

Atomistic Mechanism of Boron Diffusion in Silicon

Davide De Salvador,^{1,*} Enrico Napolitani,¹ Salvatore Mirabella,² Gabriele Bisognin,¹ Giuliana Impellizzeri,² Alberto Carnera,¹ and Francesco Priolo²

¹MATIS INFN-CNR and Padova University, Physics Department, via Marzolo 8, 35131 Padova, Italy

²MATIS INFN-CNR and Catania University, Physics and Astronomy Department, via S. Sofia 64, 95123 Catania, Italy

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B diffuses in crystalline Si by reacting with a Si self-interstitial (I) with a frequency g and so forming a fast migrating BI complex that can migrate for an average length λ . We experimentally demonstrate that both g and λ strongly depend on the free hole concentration p . At low p , g has a constant trend and λ increases with p , while at high p , g has a superlinear trend and λ decreases with p . This demonstrates that BI forms in the two regimes by interaction with neutral and double positive I , respectively, and its charge state has to change by interaction with free holes before diffusing.

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Diffusion of impurities in semiconductors is an elementary process relevant for electronic device production. A complete knowledge of the atomistic mechanism of impurity diffusion is a fundamental issue to control the doping profiles in nanometric regions [1]. Diffusion mechanism of boron in crystalline silicon is one of the most important cases not completely explained in spite of 30 years of activity on this topic [2]. B generally substitutes Si atoms in the crystalline lattice and needs to interact with Si self-interstitial defects (I) in order to diffuse [3,4]. After the interaction, a bonded BI complex forms and migrates in the Si lattice with a mean free path (λ) before it spontaneously breaks into the I and the substitutional boron (B_s) components, thus stopping its movement [5–8]. This phenomenon was experimentally evidenced by looking at the diffusion shape of a sharp B peak (B δ doping) [5,6] when its average broadening is comparable to or lower than the mean free path. Under this condition, proper data analysis and profiling technique give experimental access to the interaction rate between boron and I (hereafter called g) and to the mean free path λ of the mobile species [5,6]. For higher broadening of the delta doping (longer annealing time), equations proposed in Refs. [5,6] merge with the Fick's equations regulated by the macroscopic parameter D (diffusivity) that can be calculated by $D = g\lambda^2$.

It was largely demonstrated that the free charge availability in Si strongly influences the diffusion coefficient of B; in particular, Ref. [9] showed that B diffusivity linearly increases with the hole concentration p in a wide range of temperatures (870–1250 °C) under both p - and n -type doping conditions, later confirmed by more recent results [10,11]. This fact, as will be shown in the following, is a consequence of the neutral charge state of the mobile BI complex. On the other hand, different structures for the BI complex are proposed by theoretical studies [7,8,12,13]. In general, it was demonstrated that the structure, the formation energy, and the migration barrier of these complexes strongly depend on the charge state. Neutral and negatively

and positively charged BI complexes were considered, but a general consensus on which one is the most relevant for diffusion has not been reached yet (neutral according to Refs. [8,13], negative according to Ref. [12]). Moreover, the charge state of the I s that promotes the BI complex formation is still a debated subject: neutral, charged, and doubly charged I were considered in the literature [2]. The experimental linear trend of the diffusivity with p concentration strongly suggests the interaction of substitutional B with a positively charged point defect, namely, I^+ , that has a population linearly increasing with p [3]. On the other hand, a theoretical work proposed I^{2+} defects [7], and a modeling paper [14], based on recent Si self-diffusion experiments [15,16], considered I^- , I^0 , and I^+ as the interstitial charge states that promote the BI complex formation. More recently, the same group of Refs. [15,16] proposed instead a negative- U energy scheme for donor states of the interstitial, i.e., asserted that neutral and doubly positively charged I are energetically favored [17].

In summary, the need for solid experimental evidence allowing one to discriminate different reaction paths among B, I , and free charges that bring to B diffusion is evident. In this work, we report a very accurate experimental study of the atomistic parameters (D , g , and λ) of B diffusion in Si as a function of the hole concentration. Our data show that the charge state of the BI mobile complex is neutral. At low p , the BI complex is formed in a negative BI^- state by interaction with an I^0 while, at high p , a positive BI^+ is formed by interaction with an I^{2+} . As a consequence, such complexes have to interact with free charges in order to become neutral and move into the lattice.

The basic idea of the experiment is to analyze the diffusion of a sharp ^{11}B spike suitable for the simultaneous determination of λ and g , embedded in different ^{10}B and P backgrounds in order to change the Fermi level and, thus, the hole concentration. The processes adopted for the sample preparation are schematically presented in Fig. 1.

