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Attractive interaction of Indium with point defects and silicon in GeSi

R. Govindaraj and R. Sielemann

Hahn-Meitner Institute, Glienicker Strasse, 100, Berlin, Germany

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Abstract

In electron irradiated Ge$_{0.98}$Si$_{0.02}$, In-vacancy and In-interstitial complexes were observed in analogy with defects in pure Ge. Isochronal annealing measurements reveal that the temperature of dissociation of In-defect complexes deviate from pure Ge subjected to identical e-irradiation, which is explained on the basis of strain induced by undersized silicon atoms affecting the binding energy of In-V and In-I complexes. Besides the pairing with intrinsic defects the interaction of In with Si atoms is observed resulting in several different configurations. Complementary experiments performed in Ge$_{0.98}$Si$_{0.02}$ and Ge$_{0.94}$Si$_{0.06}$ elucidate the attractive interaction between In and Si.

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Germanium-silicon (Ge\textsubscript{x}Si\textsubscript{1−x}) alloy, is an exciting material for band gap engineering and the integration of fast analog circuits\textsuperscript{1,2,3}, due to tunable lattice constant and band gap energy with \( x \). Interactions of indium (an important acceptor impurity in Ge/ Si system) with point defects have been carried out in detail in Ge, as a function of electronic chemical potential by Perturbed angular correlation (PAC) spectroscopy\textsuperscript{4,5}. PAC method has been applied to defect studies in elemental and compound semiconductors\textsuperscript{6}. Of special importance for the PAC study of semiconductors is the need for only a dilute concentration of probe atoms (typically 10\textsuperscript{13} cm\textsuperscript{−3} to 10\textsuperscript{14} cm\textsuperscript{−3}) and the possibility of studying the sample at different temperatures. The present PAC experiment illustrates the interaction between the electron irradiation induced defects and indium atoms in Ge\textsubscript{0.98}Si\textsubscript{0.02}, thus elucidating the role of 2 at% silicon in the formation and evolution of point defects.

Ge\textsubscript{0.98}Si\textsubscript{0.02} crystals (n-type and \( n_e = 10^{15} \) cm\textsuperscript{−3}) were grown along <110> by Czochralski technique as reported\textsuperscript{2}. \( ^{111}\text{In} \) concentration \( \leq 5 \times 10^{13} \) cm\textsuperscript{−3} of probe atoms are recoil implanted uniformly to a depth of 4 \( \mu \)m as reported earlier\textsuperscript{4,5}. The coincidence spectra between 171 and 245 keV \( \gamma \) rays of \( ^{111}\text{Cd} \) were measured using a four BaF\textsubscript{2} detector PAC spectrometer with a time resolution of 660 ps\textsuperscript{5}. The measured perturbation function \( R(t) \) were analysed for static quadrupole interactions as \( R(t) = A_2 (f_o \exp(-\Delta_0 t) + \sum_{i=1}^{n} f_i G_i(t)) \), with the perturbation factor \( G(t) \) is given as \( \sum_{m=0}^{3} S_{2m} (\eta) \cos(g_n (\eta) \omega_m t) \exp(-g_n (\eta) \delta_m \omega_m t) \) where \( n \) is determined by the number of frequency components occurring in the \( R(t) \) spectrum. The frequencies \( \nu_Q \) are related to \( \omega_m \) by \( \omega_m = (m \pi / 10) \nu_Q \), when the interaction is axially symmetric. The parameters evaluated are \( \nu_Q \) (=\( eQV_{zz}/h \)), width of Lorentzian distribution of quadrupole frequencies \( \delta \) as experienced by the fraction \( f \) of probe atoms\textsuperscript{5}. \( A_2 \) is the effective anisotropy of the \( \gamma - \gamma \) cascade and \( \Delta_0 \) denotes the width of the Lorentzian distribution of quadrupole frequencies with a mean at 0 MHz. While \( \delta_m = \Delta \nu_{Qm}/\nu_{Qm} \), where \( \Delta \nu_{Qm} \) is the spread of interaction strength. PAC measurements were carried out in \( ^{111}\text{In} \) recoil implanted Ge\textsubscript{0.98}Si\textsubscript{0.02}. Subsequent to annealing at 823 K, the sample was irradiated with electron of energy 2 MeV to a dose of 10\textsuperscript{15} e/cm\textsuperscript{2} at 77 K to produce frenkal pairs in a controlled manner and isochronal annealing measurements have been carried out. Measurements have also been carried out in \( ^{111}\text{In} \) recoil implanted Ge\textsubscript{0.94}Si\textsubscript{0.06} to further elucidate the role of Si.

