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J. Phys.: Condens. Matter **17** (2005) S2171–S2184 doi:10.1088/0953-8984/17/22/004

Interstitial-carbon-related defects in relaxed SiGe alloy: the effect of alloying

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Received 6 October 2004
Published 20 May 2005
Online at stacks.iop.org/JPhysCM/17/S2171

Abstract
C_i and C_iC_s are two main defects produced via the Watkins replacement mechanism when Si-based materials containing carbon are subjected to particle irradiation. In the present article we re-examine our experimental observations reported on these defects in relaxed $Si_{1-x}Ge_x$ alloy layers in the light of very recent and thorough theoretical investigations (Venezuela *et al* 2004 *Phys. Rev.* B **69** 115209 and Balsas *et al* 2004 *Phys. Rev.* B **70** 085201). In addressing these defects two main issues are taken up. Firstly, the role of alloying upon the position of the electrical levels in the bandgap is considered: a linear shift towards the valence band with the same rate of all related levels is observed experimentally and predicted theoretically. Secondly, the dynamics of migration of interstitial carbon (C_i) in the process of forming C_iC_s is analysed. Our suggestion that C_i migrates via Si-based paths has now found theoretical justification.

1. Introduction

The interstitial-carbon defect, C_i, being isoelectronic to silicon, is of particular importance as it may provide important clues as to the configuration and dynamical properties of the isolated silicon self-interstitial, the direct observation of which is still lacking. The interstitial-carbon defect is also an interesting defect as it introduces an acceptor level near the conduction band and a donor level near the valence band, both levels being rather shallow. Strain-relaxed, epitaxial $Si_{1-x}Ge_x$ layers enable one to study the behaviour of different charge states of a defect when the band structure changes with composition. One of the main questions to ask is whether the energy difference between two levels (the so-called Hubbard energy U) and, hence, the degree of lattice relaxation accompanying the capture of the extra electron is composition dependent.

The C_i defect, created in strain-relaxed $Si_{1-x}Ge_x$ layers by 2 MeV proton irradiations, has been studied by us using deep-level transient spectroscopy (DLTS). In n- and p-type $Si_{1-x}Ge_x$ both the $(-/0)$-acceptor level and the $(0/+)$-donor level were followed as a function of x in the

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range $0 \leqslant x \leqslant 0.50$ [1–3]. Both the acceptor and donor levels were found to move deeper into the bandgap with increasing x, and no pinning to any of the band edges was observed for any of these levels. The main implication for the donor level when increasing the Ge composition is that it becomes gradually shallower until it merges with the valence band for $x \approx 37\%$.

Being mobile at rather low temperatures, C_i might be trapped by some of the substitutional carbon atoms (C_s) that escaped the Watkins replacement mechanism. In n-type $Si_{1-x}Ge_x$ the C_iC_s pair induces an acceptor level slightly deeper than $C_i^{-/0}$. Increasing the Ge content in the alloy makes the corresponding level move with the same rate as for both C_i-related levels. Our proposal was that the similar core structures of $C_i^{-/0}$ and $C_iC_s^{-/0}$, in which the trapped electron resides primarily in the non-bonding p orbital of the interstitial Si atom shared by the two defects, could be responsible for the mutual pinning of $C_i^{-/0}$ and $C_iC_s^{-/0}$.

Quantitative analysis of the annealing of C_i, resulting in a migration and subsequent pairing with C_s, was carried out in n-type material [2], where a strong dependence on the composition was observed. Whereas C_i anneals in pure Si during a 15 min heat treatment at a temperature of 320 K, a temperature above 500 K is needed in $Si_{0.50}Ge_{0.50}$. This was a challenging observation as it might reflect a retarded diffusion of C_i in $Si_{1-x}Ge_x$ with increasing x, similar to what has been observed, but not yet satisfactorily explained, for high temperature diffusion of interstitial boron, B_i, in $Si_{1-x}Ge_x$ for $x \leqslant 0.50$ [4], a defect which also has an interstitialcy structure [5]. In the case of interstitial carbon, we argued [3] that a Si path constitutes the only route for C_i to move.

Very recently, two theoretical approaches have been dedicated to both C_i and C_iC_s defects and their dynamics [6, 7]. All of our results and attempts to explain the experimental observations have been given a fundamental and quantitative justification in these papers. Below, we recall the main experimental results and detail the main inputs of the two theoretical studies.

2. Experimental conditions

n- and p-type $Si_{1-x}Ge_x$ layers were grown in similar ways by molecular-beam epitaxy (MBE) on (001) Si substrates using the compositional grading technique [8]. This technique is capable of producing high-quality $Si_{1-x}Ge_x$ layers with respect to structural, optical, and electrical characteristics [9]. The carbon concentration in the MBE-grown samples is relatively high, in the range of 10^{17}–10^{18} cm^{-3}, as determined by secondary ion mass spectrometry (SIMS), whereas the oxygen concentration is far below the SIMS detection limit of $\sim 1 \times 10^{17}$ cm^{-3}. The oxygen concentration is even below 10^{16} cm^{-3} as the two well known oxygen-related defects VO_i and C_iO_i are always found at concentrations smaller than in commercial FZ samples. The strain-relaxed $Si_{1-x}Ge_x$ layers were 4 μm thick, doped with either Sb to 2–5 $\times 10^{15}$ cm^{-3} (the n-type layers) or with B to 3–10 $\times 10^{15}$ cm^{-3} (the p-type layers). On top of these layers, 0.5 μm thick layers doped to high concentrations ($\sim 5 \times 10^{19}$ cm^{-3}) of either B (on the n-type layers) or Sb (on the p-type layers) were grown. Mesa diodes were subsequently formed by photolithography. Irradiations were performed with either 2 MeV electrons or 2 MeV protons to doses of 1–4 $\times 10^{15}$ or 3–5 $\times 10^{12}$ cm^{-2}, respectively. Electrons of this energy pass through the diodes whereas the protons stop at a depth of 60 μm, which is far beyond the investigated zone of a few micrometres from the top of the diode. The diodes were irradiated and kept at room temperature (RT) prior to measurement except for the diodes of small x, which were irradiated and kept at 270 K until they were subjected to measurement. The storage at 270 K was used in order to impede the transformation of the C_i defect into C_iC_s, which is known to take place at a temperature only slightly above room temperature for small x values [10].

