Iso-concentration study of atomistic mechanism of B diffusion in Si

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Abstract

B diffuses in crystalline Si by reacting with Si self-interstitial (I) with a frequency g, forming a BI complex that can migrate for an average length λ. We experimentally measured both g and λ as a function of the hole concentration p by means of iso-concentration experiments on B delta-layers both under p- and n-doping conditions. On the basis of these data, we propose a comprehensive model that fixes the interplay among free charge, I and BI charge states that determines the B diffusion. Pairing effect with donors was also considered.
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1. Introduction

Diffusion of B in Si is a crucial elementary process relevant for the modelling of p-junctions [1,2]. B generally perfectly substitutes Si atoms in the crystalline lattice and needs to interact with Si self-interstitial defects (I_s) in order to diffuse [3,4]. After the interaction, a bonded BI complex forms (kick-out) 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 (kick-in) [5–8]. This phenomenon was experimentally evidenced by looking at the diffusion shape of a sharp B peak (B delta doping) [5,6]. It was demonstrated that the Fick equation, regulated by the diffusion coefficient D, does not accurately describe the diffusion profiles but two separate "atomistic" physical parameters have to be used in order to properly describe the experimental data: the mean free path of the mobile species (λ) and the interaction rate between B and I (kick-out rate g). A proper profiling technique and data analysis can give experimental access to g and λ separately, while the macroscopic parameter D is connected to g and λ by the relation $D = g\lambda^2$ [5,6].

It was largely demonstrated that the free charge availability in Si strongly influences the diffusion coefficient of B; in particular an earlier paper [9], later confirmed by more recent results [10,11], showed that B diffusivity linearly increases with the hole concentration p in a wide range of temperatures (870–1250 °C). This fact is a consequence of the neutral charge state of the mobile BI complex [2]. 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 this complex strongly depend on its charge state. Neutral, negatively and positively charged BI complexes were considered but a general consensus on which is the most relevant complex for diffusion has not yet been reached (neutral according to [8,13], negative according to [12]).

A general consensus is not reached also about the predominant charge state of the I that promotes the BI complex formation: neutral, charged and doubly charged I

were considered in 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^{++} 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 [15,16] proposed instead a negative-U energy scheme for donor states of the interstitial, i.e. they asserted that neutral and doubly positively charged I are energetically favoured [17].

Another important phenomenon, that plays a role in n-doping conditions that are reached by co-doping B with donor species, is the pairing among B and the donors. It consists in the formation of donor–acceptor substitutional pairs, which are energetically favoured by coulombic attraction [2]. This phenomenon reduces B diffusion under co-doping, since it increases the energy cost for the BI formation and reduces the amount of B effectively available for diffusion. It was noticed that the D reduction due to pair can not be disentangled by a possible diffusion component of a BI^- species, which can be predominant in n-doping conditions [2]. In other words the absolute extent of B diffusion by BI^- intermediate species and B pairing D reduction cannot be determined by usual diffusion experiment.

In summary the need for solid experimental evidences, that can allow to discriminate between different reaction paths among B, I and free charges that bring to B diffusion, is evident. In this work, we report a experimental study of the atomistic parameters (D, g and λ) of B diffusion in Si as a function of the holes concentration. Our data shows that the BI complexes are formed by two possible interactions with a neutral I^0 or a double positively charge I^{++}, forming BI^- and BI^+ species, respectively. In p-doped and slightly n-doped conditions the linear trend of the diffusivity demonstrates that both BI^- and BI^+ have to change their charge status, by interacting with free holes, to form BI^0 and diffuse. Moreover, a preliminary analysis of n-doped data shows that the experimental determination of g and λ allows to distinguish between BI^- diffusion and pairing, providing a determination of the small BI^- diffusion component and of the pairing energy.

