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Iron in relaxed $Si_{1-x}Ge_x$ alloy: Band gap related levels, diffusion, and alloying effects

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The microscopic behavior of iron in relaxed $Si_{1-x}Ge_x$ alloy is addressed in the present work where various new aspects are highlighted. In *p*-type materials two types of defects involving iron may coexist under equilibrium; the isolated form, Fe_i, and the iron-acceptor pair, Fe_i-A_s. The latter complex is favored over the former because it is thermodynamically more stable. In each case the iron atom stabilizes at the interstitial tetrahedral site. When boron is the acceptor impurity, both the isolated and the paired forms introduce donor-like levels, distant from each other by 0.28 eV. In the relaxed $Si_{1-x}Ge_x$ bulk alloy, these levels are shown to remain separated by the same amount. However, they shift toward the valence band much faster than the shrinkage of the band gap when the Ge content is increased. The consequence is that the pair-related donor level merges with the valence band at a fairly low alloy composition ($x \geqslant 7\%$) while the iron donor level is predicted to disappear from the gap for $x \geqslant 25\%$. We also show that neither the entropy nor the enthalpy of migration of free iron, whose experimental determination requires one to take into account the above-mentioned shift, are affected by alloying. Therefore, the fast diffusing character, attributed to iron in silicon, still holds in the alloy. The origin of spectral broadening, related to the chemical disorder, is discussed. Finally, the major technological implication emerging from our new findings is addressed. In particular, we show that both the gettering by segregation, routinely used in silicon, and the field-induced outdiffusion, established in *n*-type silicon ten years ago, are totally inefficient in the $Si_{1-x}Ge_x$ alloy.

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I. INTRODUCTION

Among the 3*d* metal impurities in silicon, known for their detrimental effects in device technology, iron has attracted the greatest attention. Its properties, now very well established, allow this species to be used as a probe to test concepts developed for modeling electrical properties, thermodynamic, transport behavior, precipitation, and gettering phenomena.[1] In the following, we summarize the main aspects of iron in silicon that are relevant for this article. Then, we motivate the need for investigating iron in $Si_{1-x}Ge_x$ alloy materials.

In single silicon crystal, Fe diffuses basically through a pure interstitial mechanism based on an exchange between the hexagonal and tetrahedral sites, the latter being the stable site while the former constitutes the saddle point.[2] The fact that silicon is an open lattice and the migration of Fe_i does not involve intrinsic point defects implies both a low activation entropy and enthalpy, characteristic for a species not constrained to the crystal lattice symmetry. A simple model, based on the polarization energy, developed by Weisser[2] in the early 1960s, predicts a charge state dependent migration for impurities diffusing via pure interstitial paths. But, it has only lately been demonstrated[3,4] that the migration enthalpy of iron is incremented by roughly 0.10 eV for each additional charge in going from Fe_i^{++} to Fe_i^0. In *p*-type silicon, the negative charge state of the acceptor induces an instability. A new minimum of the free energy results thus from a long-range Coulombic attraction between the positively charged Fe_i^+ and the negatively charged dopant. This property is currently used to determine the migration parameters as we shall see in the following. Under equilibrium such a system accommodates two configurations; a metastable one consisting of free interstitial Fe_i and a stable one represented by the Fe_i-A_s pair, where A_s stands for the substitutional acceptor. This pair adopts the ⟨111⟩ axial symmetry where Fe_i stabilizes at the adjacent tetrahedral site. Subsequently, the same pair was found to accommodate a second configuration, where Fe_i sits at the next hexagonal site along the ⟨100⟩ direction. Although slightly higher in energy, and thus less stable, a significant fraction of the pairs aligned along the ⟨100⟩ direction can, under special experimental conditions, be observed.[3] Electrically, the pair formation results in a deactivation of the acceptor. Free interstitial $Fe_i^{0/+}$ introduces a level at 0.38 eV above the valence band and exhibits a barrier for the capture of holes of 0.048 eV.[4,5] On the other hand, the hole traps representing both configurations of the Fe_i-A_s pair depend on the nature of the A_s dopant.[3] In boron-doped silicon, the case of interest in the present work, the most stable configuration induces a level located at 0.10 eV above the valence band. Finally, an electron trap, located at 0.23 eV below the conduction band, has also been firmly established as being the second charge state of the same stable pair.[6]