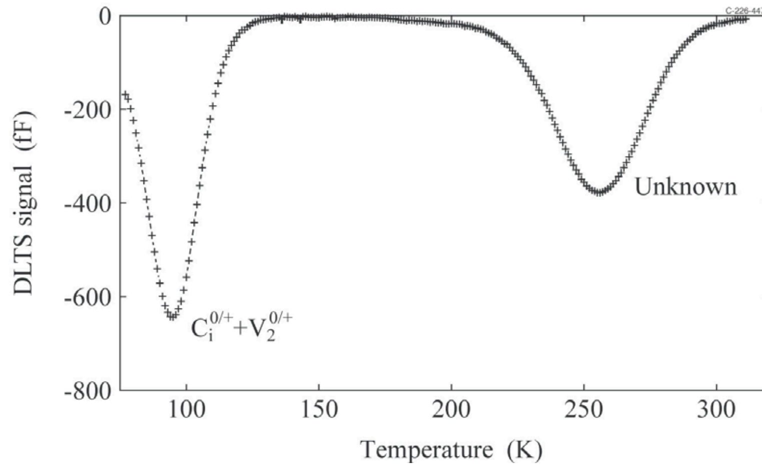

Figure 1. DLTS-temperature scan of electron-irradiated $Si_{0.84}Ge_{0.16}$ n^+p-diode, recorded using a repetition rate of 250 Hz [3]. The 'DLTS fingerprints' of the two lines are $\Delta H_p = 0.16$ eV, $\sigma_p = 2 \times 10^{-14}$ cm^2, for the shallow peak and $\Delta H_p = 0.46$ eV, $\sigma_p = 1 \times 10^{-14}$ cm^2, for the unknown peak respectively.

3. Experimental results and recent theoretical outcome

3.1. Electronic properties

A representative DLTS spectrum of a p-type $Si_{0.84}Ge_{0.16}$ diode after electron irradiation to a dose of 3×10^{15} cm^{-2} is shown in figure 1. It has already been demonstrated [1] that the shallower line is composed of two lines, emerging from the donor levels of the di-vacancy, $V_2^{0/+}$, and the interstitial carbon, $C_i^{0/+}$. Two related features are worth mentioning. Firstly, the $C_i^{0/+}$ anneals at a lower temperature than does the $V_2^{0/+}$ defect for all compositions below $x = 0.50$, and secondly, the intensity of the $V_2^{0/+}$ line is always much smaller than that of the $C_i^{0/+}$ line. Thus, before annealing, the 'DLTS fingerprints' (ionization enthalpy and apparent capture cross section) of this line are those of the $C_i^{0/+}$ defect and after annealing of the $C_i^{0/+}$ defect they are those of the $V_2^{0/+}$ defect. The line labelled 'unknown', which is of no concern here, has not been unambiguously identified but probably involves the Ge–V–B complex supported by an observed variation with irradiation dose, Ge composition, and B concentration.

Figure 2 represents two DLTS spectra recorded in an n-type $Si_{0.95}Ge_{0.05}$ diode subjected to similar irradiation conditions as above [2]. Here the analysis is much easier than in the case of p-type alloy as no overlapping with other major irradiation-induced levels can be expected. The double-acceptor level of the di-vacancy is clearly away from the carbon-related lines and there is no risk for the acceptor level $C_i^{-/0}$ to overlap with the A centre (VO_i), which is an important irradiation defect. The samples used in this study are indeed MBE grown with no oxygen. The spectrum recorded after annealing the diode *in situ* at 370 K for 15 min contains the acceptor level $C_iC_s^{-/0}$, which is also clearly distinguished. We will come to the dynamics of this conversion in the second part of the present review.

The electron-ionization enthalpies of the two charge states $C_i^{0/+}$ and $C_i^{-/0}$ are reported in figure 3. The hole-ionization enthalpy ΔH_p of the donor level has been converted to ΔH_n, the electron-ionization enthalpy relative to the conduction band edge, by using the simple conservation law $\Delta H_p + \Delta H_n = \Delta H_{cv}$, where ΔH_{cv} is the bandgap enthalpy. In agreement with van de Walle and Martin [11], we assume that the reduction of the bandgap is entirely

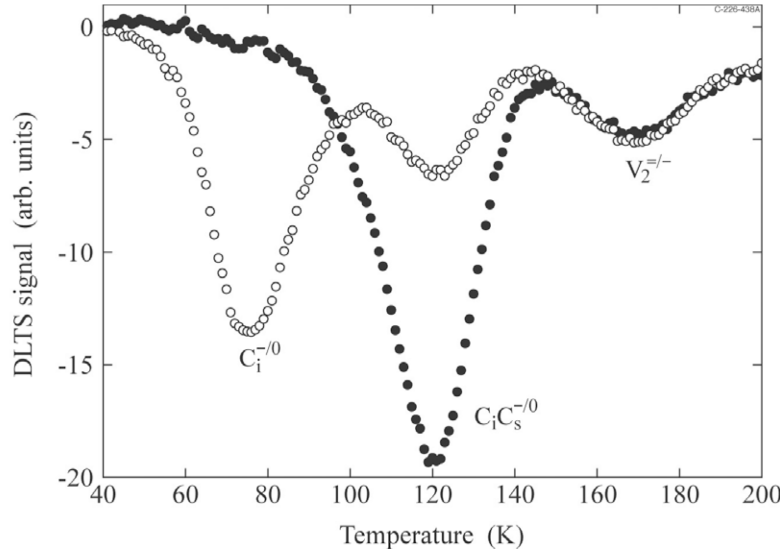

Figure 2. DLTS spectra of a $Si_{0.95}Ge_{0.05}$ diode immediately after proton irradiation (○) and after annealing at 370 K for 15 min (●) [2]. The spectra were recorded using a repetition rate of 2.5 kHz.

reflected in the valence band shift and thus the bandgap enthalpy $\Delta H_{cv}(x, T)$ is given by [12]

$$\Delta H_{cv}(x, T) = 1.17 + \frac{\alpha\beta T^2}{(\beta + T)^2} - 0.43x + 0.206x^2 \text{ eV} \quad (1)$$

where $\alpha = 4.9 \times 10^{-4}$ eV K^{-1} and $\beta = 655$ K [13]. The bandgap enthalpy of figure 3 has been calculated for a temperature of 100 K; this is a reasonable compromise, considering the temperature positions of the DLTS peaks for both the acceptor and donor states.

