# Lattice location and thermal evolution of small B complexes in crystalline Si

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The lattice location of B in Si has been investigated by channelling analyses using nuclear reactions (650 keV proton beam, $^{11}B(p,\alpha)^{8}Be$). The formation at room temperature of a specific, small B complex in presence of an excess of point defects has been inferred. In particular, B implanted in Si or B substitutional dissolved in Si and irradiated with proton beam form a unique B complex with B atoms not randomly located. The angular scans along the ⟨100⟩ and ⟨110⟩ axes are compatible with B–B pairs aligned along the ⟨100⟩ axis. The thermal annealing in the 200–950 °C range of the B complexes, analyzed by lattice location and carrier concentration measurements, depends on the residual defect density in the lattice. The B complexes dissolve at low temperature if no excess of Si self-interstitials (Is) exists or they evolve into large B clusters and then dissolve at high temperature if Is supersaturation holds. *© 2005 American Institute of Physics*.
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The interest of B doping in Si is still of relevance because of the fascinating basic physics involved in this system and its extensive use in integrated circuits fabrication. The required continuous device scaling down[1] drives to deeper knowledge on dopant diffusion, defects interaction, precipitation at high concentration, dissolution, and electrical activation. Ion implantation has become a standard industrial technique to selectively introduce dopants in crystalline Si.[2] However, at the fluences used for Si doping by B implantation ($10^{15}$ cm$^{-2}$), the crystalline lattice is heavily damaged and B is electrically inactive. During the postimplant thermal treatments required to activate the dopant and recover the lattice damage, undesired effects, such as transient enhanced diffusion of B atoms[3] and precipitation into electrically inactive boron-interstitial-clusters (BICs)[4,5] well below the B equilibrium solid solubility, occur. This behavior has been modeled in terms of interaction of B with Si self-interstitials (Is), with the concentration of the latter in ion implanted Si being several orders of magnitude higher than at equilibrium. The detrimental effect of the excess of Is is further supported by the observation that B clustering does not occur below the solubility limit ($4\times10^{20}$ atoms/cm$^3$) during solid phase epitaxial regrowth (SPEG).[6] Several strategies based on defect engineering have been developed to overcome the problems related to the anomalous diffusion of B implanted in crystalline Si.[7]

Many theoretical efforts have been spent to detail BIC's nature, location, and energies[5,8,9] while a few experimental works show their composition, thermal dissolution, and electrical activation.[10–12] Diffusion-based investigations, by secondary ion mass spectrometry, are limited to the high-temperature regime, where B diffusion is detectable.[10,11] Nevertheless, some crucial information about the lattice location of BICs and their thermal evolution from the room temperature (RT) to 800 °C are still missing.

In a previous work,[13] we showed that substitutional B in Si undergoes off-lattice displacement at RT during irradiation with $H^+$ beams as a consequence of B interaction with Is generated by irradiation. The amount of displaced B increased with irradiation fluence until saturation, at which point, the formation of B–B pairs stable in presence of excess Is was supposed.

In this work, we study the lattice location of small B complexes obtained both through irradiation of substitutional B and by implanting B in crystalline Si. Identical angular scans suggest that the same B complex is formed in both cases in spite of the different conditions. In addition, the damage recovery and the electrical activation of such B complexes subjected to thermal treatment in the 200–950 °C range will be presented and discussed.

(100) *n*-type Si substrates were used in this experiment and two sets of samples have been prepared: (1) *proton-irradiated samples*—They consist of 400 nm thick Si layer uniformly doped with a B concentration of $1\times10^{20}$ atoms/cm$^3$ irradiated with a 650 keV $H^+$ beam at a fluence of $1\times10^{17}$ cm$^{-2}$ (above the saturation fluence according to Ref. 13). The B-doped layer was obtained either by molecular-beam epitaxy (MBE) or SPEG of B implanted at multiple energies into preamorphized Si. (2) *B implanted samples*—A 50 keV $^{11}B^+$ beam was implanted (7° tilt) at RT into crystalline substrate at a fluence of $2\times10^{15}$ cm$^{-2}$ ($1.5\times10^{20}$ B/cm$^3$ peak concentration, projected range ~200 nm).[14]

Channelling measurements have been performed using the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction at 650 keV proton beam and detecting emitted $\alpha$ particles. For details on this technique, see Ref. 13. The angular scans, reported in Fig. 1, have been obtained by measuring the yield of B ($\chi_B$) and Si ($\chi_{Si}$) normalized to the random yield as function of the tilt angle swept by the proton beam about a crystal axis [⟨100⟩ in Fig. 1(a) or ⟨110⟩ in Fig. 1(b)] inside the (100) plane.[15]

