Mechanism of Boron Diffusion in Amorphous Silicon

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We have elucidated the mechanism for B migration in the amorphous (*a*-) Si network. B diffusivity in *a*-Si is much higher than in crystalline Si; it is transient and increases with B concentration up to 2×10^{20} B/cm^3. At higher density, B atoms in *a*-Si quickly precipitate. B diffusion is indirect, mediated by dangling bonds (DB) present in *a*-Si. The density of DB is enhanced by B accommodation in the *a*-Si network and decreases because of *a*-Si relaxation. Accurate data simulations allow one to extract the DB diffusivity, whose activation energy is 2.6 eV. Implications of these results are discussed.

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Boron is the main *p*-type dopant in silicon. The understanding and control of its diffusion properties represent a crucial issue for the continuous scaling down of microelectronic devices. In addition, B in Si represents a proper model system, as its fundamental atomistic processes can be investigated in a material prepared with unprecedented purity and accuracy. In fact, B diffusion in crystalline (*c*-) Si has been the subject of intensive investigation for over 30 years [1–3]. Nevertheless, only very recently the fundamental atomistic mechanisms have been fully assessed in *c*-Si, showing that B interacts with Si self-interstitials (I), in their neutral or doubly positively charged state, and with free charges, to form a mobile BI complex [4].

In the fabrication of electronic devices B is typically introduced in *c*-Si by ion implantation. This is a quite dramatic process, breaking several bonds and producing a large supersaturation of Is, well above their equilibrium value. The subsequent annealing, used to restore the crystal lattice and activate the dopant, produces a transient enhanced diffusion (TED) of B, until the I supersaturation is exhausted [5]. To separate dopants from damage and to reduce ion channeling and TED effects, B is implanted in the amorphous (*a*-) phase and *a*-Si is then recrystallized by solid phase epitaxy (SPE) [6].

Amorphous Si is a well-defined metastable thermodynamical phase, in which fourfold-coordinated Si atoms form an ideal continuous random network where short range order is maintained while long range order is lost. It has been shown that defects in the *a*-Si network are very different from those in the crystalline phase, and they are represented by dangling bonds (DB), i.e., threefold-coordinated Si atoms, and floating bonds (FB), i.e., fivefold-coordinated atoms [7–9]. Once prepared by ion implantation, *a*-Si is full of defects (unrelaxed state) and upon annealing it continuously modifies through defect annihilation and bond rearrangement into a relaxed state [10]. This structural relaxation process has been studied in details around 20 years ago by calorimetry, Raman spectroscopy, and optical and conductivity measurements [10–12], showing also the role of defects in *a*-Si as efficient trap centers for the metal impurities [13].

Boron diffusion in *a*-Si represents a fascinating process in a network with properties different from *c*-Si and continuously changing upon annealing. Comprehension and control of this phenomenon is also relevant for technological applications since B is often introduced in *a*-Si prior to epitaxy, and changes in the B profiles before regrowth will significantly affect the final electrical properties of the devices [14]. In spite of this, B diffusion in *a*-Si has been totally neglected until only very recently when initial evidence of B diffusion [15,16] and clustering [17] in *a*-Si have been provided.

In this Letter we conducted accurate experiments on B diffusion and clustering in *a*-Si by using sharp doped layers grown by molecular beam epitaxy (MBE). The mechanism for B diffusion is modeled to be mediated by the defects present in the *a*-Si network whose concentration is temperature and time dependent and is enhanced by the presence of B itself. B diffusivity is observed to be several orders of magnitude higher than its crystalline counterpart, while defect diffusion in the amorphous network is found to occur with a single activation energy of around 2.6 eV. This value is very close to the activation energy for SPE, strongly suggesting that the same defect could be responsible for both processes.