It appears from figure 3 that neither the acceptor nor the donor levels are pinned to any of the band edges, both moving away from the conduction band with a rate of $+0.30x \pm 0.02$ eV. They remain at a constant Hubbard energy separation of about 0.8 eV from each other while the composition is varied. However, the main consequence of alloying is that the donor level merges with the valence band for $x \approx 37\%$, leaving the acceptor level $C_i^{-/0}$ as the only representative charge state of the interstitial carbon.

In figure 4, we report the electron-ionization enthalpies for both acceptor states $C_i^{-/0}$ and $C_iC_s^{-/0}$. The remarkable feature is again their mutual pinning while they both move deeper into the bandgap with increasing alloy composition. This may find a logical explanation with reference to an early work carried out in silicon by Watkins and Brower [14] and Song *et al* [15]. The major inputs pointed out by these authors are worth mentioning here to understand the effect of alloying: the EPR signal related to the interstitial carbon appeared to be consistent with the C_{2v} symmetry, a configuration corresponding to a $\langle 100\rangle Si_i$–C_i interstitialcy where both Si and C atoms share the same substitutional site [15]. The consequence is that each of the two atoms is threefold coordinated, developing thus only three bonds with the respective first nearest neighbours [15]. In such a configuration, the unpaired electron of C_i^+ was found to reside on the p orbital on the C_i atom, the p orbital on the Si_i being empty. However, to form C_i^- we must add two electrons. The unpaired electron was then found to reside in the nonbonding p orbital on the Si_i atom, the corresponding p orbital on the C_i atom being saturated. But the major difference resulting from EPR analysis is that in the case of C_i^+ the unpaired electron

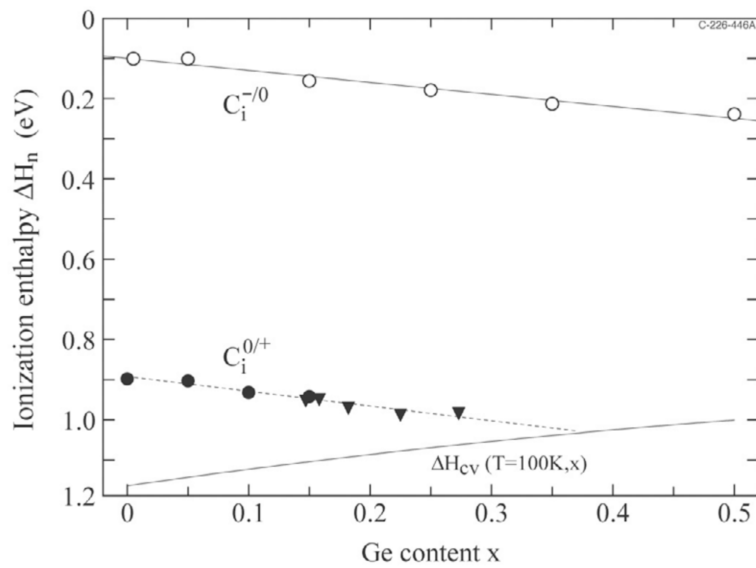

Figure 3. Ionization enthalpies as a function of the Ge content x of the $Si_{1-x}Ge_x$ epitaxial layers for the $C_i^{-/0}$ defect [3]: (O) from [2] and the $C_i^{0/+}$ defect; (▼,●) from [3] (▼) and from [1] (●). The uncertainties of the ionization enthalpies are similar to the size of the markers. In agreement with [12] the energy of the conduction band is assumed to be constant in the investigated composition range. The lines are linear fits, leading to a rate of shift away from the conduction band of $\pm 0.30x$ eV.

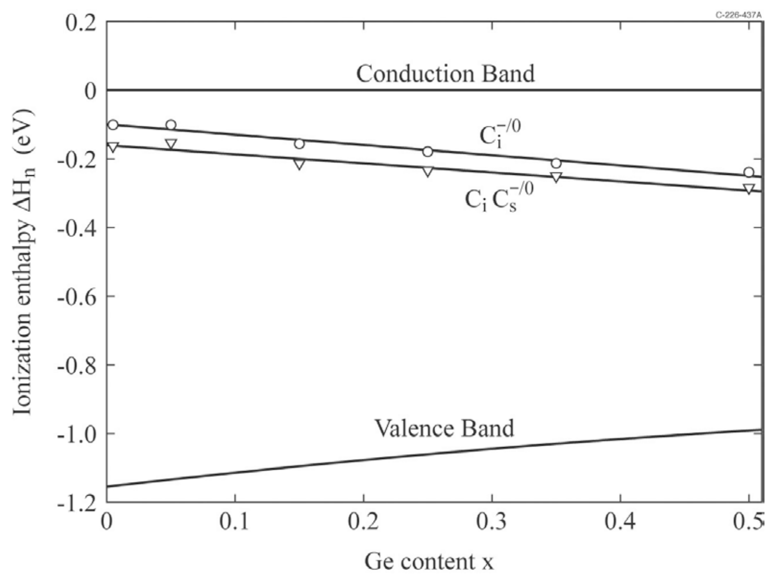

Figure 4. Ionization enthalpies as a function of alloy composition of the $Si_{1-x}Ge_x$ epitaxial layers for the C_i (O) and the C_iC_s (∇) defects [2]. Also shown are the energies of the conduction and valence band edges taken from [12]. The full lines through the ionization enthalpies are linear least square fits giving slopes of $+0.30x$ eV when counted from the conduction band.

was found localized on the C_i atom whereas in the case of C_i^- it was found to be rather more diffuse.

On the other hand, the electronic structure of the deepest metastable configuration of $C_iC_s^{-/0}$, which is our concern here and which is represented by the second peak in figure 2, was found to correspond basically to an isolated Si_i–C_i interstitialcy slightly perturbed by the presence of a second carbon atom replacing one of the nearest silicon atoms. The symmetry of this configuration, labelled A by Song *et al* [14], is C_{1h}.