The successful technological application of $Si_{1-x}Ge_x$ obviously raises the same practical as well as fundamental issues. However, the situation in the alloy might be complicated by the fact that the material is no longer homogeneous and its band gap strongly affected by the alloy composition, implying both chemical and energetic local fluctuations. The study of the dynamics of Fe_i and $\mathrm{Fe}_i\text{–}\mathrm{B}_s$ pairs in the crystalline alloy is thus expected to further our knowledge on the subtle coupling between defects and band gap engineering. This subject has already led to the collection of a fair amount of data for other point defects.[7–12] Our main motivation in the present study is to determine the energy level positions of both Fe_i and $\mathrm{Fe}_i\text{–}\mathrm{B}_s$, as a function of the band gap variation due to a change in the Ge content. Then the impact of alloy disorder on the diffusivity is examined, as the disorder is expected to primarily affect the channels through which free iron is supposed to migrate. It is worth noticing at this stage that a change in the level position, affecting its equilibrium electronic population, and the alloy disorder, possibly influencing the diffusion path, may have some consequence on the dynamic behavior of iron. We may, therefore, expect new trends in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$-based device processing and performance. Finally, from a fundamental point of view, local fluctuation of the defect environment due to chemical inhomogeneities may affect the electronic interactions, enabling spectroscopic broadening to become a useful source of information. All these new aspects are investigated in detail in the present work.

To our knowledge only two groups have given attention to the behavior of Fe in the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy. Hoehne *et al.*[13] carried out spin resonance on $\mathrm{Si}_{0.988}\mathrm{Ge}_{0.012}:\mathrm{Fe}_i^0$ with the aim of determining microscopic details on the local atomic arrangement around the Fe atom. Although the authors evidenced a line broadening, they were unable to elucidate the atomic structure of the defect. On the other hand, Nauka and Kamins[14] used deep level spectroscopy techniques to study some metallic species, especially $\mathrm{Fe}^{0/+}$, in relaxed as well as strained $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ layers. These authors only focused on the energy level position of Fe_i but were able to investigate a large range of alloy composition leading them to address the issue of the internal reference level with respect to the $\mathrm{Si}\text{–}\mathrm{Si}_{1-x}\mathrm{Ge}_x$ band offset. They found that, with increasing Ge content, the hole ionization enthalpy of free iron, $\Delta\mathrm{H}_p(x)[\mathrm{Fe}_i^{0/+}]$, decreases much faster than the band gap. They left untreated however the case of the $\mathrm{Fe}_i\text{–}\mathrm{B}_s$ pair as well as the iron diffusivity and the fluctuation related issues which are addressed in the following.

In this article we first detail the sample preparation and experimental procedures. Then the results are presented after having recalled the main theoretical tools allowing quantification of the diffusion process. We will show in particular that while the energetic distance between the donor levels of Fe_i and $\mathrm{Fe}_i\text{–}\mathrm{B}_s$ remains unaffected by adding Ge, the individual levels shift toward the valence band much faster than the reduction of the band gap. Therefore, we confirm that in contrast to the III–V and II–VI semiconductors, the $3d$ state cannot be used as independent, internal reference. We will also show that alloying does not affect the diffusion behavior of Fe, at least for Ge content below 12%. Finally, a discussion follows in which the main points and the major technological implications of our findings are underlined.

II. EXPERIMENTAL DETAILS

Relaxed bulk single crystalline $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ $\langle 111\rangle$ oriented samples were grown by Czochralski technique in the Ar atmosphere. The growth procedure is described in detail in Ref. 15. The alloy composition $x(=[\mathrm{Ge}]/[\mathrm{Si}])$ varies in the range of 0–12% as measured by Rutherford backscattering spectrometry. The samples were boron doped during growth with a uniform concentration ranging from 1×10^{14} to $3.5\times10^{15}\ \mathrm{cm}^{-3}$. This range of doping has been found to be useful in exploring the interplay between the energy level position and the Fermi level affecting the electronic population and thus the diffusivity.

After standard chemical polishing and cleaning, highly pure iron was scratched on one side of the wafers followed by diffusion under argon atmosphere (300 mbar) in sealed ampoules. This process was carried out at 950 °C and followed by a quenching to room temperature to impede the iron from precipitating. Schottky diodes were formed by aluminum evaporation after etching away a few microns while gold ohmic contacts were deposited on the back side of the structure. Diodes without iron, but subjected to the same high temperature heat treatment, did not indicate any signal which could be related either to process-induced defects or dislocations; the latter possibly originating from the growth process or the quenching procedure.