An error of 5% and 3% affects the minimum yield of B and Si, respectively. The Si yield is typical of a free-of-defects single crystal and the B yield closely follows the Si yield as expected for substitutional impurities. We estimated that ~95% of B is substitutional located (before proton irra-

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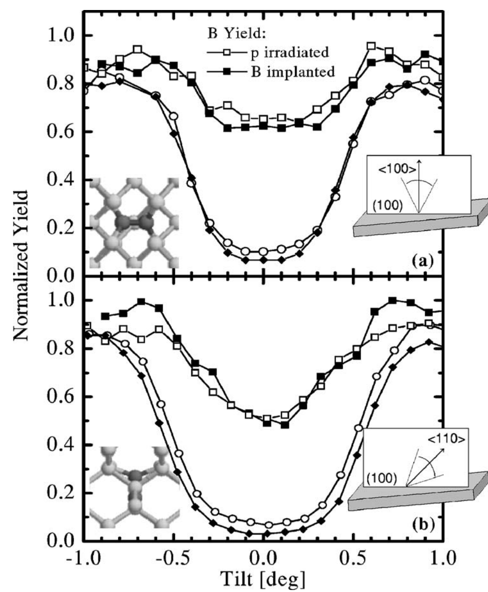


FIG. 1. Angular scans for (a) ⟨100⟩ and (b) ⟨110⟩ axes along the (100) plane: Normalized Si yield (♦); normalized B yield of proton irradiated samples (□); normalized B yield in B-implanted sample (■). For comparison, the normalized B yield in a B-doped Si before irradiation is shown by empty circles (○). The projections of B–B (dark grey) ⟨100⟩ split are shown in the insets.

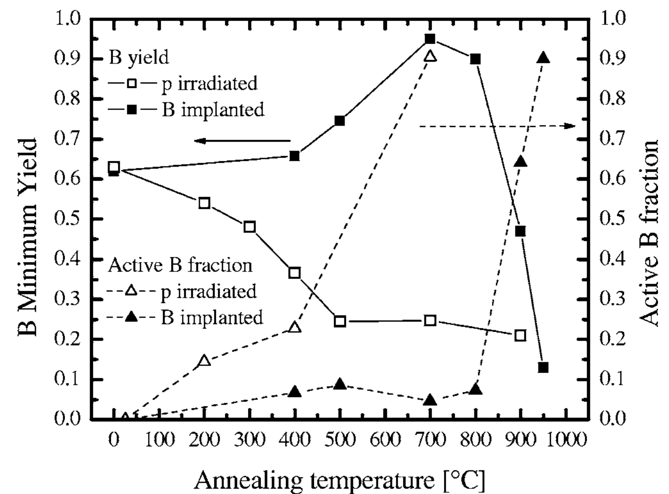


FIG. 2. Normalized yield (squares) measured along the ⟨100⟩ axis and electrical activation (triangles) vs the annealing temperature for proton irradiated ($1\times10^{17}$ $H^+/cm^2$) samples (empty symbols) and B-implanted samples (filled symbols). Each annealing step is 45 min.

diation) in agreement with the carrier concentration determined by means of the van der Pauw and Hall effect techniques (Hall scattering factor $r_H=0.75$).[16]

In proton irradiated samples, the B $\chi_{\min}$ is 65% and 50% along the ⟨100⟩ and ⟨110⟩ axes, respectively, indicating that B atoms have been displaced from substitutional sites. The $\chi_{\mathrm{Si}}$ in irradiated samples (not shown) is identical to that of an unirradiated crystal, indicating that the Si lattice is not affected by the *p* irradiation at least within the channelling sensitivity. The half-width[15] of the B angular scan is $\Psi_{1/2}(\mathrm{B})=0.39°$ for ⟨110⟩ scan, smaller than that of Si[$\Psi_{1/2}(\mathrm{Si})=0.47°$], unlike the ⟨100⟩ scan in which $\Psi_{1/2}(\mathrm{B})\approx\Psi_{1/2}(\mathrm{Si})=0.43°$. This means that in these samples, the displaced B is not randomly located since one would expect the same angular scan regardless of the chosen axis in that case. Moreover, the features of the angular scans indicated that part of the B atoms undergo large displacement toward the center of the ⟨100⟩ axis and small displacement along the ⟨110⟩. The symmetry of the displaced B could be an indication that the complex or defect involves a very limited number of B atoms, since it is likely that in large B-Is clusters, the several possible configurations will generate a B random signal in channelling analyses. Taking into account the configuration of the small B-Is clusters proposed by several groups,[9,17] our data support the formation of a ⟨100⟩ split $B_2I$ complex, similar to the one drawn[8] in the insets of Fig. 1. We cannot exclude the contribution to the measured yield of other $B_2I_x$ ($x>1$) complexes.

