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Impurities–Si interstitials interaction in Si doped with B or Ga during ion irradiation

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Abstract

Substitutional impurities (B, Ga) in Si experienced an off-lattice displacement during ion-irradiation using a H^+ or He^+ beam at room temperature in random incidence. Samples were prepared by solid phase epitaxy (SPE) of pre-amorphized Si subsequently implanted with B and Ga at a concentration of about 1×10^{20} at. cm^{-3} confined in a 300 nm thick surface region. The lattice location of impurities was performed by a channelling technique along different axes ($\langle 100 \rangle$, $\langle 110 \rangle$) using the $^{11}B(p, \alpha)^8Be$ reaction and standard RBS for B and Ga, respectively. The normalized channelling yield χ of the impurity signal increases with the ion fluence, indicating a progressive off-lattice displacement of the dopant during irradiation in random incidence, until it saturates at $\chi_F < 1$, suggesting a non-random displacement of the dopant. In particular, at saturation the off-lattice displacement of B and Ga was investigated by angular scanning, revealing different positions for each dopant. This effect has been related to the interaction of impurities with the Si self-interstitials (Si_I) generated by the impinging beam in the doped region.

1. Introduction

It is well known that silicon dopants can move inside the crystal by means of interactions with native point defects, which are able to greatly enhance atomic diffusion phenomena and to induce clustering of impurity atoms. The presence of an excess of point defects can be deleterious on the spatial gradient of the dopant concentration distribution, inducing TED (transient enhanced diffusion) phenomena. In addition the formation of impurity clusters degrades the electrical activation and charge carrier mobility, so the interaction between

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impurities and point defects in Si, such as a vacancy or a self-interstitial, constitutes a charming issue in fundamental research as well as a crucial key in fabricating high level, long time duration Si based devices [1–5].

Dopant diffusion in silicon is mediated by native point defects [6]. Substitutional dopant atoms migrate in silicon by pairing with either a Si self-interstitial I or a vacancy V, respectively, as follows: $A + I \rightarrow AI$; $A + V \rightarrow AV$, where AI is a dopant interstitial pair and AV is a dopant vacancy pair. It has been demonstrated that substitutional group III impurities diffuse prevalently by an interstitial mechanism [6, 7] and deviations from the equilibrium diffusion coefficient have been correlated to the excess of $\mathrm{Si_I}$.

In fact, $\mathrm{Si_I}$ detection is quite a difficult task because of both the very low equilibrium density and the experimental difficulties in directly evidencing these point defects. Indirect observation of $\mathrm{Si_I}$ is accessible by studying the enhancement of dopant diffusion realized by a supersaturation $\mathrm{Si_I}$ at temperature >900 °C, whilst very little information is known about the impurity–$\mathrm{Si_I}$ interaction at lower temperatures [8]. In this work we use the channelling technique [9] to study the interaction at room temperature (RT) between $\mathrm{Si_I}$, and B and Ga impurities. Particularly, we measured the off-lattice displacements of substitutional impurities when an excess of $\mathrm{Si_I}$ is produced at a controlled rate by irradiation with light ions. The off-lattice displacement rate has then been fitted by a simple model assuming that the displacement rate is limited by the capture probability of a $\mathrm{Si_I}$ by a substitutional impurity atom. As a result, the B and Ga–$\mathrm{Si_I}$ interaction cross sections at room temperature have been evaluated.