The similarity of the core structures of C_i and C_iC_s is expected not to be affected by alloying in the sense that adding Ge to the lattice would shift equally both corresponding levels, provided no Ge–C bond is formed. In a very recent theoretical investigation, using a density functional supercell method, Balsas *et al* [6] came to a full agreement with this description. These authors have shown, in particular, that C_i and C_iC_s interact weakly with Ge atoms. Instead, the defect-level location is perturbed by an indirect interaction. In other words, the alloy modifies the host and defect–host coupling properties via charge transfer within Si and Ge atoms due to their different electronegativities. The variations of this coupling together with a volume expansion occur across the alloy composition x, and this was shown to induce the observed smooth shift of the levels relative to the band edges without affecting their mutual distances. In contrast, a direct interaction of the defects with Ge atoms would have implied defect–Ge complexes, strongly affecting the binding energy of the trapped electron, and different structures would have appeared, reflecting the statistical distribution of Ge into the lattice. Balsas *et al* [6] have shown that the Ge–C bond is very unlikely to form as its formation energy requires 0.8 eV more than in a Ge-free region. These authors estimated the shift of the donor level $C_i^{0/+}$ and found the following linear relation:

$$\Delta H(\mathrm{Si}, x = 0) - \Delta H(\mathrm{Si}_{1-x}\mathrm{Ge}_x, x) = (-0.76 \pm 0.04)x \text{ eV} \tag{2}$$

which confirms that the donor level moves towards the valence band much faster than the bandgap shrinks. If we take into account the linear part of the narrowing rate of the bandgap given in equation (1), namely $-0.43x$ eV, we end up with a variation with respect to the conduction band of $+0.33x \pm 0.4$ eV, which nicely agrees with the fitting of the experimental data shown in figures 3 and 4, leading to a rate of $+0.30x \pm 0.02$ eV. To account for the slight difference between the experimental and theoretical values it would have been necessary to consider the bowing factor ($+0.206x^2$). But for the sake of clarity we consider this correction as of second order. Going a step further, Balsas *et al* [6] calculated the correlation energy, equal to the Hubbard energy, expressing the difference between the positions of the acceptor and donor states. They found for this correlation energy the relation

$$U(x) = 0.74 + 0.02x \text{ eV}. \tag{3}$$

The tiny composition dependence is below the experimental uncertainty and cannot thus be observed. Therefore, we can consider that the Hubbard energy does not depend on the alloy composition, bringing a good agreement between theory and experiment. Finally, it is also worth noticing that whether the unpaired electron is localized on the carbon p orbital in the case of $C_i^{0/+}$ or spread over many atoms in the case of $C_i^{-/0}$, although it resides mainly on the p orbital of Si_i atom, does not affect $U(x)$.

3.2. Dynamical and structural properties

As we mentioned above, the C_i defect is one of the first products of the Watkins replacement mechanism. In the temperature scale there is a threshold above which a second reaction follows where the mobile C_i may encounter a substitutional carbon atom that escaped the replacement mechanism. The pair C_iC_s is then formed and in silicon this pair is stable up to 500 K. In oxygen free samples and as long as the inequality $[C_s] \gg [Sb_s]$ is fulfilled, which is the case in

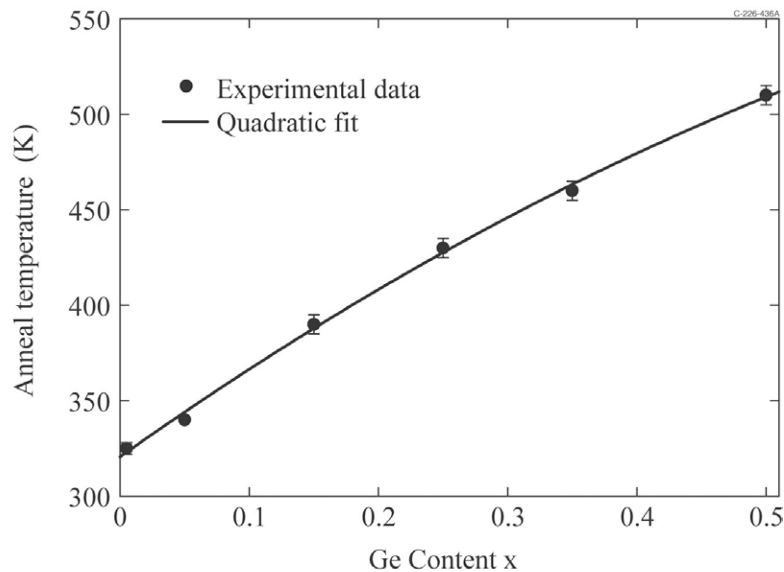

Figure 5. Anneal temperature of the C_i defect as a function of the alloy composition [2]. The full line is a quadratic fit to the points.

the present review, the two major competing products C_iO_i and C_iSb_s will not be formed. So far, the latter pair has never been observed, but the parallel is made with the well established C_iP_s pair, which does form. Under these conditions, a one to one conversion of C_i to C_iC_s, illustrated in figure 2, may thus be achieved, simplifying considerably the analysis.

In an early work, we have reported that the annealing temperature of the C_i defect in n-type $Si_{1-x}Ge_x$ alloy was strongly dependent on the Ge content of the alloy [2]. Concordant values with the n-type alloys were found when similar isochronal annealing experiments of the C_i defect were carried out for a few selected p-type $Si_{1-x}Ge_x$ alloys ($x = 0.05$, 0.15, and 0.27). In our moderately doped n- and p-type materials, and whether the bias is on or off, the three charge states, positive, neutral and negative, can be probed in the investigated temperature range. No indication was found for any charge state effect. Figure 5 illustrates this apparent stability for the neutral charge state (bias off) where an increase from 325 to 500 K in going from Si to $Si_{0.5}Ge_{0.5}$ is necessary to get rid of C_i [2]. Because the C_i defect anneals by migration to a substitutional carbon impurity, C_s, thus forming the more stable C_iC_s, it was suggested that the migration energy of C_i increases in the alloy [2].

