

## Room Temperature Migration of Boron in Crystalline Silicon

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(Received 7 May 2004; published 30 July 2004)

We demonstrate that substitutional  $B$  in silicon can migrate even at room temperature and below, stimulated by a high interstitial flux. Once mobile  $B$  is formed, it migrates for long distances with a diffusivity  $>5 \times 10^{-13}$  cm<sup>2</sup>/s, until it assumes an immobile configuration with a migration length independent of the temperature. This phenomenon is present during secondary ion mass spectrometry (SIMS) analyses of  $B$  profiles, altering the profile during the analysis itself. These results shed new light on all the data based on SIMS analyses and reported in literature in the last decades.

DOI: 10.1103/PhysRevLett.93.055901

PACS numbers: 66.30.Jt, 68.49.Sf, 68.55.Ln

Despite the enormous scientific efforts spent over the last decades, the present knowledge on the point defects and dopant diffusion and interaction in Si between themselves and with substrate impurities still has many important open points, from both an experimental and a theoretical point of view. In particular, understanding the behavior of the above phenomena in the room temperature (RT) regime is extremely challenging, and very few experiments have been reported so far. It has been recognized, by performing experiments on the electrical deactivation of dopants, that the silicon self-interstitial ( $I$ ) defects produced by ion implantation through the interstitial-vacancy ( $I$ - $V$ ) Frenkel pairs generation mechanism, can migrate even at RT for several microns [1] with a diffusion coefficient greater than  $1 \times 10^{-7}$  cm<sup>2</sup>/s [2]. The penetration length is limited by the trapping either by dopants, which as a result are brought in a nonelectrically active configuration [1,3], or by other impurities such as C [1].

Even less knowledge is available on dopant diffusion at RT. The most studied dopant, in all the temperature regimes, is boron, as it is the most used  $p$ -type dopant for devices. At temperatures above 450 °C it is well recognized, both experimentally [4–6] and theoretically [7–11], that the diffusion of electrically active  $B$ , i.e., substitutional  $B$  ( $B_s$ ), proceeds via an interstitial(cy) mechanism through the following reactions:



In order to migrate,  $B_s$  has to interact with an  $I$  through reaction (1), by forming a mobile boron species,  $B_m$ , which can then migrate for long distances before returning to a substitutional position through the inverse reaction (2). By performing a detailed analysis of the diffusion of very thin  $B$  doped layers (deltas) in silicon, Cowern *et al.* [5] estimated experimentally that the frequency of reaction (1)  $g$ , i.e., the  $B_m$  generation rate, is mostly limited by the availability of  $I$ 's, with a low

reaction barrier  $<0.2$  eV [5,6]. The migration length  $\lambda$  of  $B_m$ , before the reaction (2) occurs, was found to be 10 nm at 625 °C, and to decrease by increasing the temperature with an activation energy of  $0.4 \pm 0.2$  eV [5,6].

At RT, it is still controversial if reaction (1) remains a viable path for  $B_s$  diffusion. No limitations come from the diffusion of  $I$ 's, which are highly mobile at RT. Moreover,  $B_m$  has been observed to diffuse at RT for long distances in experiments where  $B_m$  was generated directly by ion implantation [2]. Concerning the energetics of reaction (1), recent calculations [8–11] have shown that it should have a very small or even zero [8] energy barrier, without any intermediate metastable complex. Therefore, even if the diffusivity of  $B_m$  is still unknown, substitutional  $B$  should in principle be able to diffuse even at RT, and for long distances. In spite of that, to our knowledge, no room temperature broadening of any substitutional  $B$  chemical profile has been reported in literature so far, even in conditions well out of equilibrium [6,12].

In this Letter we demonstrate that  $B_s$  can indeed migrate for long distances even at RT and below, if stimulated by a sufficiently high self-interstitial flux. The phenomenon occurs during the secondary ion mass spectrometry (SIMS) measurements of the chemical  $B$  profile. As it has never been considered in the past, and SIMS is the only known technique able to measure the chemical profile of boron, it probably explains why no RT diffusion of  $B_s$  has been experimentally observed up to now. We describe some of the phenomena involved in the RT  $B$  diffusion, and, for the first time, we measure a lower limit for the diffusion coefficient of the mobile species  $B_m$ .