The quadrupole parameters in \( ^{111}\text{In} \) recoil implanted sample at room temperature are
listed in Table-I. Based on the reported results, $f_1$ and $f_2$ are identified to be due to In-vacancy (52 MHz, $\eta = 0$) and In-interstitial (415 MHz, $\eta = 0$) complexes respectively. Computationally these are deduced to be split vacancy with C$_d$ (on the bond centre) and C$_d$-self-interstitial complex with split configuration respectively. A sharp slope in the $R(t)$ spectrum (Cf Fig.1a) around $t \approx 0$ ns is mostly contributed by $^{111}$Sn recoil implanted defects located at next nearest neighboring environment of the probe atoms. PAC spectrum in the recoil implanted Ge$_{0.98}$Si$_{0.02}$ (Fig.1a) is distinctly different from that of Ge$_{0.98}^{111}$Ge. In $^{111}$In implanted n-Ge (with charge carrier concentration $n_e \approx 10^{15}$ e$^-$/cm$^3$) it is observed that interstitials are predominantly present compared to vacancies. In the present sample (n-Ge$_{0.98}$Si$_{0.02}$ of similar $n_e$) we observe that both vacancies and interstitials are predominantly present (Cf. Table-I), thus bringing out the significant role played by silicon in stabilising vacancies at the cost of interstitials, the details of which are discussed subsequently.

The sample is annealed at 888 K for 15 minutes (Cf. Fig 1b) to restore all the probe atoms at defect free substitutional sites. The fractions $f_3$ and $f_4$ are plausibly interpreted as In-Si$_2$ complex and In-Si clusters, the discussion on these assignment is presented in the later part of this work.

Results of PAC measurements in the e-irradiated sample are compiled in Table-I. Corresponding PAC spectra are shown in Fig 1. In Ge$_{0.98}$Si$_{0.02}$, the fractions $f_1$ (In-V$_0$) and $f_2$ (interstitial-In) disappear following annealing treatments at 450 and 350 K respectively (Cf. Fig.2), whereas in pure Ge subjected to electron irradiation it has been observed that In-I$_0$, In-V$_0$ complexes dissociate around 380 and 400 K respectively. These results imply an accelerated recovery of In-I$_0$ complex and a retarded dissociation of In-V$_0$ complex in the case of Ge$_{0.98}$Si$_{0.02}$ compared with pure Ge subjected to identical electron irradiation. The difference in recovery stages can be understood due to the strain developed at undersized silicon atoms ($r_{Ge} = 1.22$ Å and $r_{Si} = 1.17$ Å). The strain developed at Si might have an influence over a few neighbors affecting the displacement fields of interstitial and vacancies thus resulting in a change of binding energy of In-V$_0$ and In-I$_0$ complexes. Silicon being undersized than Ge would have more binding to interstitial complex contributing for the lower binding energy of In-I$_0$ complex in Ge$_{0.98}$Si$_{0.02}$ than in pure Ge, while the same effect contributes for an increased binding energy of In-V$_0$ complex. The fractions $f_3$ and
| Sample treatment                                      | index | $\nu_Q$ (MHz) | $\eta_i$ | $f_i$     | Identification                      |
|------------------------------------------------------|-------|---------------|---------|----------|-------------------------------------|
| $^{111}$Sn recoil implanted                          | 0     | 0             | 0       | 0.83±0.01| substitutional probe atoms          |
| Ge$_{0.98}$Si$_{0.02}$                                | 1     | 52±1          | 0       | 0.10±0.02| In-V$_O$                           |
|                                                      | 2     | 415±2         | 0       | 0.07±0.01| In-I$_O$                           |
| $^{111}$Sn recoil implanted and annealed (at 880 K) Ge$_{0.98}$Si$_{0.02}$ | 3     | 11±2          | 0.3     | 0.31±0.03| In-Si$_2$ / In-Si complex           |
|                                                      | 4     | 34±3          | 0       | 0.05±0.01| In-Si clusters                      |
| electron irradiated                                  | 0     | 0             | 0       | 0.59±0.02| substitutional probe atoms          |
| Ge$_{0.98}$Si$_{0.02}$                                | 1     | 52±1          | 0       | 0.12±0.01| In-V$_O$                           |
| and annealed at 338 K                                | 2     | 415±2         | 0       | 0.09±0.01| In-I$_O$                           |
|                                                      | 3     | 15±3          | 0.35    | 0.2±0.03 | In-Si$_2$ / In-Si complex           |
| electron irradiated                                  | 0     | 0             | 0       | 0.64±0.03| substitutional probe atoms          |
| Ge$_{0.98}$Si$_{0.02}$ and annealed at 880 K          | 1     | 52±1          | 0       | 0.11±0.01| In-V$_O$                           |
|                                                      | 2     | 415±2         | 0       | 0.05±0.01| In-I$_O$                           |
|                                                      | 3     | 15±3          | 0.35    | 0.2±0.03 | In-Si$_2$ / In-Si complex           |
| electron irradiated                                  | 0     | 0             | 0       | 0.74±0.03| substitutional probe atoms          |
| Ge$_{0.98}$Si$_{0.02}$ and annealed at 880 K          | 3     | 11±2          | 0.32    | 0.2±0.02 | In-Si$_2$ / In-Si complex           |
|                                                      | 4     | 96±2          | 0       | 0.06±0.01| In-Si$_2$ / In-Si complex           |
| $^{111}$Sn recoil implanted and annealed (at 880 K) Ge$_{0.94}$Si$_{0.06}$ | 0     | 0             | 0       | 0.48±0.04| substitutional probe atoms          |
|                                                      | 3     | 10±2          | 0.4     | 0.43±0.02| In-Si$_2$ / In-Si complex           |
|                                                      | 4     | 62±3          | 0       | 0.09±0.02| In-Si$_2$ / In-Si complex           |
| $e^{-}$ irradiated and annealed (at 880 K) Ge        | 0     | 0             | 0       | 1        | substitutional probe atoms          |