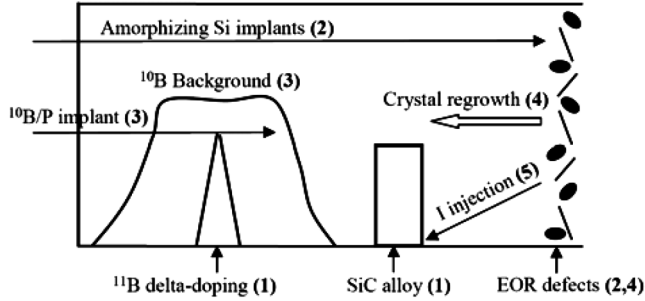


FIG. 1. Schematic view of the experiment. (1) Epitaxial growth of silicon with delta-doped B and a Si_{1-x}C_x alloy barrier. (2) Amorphizing Si implants. (3) Multiple ¹⁰B (or ³¹P) implants to insert a B (P) background around delta-doped B. (4) Solid phase epitaxial regrowth. (5) Diffusion annealing.

The samples were grown by molecular beam epitaxy, inserting a B spike (at the depth of 180 nm, using a natural isotopic abundance solid B source) and a Si_{1-x}C_x alloy layer (between 390 and 440 nm, C concentration $x = 0.3$ at. %). Subsequently, this structure was amorphized down to a depth of 500 nm by implanting Si ions. Multiple ¹⁰B implants were performed to produce the background box that results to be constant within $\pm 5\%$ in the range between 80 and 320 nm. Depending on the ¹⁰B implantation fluence, the box concentration ranged from 5×10^{18} to 7.5×10^{19} B/cm³. In order to explore B diffusion in *n*-doping conditions, one sample was produced by multiple ion implants with a 3×10^{18} atoms/cm³ phosphorus background. The structures were recrystallized through solid phase epitaxy induced by rapid thermal annealing at 700 °C in an inert N₂ atmosphere with an annealing of 15 s for *p*-doped samples and 10 min for the *n*-doped specimen. Annealings to induce a moderate diffusion of the spike, suitable for λ and g determination, were then performed at the same temperature for many different times ranging from 100 s to 32 h. During such annealings, the residual damage formed just below the amorphization depth [end of range (EOR) defects] could inject interstitials above the equilibrium concentration and perturb the experiment [18,19]. The substitutional C in the Si_{1-x}C_x alloy layer stops the *I* flux by forming C-*I* precipitates [20–22], thus preventing nonequilibrium diffusion phenomena at the B spike. We verified that the amount of substitutional C in our samples is enough to avoid any *I*s supersaturation, since about 90% of C is still in substitutional sites even after the longest annealing. This was measured by nuclear reaction analysis and high resolution x-ray diffraction. In the same way, we also verified that the B background is fully substitutional both before and after the annealings.

In order to provide λ and g determination with high accuracy and sensitivity, the profiling technique is crucial. We performed secondary ion mass spectrometry (SIMS) measurements with the sample frozen at -70 °C during the analysis. As recently demonstrated by our group, low

temperature prevents measurement artefacts due to long-range room temperature diffusion phenomena of B induced by the point defects injected by the sputtering beam [23]. Moreover, we flooded the samples during the analyses with a jet of O₂ gas as described in Ref. [24]. This allows us to considerably increase (up to a factor of 20) the B⁺ yield (some 10⁴ counts/s are collected at the top of the delta doping spike) without losing depth resolution [24]. As a consequence of the whole procedure, the errors for determining the diffusion g and λ parameters are, respectively, a factor of about 6 and 3 lower than for standard measurement conditions, i.e., at room temperature and in ultrahigh vacuum.

In Fig. 2, we show an example of how delta-doped ¹¹B diffuses in a sample with a 5×10^{18} atoms/cm³ ¹⁰B background. Solid circles trace the B concentration profile of the as-regrown sample, while open symbols concern the B profile after a 1 h diffusion at 700 °C. The dashed line is the best fit to the diffused data obtained by numerically “diffusing” the as-regrown profile according to the equations of Ref. [5]. λ and g parameters were optimized by an automatic minimization of χ^2 . In order to evidence the sensitivity to the atomistic parameters, two other simulations with the same diffusivity but different g and λ values are also reported in Fig. 2.