In SIMS [13], an  $O_2^+$  beam with energy of a few keV is used to sputter the sample, and the secondary ions are extracted and counted as a function of the sputtering time. In the case of boron,  $B^+$  is detected, and its yield is proportional to the real  $B$  concentration at the corresponding eroded depth, which generally increases linearly with the sputtering time. The depth resolution in SIMS is usually assumed to be limited only by the ion

beam mixing produced by the sputtering beam, which is known to alter a very shallow layer [14]. The characteristic SIMS resolution function is therefore considered to be a Gaussian with single exponential trailing and leading tails with decay length of the same order of the mixing altered layer, i.e., only a few nm's [14]. Our findings demonstrate that SIMS analyses, due to RT long range migration phenomena of  $B$  induced by the sputtering beam, present major artifacts never considered before. These results shed new light on many past literature data, which need to be carefully revised on the basis of these new findings.

Crystalline silicon ( $c$ -Si) samples grown by molecular beam epitaxy (MBE) with substitutional  $B$  delta doping profiles were analyzed by a Cameca IMS-4f SIMS by using  $O_2^+$  ions with different beam energies and currents. Some of the samples were analyzed both before and after amorphization, and also at different temperatures, heating or cooling the sample during the analysis with a liquid nitrogen-thermo resistance temperature controlled stage fabricated on purpose. Figure 1(a) shows the SIMS profiles of a boron delta obtained from the same sample before and after amorphization performed by implanting at liquid nitrogen temperature  $250\text{ keV}$ ,  $3 \times 10^{15}\text{ cm}^{-2}$   $Si^-$  ions. Both measurements were done at RT with a  $3\text{ keV}$  beam with an erosion rate of  $1.6\text{ nm/s}$ . Unexpectedly, the delta measured in  $c$ -Si appears much more broadened than in amorphous-Si ( $a$ -Si): long tails are present on both sides of the delta. Similar tails are present in other measurements reported in literature, which led to several fundamental results on the physics of point defects and dopant diffusion [5,6,15]. It is clearly unbelievable that the amorphization implant could produce a shrinkage of the profile. Therefore, a strong  $B$  redistribution has occurred during the measurement in  $c$ -Si, not occurring in  $a$ -Si.

In Fig. 1(b) we have measured the same  $c$ -Si sample as in Fig. 1(a), using exactly the same measurement conditions except for the sample temperature, that was varied from  $+65^\circ\text{C}$  to  $-75^\circ\text{C}$ . Again unexpectedly, as no temperature dependence has been investigated so far for the SIMS measurements of  $B$  in silicon, the profiles differ significantly from one another. Long tails are present in the profiles obtained at the higher temperatures, while they reduce significantly by reducing the temperature. At  $-75^\circ\text{C}$  the tails are almost not present, and the profile resembles the ideal resolution function of SIMS, with single exponential leading and trailing edges except for small tails present at concentrations below  $10^{16}\text{ cm}^{-3}$ . At this low temperature the anomalous broadening is completely suppressed as an identical profile has been found already at  $-50^\circ\text{C}$  (not shown). Therefore, a long range, temperature dependent migration of boron occurs during the measurements in  $c$ -Si, not occurring below  $-50^\circ\text{C}$ . At  $-5^\circ\text{C}$  and above, the migration is qualitatively similar to the diffusion observed at higher temperatures in nonequilibrium conditions [6].