2. Experimental details

The B or Ga doped Si samples were prepared by implanting $^{11}\mathrm{B}^+$ and $^{69}\mathrm{Ga}^+$, respectively, at RT into a 550 nm thick layer of pre-amorphized Si (by Si implantation at liquid nitrogen temperature). The substrate was ⟨100⟩ oriented Cz-Si, n type, $\rho = 1.5$–$4\ \Omega$ cm. The ion implantation energies and fluences were varied in order to obtain a constant concentration of 2×10^{20} B cm^{-3} and 1×10^{20} Ga cm^{-3} in a 300 nm surface region. Samples were annealed in a vacuum furnace ($p \sim 10^{-7}$ mbar) at 580 °C for 1 h to crystallize amorphous Si by SPE. Complete electrical activation (>90%) of p-doped (B or Ga) Si crystals was checked by Hall effect measurements. It is well known that electrically active dopant atoms are substitutional in the Si lattice and therefore ion-channelling analyses can be used to determine the fraction of active impurities by measuring the substitutional dopant concentration. The nuclear reaction $^{11}\mathrm{B}(\mathrm{p}, \alpha)^{8}\mathrm{Be}$ at 650 keV proton energy was used to reveal B in Si [9]. The lattice location of B atoms was determined by measuring the ratio of the aligned to the random α spectrum (normalized channelling yield χ) along different axes. Standard RBS-channelling analyses using a 2 MeV He$^+$ beam have been performed to investigate the Ga lattice location. After SPE the substitutional fraction of B and Ga were ~90%, in agreement with the electrical data measured by the Hall effect (not shown).

The excess of $\mathrm{Si_I}$ was generated at a controlled rate by irradiation with a 650 keV H$^+$ or 2.0 MeV He$^+$ beam randomly incident on the sample and the channelling yield χ of B or Ga atoms was measured as function of $\mathrm{Si_I}$ fluence. The size of the beam spot was 1 mm^2 and the typical beam current was 50 nA. We tested that the impurity displacement rate was independent of the beam current in the 5–100 nA range. The channelled beam does not modify the B location for the ion fluence typical of channelling analyses ($\sim 5 \times 10^{15}$ ion cm^{-2}) but Ga underwent a displacement. By comparison of the Ga displacement rate produced by channelling and random irradiations we have estimated that channelling irradiation at a fluence Φ_{ch} is equivalent to a random irradiation at a fluence $\Phi_{\mathrm{rn}} = 0.015\Phi_{\mathrm{ch}}$. More details of the experiment are reported in previous work [10, 11].

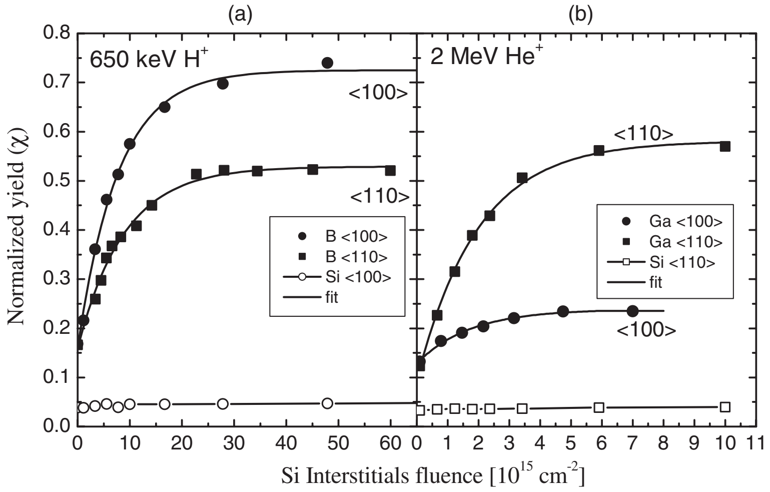

Figure 1. (a) ⟨100⟩ (●) and ⟨110⟩ (■) B normalized yields measured as a function of the Si$_{\mathrm{I}}$ fluence generated by the passing H$^+$ beam (650 keV). The solid lines are the fits of the data using $\sigma = (1.1 \pm 0.1) \times 10^{-16}$ cm^2, by the exponential law reported in the text. The sample is B doped Si with maximum concentration of 2×10^{20} at. cm^{-3}. The channelling yield of Si signal along the ⟨100⟩ axis is also reported (○). (b) ⟨100⟩ (●) and ⟨110⟩ (■) Ga normalized yields measured as a function of the Si$_{\mathrm{I}}$ fluence generated by the passing He beam (2 MeV). The solid lines are the fits of the data using $\sigma = (5.0 \pm 0.1) \times 10^{-16}$ cm^2, by the exponential law reported in the text. The sample is Ga doped Si with maximum concentration of 1×10^{20} at. cm^{-3}. The channelling yield of Si signal along the ⟨110⟩ axis is also reported (□).