Deep level transient spectroscopy (DLTS) measurements were recorded with two commercial systems. The first one is a Semitrap spectrometer using the lock-in principle to process the capacitance transient signal. The second one is a Biorad system, based on the hypothesis of a pure exponential transient in which electronic sampling at two distant points along the time scale are enough to reproduce the observed time constant.

III. BASIC THEORETICAL TOOLS

The most stable form of Fe in the lattice, resulting from a minimization of the free energy of the system $p\text{-}\mathrm{Si}_{1-x}\mathrm{Ge}_x:\mathrm{Fe}$, is the $\mathrm{Fe}_i\text{–}\mathrm{B}_s$ pair. As stated in the Introduction, the formation of such a pair is a consequence of the Coulombic attraction[3,4] between the immobile B_s^- and the mobile Fe_i^+. At moderate doping levels and low Fe concentrations, the pair is formed within a few tens of minutes at room temperature, which is the time required for diode preparation. There are, however, accessible conditions under which Fe_i may be detached from boron and driven far away at the atomic scale. Such a metastable configuration could be kept long enough to allow observations of the isolated species in the substrate. This is done by thermally dissociating the pair according to

$$\mathrm{B}_s^-\mathrm{Fe}_i^+ \leftrightarrow \mathrm{B}_s^- + \mathrm{Fe}_i^+ . \tag{1}$$

However, if heating is a necessary condition for the reaction to be driven to the right, it does not suffice. Knowing that the binding energy of the pair is 0.65 eV in silicon,[16] the law of mass action enables a negligible equilibrium fraction of free Fe_i. To overcome this difficulty and thus favor a higher concentration of isolated Fe_i, a charge state conversion from positive to neutral is needed for each thermally dissociated Fe_i^+. This is done by reverse biasing the diode while heating according to

$$\mathrm{Fe}_i^+ \xrightarrow{V_r} \mathrm{Fe}_i^0. \tag{2}$$

Biasing prevents each dissociated Fe_i^+ from undergoing a Coulombic attraction by B_s^-. Basically, the procedure allows a band bending such as the pseudo-Fermi level in the depleted region is pushed above the iron-related level ($Fe_i^{0/+}$) converting each Fe_i^+ resulting form reaction (1) to Fe_i^0. Whereas reactions (1) and (2) are conducted at temperatures typically above 360 K, the reverse bias is kept until the diode is cooled below room temperature, where free Fe_i is no longer mobile and DLTS measurement can be safely carried out. The Fe-related signal appears in a temperature range determined by the rate window capabilities of the technique, typically from 200 to 280 K.

On the other hand, reaction (1) left to itself under 0 V results in the pair formation until equilibrium is reached. This allows to study the $Fe_i^+-B_s^-$ pair-related level which gives rise to a DLTS peak around 60 K. The corresponding pairing kinetics enables us to determine the diffusion coefficient of free Fe_i^+. Reaction (1) being diffusion limited, the rate of pairing is written as follows,[17]

$$\frac{d[\mathrm{Fe}](t)}{dt} = -4\pi\{R_+D_+f^+ + R_0D_0f^0\}[\mathrm{Fe}](t)[B_s](t). \tag{3}$$

In this equation f^+ is the fraction of ionized iron at equilibrium in the neutral region of the diode. It is given by

$$f^+ = \frac{[\mathrm{Fe}_i^+]}{[\mathrm{Fe}_i^+]+[\mathrm{Fe}_i^0]} = \frac{c_p}{c_p+e_p}, \tag{4}$$

where c_p and e_p are, respectively, the hole capture and emission rates and $f^+ = 1 - f^0$ stands for the fraction of positively charged iron. Finally, D_+ represents the diffusion coefficient and R_+ the capture radius of Fe_i^+ by the immobile B_s^-. The same definition holds for D_0, R_0, and f^0 corresponding to Fe_i^0.