This interpretation has been revised since then by looking at the C_i annealing kinetics in more detail [3]. Quantitative information about the annealing kinetics can indeed be obtained from isothermal-annealing experiments carried out at different temperatures. An example is given in figure 6 for an n-type $Si_{0.95}Ge_{0.05}$ diode showing the C_i concentration, $[C_i]$, the C_iC_s concentration, $[C_iC_s]$, and their sum, $[C_i] + [C_iC_s]$, as a function of annealing time at a temperature of 325 K. We see that this sum remains unaffected during the whole isothermal annealing sequence. This observation, which holds in the entire temperature range, is a clear demonstration that a one to one conversion is taking place and no alternative trap for C_i is disturbing the C_iC_s formation as stated above. It is thus natural to expect a first order behaviour for the C_i decay and the C_iC_s formation. Numerical fit to the data show indeed that both $[C_i]$ and $[C_iC_s]$ follow pure exponential shapes of the form $A_i \exp(-t/\tau_i)$, where $1/\tau_i$ is the temperature-dependent rate constant (the rate constant includes both the rate of migration

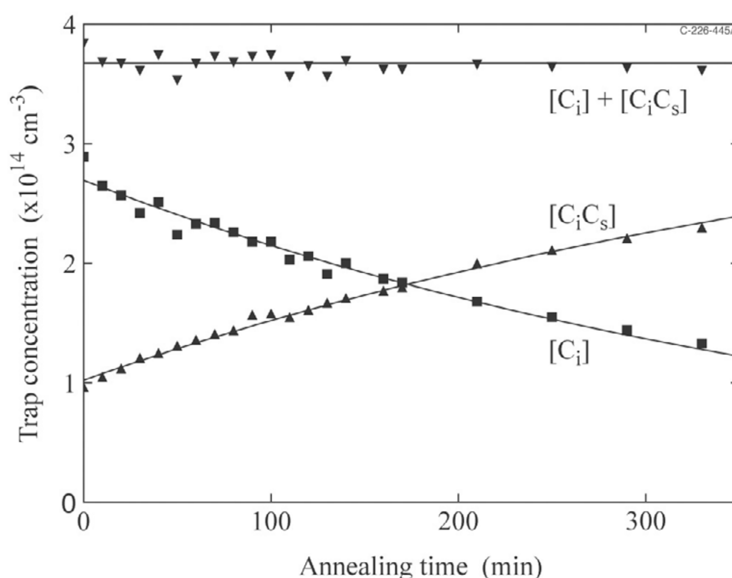

Figure 6. Results from an isothermal-annealing experiment of a $Si_{0.95}Ge_{0.05}$ p^+n diode at a temperature of 325 K. The solid curves are exponential fits to the experimental data [3].

and the rate of C_iC_s formation) [16]. But the striking feature emerging from the analysis of the data of figure 6 is that the rate constant for the annealing of C_i, $1/\tau_1$, and the rate constant for the in-growth of C_iC_s, $1/\tau_2$, are identical, $1/\tau_1 = 1/\tau_2 = 1/\tau$. This parameter thus reflects the rate constant of the single reaction $C_i + C_s \rightarrow C_iC_s$ and there is only one single limiting process for the C_iC_s formation as will be confirmed below. This point is further clarified by considering the Arrhenius plots of the rate $1/\tau = (1/\tau_0)\exp(-\Delta H_a/kT)$, where $1/\tau_0$ is the frequency factor and ΔH_a is the activation enthalpy characteristic of the annealing process. The data are reported in table 1 and compared to those extracted from pure silicon by Song and Watkins [15]. It is worth mentioning that these authors found only a tiny difference between p- and n-type silicon with or without bias during annealing, confirming that the charge state of C_i has no influence. On the other hand, the 10^5–10^8 range of the pre-exponential factors of the annealing kinetics strongly suggests long-range migration of interstitial carbon. Finally, the physical meaning of the activation enthalpy is refined by comparing the data obtained for reorientation of C_i, which involves a single-jump process [15], to the present data involving a long range process. Within the experimental uncertainties, Song and Watkins found 0.77–0.80 eV for the barrier of reorientation which is clearly very close to the value corresponding to the long range process[3] and to ours. It may thus be concluded that, irrespective of the alloy composition, the activation enthalpy is actually a migration enthalpy and the diffusion of C_i is the only limiting process to the formation of C_iC_s. In other words, the energy barrier for the formation of the C_iC_s defect is non-existent or negligible, otherwise the activation enthalpy of annealing would be larger than the reorientation energy barrier. It is worth mentioning that the above values are lower than those published by Tipping and Newman [17], who found 0.87 eV. This discrepancy may find its origin in the fact that these authors invoke an intermediate

[3] The C_i defect shows a preferential alignment under certain temperature conditions when external stress is applied; it is the reorientation from this alignment which was studied [15]. The same activation energy is expected for reorientation and annealing if the reorientation and single diffusional jump mechanism are the same [15].

Table 1. Data related to recovery time constant of the annealing kinetics of $C_i^{-/0}$ which is a long range process. The activation enthalpy resulting from the stress alignment, which stems from a single process, is also reported.

Material	Migration enthalpy ΔH_m (eV)	Prefactor $1/\tau_0$ (s^{-1})	Comments
Si	0.77		From alignment [15]
	0.74	$(0.5–1) \times 10^8$	From annealing [15]
$Si_{0.95}Ge_{0.05}$	0.76 ± 0.03	2×10^7	From annealing [3]
$Si_{0.85}Ge_{0.15}$	0.75 ± 0.03	6×10^5	From annealing [3]

electrically inactive state in the process of formation of C_iC_s, which clearly would lead the kinetics to deviate from a pure exponential behaviour, in contradiction with our findings [3].

