational amplitudes of different defects are neglected, and reactions are assumed to be diffusion limited.

Interactions between B and defects occur already during implantation at room temperature, since free I and V are mobile.[12,13] The interstitial B (B_i) is also mobile, but the B–Si interstitial pairs ($B-I$) are not mobile at room temperature.[3] The B in $B-I$ pairs or B_i may become substitutional (B_s) through the interaction with a free V (Frank–Turnbull mechanism). They also can interact with an additional free I and form an immobile complex,[5] such as BI_2. Therefore, after the room temperature implant most of the B

[a]Permanent address: University of Valladolid, Campus Miguel Delibes s/n, 47011 Valladolid, Spain; electronic mail: lourdes@ele.uva.es

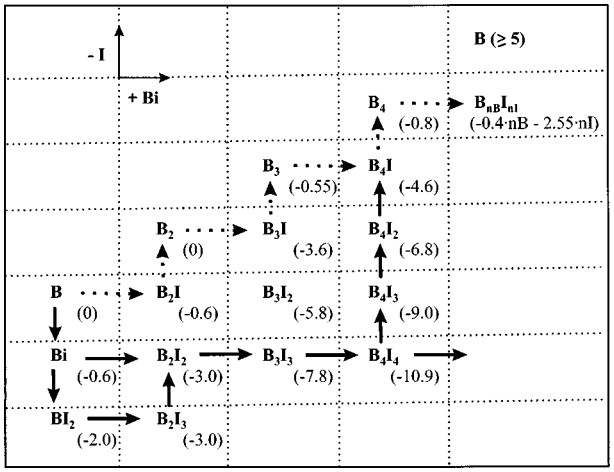

FIG. 1. Energy in eV of B clusters and schematic of the different paths for the growth of B clusters. The dashed line corresponds to a generic low interstitial content path. The solid line corresponds to a high interstitial content path. The energies in the table determine a predominant high interstitial content path. The clusters with high interstitial content release Si interstitials when the interstitial supersaturation decreases.

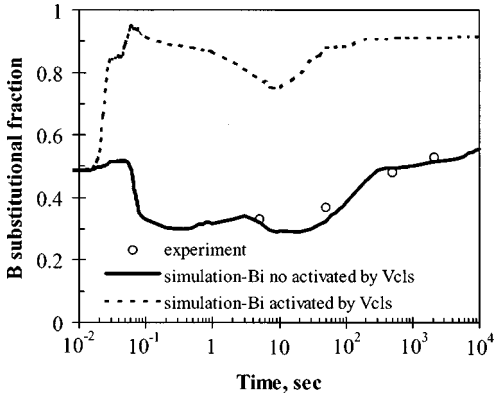

FIG. 2. Time evolution of the substitutional fraction of a single B marker layer during a postimplant anneal at 800 °C. The initial B spike (20 nm wide, 100 nm below the surface, B concentration $4.5\times10^{19}\,\mathrm{cm}^{-3}$) is implanted with 40 keV $9\times10^{13}\,\mathrm{cm}^{-2}$ Si ions. Symbols correspond to the experimental data, extracted as the ratio of the B in the diffusion tail to the total amount of B. The solid line corresponds to the model in which we do not include the interaction of B_i with vacancy clusters. The dashed line assumes that B_i becomes B_s when interacting with vacancy clusters. In both cases the parameters in Fig. 1 are used. Our model, in agreement with the experimental results, shows that B clusters are already formed in the first 5 s and some dissolution occurs during the first 30 min. The total dissolution of the B clusters takes several hours at 800 °C.

atoms are distributed between different immobile configurations: B_s, B–I pairs, and BI_2. The I and V that survive recombination are mostly stored in stable and immobile clusters (I_{cls} and V_{cls}, respectively).