2. Experiment description

The basic idea of the experiment is to analyze the diffusion of a sharp ^{11}B delta doping, suitable for the simultaneous determination of D, λ and g; the ^{11}B was embedded in different ^{10}B and P backgrounds in order to change the Fermi-level and therefore the hole concentration. Fig. 1 shows the chemical profiles of the elements present in a typical sample. The samples were grown by molecular beam epitaxy (MBE), with a B spike at the depth of 180 nm, using a natural isotopic abundance solid B source (the ^{11}B profile of the spike is the continuous line
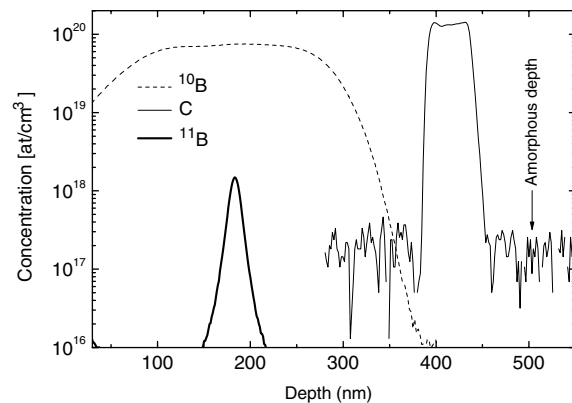

Fig. 1. Chemical profiles of ^{10}B (dashed line), ^{11}B (continuous line) and C (thin continuous line) on a typical sample. The C background is constant up to the surface and is not shown for the sake of clarity. The amorphising depth is marked by an arrow.

in Fig. 1). Moreover, a $Si_{1-x}C_x$ alloy layer between 390 and 440 nm, was grown (continuous thin line in Fig. 1). Subsequently, this structure was amorphized down to a depth of 500 nm by implanting Si ions. Multiple ^{10}B implants were performed to produce the background box that results to have a B concentration constant within $\pm 5\%$ in the range between 110 and 250 nm (dashed line in Fig. 1). Depending on the ^{10}B implantation fluence, the box concentration ranged from 5×10^{18} to 7.5×10^{19} B/cm^3. In order to explore B diffusion in n-doping conditions two samples were produced by multiple ion implants with 3×10^{18} and 1×10^{19} at/cm^3 phosphorus backgrounds. The structures were re-crystallized through solid phase epitaxy induced by rapid thermal annealing (RTA) at 700 °C, in inert N_2 atmosphere, with an annealing time of 15 s for p-doped samples and 10 min for the n-doped ones. Annealings to induce diffusion were then performed at the same temperature for many different times ranging from 100 s to 40 h. During such annealings the residual damage formed just below the amorphization depth (end of range defects) can inject interstitials so bringing the I's population above the equilibrium concentration, invalidating the experiment [18,19]. The $Si_{1-x}C_x$ alloy layer stops such I flux towards the surface and prevents, as a consequence, non-equilibrium diffusion phenomena [20]. We verified that all B is substitutionally located in the Si lattice, both before and after the annealings by means of high resolution X-ray diffraction and nuclear reaction analysis in channeling configuration.

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) measurement with the sample frozen at -70 °C during the analysis. In fact, low temperature prevents measurement artefacts due to long-range room temperature B diffusion phenomena induced by the point defects injected by the sputtering beam (see [21]). Moreover, we flooded the samples during the analyses with a jet of O_2 gas as described in [22]. This allows to considerably increase (up

to a factor of 20) the B^+ yield, without loosing depth resolution [22].

3. Results and discussion

In Fig. 2, we show two examples of ^{11}B profiles for the 5×10^{18} at/cm^3 (circles) and 7.5×10^{19} at/cm^3 (triangles) ^{10}B background after diffusion for 1 h and 200 s, respectively. The two profiles present quite different shapes: the first has two exponential (linear in log-scale) tails characteristic of BI mediated diffusion with a long BI mean free path, while the second has a gaussian (parabolic in log-scale) shape characteristic of a Fick diffusion or of a small mean free path. The lines are the best fits to the diffused data obtained by numerically "diffusing" the as-regrown profile according to the equations of [5]. The fits allow to quantify the two different mean free path values (together with g and D) and it confirms the above qualitative description.

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 Fig. 3(a–c), respectively. n_i is equal to 0.92×10^{18} cm^{-3} at the diffusion temperature of 700 °C [3]. p is calculated starting from the background B concentration according to Boltzmann statistics and considering a full ionization of substitutional B as demonstrated in [23].