Table 1 indicates that the observed retardation in the decay of C_i, when the alloy composition is increased, is clearly a result of a decreasing frequency factor. To understand the ultimate cause of this retardation, we express the annealing rate according to its thermodynamic definition,

$$\frac{1}{\tau} = \frac{1}{\tau_{00}} \exp\left(\frac{\Delta S_m}{k}\right) \exp\left(-\frac{\Delta H_m}{kT}\right) \tag{4}$$

with

$$\frac{1}{\tau_{00}} = 4\pi R n l^2 \nu_a \, [C_s] \, . \tag{5}$$

In equation (5) R is the capture radius, n is the number of possible jump directions which is not affected in the present case as the structure of the alloy remains diamond-like, l is the jump length and ν_a is the attempt-to-escape frequency. Song and Watkins [15] and Song *et al* [18] have reported frequency factors for pure silicon ($x = 0$) of $1/\tau_0 = 2 \times 10^8$ and 5×10^7 s^{-1}, respectively, thus a factor of two to ten larger than the value found for $Si_{0.95}Ge_{0.05}$. Song and Watkins [15] were using Si samples of a somewhat larger C_s concentration than used in the present investigation (about a factor of ten). Thus, as expected from the equations above, the factor of two to ten can easily be explained. However, while in the present experiments the substitutional carbon concentration is constant within 20% throughout the Ge composition range[4], a reduction of the frequency factor of about a factor of 330 in going from Si to $Si_{0.85}Ge_{0.15}$ cannot be explained as an effect of a change in the carbon concentration.

A variety of mechanisms could in principle account for the observed rate-limited process. Among them, the charge state effects should be excluded as shown above. The capture radius R is controlled by short-range elastic interactions, and is unlikely to play any significant role. The alloying, however, will affect in a subtle manner the product $l^2 \times \nu_a$. The diffusion jump length l is increased due to the expansion of the lattice of the alloy, leading thus to a very slight increase of the frequency factor, which is opposite to the observation. On the other hand, the alloy attempt-to-escape frequency ν_a decreases when mixing Ge and Si, as can be estimated from the Vegard law for the distribution of the alloy Debye frequency between those of Si and Ge. But, such a decrease is by far not large enough to account for the observation.

Our suggestion was thus to consider the migration entropy, ΔS_m, the only parameter susceptible to significantly affecting the frequency pre-factor of equation (4). In this scheme

[4] We estimated the constancy of the substitutional carbon concentration through the x range by irradiating a set of $Si_{1-x}Ge_x$ diodes with exactly the same proton dose. The intensity of the C_i line, before any annealing, was found to be constant within 20%. We take this as a demonstration that the substitutional carbon concentration is constant within about 20%.

$\Delta S_m(x)$ must be a decreasing function of x, which is possible only if the number of pathways mediating the C_i diffusion is reduced with increasing Ge content. The concordance of ΔH_m found in the present work with the reorientation barrier, measured by EPR [15] in silicon, and which is a local atomic process, is in favour of dynamic paths involving Si atoms only and explains at once why the enthalpy of migration is kept invariant. The migration path involving the Ge atom would have a larger energy barrier and would thus be avoided. This suggestion assumes implicitly that the formation of C_i in the proximity of a Ge atom would be unlikely. A firm statement on this matter could only come from theoretical investigations, which have been made very recently by Venezuela *et al* [7], who have used *ab initio* total-energy calculations to determine the structure of C_i and C_s as well as their formation energies in different atomic configurations involving Ge atoms. After having demonstrated that the split $\langle 100 \rangle$ configuration of C_i is energetically the most favourable for both Si and Ge, these authors assumed that the same configuration holds for the alloy as well. They undertook then to calculate the formation energies for both C_i and C_s in the alloy and found firstly that, under thermal equilibrium, the formation energy of C_i is significantly higher than for C_s in both elemental semiconductors. Therefore, under growth conditions which take place at thermal equilibrium, substitutional carbon, C_s, is more favourable than C_i, which is in agreement with the experiment. Secondly, in the alloy C_i may have four different nearest neighbours: Si_3Ge_0, Si_2Ge_1, Si_1Ge_2, and Si_0Ge_3. The calculations carried out by Venezuela *et al* [7] with two compositions are shown in figure 7. The highest Si content alloy corresponds to one of our experimentally investigated materials, namely $Si_{0.85}Ge_{0.15}$. Clearly, the formation energy increases by roughly 0.38 eV per extra Si–Ge bond. It is interesting to notice that with increasing alloy composition, the formation energy of C_i decreases. The explanation is straightforward on the basis of the strain versus chemical energy: the cluster formed by C_i and its three neighbours is indeed under compressive strain. But the authors above have also shown that the formation energy of C_i decreases linearly with the lattice parameter. Therefore, in $Si_{1-x}Ge_x$ as the composition increases, the lattice parameter increases, allowing the compressive strain of the cluster to be relieved, thus lowering the formation energy of C_i for each configuration. This result is worth remembering when a tentative parallel is attempted with boron, another interstitialcy defect which seems to be retarded in $Si_{1-x}Ge_x$ alloy as well.

What figure 7 shows more importantly is that the formation energy of C_i in $Si_{1-x}Ge_x$ is lower for higher concentrations of Si atoms at the nearest-neighbour sites. This is in agreement with the finding that the formation energy of C_i is lower by 0.74 in Si than in Ge. The case of second neighbours has also been considered by Venezuela *et al* [7], who found a negligible contribution of the order of 20 meV. Therefore, restricting to the first nearest neighbours only can be considered as a good approximation. Given the formation energies obtained by these authors, the equilibrium relative population fractions of each first nearest neighbour configuration is straightforward. At thermal equilibrium, this fraction is given by

$$f^{\mathrm{cong}}(x,T) = \frac{P^{\mathrm{conf}}(x)\exp[-E_{\mathrm{f}}^{\mathrm{conf}}(x)/kT]}{\sum_{\mathrm{conf}} P^{\mathrm{conf}}(x)\exp[-E_{\mathrm{f}}^{\mathrm{conf}}(x)/kT]} \tag{6}$$

where $E_{\mathrm{f}}^{\mathrm{conf}}(x)$ is the formation energy of C_i with a given configuration in the alloy of composition x and $P^{\mathrm{conf}}(x)$ is the probability for that given configuration to exist in the same alloy. The probability $P^{\mathrm{conf}}(x)$ of the neighbours to the interstitial carbon being Si_nGe_{3-n}, describing each of the four possibilities mentioned above, is expressed as

$$P^{\mathrm{conf}}(x) = \frac{3\downarrow}{n\downarrow(3-n)\downarrow} x^n (1-x)^{3-n}. \tag{7}$$

