Interstitial-carbon defects in $Si_{1-x}Ge_x$

A. Nylandsted Larsen,* A. Bro Hansen, D. Reitze,† J.-J. Goubel,‡ and J. Fage-Pedersen
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

A. Mesli
Laboratoire LPSE, 4 rue des Frères Lumière, F-68093 Mulhouse Cedex, France
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The interstial-carbon (C_i) defect in molecular-beam epitaxy grown, strain relaxed *n*-or *p*-type $Si_{1-x}Ge_x$ for $0 \leqslant x \leqslant 0.50$ has been created by 2-MeV proton or electron irradiations, and studied by deep-level transient spectroscopy on p^+n- and n^+p-mesa diodes. The energy difference between the shallow acceptor and donor levels of the C_i defect remains at a constant value of 0.8 eV as the Ge content is varied. The migration enthalpy of C_i is independent of composition in the composition range $0 \leqslant x \leqslant 0.15$. The observed increased stability of the C_i defect with increasing *x* is the result of a decrease in the entropy of the process.

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The interstitial-carbon defect C_i in strain-relaxed, epitaxial $Si_{1-x}Ge_x$ layers is a fascinating defect as it introduces an acceptor level near the conduction band and a donor level near the valence band, both levels being rather shallow. Thus, the system enables one for the first time to study the behavior of different charge states of an interstitial-type defect when the band structure changes with composition. An obvious question to raise, partly motivating the present investigation, is whether the energy difference between the two levels (the so-called Hubbard energy *U*) and, hence, the degree of lattice relaxation accompanying the capture of the extra electron, is independent of composition.

The C_i defect, created in strain-relaxed $Si_{1-x}Ge_x$ layers by 2-MeV proton irradiations, has previously been studied by us using deep-level transient spectroscopy (DLTS) (Refs. 1, 2). In *n*-type $Si_{1-x}Ge_x$ the (−/0)-acceptor level was followed as a function of *x* in the range $0.05 \leqslant x \leqslant 0.50$ (Ref. 2), whereas in *p*-type $Si_{1-x}Ge_x$ the (0/+)-donor level was followed in the range $0 \leqslant x \leqslant 0.15$ (Ref. 1). The acceptor level was found to move deeper into the band gap with increasing *x*, while the donor level was found to become gradually more shallow, and no pinning to any of the band edges was observed. However, in *n*-type $Si_{1-x}Ge_x$ the energy difference between the acceptor level of C_i and the acceptor level of C_iC_s was observed to be independent of *x*. This could be understood with reference to the similar core structure of the two defects, in which the trapped electron resides primarily in the nonbonding *p* orbital of the similar interstitial Si atom involved in the two defects.

The annealing of C_i, which takes place by the migration of C_i and subsequent pairing with impurities, was studied 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 is 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 clarified, for high-temperature diffusion of B in $Si_{1-x}Ge_x$ for $x \leqslant 0.50$ (Ref. 3), which is also an interstitially-mediated diffuser.[4]

In the present investigation, we have extended the composition range of the *p*-type material to $x = 0.50$ in order to make possible a more precise comparison between the movements of the two C_i levels as a function of the alloy composition. In addition, we provide for the first time, a quantitative analysis of the annealing kinetics of the C_i defect in *n*-type $Si_{0.95}Ge_{0.05}$ and $Si_{0.85}Ge_{0.15}$.