During the annealing at 800 °C, the I_{cls} ripen and dissolve, and the free I that they release interact with B atoms. The formation of B clusters happens by the addition of B_i to the preexisting BI_2 precursors.[5] This requires the diffusion of the B_i over a distance of several nm. In the early stages of the annealing, when a large concentration of I and V in clusters is still present ($>10^{19}\,\mathrm{cm}^{-3}$), the mobile B_i atoms have a large probability of interacting with them without reaching the BI_2 precursors. Therefore, it is important to consider the possible interaction between B_i and I_{cls} and V_{cls}. No theoretical calculations have been carried out for such interactions. Our interpretation is based on experimental results described below, with B marker layers implanted with Si ions or during oxidation.[1,2,5,14,15]

The I_{cls} (311 defects) are formed in the region of maximum damage, which is close to the projected range of the implanted ions.[16] However, the damaged region during implantation extends further. If we include in the model an interaction between B_i and I_{cls}, and simulate a 40 keV Si implant on B marker layers, we observe an accumulation of B atoms in the position of the stable I_{cls}, outside the initial position of the B marker layer. Since experiments do not yield any evidence that the B clusters occur outside the initial zones of the B markers,[17] we conclude that B_i and I_{cls} do not interact or the interaction is not strong enough to immobilize the B atoms in I_{cls}.

If we assume that a V_{cls} absorbs the Si interstitial from the B_i, leaving a B_s, the growth of B clusters during the early stages of the anneal is not possible since the diffusion path of the mobile B_i is interrupted by the high concentration of V_{cls}. The simulation of a Si implant in samples containing B markers leads to an almost complete activation of B, for very short anneal times (see Fig. 2), as reported also by Caturla *et al.*[7] for B implants. This contradicts experimental results that show that B clusters are present after a Si implant of 40 keV and 5 s anneal at 800 °C.[5] Also a significant fraction of immobile B is observed in B markers placed in the vacancy rich region of a 2 MeV Si $10^{16}\,\mathrm{cm}^{-2}$ implant at 300 °C, while the rest of the B diffuses.[15] This indicates that B clusters start forming at low temperatures in the early stages of the annealing, and that a high concentration of V_{cls} does not suppress their formation, provided that a high concentration of Si interstitials is also present. Therefore, we must conclude that there is little or no interaction between B_i and V_{cls}.

Suppressing the interaction between B_i and both I_{cls} and V_{cls}, the mobile B_i can diffuse freely until it becomes substitutional by kicking out an I, captures a free V, or until it interacts with a free I or other B atoms to form B clusters. Still, two main paths are possible for the growth of B clusters, as shown in the schematic of Fig. 1. In general, both paths act simultaneously and all the configurations of the B clusters ($B_{nB}I_{nI}$) are possible. The predominance of one of the path versus the other is determined by the relative stability of the B clusters and the concentration of B and I. In the *low interstitial content* path (dashed line), new B_i are added to preexisting B clusters, but Si interstitials are rapidly emitted leaving B complexes with low interstitial content ($B_2I, B_2, B_3I, B_3\ldots$).[18] Through this path, B clusters could be formed in the presence of low interstitial supersaturation as long as the B concentration is high enough. This implies that B clusters would be formed during the plus one regime, or even under oxidation conditions. However, experiments indicate that the B marker layers do not cluster under oxidation conditions[14] [see also Fig. 3(b)]. Further, in ion-implanted Si, B clusters are formed in the first 5 s of the anneal at 800 °C. During the remainder of the anneal, which occurs at much lower interstitial concentration, the fraction of B in clusters actually decreases[5] (see Fig. 2).