The whole set of data in Fig. 3 furnishes very detailed information about B diffusion mechanism, that allow to answer, by a proper modelization, many questions still open in the literature. The data are consistently reproduced (continuous lines) by exploiting the following hypotheses: (i) the diffusion is mainly due to BI^0 mobile species and to a small extent to BI^-. The presence of these two mobile species introduces a linear and a constant term in the D trend versus p/n_i (Fig. 3(a)), respectively ($D = D_{BI}^- + D_{BI}^0(p/n)$). (ii) The diffusion is reduced by the pairing with P under n-doping conditions. The functional form of such a reduction was

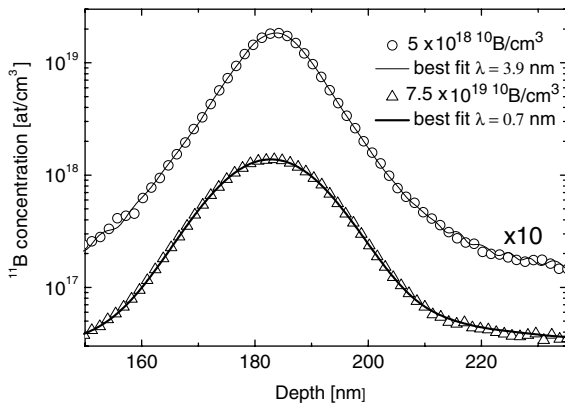Fig. 3. Diffusivity (D), generation rate (g) and mean free path (λ) (panels (a–c), respectively), as a function of the hole concentration normalized to intrinsic carrier concentration at the annealing temperature of 700 °C. Continuous lines are the best fit to the data obtained by the modelling described in the text.

Fig. 2. SIMS measurements of concentration profiles of ^{11}B spike after diffusion annealing for samples with a 5×10^{18} at/cm^3 (circles) and a 7.5×10^{19} at/cm^3 (triangles) ^{10}B background. The lines are the best fits to the data obtained with $\lambda = 3.9$ nm and $\lambda = 0.8$ nm, respectively. Data relative to 5×10^{18} at/cm^3 sample are multiplied by a factor 10 for the sake of clarity.

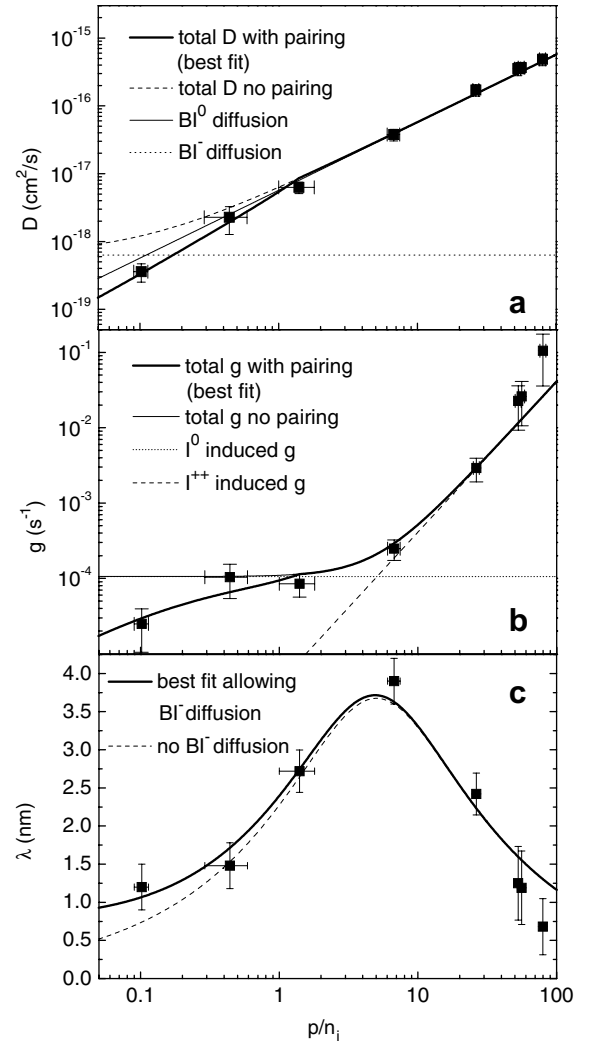taken by [2,11] and it depends on the binding energy E_{BP} among substitutional B and P. (iii) The pairing affects the interaction rate g among B_s and the interstitial in the same way as it does for D, since it decreases the number of B available to undergo kick-out. In fact a fraction of B atoms trapped in pairs needs a larger energy to promote the formation of BI and therefore it does not effectively contribution to g and to D. On the other hand, the pairing negligibly affects the mobile species mean free path. The mean free path indeed depends on the diffusivity of the mobile species and on the probability of BI breaking (kick-in reaction). Such quantities will be affected when BI species is in the proximity of P atoms but this occurs for a very reduced fraction of the BI path because of the relatively low P concentration (1×10^{19} at/cm^3 at maximum). Therefore kick-in and BI diffusion (and therefore λ) will be in the greater part regulated by the unperturbed lattice energetics. (iv) The interaction with interstitials that promotes the formation