A 350 nm thick Si layer was grown by MBE on top of a silicon on insulator (SOI) substrate. The layer contained two 20 nm thick B-doped regions at concentrations of 7×10^{19} and 8×10^{20} B/cm^3 (hereafter named as low- or high-B box, respectively), as drawn in the inset of Fig. 1. The MBE growth details were described elsewhere [18]. Later on, the sample was implanted at the liquid nitrogen temperature with Si$^-$ ions (4×10^{15} Si/cm^3 at 400 keV and 2×10^{15} Si/cm^3 at 20 keV) realizing a continuous amorphous layer from the surface down to about 1 μm, well below the oxide layer. Such a SiO_2 barrier stops the SPE

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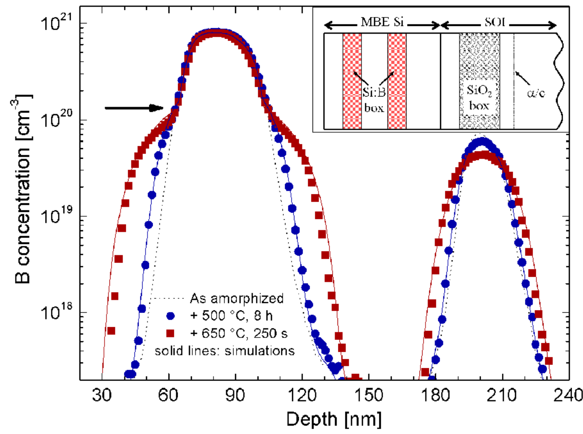

FIG. 1 (color online). B SIMS profiles in the as-amorphized sample (dotted line) and after annealing at 500 °C, 8 h (circles) or at 650 °C, 250 s (squares). Best fit results (solid lines) and sample drawing (inset) are also shown.

regrowth maintaining the B-doped region in the amorphous state for a relatively long time, up to the occurrence of the random nucleation and growth [19,20]. B profiles were measured by secondary ion mass spectrometry (SIMS) [21]. By joining the extremely high B concentration gradient with such an SOI approach, we studied, with very high accuracy and over more than three decades in the concentration values, the B diffusion in a-Si in the wide temperature range of 450–650 °C. In addition, the spacing between the B distribution and the sample surface prevents any dopant outgoing effect.

In Fig. 1 an overview of the main features of B diffusion is given. The symbols indicate the B diffused SIMS profiles after annealing at 500 °C, 8 h (circles) or 650 °C, 250 s (squares) performed on the as-amorphized sample (dotted line). Solid lines hereafter represent the simulated diffusion profiles based upon the model proposed later on. It is clear that B diffusion is much higher in a-Si than in c-Si, where the mean diffusion length after similar thermal budgets would be negligible (10^{-2}–10^{-3} nm [22]). Moreover, clustering of B atoms above $\sim(1\text{–}2)\times 10^{20}$ B/cm^3 is observed, as indicated by the kink in the high-B box profile (see the arrow). Such a kink has been noted at the same concentration as soon as B diffusion is detectable and up to the longest time used at all temperatures. This suggests that B precipitation in a-Si occurs through quick formation of a B complex, which is quite stable against dissolution, in agreement with our recent results [17] and theoretical predictions [23]. The observed B diffusion does not obey a standard Fick's law with constant and homogeneous diffusivity (D_B), since after annealing the concentration gradient significantly increases, opposite to what is expected, and both B boxes assume a "boxlike" shape with wide shoulders and narrow tails. As a first approximation, a B diffusivity univocally increasing with B concentration (n_B) can be assumed to account for the boxlike shape. Nonetheless, from Fig. 1 we see that for a fixed concentration the high-B box shows a larger diffusion than the low-B box, and thus a univocal relation between D_B and n_B cannot be found, as also simulation attempts demonstrated. Hence, diffusivity seems to feel the global amount of B present in the surroundings, being higher in the high-B box.