3. Results and discussion

The channelling yield along the different crystallographic directions, increased progressively with increasing ion fluence for both Ga and B impurities. The displacement of B and Ga atoms cannot be attributed to direct knock-on by the incoming beam since its probability is negligible but it is likely to be mediated by the interaction with Si$_{\mathrm{I}}$ generated by the ion beam. For this reason the normalized channelling yield of B and Ga is reported in figures 1(a) and (b), respectively, as a function of the fluence of the excess of Si$_{\mathrm{I}}$ produced by the impinging beam. The latter was calculated by integrating the Si$_{\mathrm{I}}$ concentration profile (calculated by SRIM [12]) over the 300 nm region where the impurities are confined. In figure 1(a) the normalized yield χ relative to the B signal for ⟨100⟩ and ⟨110⟩ channelling is reported as a function of the interstitial fluence (N_{I}) for 650 keV H$^+$ irradiation. The normalized Si channelling yield below the surface peak in the proton spectrum was ∼4%, typical of a free-of-defects crystal, and it remains constant under irradiation, indicating that no damage is accumulated in the Si lattice. The B yield started to increase monotonically with interstitial fluence above 1×10^{15} cm^{-2}, until saturation occurred at a fluence of $\sim 1.5 \times 10^{16}$ cm^{-2}. The saturation values (χ_{F}) for ⟨100⟩ and ⟨110⟩ channelling are ∼70% and 50%, respectively, and this difference is a clear indication of a non-random B displacement. A similar progressive displacement is observed during irradiation with a 2.0 MeV He beam of the Ga implanted samples. The channelling yield of Ga is reported in figure 1(b) as a function of the Si$_{\mathrm{I}}$ fluence. Even in this case the Si channelling yield remains constant to ∼4% during irradiation. The Ga displacement is faster than that of B and saturation occurs at a fluence of $\sim 4 \times 10^{15}$ Si$_{\mathrm{I}}$ cm^{-2}. The saturation value for ⟨110⟩ channelling is definitely ∼60% higher with respect to ⟨100⟩ channelling, indicating, as in the case of B, a non-random displacement of Ga. It should be noted that the Ga channelling

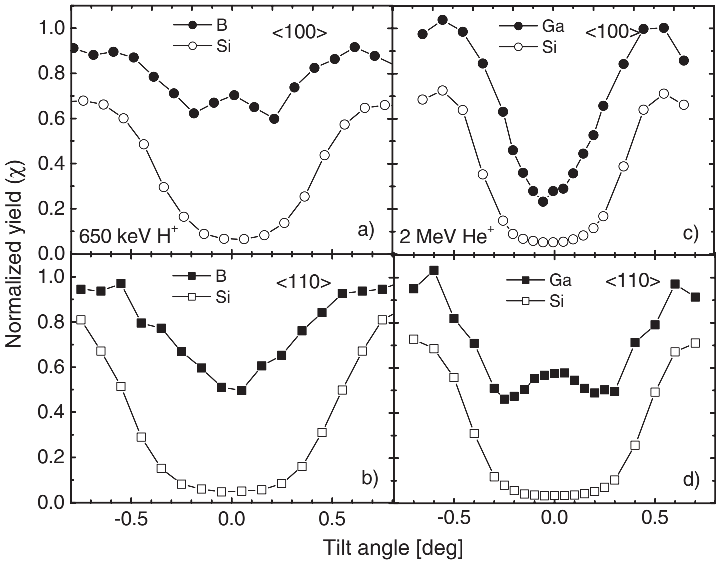

Figure 2. Normalized yield from the impurity atoms and the Si atoms in the doped region as function of the angle between the incident beam and various low index axes along the (100) plane: for B and Si signals along the ⟨100⟩ (a) and ⟨110⟩ (b) axes using a 650 keV H^+ beam, for Ga and Si signals along the ⟨100⟩ (c) and ⟨110⟩ (d) axes using 2 MeV He^+ beam.