of the BI complex is driven by neutral I^0 and double positive I^{++}. The populations of such species have a constant and a quadratic trend with p/n_i [3] (Fig. 3(b)) thus introducing a constant g_I^0 and a quadratic $g_I^{++}(p/n_i)^2$ term in the kick-out frequency trend versus p/n_i ($g = g_I^0 + g_I^{++}(p/n_i)$). (v) λ is connected to D and g by the relation: $\lambda = (D/g)^{1/2}$ [5,6].

The above model, with the five free parameters defined above (D_{BI}^-, D_{BI}^0, g_I^0, g_I^{++} and E_{BP}), allows to produce the continuous lines in Fig. 3(a–c) that very satisfactorily fit the data for D, g and λ. Adding more parameters (such as, for example a quadratic term for D, that would be linked to D_{BI}^+ diffusion or a linear term in g that would be linked to the interaction with a I^+ interstitial) does not improve the fit or, in some cases, give non physical (negative) parameters. The best fit values are $D_{BI}^- = 6.3 \times 10^{-19}$ cm^2/s, $D_{BI}^0 = 5.7 \times 10^{-18}$ cm^2/s, $g_I^0 = 1.06 \times 10^{-4}$ s^{-1}, $g_I^{++} = 0.42 \times 10^{-5}$ s^{-1} and $E_{BP} = 0.68$ eV. Notice how E_{BP} among 0.4 and 0.7 eV are reported in literature [2].

$D_{BI}^0(p/n_i)$ term dominates the diffusion in a very wide range of doping from p- to slightly n-conditions. In this regime ($p/n_i > 0.3$) pairing does not play a significant role and experimental data are well fitted, inside the error bars, without considering it (dashed lines in Fig. 3(a) and (b)). g is clearly the sum of a constant and a quadratic components thus assessing the I^0 and I^{++} contribution. In this regime λ traces a bell as a function of p/n_i. This is a consequence of the charge exchange that must occur to transform the BI^- and BI^+ species (primarily produced by interaction of I^0 and I^{++} with B_s^-) into the mobile BI^0 species. When $p/n_i < 4$ BI^- is produced and it has to get an hole to move, so BI mean free path increases by increasing the hole availability. On the contrary when $p/n_i > 4$ BI^+ is produced and it has to loose a hole to move. This is less probable to occur the higher is p thus reducing λ.