The *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, as described elsewhere.[5] We have previously demonstrated that this technique is capable of producing high-quality $Si_{1-x}Ge_x$ layers with respect to structural, optical, and electrical characteristics.[6] The carbon concentration in our 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 below the SIMS detection limit of $\sim 1\times10^{17}\,cm^{-3}$ (oxygen related defects, such as VO_i and C_iO_i, are always found at concentrations smaller than in commercial floating-zone (FZ) samples, demonstrating that the actual O concentration is probably below $\sim 10^{15}\,cm^{-3}$). The strain-relaxed $Si_{1-x}Ge_x$ layers were 4 μm thick, doped with either Sb to concentrations between 2×10^{15} and $5\times10^{15}\,cm^{-3}$ (the *n*-type layers) or with B to concentrations between 3×10^{15} and $10\times10^{15}\,cm^{-3}$ (the *p*-type layers). On top of these layers, 0.5-μm-thick layers doped to high concentrations ($\sim 5\times10^{19}\,cm^{-3}$) of either B (on the *n*-type layers) or Sb (on the *p*-type layers) were grown. The p^+n- and n^+p-mesa diodes were then fabricated using photolithographic techniques. Irradiations were performed with either 2-MeV electrons or 2-MeV protons to doses of 1×10^{-14} to $4\times10^{15}\,cm^{-2}$ or 3×10^{12} to $5\times10^{12}\,cm^{-2}$, respectively. Electrons of this energy pass through the diodes, whereas the protons stop at a depth of $\sim$50 μm that is far beyond the investigated zone of a few micrometer from the top of the diode. The diodes were irradiated and kept at room temperature 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.

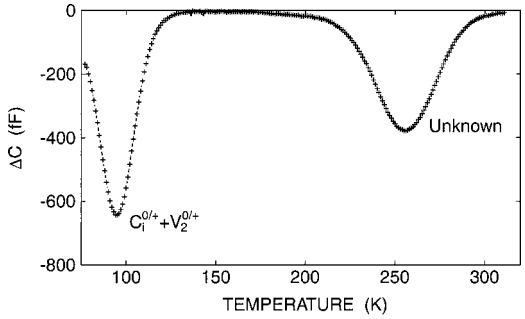

FIG. 1. DLTS-temperature scan of electron irradiated $Si_{0.84}Ge_{0.16}$ n^+p diode, recorded using a repetition rate of 250 Hz. The "DLTS finger prints" of the two lines are $\Delta H_p = 0.16$ eV, $\sigma_c = 2\times10^{14}$ cm^2 and $\Delta H_p = 0.46$ eV, $\sigma_c = 1\times10^{14}$ cm^2, mentioned according to increasing temperature in the spectrum.

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 Fig. 1. It was already demonstrated in Ref. 1 for $x=0.05$ and 0.15 that the line labeled $C_i^{0/+}$ $V_2^{0/+}$ in the spectrum (labeled line H_1+H_2 in Ref. 1) is composed of two lines, emerging from the donor level of the divacancy $V_2^{0/+}$ and the donor level of interstitial carbon, $C_i^{0/+}$. It is very fortunate that $C_i^{0/+}$ anneals at a lower temperature than does $V_2^{0/+}$ for all compositions below $x=0.50$ (Ref. 7), and that 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 finger prints" (ionization enthalpy and apparent capture cross section) of the $C_i^{0/+}+V_2^{0/+}$ 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 labeled "unknown," which is of no concern in this work, seemingly involves the complex Ge-V-B documented by the observed variation with irradiation dose, Ge composition, and B concentration.

The electron-ionization enthalpies ΔH_n of the two charge states $C_i^{0/+}$ and $C_i^{-/0}$ are reported in Fig. 2. The hole-

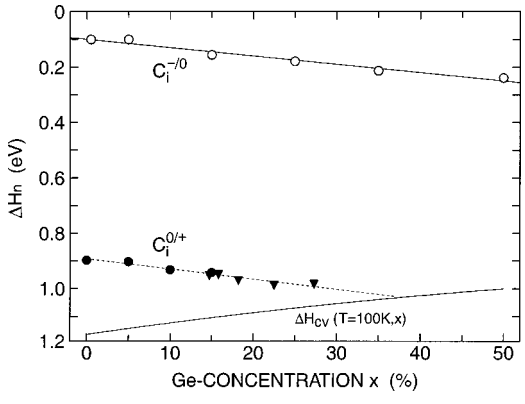

FIG. 2. Ionization enthalpies as a function of the Ge content *x* of the $Si_{1-x}Ge_x$ epitaxial layers for the $C_i^{-/0}$ defect (○) from Ref. 2 and the $C_i^{0/+}$ defect (▼, ●) from the present investigation (▼) and from Ref. 1 (●). The uncertainties of the ionization enthalpies are similar to the size of the markers. In agreement with Ref. 9, the energy of the conduction band is assumed to be constant in the investigated composition range. The lines are linear fits to the data points to guide the eye.

