Room-temperature boron displacement in crystalline silicon induced by proton irradiation

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The effect induced by proton irradiation on B-doped crystalline Si at room temperature is investigated in detail. The displacement of B atoms out of substitutional lattice sites is shown to be induced at room temperature by proton irradiation at energies ranging between 300 and 1300 keV. This phenomenon was studied by means of channeling and nuclear reaction analysis techniques using the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction at 650 keV proton energy. For all the irradiation energies used, the fraction of displaced B atoms increases exponentially with proton irradiation fluence until saturation occurs. The B displacement rate strongly increases by decreasing the irradiation energy. We show that B off-lattice displacement is not due to a direct interaction of the proton beam with B atoms, but to the Si self-interstitials (I_{Si}) generated in the lattice by the irradiating beam. The displacement results from the formation of a mobile B-I_{Si} pair when a I_{Si} is trapped by a substitutional B. The measured damage rate has been interpreted in terms of the I_{Si}-B substitutional trapping probability and the resulting cross section at room temperature is $(1.00\pm0.05)\times10^{-16}$ cm^2. [DOI: 10.1063/1.1868874]

Boron incorporation in crystalline Si represents one of the most efficient way to *p*-type dope the semiconductor in microelectronic technology nowadays. Indeed, obtaining and maintaining a good electrical activation of B is a crucial key in fabricating high-level, long-time-duration Si-based devices. On this basis, the interaction between B atoms and intrinsic point defects in Si, such as vacancy or self-interstitial (I_{Si}), constitutes a charming issue in fundamental research as well as a strategic challenge for technological reasons, since it determines the dopant diffusion, its electrical activation and clustering.[1–9] It is well known that electrically active B atoms are substitutional in the Si lattice, so that the nuclear reaction analysis (NRA) using the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction at fixed proton energy of 650 keV,[10–12] could be used to determine the fraction of activated B from measurements of the dopant site lattice location. Nonetheless, more than ten years ago, it was shown that ion-beam analysis could induce an off-lattice displacement for different dopants such as B (Refs. 13,14) Ga, Sb, and As (Ref. 15) in crystalline Si. The microscopic mechanism responsible for this process was not clarified, although there is evidence that dopant displacement induced by ion irradiation has a great impact on the electronic device manufacturing processes and on the analysis of materials for their development. In fact, from a device manufacturing perspective, irradiation-induced dopant displacement could be a strategic subject of research because every device application in space, such as satellite telecommunications, suffers from a persistent cosmic irradiation. On the other hand, ion-beam irradiation has been used in ultrashallow junction fabrication by tuning the vacancy/self-interstitial balance in the point defect engineering approach.[16] Therefore, an accurate knowledge of the physical mechanism underlying ion-beam irradiation and related damage is highly demanded.

We investigate here the B displacement during irradiation with a proton beam at room temperature. To this end, we irradiated the B-doped crystal with proton beams at different energies, while we measured the B off-lattice displacement. The B displacement rate and its dependence on the irradiation energy is studied in a coherent simple model that assumes an interaction between I_{Si} generated by the irradiating beam and B substitutional atoms. As a result, the B-I_{Si} interaction cross section at room temperature is evaluated.