The D_{BI}^- contribute becomes comparable to $D_{BI}^0(p/n_i)$ at about $p/n_i = 0.3$ (Fig. 3(a)). When $p/n_i < 0.3$ pairing is also important as can be noted by comparing the dashed and continuous line in Fig. 3(a). It is evident (as considered in [2]) that the pairing and BI^- contribution can not be simply deduced by Fig. 3(a), i.e. only by measuring D: for example a null BI^- contribution and a less effective pairing effect (lower E_{BP}) could bring to a good fit of the data as well. Instead, pairing is evidenced by the g plot (Fig. 3(b)) that is not affected by the nature of the mobile species. The abrupt decrease of g when $p/n_i = 0.1$ with respect to the extrapolation of the trend determined by the other data (dashed line) demonstrates that pairing occurs and allows to quantify the role of the paired dopants by fixing the E_{BP} parameter. On the contrary the trend of λ does not depend on pairing but only on the kind of mobile species. The BI^- diffusion component prevents λ going down rapidly what would occur in absence of a BI^- contribution,

since less holes ara available (dashed line, Fig. 3(c)). As a matter of fact when p/n_i tends to zero BI^- does not transform into BI^0 and this would give a null mean free path in the case that BI^- would be an immobile specie. Instead, a BI^- diffusion component allows to correctly reproduce D and λ values at $p/n_i = 0.1$.

Of course, while the first part of the model concerning the $p/n_i > 0.3$ regime is strongly supported by a lot of data and has to be considered well assessed, the last part of the model regarding $p/n_i < 0.3$ regime that fixes both E_{BP} and D_{BI}^- parameters only depends on D, g and λ evaluated on a single doped sample and therefore has to be considered only preliminar. Work is in progress to extend such investigation to higher n-doping regime and to different n-co-doping species.

Acknowledgements

References

[1] Semiconductor Industry Association, International technology roadmap for semiconductors (2005). <http://www.itrs.net/Common/2005ITRS/Home2005.htm>.
[2] P. Pichler, in: S. Selberherr (Ed.), Intrinsic Point Defects, Impurities, and their Diffusion in Silicon, Springer, Wein, NewYork, 2004.
[3] P.M. Fahey, P.B. Griffin, J.D. Plummer, Rev. Mod. Phys. 61 (1989) 289.
[4] U. Goesele, T.Y. Tan, in: J.W. Corbett, S. Mahayan (Eds.), Defects in Semiconductors II, 45, North-Holland, New York, 1983.
[5] N.E.B. Cowern, K.T. F Jassen, G.F.A. van de Walle, D.J. Gravesteijn, Phys. Rev. Lett. 65 (1990) 2434.
[6] N.E.B. Cowern, K.T. F Jassen, G.F.A. van de Walle, D.J. Gravesteijn, C.J. Vriezema, Phys. Rev. Lett. 67 (1991) 212.
[7] B. Sadigh et al., Phys. Rev. Lett. 83 (1999) 4341.
[8] W. Windl, M.M. Bunea, R. Stumpf, S.T. Dunham, M.P. Masquelier, Phys. Rev. Lett. 83 (1999) 4345.
[9] B.R. Fair, P.N. Pappas, J. Electrochem. Soc. 122 (1975) 1241.
[10] M. Miyake, J. Appl. Phys. 57 (1984) 1861.
[11] A.F.W. Willoughby et al., J. Appl. Phys. 59 (1986) 2392.
[12] J.W. Jeong, A. Oshiyama, Phys. Rev. B 64 (2001) 235204.
[13] L. Lin, T. Kirichenko, B.R. Sahu, G.S. Hwang, S.K. Banerjee, Phys. Rev. B 72 (2005) 205206.
[14] I. Martin-Bragado et al., Phys. Rev. B 72 (2005) 35202.
[15] H.H. Silvestri, Mater. Res. Soc. Proc. 719 (2002) F13.10.
[16] H.A. Bracht, H.H. Silvestri, E.E. Hallerb, Solid State Commun. 133 (2005) 727.
[17] H. Bracht, Physica B 376–377 (2006) 11.
[18] K.J. Jones et al., Appl. Phys. Lett. 68 (1996) 2672.
[19] E. Lampin, V. Senez, A. Claverie, J. Appl. Phys. 85 (1999) 8137.
[20] E. Napolitani et al., Appl. Phys. Lett. 79 (2001) 4145.
[21] E. Napolitani et al., Phys. Rev. Lett. 93 (2004) 055901.
[22] E. Napolitani et al., J. Vac. Sci. Technol. B 24 (2006) 394.
[23] X. Luo, S.B. Zhang, S.H. Wei, Phys. Rev. Lett. 90 (2003) 026103.