The kinetics equation (3) can be simplified further if we consider two important facts. First, the experimental conditions are arranged such that the iron atoms are diluted, satisfying the condition $[\mathrm{Fe}_i] \ll [\mathrm{B}_s]$. This allows the boron concentration to be kept almost unaffected, that is $[\mathrm{B}](t) \approx [\mathrm{B}]_0$. The consequence is important in the sense that the kinetics is of the first order as we shall demonstrate in the following. Second, although rigorously both positive and neutral iron should be considered in Eq. (3), in practice the ratio D_+/D_0 is of the order of 50 in the accessible temperature range.[4] This allows one to neglect the contribution of the neutral species. Finally, owing to the simple Thomson model,[18] the capture radius R_+ is well described by the equipartition condition given by

$$\frac{e^2}{4\pi\varepsilon_0\varepsilon_r R_+} = \frac{3}{2}kT, \tag{5}$$

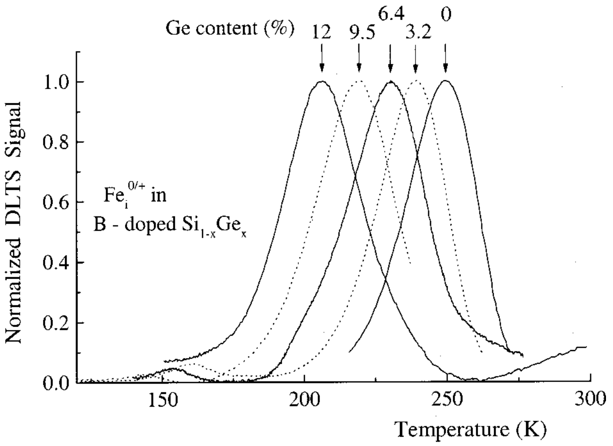

FIG. 1. Fe-donor related DLTS spectra as obtained in Fe-contaminated boron-doped $Si_{1-x}Ge_x$ for different Ge contents x. The spectra were recorded with the BioRad system using the rate window $e_0 = 200\ \mathrm{s}^{-1}$, a pulse width of 200 μs, and a reverse bias of $V_r = -2$ V while the filling bias was $V_f = 0$ V.

where the left-hand side represents the electrostatic Coulombic energy of attraction between Fe_i^+ and B_s^-. It is a simple matter to show that within the temperature range of the present investigation, the capture radius R_+ is of the order of 50 Å. On the other hand, the capture radius of neutral iron R_0 is controlled by a very short range potential (chemical forces) which does not extend beyond 5 Å. All these considerations lead us to justify dropping of the term $R_0D_0f^0$ in Eq. (3). As a matter of fact, the neutral species Fe^0 can easily be analyzed in an n-type substrate as we have shown a decade ago.[4] The injection into Eq. (3) of both the capture radius R_+, extracted from Eq. (5), and f^+, given by Eq. (4), enables one to extract the time constant for pairing. This quantity, being determined experimentally, is linked to the dynamic parameters of Fe_i^+ according to

$$\frac{1}{\tau_{\mathrm{exp}}} = 4\pi R_+ f^+ D_+ [\mathrm{B}_s]. \tag{6}$$

The only unknown is the diffusion coefficient $D_+(T)$, which is extracted from a simple Arrhenius plot. This procedure was successfully used in the past in silicon where very often the parameter f^+ was purposely set to unity. This is in general justified as long as the acceptor doping level is above $5\times10^{14}\ \mathrm{cm}^{-3}$, allowing the Fermi level to be far below the trap which corresponds to $c_p \gg e_p$ in Eq. (4). We shall see that this might be a crucial issue in $Si_{1-x}Ge_x$ where the relative position of the Fermi level and the trap strongly depend on the alloy composition x.

IV. EXPERIMENTAL RESULTS

A. Level positions in the band gap

Starting with isolated Fe_i, a set of DLTS spectra are displayed in Fig. 1 for different alloy compositions. The spectra are recorded following the procedure described by reactions (1) and (2). A reverse bias of -5 V, used to impede a reassociation of the mobile species Fe_i with the immobile B_s, was deliberately higher than the reverse bias used for DLTS in order to analyze a region of uniform Fe_i concentration. For the sake of clarity, the temperature range is intentionally restricted to 150–300 K where only the donor level ($\mathrm{Fe}_i^{0/+}$) is observed. The main striking feature is a very significant shift of the iron donor related peak toward lower temperatures when the Ge content is increased. This behavior indicates an effective increase of the hole exchange rate which, based on our knowledge of the *p*-Si:Fe system, can be extended to take into account the alloy effect. The new rate is given by

$$e_p(x,T)=\sigma_{p0}(x)v_p(T)N_v(T)\exp\left[\frac{\Delta S_p(x,T)}{k}\right]\times\exp\left[-\frac{\Delta H_p(x,T)+\Delta E_\sigma}{kT}\right]. \qquad (7)$$