A 400-nm-thick Si layer uniformly doped with a B concentration of 1×10^{20} at./cm^3 was grown by molecular-beam epitaxy (MBE) on an *n*-type (100) Si substrate. The base pressure of MBE chamber was 5×10^{-11} mbar, while the Si deposition rate was 1 Å/s and the substrate temperature during the growth was kept at 450 °C. Electrical measurements performed on the as-grown sample by means of the Van der Pauw technique gave a B active dose of about 4×10^{15} B/cm^2, meaning that almost all the incorporated B atoms are electrically active. Channeling analyses confirmed that 90% of B was substitutional in the lattice. The sample was cut in small pieces and mounted upon a four-movement (three-axis) goniometer in a standard scattering chamber with a pressure lower than 6×10^{-7} mbar. A 3.5 MeV Singletron accelerator (HVEE) was used to perform irradiation of the samples at room temperature, using H^+ beam with energies ranging from 325 to 1300 keV and fluences up to 4×10^{17} H^+/cm^2 at a fixed current of 50 nA. The beam spot was 1 mm^2, and the beam was incident at a random direction on the sample. Each irradiation was followed by *in situ* NRA-channeling measurements along the ⟨100⟩ axis, using the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction at E_p=650 keV. The crystalline quality of the Si lattice has been monitored by simultaneously detecting the backscattered protons through a dedicated detector. The proton fluence for each channeling analysis was 5×10^{15} H^+/cm^2, to avoid sample modification during analysis. The detector of the α particle has been covered by a 10 μm Mylar™ foil,[17] in order to detect the gen-

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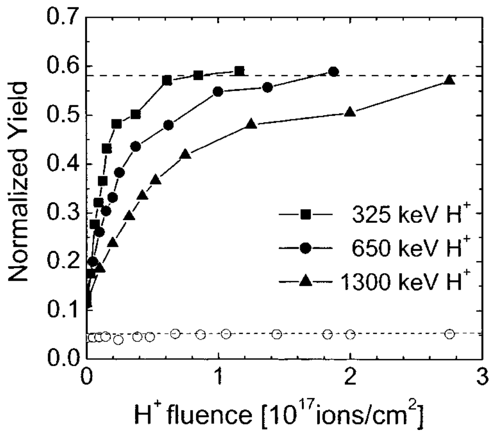

FIG. 1. ⟨100⟩ B normalized yields measured by NRA as a function of the irradiation fluence for different energies of the proton beam: 325 keV (■), 650 keV (●), and 1300 keV (▲). The minimum Si yield (○) is also reported.

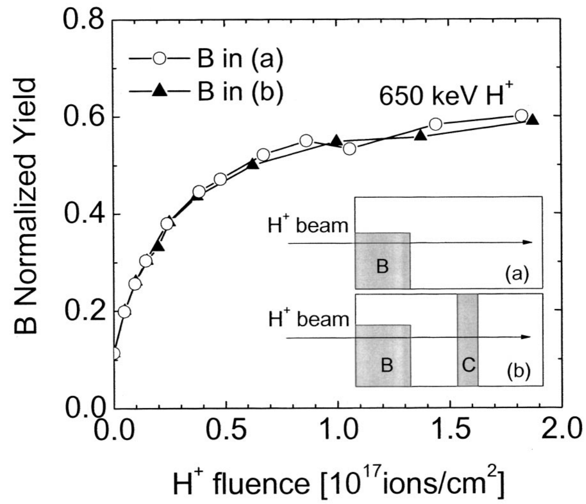

FIG. 2. ⟨100⟩ B normalized yields measured by NRA as a function of fluence for proton irradiation at 650 keV for the sample with the Si:C box (▲) and without (○). The (a) and (b) samples are schematically indicated in the inset.

erated α-particle energy spectrum suppressing all the backscattered protons. The energy integrated α particles yield is proportional to the B dose seen by the proton incident beam, and the normalized yield (χ_B) is proportional to the fraction of B displaced out of lattice. In Fig. 1, the channeling yield as a function of the H^+ fluence is reported for three different irradiation energies (325, 650, and 1300 keV). The silicon minimum yield, measured just below the surface peak after irradiations at a proton energy of 1300 keV, is also shown. The relative experimental error on a single measurement is lower than 5%. An increase of χ_B with the irradiation fluence, is evident although the Si minimum yield remains constant. The χ_B curves increases exponentially until they reaches saturation. This result implies that the proton irradiation induces at room temperature a selective displacement of B atoms from substitutional positions. On the other hand, no evidence of Si displacement is observed, even at the highest proton fluences.