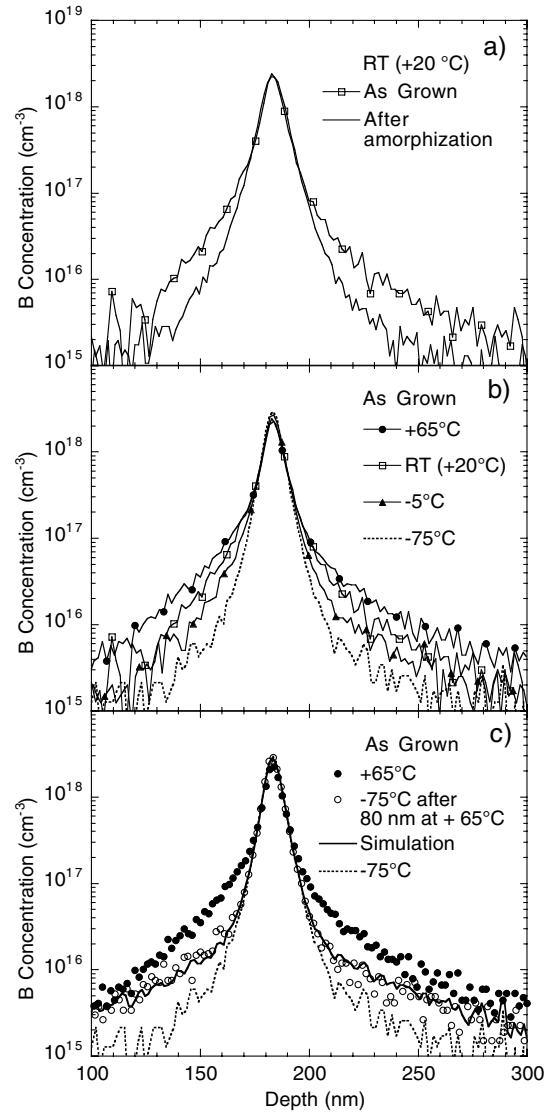


FIG. 1. B concentration profiles of a  $B$  delta grown by MBE in  $c$ -Si, measured by SIMS in different conditions: (a) at room temperature, before and after amorphization; (b) at different temperatures in crystalline silicon; (c) at  $-75^\circ\text{C}$  after sputtering at  $+65^\circ\text{C}$  for  $80\text{ nm}$ , compared to the measurements obtained entirely at  $-75^\circ\text{C}$  or  $+65^\circ\text{C}$ ; the simulation is derived from the model presented in Ref. [5]. See the text for more details.

We have estimated, by considering the temperature measurement uncertainties and the local sample heating due to the sputtering beam, that the temperatures in Fig. 1(b) represent the temperature of the sample eroded zone within  $\pm 5^\circ\text{C}$ . In addition, we have observed exactly the same profiles as in Fig. 1(b) by repeating the measurements with a beam current a factor of 4 lower (not shown), i.e., with an erosion rate a factor of 4 lower. This definitely demonstrates that direct beam heating has no influence in the observed broadening. The last experiment tells us an additional important point. The measurement time has no role at all. Therefore, the phenomena we are observing are not diffusion limited, while they have to be

limited by trapping or reconfiguration mechanisms such as reaction (2).

Figures 1(a) and 1(b) convincingly demonstrate that  $B_s$  is able to diffuse for long distances even at RT and below in *c*-Si. Therefore, consistent with what is expected from theoretical results and previous experimental findings, at least the reaction (1) occurs at RT. In *a*-Si, trapping by the dangling bonds of the disordered material suppresses instead any long range migration phenomenon. In order to produce the observed huge diffusion in *c*-Si, a large amount of  $I$ 's has to take part to reaction (1). It has already been reported that ion implantation can inject  $I$ 's, which migrate very fast for long distances at RT [1]. In our experiment the  $O_2^+$  implantation doses used to sputter the sample are indeed enormous ( $\sim 1 \times 10^{18} \text{ cm}^{-2}$  for a single measurement). The  $I$ 's are able to escape only from the extreme tail of the collision cascade, i.e., where the beam produces dilute concentrations of  $I$ 's and  $V$ 's without the formation of immobile clusters or amorphous pockets, which may act as traps for the point defects [1]. Even if the defect injection during ion implantation at RT reaches saturation very quickly [1], in our experiment the erosion front advances with time exposing, as the measurement proceeds, new and defect-free material. Consequently, the amount of  $I$ 's injected can be significantly higher than in previous experiments [1,6,12]. Figure 1(b) suggests also that reaction (2) is quite unlikely at RT. In fact, by extrapolating the values reported in literature at temperatures greater than  $450^\circ\text{C}$ , the migration length  $\lambda$  is predicted to be several hundreds of microns at RT. The slope of the tails of the profiles is instead on the order of only about a few tens of nm's.