The use of this relationship to extract the hole ionization enthalpy necessitates some clarifications as T is not the only variable. First, the hole effective mass involved in the product $v_p(T)N_v(T)$ is essentially determined by its value in silicon,[10] justifying the fact that *x* is not explicitly included in this product. Therefore, $v_p(T)N_v(T)$ reduces to the well-known parabolic form bT^2, where *b* is a constant.[10] Second, the hole capture cross section $\sigma_p(x,T)$ expresses a thermally activated process taking the form $\sigma_p(x,T)=\sigma_{p0}(x)\exp(-\Delta E_\sigma/kT)$. The temperature dependence appears in the exponential only. This has been experimentally demonstrated in silicon,[4] where ΔE_σ has been found to be 0.048 eV, a value small enough to be considered as *x* independent. But this may not be the case for $\sigma_{p0}(x)$.

These considerations allow us to confidently state that the whole preexponential factor in relation (7) keeps its temperature parabolic form, irrespective of the alloy composition, leading in principle to a straightforward determination of $\Delta S_p(x,T)$ and $\Delta H_p(x,T)$.[10] But this requires that we know *a priori* the temperature dependence of these two functions, which is not obvious. Fortunately, some hints can be gained from previous studies. To begin with, in silicon, $\Delta S_p(0,T)$—expressing the sum of a configurational entropy change $[\Delta S_p^{\mathrm{conf}}=-k\ln(2)]$ and a more complex vibrational contribution $\Delta S_p^{\mathrm{vib}}(0,T)$—reduces to the former which is temperature independent.[19] The fact that the vibrational contribution is not significant can be expected for impurities stabilizing at pure interstitial sites, configurations not involving the covalent bonds, and thus very weakly coupled to the lattice.[2,19] It is highly likely that the same situation holds in the alloy.

Finally, the hole ionization enthalpy $\Delta H_p(x,T)$ can at most take up the temperature dependence of the band gap, which is known,[20,21] and thus possibly accounted for.[10] In the present case, however, it will be demonstrated that the impact of the Ge content is by far much more important than a possible thermal shift of the iron level. In conclusion, we can confidently drop the variable T in the activation energy and write $\Delta H_p(x,T)+\Delta E_\sigma\approx\Delta H_p(x)+\Delta E_\sigma$. The emission rates $e_p(x,T)$, normalized to T^2, as a function of $10^3/T$ are plotted in Fig. 2. The extrapolation to $T=\infty$ shows that, within the experimental uncertainties, the prefactor of relation (7) remains almost unaffected, thus confirming all the above-mentioned assertions. The capture cross section $\sigma_{p0}(x)$ is found to vary in the range $(2-6)\times10^{-16}$ cm^2, an interval that is much more narrower than expected from the uncertainties inherent to the extrapolation procedure in the Arrhenius law. Therefore, there is no evidence for any impact of the alloy, either on the capture cross section or on the ionization entropy which remains essentially determined by the configurational contribution $[\Delta S_p^{\mathrm{vib}}(x,T)\approx0]$. It, therefore, becomes straightforward to extract the hole ionization enthalpy of $\mathrm{Fe}_i^{0/+}$ provided a correction to the activation barrier for capture ($\Delta E_\sigma=0.048$ eV) is applied to the data of Fig. 2 as we will see in the following

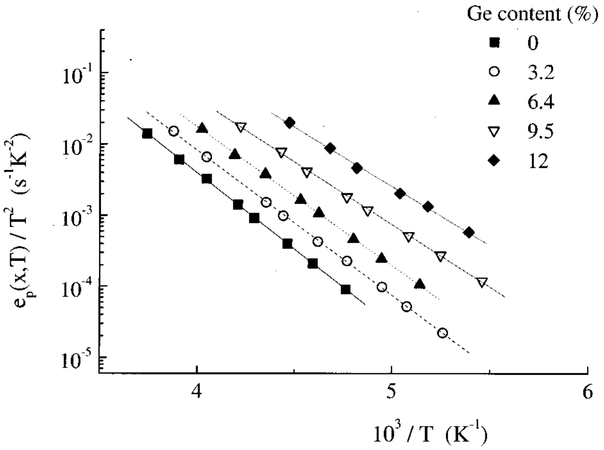

FIG. 2. Arrhenius plots of the hole emission rates for different Ge contents. Within the experimental uncertainties, the extrapolation to $T=\infty$ leads to a convergence of all the data.