We observe that all the χ_B curves start at the same initial χ_B value (χ_0) and obtain, regardless of the irradiation energy, about the same saturation value (χ_F), even if the damaging rate strongly depends on the irradiation energy. The χ_0 value (~0.1) is related to the nonsubstitutional B fraction in the as-grown sample, in agreement with the electrical measurement, while the saturation value (~0.6), lower than unity, indicates that not all the B atoms are displaced from the substitutional site. Moreover, the damage rate decreases with increasing the irradiation energy, indicating that the B displacement is strongly correlated not only to the total irradiating fluence, but also to the energy deposited by the irradiating beam.

In order to explain the B displacement induced by the H^+ beam, we could assume a direct interaction between the H^+ beam and the B atom or, alternatively, an indirect effect related to the beam energy loss. However, the probability of a direct interaction B-H^+ is negligible. In fact, assuming Coulomb interaction and a B displacement energy of the same order of the Si displacement (~15 eV),[18] it is possible to roughly estimate the ratio between the H^+-induced B displacements versus the Si ones, as follows: $P_{H^+\text{-}B}/P_{H^+\text{-}Si} \propto (C_B/C_{Si})(Z_B/Z_{Si})^2 \approx 2.6\times10^{-4}$, where C_B and C_{Si} are the atomic densities for boron and silicon, respectively. Thus, a fluence of $\sim5\times10^{16}$ H^+/cm^2 at 650 keV displaces approximately 3.8×10^{20} Si/cm^3 (calculated by TRIM code simulations[19]) so that 1×10^{17} B/cm^3 are displaced. Thus, the probability of a direct B displacement is negligible in this experiment.

Thus, an indirect effect related to the beam interaction with the Si matrix, through elastic or anelastic energy loss, has to be invoked.

Earlier work from Smulder and Swanson[13,14] demonstrated that no B off-lattice displacement occurs at very low temperature. In fact, they did not detect any B displacement after irradiation at 35 K with a 700 keV H beam at a dose of 4×10^{16} H^+/cm^{-2}, while a strong B displacement was observed after the sample thermalization at RT. Therefore, the B displacement did not occur during the irradiation but after it, so that it cannot be due to the anelastic energy loss of the beam.

On the other hand, it is well known that the elastic energy loss of the beam produces point defects along the ion path. The highest I_{Si} concentration is generated at a depth close to the projected range. It is known that I_{Si} can diffuse for several micrometers at RT,[20] so it could be possible that B off-lattice displacement is due to interactions with I_{Si} generated along the ion track that reach the B-doped region forming a mobile B-I_{Si} couple.[4–7] To disentangle the contribution of I_{Si} generated in the B-doped region from that due to I_{Si} generated along the ion track during B displacement process, a similar B-doped sample was grown by MBE containing also a $Si_{1-y}C_y$ alloy box (thickness of 100 nm, $y\sim0.01$) located at 100 nm below the B-doped layer, as schematically depicted in Fig. 2. In fact, it has been demonstrated by several experiments[1,16] that substitutional C in Si is able to trap I_{Si} even at RT. We expect therefore variation in the damage rate if I_{Si} produced deeper in the sample contribute to the displacement. This new sample, with fully substitutional C, was irradiated and analyzed in the same manner as the previous one, and the two χ_B curves relative to sample without (a) and with C (b) are plotted against the irradiation fluence in Fig. 2, for the 650 keV H^+ irradiation. It is noteworthy that no difference appears, either for this irradiation energy or for the others (not shown). This clearly demon-

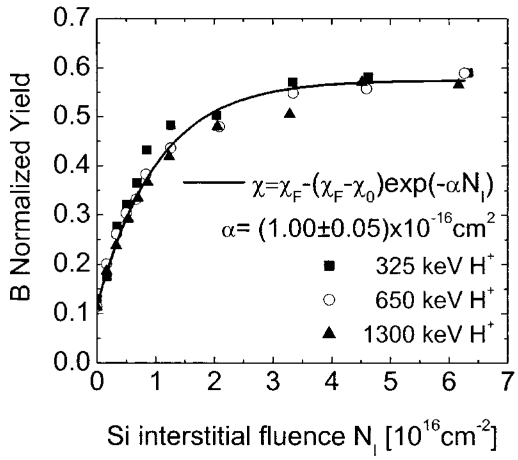

FIG. 3. ⟨100⟩ normalized yields plotted as a function of the Si self-interstitial fluence generated by the passing proton beam [325 keV (■), 650 keV (○), and 1300 keV (▲)]. The solid line is the fit of the data using a B-I_{Si} interaction cross section $\alpha=(1.00\pm0.05)\times10^{-16}$ cm^2.