The observed diffusion has also a marked transient character. This is shown in Fig. 2 where the SIMS profiles of the high-B box as-amorphized (dotted lines), after 10 s (squares), 50 s (triangles), or 100 s (diamonds) at 650 °C are reported. SIMS data clearly indicate a B diffusivity that decreases with time, in agreement with Ref. [16]. During annealing, the a-Si relaxes reducing the defect density, and this could affect B diffusion, if mediated by such defects. Still, the relaxation at 650 °C is extinguished within 2 s [12] and the observed transient B diffusion has a quite larger time scale. As a counterproof, we de-relaxed a sample annealed at 650 °C, 50 s by implanting Ge ions [300 keV, 6×10^{13} cm^{-2}, corresponding to a 0.1 DPA (displacement per atom)]. This process raises up the defect density as in the unrelaxed state [12], not affecting the B profile. A further annealing at 650 °C, 50 s on such a de-relaxed sample gives a diffusion (stars) not distinguishable from the 650 °C, 100 s sample, saying that the defect annihilation during the relaxation does not have a significant role on the overall B diffusion.

A rough estimate of the B diffusivity can be extracted by the low-B box, by calculating the squared variance (σ^2) of the diffused B distribution with respect to the as-amorphized case (${\sigma^2}_0$), divided by twice the annealing time (t): $D_{\mathrm{eff}} = (\sigma^2 - {\sigma^2}_0)/2t$. This calculated B effective diffusivity, reported in Fig. 3 (circles) for all the annealing processes, should return a constant value in the case of Fick-like behavior. In this case, it confirms the non-Fick-like trend and allows one to quantify the transient behavior of diffusion. An evident decrease of D_{eff} is observed in all

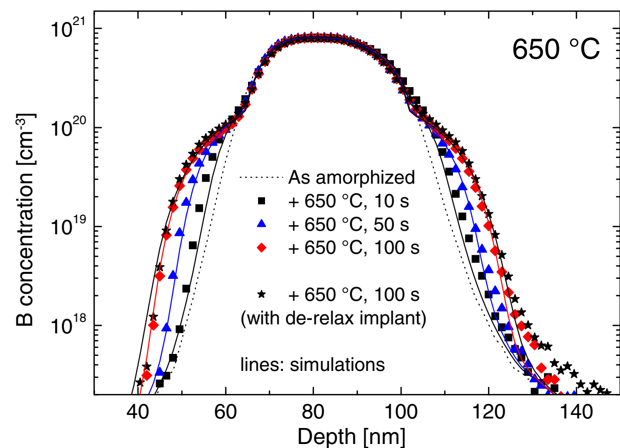

FIG. 2 (color online). B SIMS profile of the high B box in the as-amorphized sample (dotted line) and after annealing at 650 °C, for 10 s (squares), 50 s (triangles), or 100 s (diamonds). A de-relax Ge implantation (300 keV, 6×10^{13} cm^{-2}) was performed in one case (stars) in the middle of the 100 s annealing. Best fit results (solid lines) are shown.

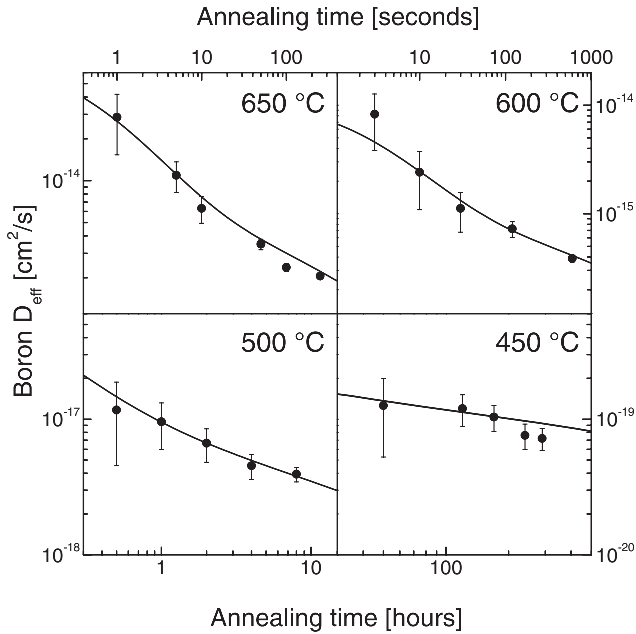

FIG. 3. Time evolution of the effective B diffusivity extracted from the low B box for all the annealing processes. Simulations of D_{eff} (solid lines) are shown.

the cases within a quite wide time scale. It is worthwhile to note that, at all temperatures, the a-Si relaxation time reported in literature [12] is much shorter (10 to 100 times) than the observed diffusivity transient.