The study of the FeB related level requires a trapping process of free Fe_i^+ by immobile B_s^-. This is done by leaving the sample at 300 K under 0 V allowing reaction (1) to proceed to the left. A DLTS signal related to the hole transition from the pair $(\mathrm{Fe}_i\mathrm{B}_s)^{0/+}$ appears at the expense of the isolated iron donor level $\mathrm{Fe}_i^{0/+}$ as shown in Fig. 3. Again, for the sake of clarity, the temperature range is deliberately restricted to values lower than 100 K. We will see in the following that if there is no loss of iron in the process of pair formation, a one to one correspondence must exist between the two iron-related signals. The Ge content dependent amplitude of the FeB signal depicted in Fig. 3 should not be considered seriously for two main reasons. First, the reverse bias used for DLTS analysis is of -5 V in the case of silicon while it is only of -1 V for the other samples. Therefore, the investigated depth does not have the same extent. Second, as mentioned previously, different $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ samples may contain different amount of dislocations affecting the concentration of electrically active iron incorporated during the diffusion process. Figure 3 reveals, however, a very significant shift of the DLTS signal toward lower temperatures, expressing a large increase of the emission rate as in the case of $\mathrm{Fe}_i^{0/+}$. The practical consequence of such a shift and of the shallow character of the level is that it becomes no longer

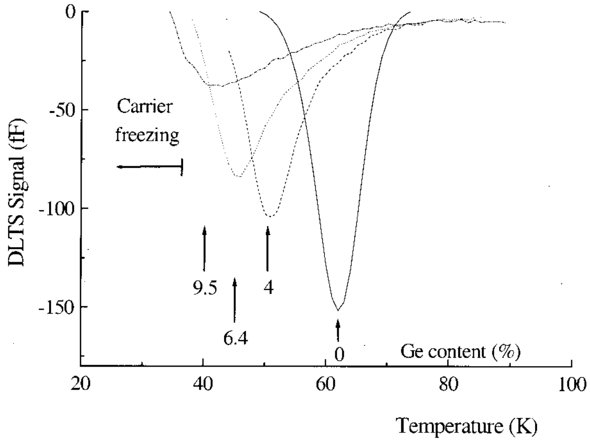

FIG. 3. FeB donor-related DLTS spectra recorded in the same samples as in Figs. 1 and 2. The spectra were recorded with the Semitrap system using the rate window $e_0 = 1647\ s^{-1}$. The spectrum in silicon was recorded with a reverse bias of $V_r = -5$ V while in the alloy a value of $V_r = -1$ V was applied. In both cases a pulse width of 250 μs and a filling bias of $V_f = 0$ V were used.

possible to investigate Ge content larger than ~7% as the related DLTS peak inevitably approaches the carrier freezing regime. This is illustrated in Fig. 3 through a drop and a significant distortion of the signal recorded on the sample with Ge content of 9.5%. Close or above this value a rigorous analysis becomes questionable unless very high experimental rate windows are available. We will therefore focus our attention on samples with alloy composition less than 7%. It is noteworthy that the sample with $x = 3.2\%$ is not considered here. Because of the carrier freezing limitation noticed previously, its doping level is too low to enable an easy analysis. A sample with $x = 4\%$ and a fairly high doping level is used instead. Another difficulty emerges from the loss of symmetry of the DLTS signal as soon as we depart from pure silicon. Figure 4 illustrates this effect through the shoulder labeled H1. Assigning this shoulder to an unknown level allows a better quantitative account of the whole signal. In particular it enables a better estimate of the thermal position of the DLTS peak related to the FeB donor level as can be seen in Fig. 4. Then, similarly to above, the hole emission rate $e_p(x, T_m)$ of the pair $Fe_iB_s^{0/+}$ can be monitored, allowing one to extract the corresponding hole ionization enthalpy $\Delta H_p(x)[Fe_iB_s^{0/+}]$.