yield at saturation is higher along the ⟨110⟩ with respect to the ⟨100⟩ axis, opposite to case of B. This inversion indicates that the lattice location of displaced Ga atoms is different from that of B atoms [9] as confirmed by the angular scan measurements reported in figure 2.

Angular scans across the ⟨100⟩ and ⟨110⟩ axes along the (100) plane have been performed for B and Ga doped Si samples after irradiation at a fluence above χ_B and χ_{Ga} saturated, respectively.

In figure 2 the normalized yields from the B (figures 2(a) and (b)) or Ga (figures 2(c) and (d)) impurity atoms and the Si atoms in the doped region as function of the angle between the incident beam (650 keV H^+ or 2 MeV He^+) and various low index axes along the (100) plane are reported.

The angular scan of B shows a lot of differences with respect to Ga. In particular for B along the ⟨100⟩ axis a small peak is evident and along the ⟨110⟩ axis there is significant attenuation in the scattering yield with a minimum at mid-channel. This kind of configuration occurs when a fraction of the impurity atoms are displaced along the ⟨100⟩ axis with respect to the ideal substitutional position. Theoretical calculations indicated that B is displaced along the 100 direction when the lowest energy pairs are formed as a consequence of the migration in the presence of an excess of Si_I [4, 14]. The ⟨100⟩ angular scan for Ga shows a pronounced attenuation with a minimum at 0 degrees tilt with a narrower dip with respect to the Si, whilst a significant peak is observed in the ⟨110⟩ channel in contrast to the B signal, indicating that a fraction of the Ga atoms occupy a position which is shadowed along the ⟨100⟩ direction and near to the centre of the ⟨110⟩ channel; such a position [9] is indicated as the tetrahedral interstitial site (Ga_T). As reported by first principle calculations, the tetrahedral interstitial site is the lowest energy position for Ga atoms interacting with Si_I, in particular it is quite likely that this is due to the formation of Ga_{Si}–Ga_T complexes [15].

The experimental data of the figure 1 can be fitted by the following expression:

$$\chi = \chi_F - (\chi_F - \chi_0)\mathrm{e}^{-\sigma N_\mathrm{I}} \tag{1}$$

where χ_0 is the χ of the non-irradiated sample, N_I is the $\mathrm{Si_I}$ fluence, and σ is a fitting parameter that can be interpreted as the effective cross-section for the capture of $\mathrm{Si_I}$ by substitutional dopants. The best-fit curves are indicated in figure 1 by a solid line for both axes and impurities, the fitting parameter σ resulted $(1.1 \pm 0.1) \times 10^{-16}$ cm^2 and $(5.0 \pm 0.1) \times 10^{-16}$ cm^2 for B (figure 1(a)) and Ga (figure 1(b)), respectively. The model used to describe the off-lattice displacement process assumes that: (a) the impurity A binds an interstitial I by forming a mobile pair AI, (b) A migrates in this complex form (AI), (the estimated migration barrier is ~1 eV); (c) the high dopant density (A–A distance ~2 nm) favours complex formation so the migrating A binds with a substitutional A into a more stable A–A complex; (d) the process ends when there are no more unpaired substitutional impurities. Assuming that the limiting step is the $\mathrm{Si_I}$ capture process it is possible (more details are reported in Piro *et al* [13]) to obtain the following expression for χ:

$$\chi(t) = \chi_F - (\chi_F - \chi_0)\exp(-\gamma\sigma_T G_\mathrm{I} t) \tag{2}$$