Given such a scenario, a predictive formula or just a simple activation energy for B diffusion in a-Si requires a detailed comprehension of the mechanism underlying the B migration. This phenomenon has a not univocal concentration dependence and it is transient. Moreover, the excess of point defects caused by ion implantation appears not to have significant effects on B diffusion and, further, cannot explain the concentration dependent diffusion feature. Still, Muller *et al.* [24] observed that in thermally relaxed a-Si, impurities are usually incorporated within a threefold coordination site and a large kinetic barrier exists against the conversion to the tetrahedral site. Thus, B atom, fourfold-coordinated in c-Si, upon amorphization is accommodated into a threefold-coordinated site, breaking one Si-B bond and generating an excess of DB in the network. Muller *et al.* [24] proposed that these DB are saturated by H in hydrogenated a-Si; in pure material, however, we propose that the DB excess distributes into the network. We indeed observed, by Cu decoration technique [25], that B-doped a-Si layers are richer in dangling bonds than undoped matrices, both just after amorphization and during subsequent annealing (not shown). In the following, such a DB excess is exploited to model the collected data by assuming that B migration in a-Si occurs via an indirect mechanism. Boron jumps between adjacent threefold coordination sites through the temporary restoring of a metastable, fourfold-coordinated B, by the capture and release of one DB.

Based on these considerations, the B migration in a-Si has been satisfactorily simulated (solid lines in Figs. 1–3) within the following rate equation model:

$$\frac{\partial n_{\mathrm{B}}}{\partial t} = \alpha \frac{\partial^2 (n_{\mathrm{B}} n_d)}{\partial x^2}, \quad (1)$$

$$\frac{\partial n_d}{\partial t} = \alpha \frac{\partial^2}{\partial x^2}(n_{\mathrm{B}} n_d) + D_d \frac{\partial^2 n_d}{\partial x^2} - 4\pi a (D_d + D_f) n_d n_f, \quad (2)$$

$$\frac{\partial n_f}{\partial t} = D_f \frac{\partial^2 n_f}{\partial x^2} - 4\pi a (D_d + D_f) n_d n_f, \quad (3)$$

where n and D are, respectively, the density and diffusivity of the subscript species (B for Boron, d for DB, f for FB). Equation (1) describes the time evolution of B concentration under the hypothesis that the mass flux of B is proportional (by the constant α) to the encounter probability of DB and B. Then, Eq. (2) describes the time evolution of DB, considering three terms: (i) the B-DB coupled diffusion term, (ii) the Fick-like diffusion term, and (iii) the annihilation term (supposed through a DB-FB meeting), whose capture radius (a) is assumed equal to the second nearest neighborhood distance (0.385 nm). Time evolution of FB density [Eq. (3)] comprises the last two terms alone. The starting value of n_{B} is given by the chemical profile below a threshold density (n_c) for the quick B clustering. The starting n_d and n_f profiles have a common homogeneous component n_0, representing the DB and FB density after amorphization. n_d has an additional contribution due to the B effect that is proportional (by a coefficient γ) to the starting, unclustered B concentration. Free, temperature dependent parameters of the model are n_c, α, and D_d (reasonably fixed equal to D_f), while n_0 and γ, being relative to the initial conditions of the a-Si matrix, are considered temperature independent and are simultaneously fitted for all the temperatures. Fitting more than 20 profiles, containing both the B boxes, allowed one to fix all the free parameters, correctly reproducing the data (solid lines in Figs. 1–3). In Fig. 3 the broadening of the low-B box is simulated, and D_{eff} is calculated (solid lines). n_0 resulted to be about 1.8 at. %, in agreement with theoretical calculations [8,9] and experimental data [12]. γ resulted to be 1.0 ± 0.5, confirming that one excess DB is generated by one unclustered B atom in amorphized Si. n_c was found to be temperature independent, valuing about 2.2×10^{20} B/cm^3. Finally, the Arrhenius plot for the fit results of α and D_d are shown in Fig. 4.