In order to clarify the above phenomena, we performed the following further experiment. We first sputtered our sample at  $+65^\circ\text{C}$  for only 80 nm. Then we stopped and completed the measurement at  $-75^\circ\text{C}$ . As we did not observe any significant migration at  $-75^\circ\text{C}$ , with the above two-step experiment we are sensitive only to the migration that the measurement may produce during the first 80 nm of sputtering at  $+65^\circ\text{C}$ . The result is shown in Fig. 1(c), compared to the profiles taken at  $+65^\circ\text{C}$  and  $-75^\circ\text{C}$  and already shown in Fig. 1(b). A significant  $B$  migration has already occurred while sputtering the first 80 nm, further confirming that a long range interaction of the sputtering beam with the boron delta occurs, mediated by  $I$ 's. We have then simulated the above diffusion by using the model proposed by Cowern *et al.* to describe the high temperature diffusion of  $B$  deltas [5], modified by assuming that  $B_m$  reaches an immobile configuration, rather than take part to reaction (2), with a migration length  $\lambda$ . The use of the above model is legitimated by the fact that both the surface and the ion beam induced collision cascades remain far from the diffusing delta during the high temperature step. We considered the profile obtained at  $-75^\circ\text{C}$  as a starting profile, and we fitted the profile obtained by the two-step measurement

with the  $B_m$  generation rate  $g$  and the  $B_m$  migration length  $\lambda$  as free parameters. A very good fit is obtained, as shown in Fig. 1(c). We have repeated the two-step experiment by setting the first step temperature at 0,  $+20$ , and  $+40^\circ\text{C}$  (not shown), obtaining simulation best fits of the same quality of the one reported in Fig. 1(c).

Figure 2 reports the values of  $\lambda$  and  $g$  obtained by the fits as a function of the reciprocal of the temperature.  $\lambda$  is clearly temperature independent, with a constant value of  $36 \pm 2 \text{ nm}$ . This further confirms that the inverse reaction (2), which is known to be a temperature dependent phenomenon [5,6], does not occur in our sample around RT [16]. The above athermal behavior suggests that the  $B_m$  is trapped by a defect or an impurity present in the lattice. It is possible to estimate the concentration of traps  $N_T$  needed to obtain  $\lambda = 36 \text{ nm}$ , by using the formula  $\lambda = 1/(4\pi a_T N_T)^{1/2}$  [17], where  $a_T$  is the effective capture radius. By assuming a reasonable value of  $a_T = 5 \text{ \AA}$ , we obtained  $N_T \approx 1 \times 10^{17} \text{ cm}^{-3}$ . The carbon and oxygen levels measured by SIMS in our sample ( $[C] \approx 1 \times 10^{17} \text{ cm}^{-3}$  and  $[O] \approx 1 \times 10^{18} \text{ cm}^{-3}$ ) are high enough to support the interaction of  $B_m$  with  $O_i$  or  $C_s$  by forming stable  $B_iO_i$  or  $B_iC_s$  complexes [18] as the principal trapping mechanisms (where the subscripts  $i$  and  $s$  stand for interstitial and substitutional positions, respectively).

The migration frequency  $g$  exhibits instead (Fig. 2) a clear exponential decrease with  $1/T$  with a thermal activation energy of  $\Delta E = 0.11 \pm 0.02 \text{ eV}$ . Such an activation energy could have two contributions  $\Delta E = \Delta E_{\text{injection}} + \Delta E_{\text{barrier}}$ , where  $\Delta E_{\text{injection}}$  comes from the injection of  $I$ 's by the sputtering beam, i.e., from the availability of  $I$ 's for reaction (1), which may change with temperature, and  $\Delta E_{\text{barrier}}$  is the energy barrier for the reaction (1). Unfortunately, it is not possible with our experiment to discriminate between the two phenomena.