The values of D , g , and λ as a function of the hole concentration p normalized by the intrinsic hole concentration in an undoped Si (n_i) are shown in Figs. 3(a)–3(c), respectively. Error bars on D , g , and λ are standard deviations evaluated by considering both statistical error propagation from the measurement noise and the variability of the parameters estimated on several different annealing

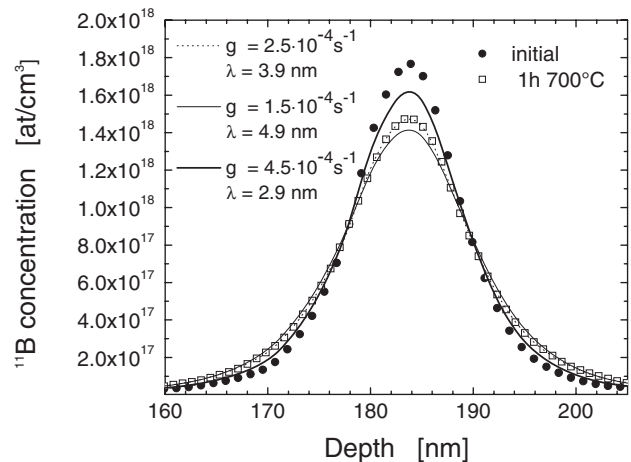


FIG. 2. SIMS measurements of concentration profiles of ¹¹B spike before (solid circles) and after (open squares) diffusion annealing at 700 °C for the sample with the 5×10^{18} atoms/cm³ ¹⁰B background. The dashed line is the best fit to the data obtained with $g = 2.5 \times 10^{-4} \text{ s}^{-1}$ and $\lambda = 3.9 \text{ nm}$. For comparison, simulations with the same D but different g and λ values are reported.

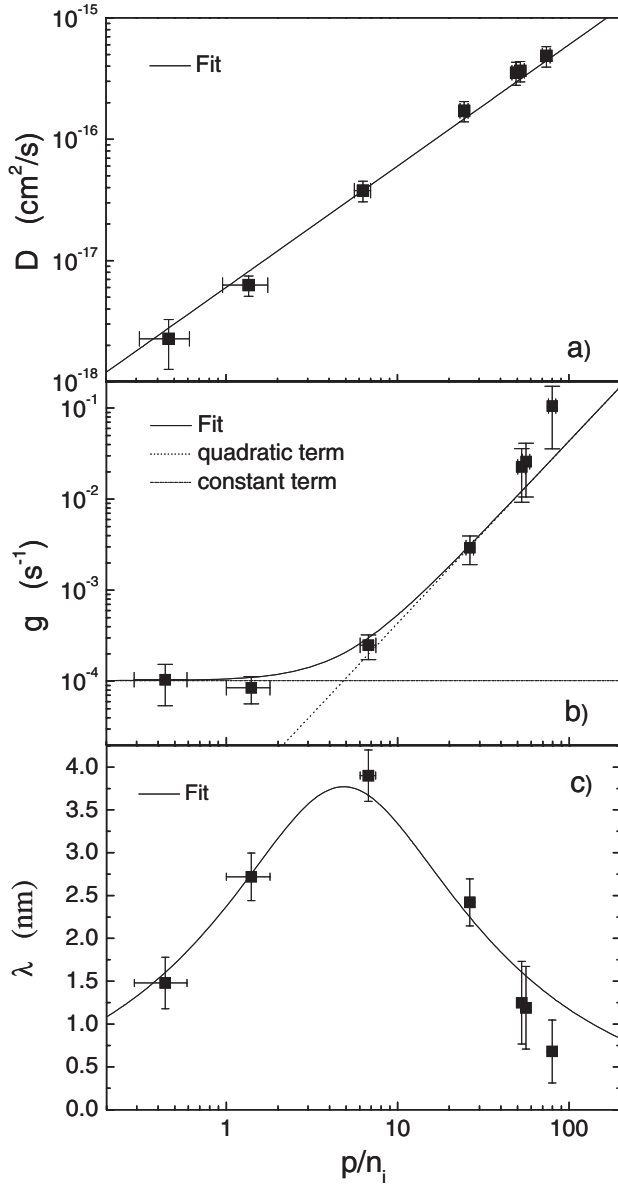


FIG. 3. (a) Diffusivity (D), (b) generation rate (g), and (c) mean free path (λ) as a function of the hole concentration normalized to the intrinsic carrier concentration at the annealing temperature of 700°C . The solid lines are fits to the data.

times on the same sample. n_i is equal to $0.99 \times 10^{18} \text{ cm}^{-3}$ at the diffusion temperature of 700°C [2,25]. p is calculated starting from the background B concentration according to Boltzmann statistics and considering a full ionization of substitutional B as demonstrated in Ref. [26].

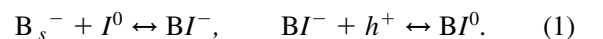
The trend of D as a function of p/n_i [Fig. 3(a)] is very well fitted by a linear function in the whole range [$D = D_0(p/n_i)$]. Adding constant or quadratic terms does not improve the fit. These data confirm the linear trend proposed in the literature [9–11] and extend it to a lower temperature (700°C instead of 870°C). As mentioned before, the linear trend of D is univocally connected to the charge state of the mobile BI complex: it indicates that

the whole diffusion process proceeds by the net exchange of a single positive charge. In fact, a process with no charge exchange would instead give a diffusivity that does not care about the hole amount, and a double charge exchange would be weighted by the probability of getting two positive charges; i.e., the diffusivity would be proportional to $(p/n_i)^2$. Rigorously, this is a consequence of the local charge conservation and law of mass action applied to each reaction that contributes to transform B_s into a mobile species. Thus, the linear trend reported in Fig. 3(a) demonstrates that B_s (which is singly negative charged before diffusion starts [23], hereafter B_s^-) has to transform into a neutral species in order to diffuse. In other words, the data demonstrate that the BI^0 complex is the mobile complex that allows B_s^- to change its position into the lattice.