ionization enthalpies 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 band-gap enthalpy. In agreement with van de Walle and Martin,[8] we assume that the reduction of the band gap is entirely reflected in the valence-band shift and, thus, the band-gap enthalpy $\Delta H_{cv}(x,T)$ is given by[9,10]

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

where $\alpha=4.9\times10^{-4}$ (eV/K) and $\beta=655$ K (Ref. 11). The band-gap enthalpy of Fig. 2 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 Fig. 2 that neither the acceptor nor the donor levels are pinned to any of the band edges, however, they remain at a constant Hubbard-energy separation of 0.8 eV from each other while the composition is varied. It also emerges from Fig. 2 that the donor level of C_i disappears from the band gap for $x>0.40$ and becomes a level in the valence band.

It was reported in Ref. 2, that the anneal temperature of the C_i defect in an *n*-type $Si_{1-x}Ge_x$ alloy was strongly dependent on the Ge content of the alloy (the anneal temperature of a defect was defined in Ref. 2 as the temperature in a 15-min isochronal-anneal sequence at which the intensity of the corresponding DLTS decreases by a factor of 2). In the present investigation, isochronal-annealing experiments of the C_i defect have been carried out for a few selected *p*-type $Si_{1-x}Ge_x$ alloys ($x=0.05$, 0.15, and 0.27); concordant values with the *n*-type alloys were found. This is not surprising, as the C_i defect in both the *p*- and *n*-type alloys is in the neutral charge state, and the results of the present experiments are, thus, merely a confirmation of the results of Ref. 2.

We have, on the other hand, looked into the C_i-annealing kinetics in some detail in the present investigation. This has been done for the two different *n*-type alloys $Si_{0.95}Ge_{0.05}$ and $Si_{0.85}Ge_{0.15}$ after 2-MeV electron irradiations. It was demonstrated in Ref. 2 for *n*-type SiGe, and confirmed in the present investigation for *p*-type SiGe, that the anneal temperature of the C_i defect increases from 50 to 125 °C in going from $Si_{0.95}Ge_{0.05}$ to $Si_{0.85}Ge_{0.15}$. 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 going from $Si_{0.95}Ge_{0.05}$ to $Si_{0.85}Ge_{0.15}$. Quantitative information about the annealing kinetics can be obtained from isothermal-anneal experiments carried out at different temperatures. An example is given in Fig. 3 for a $Si_{0.95}Ge_{0.05}$ 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 anneal time at an anneal temperature of 325 K. A numerical fit to the data shows that the changes in both $[C_i]$ and $[C_iC_S]$ follow pure exponentials of the form $A\exp(-t/\tau_i)$, where $1/\tau_i$ is the temperature-dependent rate constant (the rate constant includes both the rate of migration and the rate of C_iC_S formation) (Ref. 12).

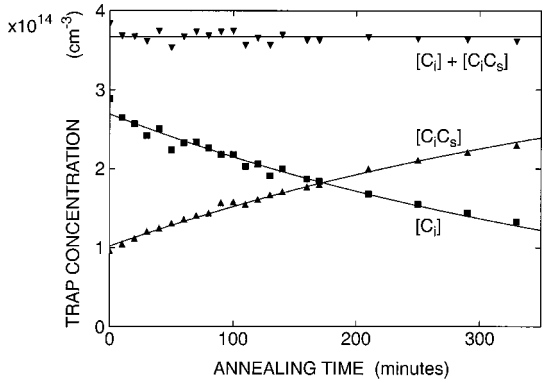

FIG. 3. Results from an isothermal-annealing experiment of a $Si_{0.95}Ge_{0.05}$ p^+n diode at a temperature of 325 K. The solid curves are exponential fits to the experimental data.