Using these two equations and the formation energies obtained by Venezuela *et al* [7], adapted to our experimental conditions, leads to the unambiguous result that the configuration

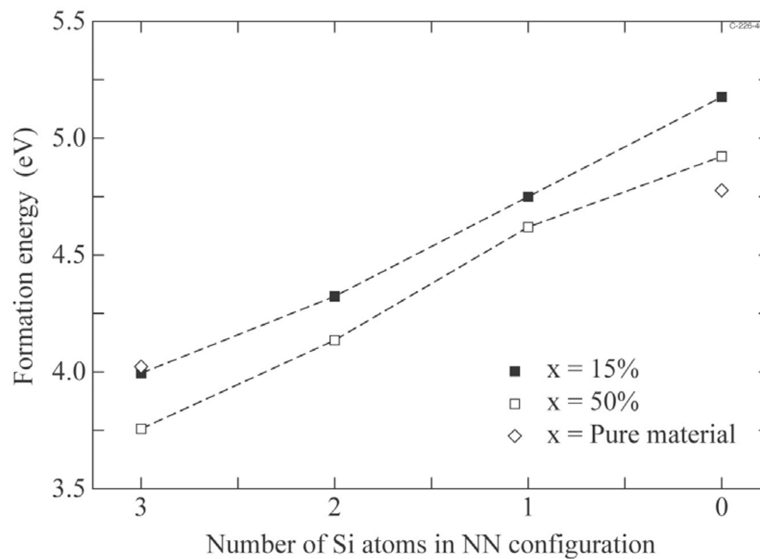

Figure 7. Formation energy for interstitial carbon, C_i, in Si_xGe_{1-x} for different atomic configurations at the nearest neighbour sites (NNs). All the data represented in this figure have been borrowed from figure 4 of [7], where the alloy labelling has to be adapted to the present work. Thus, $x = 85\%$ in [7] corresponds to $Si_{0.85}Ge_{0.15}$ in our case.

C_i:Si_3Ge_0 is populated to a value of 99.9%. This is a clear confirmation of our earlier suggestion that C_i migrates via Si-based paths. At higher temperatures (above 1100 K), the configuration involving one Ge atom, namely C_i:Si_2Ge_1, starts to be populated. A deviation from first order kinetics could then be expected as two components of the migration enthalpy may need to be taken into account.

4. Discussion

Our experimental work, now supported by thorough theoretical investigations, has shown that both energy levels introduced by C_i shift with the same rate towards the valence band when the alloy composition increases. The two related levels do not exhibit any charge-state-dependent metastability, and in this respect C_i can be considered as a simple and well defined defect. On the other hand, the observed retarded annealing process of C_i in the alloy has been shown to be entirely the result of an important reduction in the number of possible Si-based paths, which is reflected in the configurational entropy taking part in the migration process.

The case of the C_iC_s defect is very exciting in the sense that it induces four metastable configurations [19–21]. Two of the configurations give rise to two levels in the lower half of the bandgap and two near the conduction band. Among the latter, only the deepest level has been dealt with in this work, revealing a shift away from the conduction band with the same rate as for C_i-related levels. The reason for the pinning between the levels related to $C_i^{-/0}$ and at least the one we observe for $C_iC_s^{-/0}$ is found to be due to the fact that both defects have the same core electronic structure, a property determined very early in silicon [14] and demonstrated to hold in the alloy as well [2]. The failure to observe the metastable replica of $C_iC_s^{-/0}$ is due to the experimental conditions. Our DLTS spectra were indeed recorded either in the cooling or the heating mode but always while pulsing the diode. This procedure

favours the lowest negative charge state configuration, which is the one we observe, called configuration A in the work of Song *et al* [20, 21]. The detection of the second metastable state, located at 0.10 eV below the conduction band and corresponding to configuration B in the labelling of Song *et al*, would have required us to cool down the sample under reverse bias, or to use either sub-bandgap light illumination at low temperature or forward bias, both methods injecting minority carriers, prior to DLTS measurement.

We believe that the behaviour of the two metastable acceptor states of $C_iC_s^{-/0}$ is worth addressing in the alloy as the chemical disorder and its related locally inhomogeneous strain might significantly affect the dynamics of conversion from one configuration to the other. To justify this idea, let us first recall the microscopic structures of configurations A and B proposed by Song *et al* [20]. Both states A^-, $C_iC_s^-$, and A^0, $C_iC_s^0$, of configuration A correspond to the 'dumbbell' Si_i–C_i interstitialcy character of isolated C_i. As mentioned above, in this configuration, both Si_i and C_i, which share the same single lattice site, are threefold coordinated. The trapped unpaired electron was found to reside primarily in the nonbonding p orbital on the interstitial Si_i atom, slightly perturbed by the presence of the substitutional carbon. As for $C_i^{-/0}$ the unpaired electron is diffuse rather than localized on Si_i atom. This is the reason for the slight perturbation by a nearby substitutional carbon atom. The conversion to configuration B is governed by a bond switching process in which C_i transforms into C_s, thus becoming fourfold coordinated, displacing Si_i into the twofold coordinated interstitial position between the two carbon atoms. The complex is thus no longer C_iC_s as both carbon atoms are occupying substitutional sites, but it transforms into C_s–Si_i–C_s in which the unpaired electron is even more spread. But the question to address is whether the bond switching governing the conversion from configuration A to configuration B, which requires a bond breaking and reconstruction, might be affected by the presence of Ge atoms in the second NNs. If this turned out to be the case, then a second and even a third Ge nearest neighbour might play a role in the dynamics of this kind of metastability.