The g and λ trends in Figs. 3(b) and 3(c) are the crucial results of this work. These data allow one to determine the atomistic mechanism by which the mobile BI^0 complex forms. The g trend describes how the production frequency of the BI complex varies with the free hole concentration. It can be seen that g has not a linear dependence on p/n_i : the first two data clearly trace a constant trend inside the error bars, while the other g data increases 2 orders of magnitude against 1 order of magnitude variation of p/n_i . In general, g is proportional to the interstitial concentration [5,6] that differently depends on p/n_i according to the I charge state [2,3]. In more detail, a self-interstitial with a charge state q introduces a term equal to $g_q(p/n_i)^q$ in the dependence of g over p/n_i . Possible I charge states proposed in the literature range from $q = -2$ to $+2$ [2] and could, in principle, be used to fit the data in Fig. 3(b). The best fit of Fig. 3(b) (continuous line) is obtained by considering only the $q = 0$ (neutral interstitial) and $q = 2$ (doubly charged interstitial) terms. All of the other terms, if used in the fit, give null inside the errors or even non-physical (negative) g_q values.

As a consequence of the I^0 and I^{2+} interaction with B_s^- , a BI complex in negative (BI^-) or positive (BI^+) charge states is produced, respectively. Such complexes are not the diffusing species as demonstrated by the D trend analysis, but they have to transform into BI^0 by changing their charge state before B diffusion. In other words, our data demonstrate that charge exchange between an already formed BI complex and free holes must occur.

The data in Figs. 3(a) and 3(b) can be described by 3 parameters that are D_0 , g_0 , and g_2 . The same parameters allow one to well reproduce the bell-like λ experimental trend of Fig. 3(c) by means of the relation $\lambda = (D/g)^{1/2}$. Such a trend can provide a deeper understanding by the following summarizing considerations. Two reactions chains involving substitutional B, interstitials, and free holes h^+ emerge from the data: (i) At low p/n_i values ($p/n_i < 4$), the dominant reactions are



The first reaction determines the constant dependence of g on p at low hole concentration. In the second reaction, BI^- can convert back and forward to BI^0 by capturing and releasing a hole in a dynamical equilibrium. The net probability of producing the mobile BI^0 is linear with p/n_i ; as a consequence, under this regime the λ of B increases with p/n_i [low p/n_i regime in Fig. 3(c)] since the time spent by the BI complex in the neutral mobile state increases by increasing p/n_i ; i.e., the equilibrium of the second reaction is pushed towards the right by increasing hole concentration [27].

(ii) At high p/n_i values ($p/n_i > 4$), the population of I^{2+} increases [proportionally to $(p/n_i)^2$ [2]], and, therefore, a second reaction chain prevails:



The net probability of producing a BI^+ complex by the first reaction is proportional to p^2 , but the probability to convert this complex into a neutral state through the second reaction is inversely proportional to the amount of holes, since the greater p/n_i is, the higher is the probability for the mobile BI^0 complex to get a hole and to go back to BI^+ . As a consequence, at high p/n_i , λ decreases by increasing p/n_i [Fig. 3(c)].

As a final remark, we have to consider that the low relevance of the interaction between the substitutional B with I^q , with $q = 2-, 1-,$ and $1+$, can have important implications: it means that either the $I^{2-,1-,1+}$ energy costs (formation plus diffusion) are very high and therefore $I^{2-,1-,1+}$ do not contribute to self-diffusion processes in silicon (that correspond to a U-shape energy scheme for I) or a high energy barrier is present in their specific reaction with B_s^- .

In conclusion, we elucidated that: (i) BI^0 is the most important species that contributes to B diffusion in Si; (ii) charge exchange between free charges and the BI complex plays a fundamental role in understanding the atomistic diffusion process of B under extrinsic conditions; (iii) B diffusion is promoted by the interaction of B_s^- with I^0 and I^{2+} species. These results help to clarify, after 30 years of debate, the atomistic diffusion mechanism of B in Si. They also have important technological implications, providing a solid experimental background over which it is possible to build up the predictive atomistic modeling of B diffusion, needed for the process design of microelectronic devices.

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*Electronic address: desalvador@padova.infm.it

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