strates that the B displacement does not depend on I_{Si} coming from the end-of-range region, but it is induced by the interaction with I_{Si} generated within the B-doped layer.

The I_{Si} number generated by a single ion along its track in a 400-nm-thick Si layer was calculated by TRIM simulation resulting in 0.54, 0.33, and 0.16 I_{Si}/ion for the selected energies of 325, 650, and 1300 keV, respectively. The curves of Fig. 1 have been replotted in Fig. 3 as a function of the I_{Si} fluence generated by the proton beam in the doped region, and they collapse in a unique exponential damage curve, which confirms that the B displacement is determined by the excess of I_{Si}. The off-lattice displacement path could be the following: (a) trapping of I_{Si} by B_s; (b) RT migration of the mobile B-I_{Si} couple; (c) formation of stable, not mobile, B complex. The first step is energetically favored since the B-I_{Si} couple formation has a binding energy of 0.90 eV,[5] while the RT migration of B has been recently evidenced.[21] Several molecular dynamics simulations and first-principles studies of the energetics[4,6] have indicated that the lowest energy configuration is a B-B pair oriented along the ⟨100⟩ axis. Although a simple quantitative correlation between the B-B pair formation and the measured χ_B is not possible, one can reasonably deduce that the χ_B saturation at a value lower than the unity depends on this nontrivial defect configuration. In fact, a B-B pair oriented along the ⟨100⟩ axis always presents a fraction of B atoms shadowed by Si substitutional atoms, in agreement with our experimental χ_B saturation value.

If we assume that the B displacement rate is limited by I_{Si} trapping process, we expect that the rate of displaced B (C_{Disp}) is proportional to the residual substitutional B (C_{Sub}) and to the excess of I_{Si} generated by the beam (G_I), as

$$\frac{dC_{Disp}}{dt}=\alpha G_I C_{Sub}, \tag{1}$$

where α represents the B-I_{Si} interaction cross section.

By solving this equation, we obtain

$$\chi=\chi_F-(\chi_F-\chi_0)e^{-\alpha N_I}, \tag{2}$$

in which N_I is the I_{Si} fluence. The fit of the data, shown in Fig. 3 with a continuous line, has been obtained for $\alpha=(1.00\pm0.05)\times10^{-16}$ cm^2. In other words, we can state that, in our experimental conditions, the substitutional B atom has a capture radius for the generated I_{Si} of about 0.1 nm. It is worth noting that, given the starting B concentration (1×10^{20} at./cm^3), the average distance L between two substitutional B atoms in the matrix is of the order of 2 nm; thus, the probability of a B-B pair formation is reasonably high. On this basis, a lower limit for the effective B diffusion coefficient D could be roughly estimated as follows: $D=L^2/t=5\times10^{-15}$ cm^2 s^{-1}, assuming $t\sim10$ s (typical duration of the irradiation step), which agrees with existing literature data.[21]

In conclusion, we studied the displacement of B atoms out of crystalline sites induced at room temperature by proton irradiations at energies ranging between 300 and 1300 keV. We found that the displaced B fraction raises exponentially with the total irradiated fluence until a saturation value, lower than unity, is reached. We demonstrated that B off-lattice displacement rate is determined by the excess of I_{Si} which causes the formation of highly mobile B-I_{Si} pairs. A simple model has been proposed, and, on this basis, the experimental data have been fitted and the B-I_{Si} interaction cross section at room temperature, has been determined.

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