which is equation (1) found by setting $\sigma = \gamma\sigma_\mathrm{T}$ (in this way the fitting parameter σ is the trapping cross section by the factor γ) and $G_\mathrm{I} t = N_\mathrm{I}$. The parameter γ is a clustering factor that is $\gamma = 2$ when pairs of impurity atoms are formed as final complexes, according to theoretical calculations that predict pairs as the lowest energy complexes for B [4, 14] and Ga [15] in Si in the presence of an excess of $\mathrm{Si_I}$. The trapping cross section σ_T is equal to $\sigma/2$ and it is clearly independent of the particular axial channelling, while σ and the saturation χ_F values depend on the impurity species and cluster configuration.

4. Conclusion

We have shown that information on the interaction between $\mathrm{Si_I}$ and substitutional impurities at RT can be achieved using irradiation with light ions to produce the excess of $\mathrm{Si_I}$, and the ion-channelling technique to detect the impurity displacement. The results are consistent with the formation of impurity-$\mathrm{Si_I}$ pairs mobile at RT and, therefore, with diffusion controlled by the $\mathrm{Si_I}$ concentration. Diffusion ends when stable B–B or Ga–Ga complexes are formed. The rate of the impurity displacement has been used to estimate the cross section of the $\mathrm{Si_I}$ capture by substitutional impurity, and it was five times higher for Ga with respect to B. Finally, the displacement rate goes to zero when every substitutional impurity has formed stable complexes. The complexes formed by B and Ga atoms are different as indicated by the peculiar features showed by the measured angular scans performed for both the impurities along the ⟨100⟩ and ⟨110⟩ axes.

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References

[1] Jain S C, Schoenmaker W, Lindsay R, Stolk P A, Decoutere S, Willander M and Maes H E 2002 *J. Appl. Phys.* **91** 8919

[2] Stolk P A, Gossmann J H J, Eaglesham D J, Jacobson D C, Rafferty C S, Gilmer G H, Jaraìz M, Poate J M, Luftman H S and Haynes T E 1997 *J. Appl. Phys.* **81** 6031
[3] Mirabella S, Bruno E, Priolo F, De Salvador D, Napolitani E, Drigo A V and Carnera A 2003 *Appl. Phys. Lett.* **83** 680
[4] Zhu J, Diaz dela Rubia T, Yang L H, Mailhiot C and Gilmer G H 1996 *Phys. Rev.* B **54** 4741
[5] Liu X Y, Windl W and Masquelier M P 2000 *Appl. Phys. Lett.* **77** 2018
[6] Bracht H 2000 Defects and diffusion in silicon technology *MRS Bull.* **25** 22
[7] Fahey P, Iyer S S and Scilla G J 1989 *Appl. Phys. Lett.* **54** 843
[8] Venezia V C, Pelaz L, Gossmann H J L, Agarwal A and Haynes T E 2004 *Phys. Rev.* B **69** 125215
[9] Appleton B R and Foti G 1977 *Ion Beam Handbook for Material Analysis* ed J W Mayer and E Rimini (New York: Academic) p 91
[10] Romano L, Piro A M, Grimaldi M G, Lopez G M and Fiorentini V 2005 *Phys. Rev.* B **71** 165201
[11] Piro A M, Romano L, Mirabella S and Grimaldi M G 2005 *Appl. Phys. Lett.* **86** 81916
[12] Ziegler J F, Biresack J P and Littmark U 1985 *The Stopping and the Range of Ions in Solids* (New York: Pergamon)
[13] Piro A M, Romano L, Mirabella S, Grimaldi M G and Rimini E 2005 *J. Phys.: Condens. Matter* **17** S2273
[14] Alippi P, Colombo L, Ruggerone P, Sieck A, Seifert G and Frauenheim T 2001 *Phys. Rev.* B **64** 075207
[15] Lopez G M and Fiorentini V 2004 *Phys. Rev.* B **69** 155206