The alternative path for the formation of B clusters involves a *high interstitial content* (solid line in Fig. 1). In this

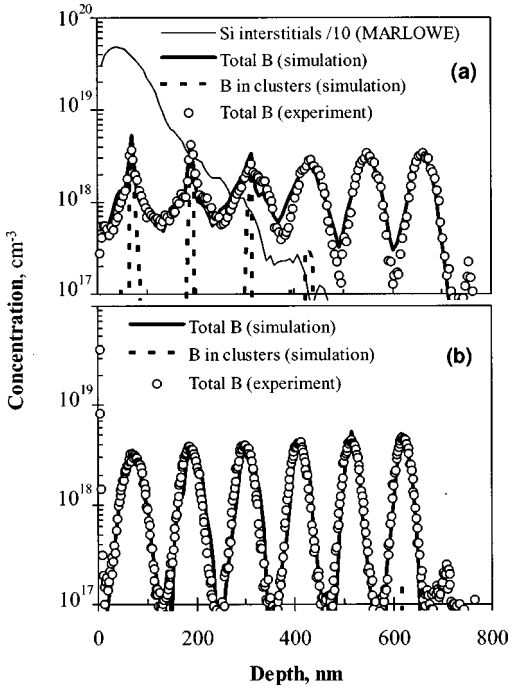

FIG. 3. (a) Secondary ion mass spectrometry (SIMS) profile of the B after a 40 keV Si $5\times10^{13}\,\mathrm{cm}^{-2}$ implant and a postimplant anneal for 10 min at 790 °C, along with the total simulated B profile and the simulated B in clusters. Also, the Si interstitials simulated by MARLOWE during the implant is plotted. The B spikes contained in the region that experience a high Si interstitial concentration during the implant experience clustering. The spikes outside that region do not cluster, although their diffusion is enhanced by the injection of Si interstitials from the damaged region. (b) SIMS profiles of the B-doped superlattice after 790 °C anneal for 15 min in an oxidizing ambient, along with the simulation results. The B markers experience enhanced diffusion due the injection of Si interstitial from the surface, but they do not cluster.

case, B_i are added to preexisting B clusters but they do not emit Si interstitials immediately. Therefore, B complexes with a high interstitial content are formed $(BI_2, B_2I_2, B_3I_3, B_4I_4 \ldots)$. The formation of such complexes is only possible under a high Si interstitial supersaturation. This happens during implantation or at the initial stages of the annealing and only inside the region of high damage [see Fig. 3(a)], in agreement with experiments.[2,5,17] When the injection of Si interstitials is small, as it is in the case of oxidizing anneals [see Fig. 3(b)] or outside the initial region of high damage [see Fig. 3(a)], the B atoms diffuse normally and no immobile B complexes are formed in the simulation and they are not detected experimentally.[2,5,14]

There are some general features that a predictive model of B clusters has to incorporate, independent of the precise values of the parameters. (i) The energies of the clusters B_2I and B_2, which are the starting point of a low interstitial content path to clustering, is high. This makes this path comparatively difficult to start. (ii) The energies of the starting clusters for the high interstitial content path (B_2I_2, B_2I_3) are lower, which makes this path more favorable, but only in the presence of a high interstitial concentration. (iii) When the interstitial concentration drops during annealing, the B clusters with high interstitial content tend to emit Si interstitials, leaving small stable configurations with low interstitial content (B_3, B_4I, B_4). (iv) The binding energies of clusters bigger than about 4 do not increase with cluster size. This is consistent with the fact that the fraction of B in clusters does not increase during the time in which most of the B diffusion takes place.[5] Bigger B clusters are formed but they are not stable at 800 °C, and after a few seconds they dissolve. (v) The most stable configuration has a ratio B:I about 4:1. The small number of I trapped in B clusters is inferred from the fact that B diffusion and clustering is observed in a sample containing a B marker with a dose 4.5 times the implanted Si dose.[5] These B clusters are stable for a long time after the 311s or I_{cls} disappear.[2] In our implementation the complex B_4I has the largest binding energy. (vi) Since the final stable B complexes have a low interstitial content, the total dissolution of the B clusters takes place under an equilibrium concentration of Si interstitials through the reverse reaction of the low interstitial path, i.e., capturing a Si interstitial and emitting a B_i. The Si interstitials needed are thermally generated interstitials, and therefore, long anneal times or high temperatures are needed to achieve a maximum activation of B, as has been observed experimentally.[2,19]

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