From the analysis of the data of Fig. 3, it appears that the rate constant for the annealing of C_i, $1/\tau_1$, and the rate constant for the ingrowth of C_iC_S, $1/\tau_2$, are identical, $1/\tau_1=1/\tau_2=1/\tau$, and that the sum $[C_i]+[C_iC_S]$ is constant during the whole isothermal-annealing sequence and in the entire temperature range, demonstrating a one to one conversion. Thus, we may conclude, that $1/\tau$ is the rate constant of the reaction $C_i+C_S\rightarrow C_iC_S$, and that C_S is the only C_i trap in these samples. The temperature-dependent rate constants were subsequently fitted to the expression: $1/\tau=(1/\tau_0)\times\exp(-\Delta H_a/kT)$, where $1/\tau_0$ is the frequency factor and ΔH_a is the activation enthalpy characteristic of the annealing process.[12] We found for the two Ge compositions:

$$Si_{0.95}Ge_{0.05}: \quad \Delta H_a=0.76\pm0.03 \text{ eV}; \quad 1/\tau_0=2\times10\ \text{s}^{-1},$$

$$Si_{0.85}Ge_{0.15}: \quad \Delta H_a=0.75\pm0.03 \text{ eV}; \quad 1/\tau_0=6\times10\ \text{s}^{-1}.$$

This is to the best of our knowledge, the first time these parameters are reported for any defect in $Si_{1-x}Ge_x$. It is evident that the activation enthalpies are identical for $Si_{0.95}Ge_{0.05}$ and $Si_{0.85}Ge_{0.15}$, and that the observed difference in annealing temperature is a result of different frequency factors. The above values are lower than those published by Tipping and Newman[13] who found 0.87 eV. This discrepancy may find its origin in the finding by those authors of an intermediate electrically inactive state in the process of formation of C_iC_s, which clearly does not follow a pure exponential behavior, in contradiction with the present case. Our values match nicely, however, those of Song and Watkins[14] who have studied the C_i defect in pure Si using electron paramagnetic resonance (EPR) and DLTS; they found that the reorientation energy barrier[15] of the C_i defect as determined by EPR is 0.77 eV and, thus, within the experimental uncertainty equal to the activation enthalpy of annealing of 0.73 eV as they determined by DLTS (Ref. 14). This observation has the important implication that the energy barrier for the formation of the C_iC_S defect is negligible, otherwise the activation enthalpy of annealing would be larger than the reorientation energy barrier. Hence, we may conclude that the observed activation enthalpy ΔH_a of annealing in pure Si is the migration enthalpy ΔH_m of the C_i defect, and we assume that the same is the case for $Si_{0.95}Ge_{0.05}$ and $Si_{0.85}Ge_{0.15}$. Thus, out of these experiments emerges the interesting result that the migration enthalpy of C_i in $Si_{1-x}Ge_x$ is independent of x in the range $0\leqslant x\leqslant0.15$. The observed increased stability of the C_i defect with increasing x is, therefore, clearly a result of a decreasing frequency factor with increasing x.

To understand the ultimate cause of this increased stability, it is worth expressing the annealing rate according to its thermodynamic definition,