Figure 5 displays the hole ionization enthalpies $\Delta H_p(x)$ for both Fe_i and Fe_iB_s donor levels, a fit to the data obtained by Nauka and Kamins in the case of the Fe-donor level,[14] and the band gap enthalpy, $\Delta H_{cv}(x,0)$. Notice that at $T = 0$ K, the band gap enthalpy is simply the Gibbs free energy $\Delta G_{cv}(x,0)$, defined also as the chemical potential for thermal generation of electron–hole pairs. In agreement with Van de Walle and Martin,[22] we assume that the reduction of the band gap is entirely reflected in the valence band shift, thus allowing an easy determination of $\Delta H_{cv}(x,0)$. Our data, although recorded in a narrow alloy composition range, agree very well with the findings of Nauka and Kamins, recorded in a wider range ($0 < x < 25\%$).

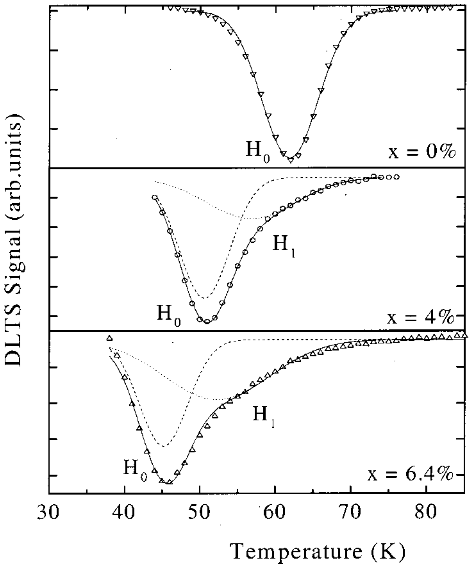

FIG. 4. Individual fits to the experimental data related to the FeB donor level (H_0) in the different alloys. The consideration of the shoulder (H_1) as an unknown point defect leads to a better account of the data. A more rigorous extraction of the hole ionization enthalpy of the FeB donor level is thus possible.

It is worth noticing, however, that both donor levels shift toward the valence band much faster than the band gap shrinks with increasing Ge content. This is surprising if we consider that the isolated $Fe_i^{0/+}$ does not involve the local covalent bonds as in the case of a substitutional impurity. Such a strong reduction of the hole ionization enthalpy may have serious implications as will be seen in the following. In the case of the FeB pair, the level is expected to be buried in the valence band for $x \geqslant 7\%$. The second interesting infor-

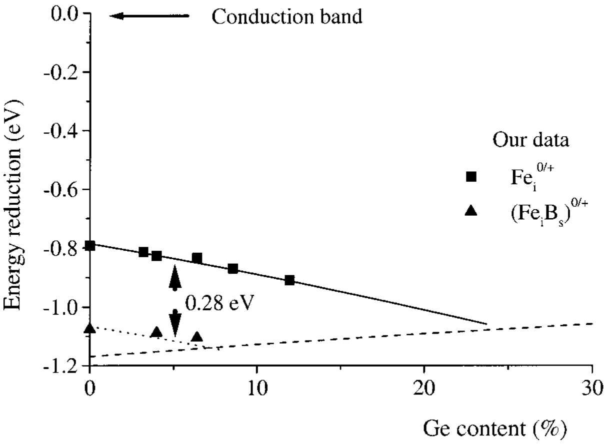

FIG. 5. Decrease of the hole ionization enthalpy at 0 K of both $Fe_i^{0/+}$ and $Fe_iB_s^{0/+}$ donor levels, as a function of the alloy composition x. The dashed curve shows the band gap shrinkage as determined by Weber and Alonso (Ref. 21). The solid curve represents the polynomial fit of Nauka and Kamins data (Ref. 14) for the Fe-donor level. The dotted curve is a simple shift of the latter by 0.28 eV which corresponds to the energy separation between the iron related levels in silicon.

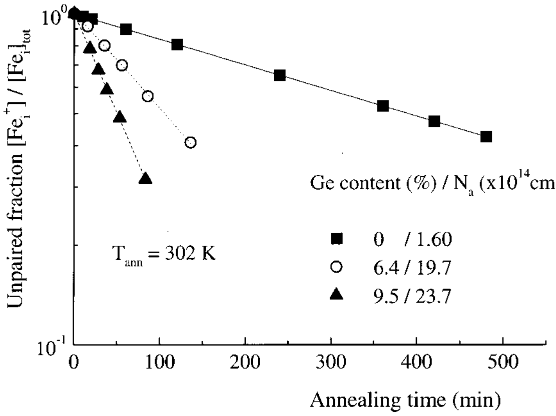

FIG. 6. Fraction of excess unpaired Fe_i vs annealing time for different alloy compositions x. The linear behavior confirms our assumption that a first-order kinetics governs reaction (1), thus simplifying the treatment of Eq. (3).