Finally, the picture that the present review attempts to draw from the full agreement between the experimental and theoretical outcomes on the dynamics of carbon would greatly benefit from a generalization to other species believed to have similar structures. This brings us to address the important issue of whether C_i and B_i but also P_i, all supposed to be interstitialcy defects, diffuse via the same mechanism. As far as $Si_{1-x}Ge_x$ is concerned, and although the present results are only fragmentary, a comparison with what is already claimed for B_i is instructive. As in the case of C_i, the diffusivity of B_i was found to decrease significantly in $Si_{1-x}Ge_x$ with increasing alloy composition. Kuo *et al* [22] proposed that a trapping of B_i by Ge might be the reason for the retardation. This suggestion, although it seems to match with a local strain relief between B and Ge, is clearly excluded in the case of C_i as the bond C_i–Ge is energetically unlikely, whereas the same strain relief argument may apply. We have shown above that the formation of C_i–Ge is not necessary to relieve the strain. The increase of the average lattice parameter of the alloy is sufficient to compensate the compressive strain of the cluster C_i:Si_3Ge_0. Now, two points need to be clearly stressed. Firstly, our data reflect the migration enthalpy only. The formation enthalpy does not play any role as C_i is formed by irradiation. Secondly, the investigated temperature ranges are very far apart from each other; near room temperature in the case of carbon, above 1000 K in the case of boron. One must thus be careful in comparing two non-overlapping temperature ranges. The most striking example is found in the case of the elementary defect in silicon, i.e. the vacancy [23], for which low and high temperature data do not match. If we assume, however, that the migration enthalpy of B_i is also composition independent, excluding the suggestion made by Kuo *et al* [22] in favour of the B–Ge bond, a match between C_i and B_i under equilibrium at high temperature would

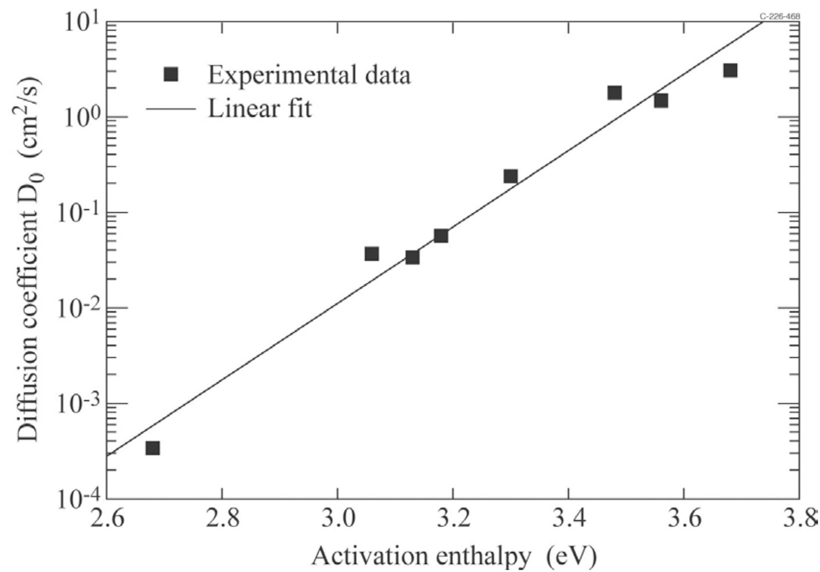

Figure 8. The Meyer–Neldel rule [25] expressed via the linear relation between the prefactor and the activation enthalpy of diffusion of boron in the $Si_{1-x}Ge_x$ alloy.

require an increase of the formation energy of C_i with the alloy composition [24]. However, this is in contradiction with the theory by Venezuela *et al* [7], which shows (see figure 7) that the formation energy of C_i decreases with the alloy composition.

To clarify these issues, we propose to compare the dynamics of carbon and boron in both the low and high temperature ranges. As B_i introduces an electron trap level in the upper half of the bandgap, the low temperature studies require us to use counter-doped n-type $Si_{1-x}Ge_x$ wafers. The samples will be irradiated to avoid the formation enthalpy as has been done for carbon containing samples. In parallel, we propose to study the diffusivity of carbon under thermal equilibrium at high temperature as has been done for boron and phosphorus. However, in this case we only have access to the activation enthalpy of the process without being able to separate the two components ΔH_m, migration enthalpy, and ΔH_f, formation enthalpy. This brings us to make a final comment. Looking at the fairly large number of diffusion data accumulated in both relaxed and strained $Si_{1-x}Ge_x$ [24], it seems rather difficult to rely on the sole strain argument, although it might play a role. The strain is not only an issue of the lattice mismatch, but it is also determined by the experimental conditions, which can vary from sample to sample and even from author to author. A simple plot of ΔH_a and the diffusion pre-exponential factor as a function of the alloy composition [24] shows that no clear trend can be obtained. Introducing tensile and compressive strains as an extra parameter, fluctuating with both the chemical disorder and experimental conditions, may indeed be more misleading than helpful. However, if we consider the relationship between the activation enthalpy and the activation entropy of the diffusion process, a clear and decisive trend is obtained. In figure 8 we show such a plot for B_i [24], irrespective of growth, strain and diffusion conditions. What is most fascinating is the fact that the same trend, known as the Meyer–Neldel rule [25], is obtained for phosphorus, not reported here, but also known to diffuse via an interstitialcy mechanism. For all species diffusing via the vacancy mechanism, the linear behaviour shown in figure 8 is not observed. We believe that this has a profound physical meaning, linking the way the atomic partners involved in the process pick up the energy

from the bath, in relation with the specific mechanism of diffusion, whether it is vacancy or interstitialcy mediated.

5. Conclusion

In conclusion, the studies reviewed in this article have demonstrated that neither the acceptor nor the donor levels of the C_i defect are pinned to any of the band edges when the composition of the $Si_{1-x}Ge_x$ is varied; however, they remain at an energy of 0.8 eV separation from each other, independent of composition. The migration enthalpy of C_i is found to be independent of composition in the investigated composition range, $0 \leqslant x \leqslant 0.15$. The experimentally observed anneal retardation of C_i is exclusively due to a decrease of the entropy of migration, a crucial parameter when discussing dynamic effects in disordered materials. We have also shown how recent and thorough theoretical considerations have brought a fundamental justification to our observations and conclusions. The outcomes discussed in this review open new issues, whose solutions would bring a significant progress into the dynamics of point defects related to alloying.

Acknowledgments

Thanks are due to John Lundsgaard Hansen for the MBE growths and to Pia Bomholt for the preparation of the diodes used in the various investigations described above. This work was supported by the Danish National Scientific Research Council. The FP6 CADRES project is acknowledged for support to attend the first CADRES Workshop at which this paper was presented.

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