The angular scans on the B-implanted sample are also shown (full squares) in Fig. 1. They are identical to those recorded on proton irradiated samples, indicating the same B location in the two samples. The Si $\chi_{\min}$ (0.1) is slightly higher than that of the unimplanted sample, and the angular half-width ($\Psi_{1/2}$) remains unchanged. It must be pointed out that it is practically impossible to obtain the same collection of angular scans along the two ⟨100⟩ and ⟨110⟩ channels with two different lattice locations of B atoms in the Si crystal.[15,18] Thus, channelling analyses indicate that the same kind of B complex is formed any time that an excess of Is is produced although different scenarios compete in proton irradiated and B implanted samples. In fact, we have calculated (by SRIM simulation)[14] that $\sim3\times10^{16}$ $\mathrm{Si/cm^2}$ are displaced in the doped layer by the 650 keV $H^+$ ions at a fluence of $1\times10^{17}$ $H^+/cm^2$, and that the probability of direct knock-on of B is negligible. So in the proton irradiated sample the ratio Is/B is ~10 and to be compared with 500 in the 50 keV $B^+$ implantation. Although these are huge difference, the B atoms appear to be similarly displaced.

We have shown[13] that in proton-irradiated samples, the fraction of clustered B increases continuously with the $H^+$ fluence (with Is fluence) until B is completely clustered and stable upon further irradiation. In B-implanted samples, we could imagine that some mobile B-Is pairs are formed in the collision cascade and, even in a dynamical situation in which interaction with other Is can occur, they will last until the B–B pairs are formed.

We investigated the evolution of the B complex after isochronal annealing (45 min, in $N_2$) in the temperature range of 200–950 °C for both *p*-irradiated and implanted samples. The minimum yield $\chi_{\mathrm{B}}$ for proton beam impinging along the ⟨100⟩ axis is shown in Fig. 2. The trend of the B lattice location evolves in the opposite way. In fact, the $\chi_{\mathrm{B}}$ of the *p*-irradiated samples monotonically decreases as the temperature increases, indicating a progressive dissolution of the B complexes; at T higher than 500 °C a consistent fraction of B is substitutional and the minimum $\chi_{\mathrm{B}}$ along the ⟨110⟩ and ⟨100⟩ axes coincides. The location of B in the substitutional site at a low temperature is also supported by measurements of the carrier concentration. B was completely inactive after irradiation, after 200 °C annealing a ~15% of B is active, and electrical activation is almost complete after 500 °C annealing. Therefore the B–B pairs dissolve at relatively low temperature and the electrical activation of B requires a limited thermal budget.

In the B-implanted sample, the minimum $\chi_{\mathrm{B}}$ increases instead after annealing up to 700 °C, and it suddenly drops at higher temperatures reaching a value of 0.1 after 950 °C

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annealing. The carrier concentration measurements indicated that only 10% of the implanted B is active up to 800 °C, and the total activation is achieved after annealing at 950 °C, in agreement with the B lattice location. Therefore, in B-implanted sample we have two regimes: at low temperatures, the B lattice location evolves toward a nearly random distribution up to 700 °C; at higher temperatures, a quick recovery of B in substitutional sites occurs. The thermal evolution of the B complex is different in the two sets of samples. This difference might be attributed to the interaction of B complex with the residual defects. In the proton-irradiated samples, the B complex evolves in a nearly free-of-defects matrix since the density of point defects produced by the $H^+$ beam is quite low, as also indicated by the channelling yield. In the B-implanted sample, a large amount of damage is left in the layer: channelling analyses using 2.0 MeV $He^+$ beam showed a disorder peak due to direct scattering from point defects corresponding to $\sim 10^{17}$ displaced $Si/cm^2$. The peak area decreases as the annealing temperature increases, and no defects have been detected after annealing at 700 °C. Many authors[3,19,20] have shown that implantation-induced damage evolves during annealing, sustaining an Is supersaturation up to 800 °C. We believe that the increase of the minimum $\chi_B$ is indicative of the formation of large B-Is clusters (due to excess of Is), and B atoms in the clusters appear randomly displaced in channelling analyses. Therefore, the initial B–B pair upon annealing at a low temperature dissolves or grows into large clusters trapping Is depending on the concentration of Is. This is in agreement with the finding of Pelaz *et al.*[21] who predicted the B clusters growth if an external Is supersaturation holds, otherwise B clusters dissolve.

In conclusion, we have shown that a well-defined stable B complex, involving probably two B atoms, is formed at RT in the presence of a supersaturation of Is. At a higher temperature, this complex evolves into large B clusters if a substantial Is supersaturation is present or dissolves (at temperature ~500 °C) if no excess of Is exists. The thermal budget necessary to activate B depends on the cluster size, and it is significantly higher when B is bonded in larger B-Is clusters.

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