$f_4$ are absent in the starting sample (in which probe atoms were recoil implanted) but only occurs following the annealing at 850 K. This observation rules out their formation due to athermal migration of defects. Also these fractions were not observed in pure Ge sample subjected to identical electron irradiation and annealed at 850 K$^5$, thus implying the association of Si atoms with these complexes. A high value of $f_3$ and non zero $\eta_3$ (Cf. Table-I) imply a simple nature of the defect but axially asymmetric. Hence the complex cannot be In-Si, as In-X (where X= P, Sb etc.,) pairs are mostly axially symmetric$^{14}$. Therefore $f_3$ is plausibly interpreted to be In-Si$_n$ complex with $n \geq 2$. This is analogous to the formation of Ge dimers aided by divacancies in electron irradiated SiGe systems$^{16}$. $f_4$ with axially symmetric configuration is interpreted to be due to In-Si clusters. The formation of In-Si complexes /clusters leading to the occurrence of $f_3$ and $f_4$ could be contributed by irradiation induced defects with an important role being played by strain at silicon atoms. Since $f_3$ and $f_4$ were observed in the probe recoil implanted sample following
annealing at 850 K, we would explore the role of the diffusion of silicon atoms in the formation of In-Si complexes. Assuming the diffusion coefficient of silicon in germanium to be around $10^{-17} \text{ cm}^2/\text{sec}$ around 823 K\cite{16}, the diffusion length can be computed to be around 40 Å for the (experimental) annealing time of 3600 seconds. In the sphere of 40 Å radius about 200 silicon atoms are present in Ge$_{0.98}$Si$_{0.02}$, implying an appreciable probability for the formation of In-Si complexes. In addition the strain developed due to undersized silicon could enhance diffusion\cite{16} leading to a higher probability for the formation of such complexes. The occurrence of In-Si complexes and In-Si clusters indicate attractive interaction between In and Si atoms. Now we will discuss the effect of Si on the electronic properties of the samples (beyond the defect recovery stages) in terms of the experimental quadrupole parameters. R(t) spectrum (Cf. Fig 4a) corresponding to electron irradiated and well annealed (at 880 K) pure n-Ge at 10 K. In the absence of any quadrupole frequency component, the Dampening parameter ($\Delta_0$) associated with $f_0$ as deduced in this case is 2.3 MHz similar to the temperature dependence of hyperfine interactions of Cd in Ge\cite{11}. Details of various electronic effects contributing for the occurrence of $\Delta_0$ is discussed elsewhere\cite{11}. Analysis of the PAC spectra in well annealed Ge$_{0.98}$Si$_{0.02}$ and Ge$_{0.94}$Si$_{0.06}$ samples (Cf. Fig 4b and 4c) at 300 K, show that the value of $\Delta_0$ are around 3.2 and 3.7 MHz respectively. The observed increase in $\Delta_0$ with increasing silicon concentration with the PAC measurements carried out at 300 K is understood based on electronic effects preferably due to higher JT distortion. Summarizing, in electron irradiated Ge$_{0.98}$Si$_{0.02}$ there is an accelerated (retarded) recovery of In-I$_0$ (In-V$_0$) complexes. The occurrence of In-Si complexes and In-Si clusters in Ge$_{0.98}$Si$_{0.02}$ and Ge$_{0.94}$Si$_{0.06}$ indicates a strong attractive interaction between In and Si.