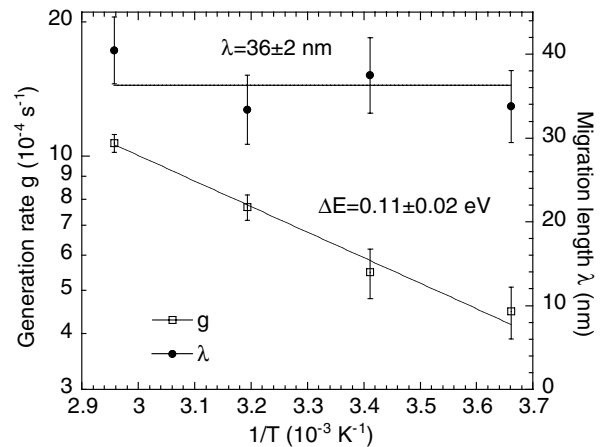


FIG. 2.  $B_m$  generation rate  $g$ , and  $B_m$  migration length  $\lambda$  versus the reciprocal of the temperature. The values were obtained by fitting the  $B$  diffusion occurring during SIMS analysis of a  $B$  delta, as shown in Fig. 1(c).

Anyway, we believe that the  $I$ 's injection will not be particularly sensitive to temperature, as it is a result of the collision cascades that involve energies much higher than the RT thermal energy. For example, the energy needed to form a  $I$ - $V$  Frenkel pair is about 15 eV. Then, it is likely that the thermal activation energy of  $0.11 \pm 0.02$  eV will represent an estimate of the energy barrier for the reaction (1) at temperatures around RT. Such a low value is in agreement with the results in this work and with other experimental estimates [5,6].

From the previous results it is also possible to estimate a lower bound for the diffusion coefficient of the  $B_m$  species at RT. The profile at RT ( $+20^\circ\text{C}$ ) in Fig. 1(b) starts to significantly differ from the profile at  $-75^\circ\text{C}$  at a depth of 120 nm. Such a difference is produced by  $B$  atoms diffusing out from the center of the delta, which is located about 60 nm deeper (i.e., at a depth of 180 nm). The above distance of 60 nm is traversed by mobile  $B_m$  in a time certainly less than the time needed to sputter 120 nm, which is 75 s. A simple calculation gives a lower limit for the  $B_m$  diffusion coefficient of  $D_{B_m} \geq 5 \times 10^{-13} \text{ cm}^2/\text{s}$ , which could be significantly increased by considering that the migrations we observe are not diffusion limited. In any case, by considering the following formula  $D_{B_m} = D_{B_m}^0 \exp(-\Delta E_m/K_B T)$ , and assuming for the preexponential factor the value calculated by Alippi *et al.* [10]  $D_{B_m}^0 \sim 1 \times 10^{-3} \text{ cm}^2/\text{s}$  (which is of the same order of magnitude as the prefactor obtained for a single hopping process with a rate equal to the Debye phonon frequency), we get an upper bound for the  $B_m$  migration energy of  $\Delta E_m \lesssim 0.56$  eV. This value is in reasonably good agreement with theoretical (between 0.4 and 0.85 eV) [8–11] determinations of the  $B_m$  migration energy.

The results presented in this Letter have enormous implications. They demonstrate that SIMS analysis introduces a huge room temperature migration of  $B$  induced by the beam-solid interactions during the analyses. This probably clarifies why no RT diffusion of  $B_s$  has been observed before. On the other hand, we show that, if the above phenomenon is properly controlled, SIMS provides a new experimental method to investigate RT diffusion phenomena:  $B_s$  is shown, for the first time, to migrate at RT, and, contrary to what is observed at much higher temperatures, the migration of the mobile species  $B_m$  is trap limited, with  $\text{C}_s$  and  $\text{O}_i$  as the most probable traps. We have also measured for the first time a lower bound for the  $B_m$  diffusion coefficient of  $5 \times 10^{-13} \text{ cm}^2/\text{s}$  at RT, which is in agreement with recent theoretical estimates. Most important, these phenomena imply also that all  $B$  profiles measured at room temperature are broader than the actual profiles before analysis. Hence, the above data force one to reconsider all of the observations obtained in the last decades by SIMS in light of possible long-range migration artifacts. Accurate profiling needs to suppress the migration phenomena that can be done either by cooling

the sample during the analysis or by “freezing” the  $B$  profile through preamorphization.

The authors thank A.V. Drigo for helpful discussions, and D. Agugiaro, L. Ramina, M. Rampazzo, and A. Pepato for technical assistance. This work has been partially supported by the MIUR projects COFIN 2002 and FIRB.

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