The proposed model explains both the peculiar concentration dependence and the transient behavior of B diffusion. The non-Fick-like diffusion is explained considering that the higher the B density, the more DB are present, promoting a faster B diffusion. Further, since DB diffusion is quicker than the B one (see Fig. 4), the DB profile broadening precedes the B one, producing a larger and lower DB profile. The excess of DB is higher in the higher

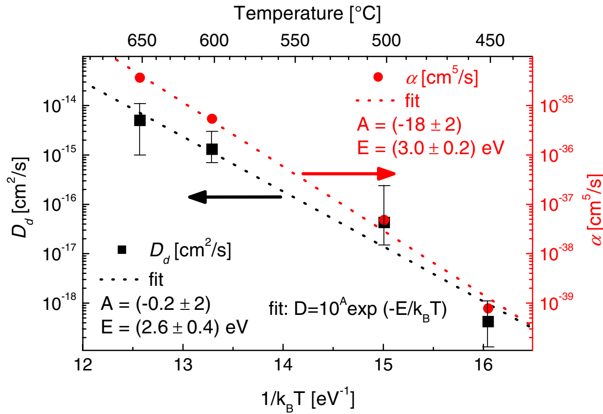

FIG. 4 (color online). Arrhenius plots for the diffusivities of dangling bond (D_d, left axis) and of B per unit dangling bond density (α, right axis). Arrhenius fits (dotted lines) and results are shown.

doped regions, accounting for the wider tail broadening in the high-B box. On the other hand, the transient diffusion is related to two distinct causes for DB density reduction. The first one is the DB-FB annihilation (whose rate is in agreement with literature data [12]), which quickly reduces the B diffusivity in the early stages of annealing. The second cause is the progressive reduction of DB density due to DB diffusion itself. Both phenomena are regulated by D_d but have quite different time scales. The annihilation needs the diffusion of DB for a small distance before meeting FB (few nanometers). The second one requests DB diffusion over the width of the box (tens of nanometers). Moreover, because of the very fast annihilation rate, the B diffusion occurring during the first transient is quite limited, as shown by the de-relax experiment correctly reproduced by the model (Fig. 2). Both DB and B diffusivities span over 6 orders of magnitude and show activation energies of 2.6 ± 0.4 and 3.0 ± 0.2 eV, respectively (Fig. 4). These values are very similar, meaning that the B migration barrier is approximately fixed by the DB diffusion barrier. It is noteworthy that SPE has a similar activation energy (2.7–2.8 eV [19]), and it is enhanced by doping. This could be not a trivial accident, since the *a*-*c* interface motion during SPE could be limited by the DB diffusion too, whose density should be enhanced by the presence of dopants.

In conclusion, the migration of B atoms in *a*-Si has been investigated and modeled to occur through the interaction with the dangling bonds of the matrix. The diffusion of B is shown to be peculiarly transient and B concentration dependent. Immobile B clusters form in *a*-Si at concentration exceeding 2×10^{20} B/cm^3, with approximately no time evolution for either formation or dissolution. B diffusion is shown to be mediated by the dangling bonds, similar to the *c*-Si case with the *I* interaction. Since B is incorporated as threefold-coordinated within amorphized Si, the DB density is locally enhanced. This effect, together with the DB diffusion, accounts for the observed B diffusion features and allows one to fully simulate all the experimental profiles. The diffusivity of dangling bonds in *a*-Si shows an activation energy of 2.6 eV, limiting the B migration without further significant kinetic barriers.

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