Results reported here are based on preliminary measurements carried out on GeSi. Detailed PAC measurements in GeSi with slightly different silicon composition and subsequent to a larger number of annealing steps have to be carried out for a complete and more detailed understanding of the aspects related to In-defect interactions as influenced by silicon in GeSi.

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Figure captions

Fig 1. TDPAC spectra in Ge\textsubscript{0.98}Si\textsubscript{0.02} for the following cases \textit{viz} (a) as \textsuperscript{111}Sn recoil implanted (b) annealed at 880 K (c) \textit{e}\textsuperscript{−} irradiated (d) annealed at 338 K (e) 425 K and (f) 923 K

Fig 2. Variation of \textit{f}_1 (In-V\textsubscript{0};52 MHz) and \textit{f}_2 (In-I\textsubscript{0};415 MHz) with annealing temperature

Fig 3. Variation of hyperfine parameters of In-Si complexes with annealing temperature

Fig 4. TDPAC spectra corresponding to annealed (at 880 K) (a) Ge (b) Ge\textsubscript{0.98}Si\textsubscript{0.02} and (c) Ge\textsubscript{0.94}Si\textsubscript{0.06}
1 B.S. Meyerson, *Scientific American* 9, 42 (1994).
2 J. Weber, *it Phys Rev* B40, 5683 (1989).
3 Temkin et al., *Appl. Phys. Lett.* 52, 1089 (1988)
4 M. Brussler, H. Metzner and R. Sielemann, *Materials Science Forum* 38, 1205 (1989)
5 H. Haesslein, R. Sielemann and C. Zistl, *Phys. Rev. Lett.* 80, 2626 (1998)
6 Th. Wichert, N. Achtziger, H. Metzner and R. Sielemann, in *Hyperfine interactions of Defects in Semiconductors*, edited by G. Langouche (Elsevier, Amsterdam, 1992), p79.
7 N. V. Abrosimov et al, *J. Crys. Growth* 174, 182 (1997)
8 R. Sielemann, *Nucl. Instr. Meth.* B146 329 (1998)
9 R. Sielemann et al, *Physica* B273-274 565 (1999)
10 H. Hohler et al, *Phys. Rev.* B70 155313 (2004)
11 A. F. Pasquevich and R. Vianden, *Phys. Rev.* B37, 10858 (1988); Also see A. F. Pasquevich and R. Vianden, *Phys. Rev.* B41, 10956 (1990)
12 A. da Siliva et al, *Phys. Rev.* B62 9903 (2000)
13 A. Fazzio et al, *Phys. Rev.* B61 R2401 (2000)
14 N. Achtziger, W. Witthuhn, *Phys. Rev.* B47 6990 (1993)
15 J. W. Corbett and J. C. Bourgoin, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, Newyork, 1975) Vol 2
16 S. M. Prokes, O. J. Glembocki and D. J. Godbey, *Appl. Phys. Lett.* 60 1087 (1992)