$$1/\tau=1/\tau_0\exp(\Delta S_m/k)\exp(-\Delta H_m/kT) \tag{2}$$

with

$$1/\tau_{00}=4\pi\times R\times n\times1^2\times\nu_a\times[C_s]. \tag{3}$$

In Eq. (3) R is the capture radius, n is the number of possible jump directions that is not affected in the present case as the structure of the alloy remains diamondlike, l is the jump length, and υ_a is the attempt-to-escape frequency. The product $1/\tau_{00}\exp(\Delta S_m/k)$ represents the frequency factor $1/\tau_0$ mentioned above. Song and Watkins[14] and Song, Benson, and Watkins[16] have reported frequency factors for pure silicon ($x=0$) of $1/\tau_0=2\times10^8$ and $5\times10^7\ \text{s}^{-1}$, respectively, thus, a factor of 2–10 larger than the value found for $Si_{0.95}Ge_{0.05}$. Song and Watkins[14] were using Si samples of a somewhat larger C_s concentration than used in the present investigation (about a factor of 10). Thus, as expected from the equations above, the factor 2–10 can easily be explained. However, while in the present experiments the substitutional carbon concentration is constant within 20% throughout the Ge-composition range,[17] a reduction of the frequency factor of about a factor of 30 in going from $Si_{0.95}Ge_{0.05}$ to $Si_{0.85}Ge_{0.15}$ cannot be explained as an effect of a change in the carbon concentration.

A variety of mechanisms can, in principle, account for the observed rate-limited process. Among them, the charge-state effects can be excluded in the carbon case because Song, Benson, and Watkins[16] carried out annealings both under zero and reverse-bias conditions and no significant difference was observed while two clearly different charge states C_i^0 and C_i^+ were probed. The capture radius R is controlled by short-range elastic interactions, and seems unlikely to play a significant role. The alloying, however, will affect in a subtle manner the product $l^2\times\upsilon_a$. 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 υ_a decreases when mixing Ge and Si, as can be estimated from the Vegard's law for the distribution of the alloy Debye frequency between those of Si and Ge. But, such a decrease is by far insufficient to account for the observation.

We are, thus, left to consider the migration entropy ΔS_m susceptible to significantly affect the frequency prefactor of Eq. (2). In our case, $\Delta S_m(x)$ must be a decreasing function of x. Possibly, the number of pathways for the diffusing species C_i is being reduced with increasing Ge content. Such a phenomenon could reflect that the C_i defect migrates via a

Si-based migration path in the SiGe alloy and, hence, that a migration path that involves Ge atoms has a larger energy barrier for diffusion and, consequently, is avoided. The concordance of ΔH_m found in the present work with the reorientation barrier measured by EPR (Ref. 14), which is a local atomic process, is in favor of dynamic paths involving Si atoms only. The fact that the entropy of an activated process plays the key role in a disordered material, has also been found very recently by us in the case of the monovacancy in $Si_{1-x}Ge_x$ and noticed in the ternary alloy ZnS_xSe_{1-x} (Ref. 18).

As mentioned previously, the high-temperature diffusion of boron in $Si_{1-x}Ge_x$ is also found to retard with increasing x up to $x=0.50$ similar to what we observe for C_i. The diffusion of boron in silicon is also mediated by an interstitial-type mechanism. A preferential pairing between a substitutional B atom and a substitutional Ge atom rendering the B atom partly immobile has been put forward to explain the retardation.[19] Hoffmann *et al.*[20] have demonstrated by infrared absorption experiments that a substitutional carbon atom in strain relaxed $Si_{1-x}Ge_x$ of $x \leqslant 0.50$ prefers a configuration with four Si neighbors. Thus, for C_i a pairing with Ge atoms is excluded. Hence, the above suggestions about the retarded C_i diffusion might be generalized to explain also the retarded B diffusion in SiGe alloys presenting thus, an alternative to the assumed B-Ge pairing.

In conclusion, these studies 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 $Si_{1-x}Ge_x$ are 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 increased stability of C_i with increasing x is exclusively due to a dramatic decrease of the entropy of migration. This effect is suggested to explain also the experimentally observed retarded B diffusion in SiGe alloys. Thus, this investigation demonstrates that the entropy is a crucial parameter when discussing dynamic effects in disordered materials.

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*Corresponding author. Email: anl@ifa.au.dk
†Project student from University of Leeds, England
‡Present address: Alcatel Microelectronics, Oudenaarde, Belgium.

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