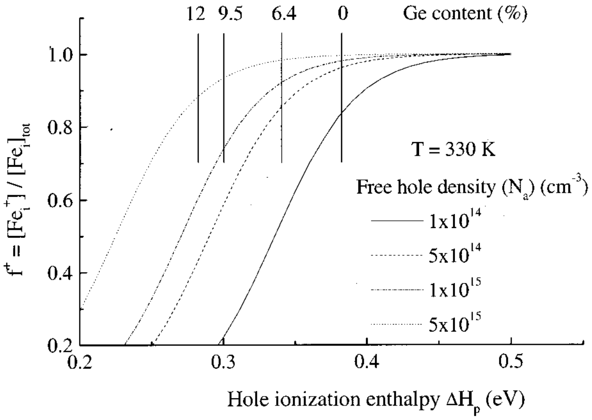

FIG. 7. Equilibrium fraction of positively charged free iron as a function of both the ionization enthalpy, determined by the Ge content in the $Si_{1-x}Ge_x$ alloy, and the free hole density determining the Fermi level position in the band gap.

mation gained from a careful observation of the data in Fig. 5 is the decrease with apparently the same rate of both ionization enthalpies. The dotted curve is indeed a simple shift of the solid curve by the quantity $\Delta H_p(0)[\mathrm{Fe}_i^{0/+}] - \Delta H_p(0)[\mathrm{Fe}_i\mathrm{B}_s^{0/+}] = 0.28$ eV.

The fact that the two levels follow each other when the band gap is reduced supports the model that the trapped hole resides primarily in the delocalized *d* orbital of the interstitial iron atom. This observation is in favor of similar core structures of both the $\mathrm{Fe}_i^{0/+}$ and $(\mathrm{Fe}_i\mathrm{B}_s)^{0/+}$ defects;[23] in $(\mathrm{Fe}_i\mathrm{B}_s)^{0/+}$ the substitutional boron atom, B_s, affects the binding energy without perturbing, or only slightly, the electronic structure.[23] Nevertheless, the shift in the ionization enthalpy with increasing alloy composition clearly indicates that the *d* orbital is sensitive to the disordered environment created by adding Ge atoms, sustained by its delocalized character. We have already established a very similar behavior in the case of the defects C_i and C_iC_s in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$,[7] confirming similar predictions made from electron-paramagnetic resonance measurements in silicon.[24,25]

B. Diffusion of Fe in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$: Fermi level effect

In our simple system, the dynamics are governed by the diffusion-limited reaction (1), in which we expect a first-order kinetic process. Such a behavior, demonstrated in silicon,[4] holds also in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys as shown in Fig. 6. When the diode is left to itself at 300 K under 0 V, allowing reaction (1) to proceed to the left, a simple trapping process of free Fe_i^+ by immobile B_s^- prevails. A quantitative analysis of this basic reaction, carried out at different temperatures, and based on relation (6) leads to the determination of the diffusion barrier $\Delta H_m(x)[\mathrm{Fe}_i^+]$ and the diffusion prefactor D_0, a parameter containing the migration entropy $\Delta S_m(x)[\mathrm{Fe}_i^+]$. In silicon, as long as the doping level satisfies the conditions $N_a \geqslant 10^{15}$ cm^{-3}, free iron is entirely ionized and thus the fraction f^+ given by relation (4) does not deviate from unity. So far, this has always been the case in the literature. However, in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$, the consideration of the factor f^+ becomes absolutely necessary as the $\mathrm{Fe}_i^{0/+}$ level has been shown to shift downwards in the band gap. For a sufficiently large Ge content, the Fe-donor level eventually crosses the Fermi level, moves below it, and acquires a neutral charge state, with the consequence that the fraction f^+ considerably reduces. A decrease in f^+ leads to an increase in the time constant as predicted by relation (6). The impact of the interplay between the doping level, controlling the Fermi level position, and the $\mathrm{Fe}_i^{0/+}$ ionization enthalpy, determined by the alloy composition, is shown in Fig. 7. It is clear that for moderately doped alloy materials, consideration of the factor f^+ becomes necessary in order to quantitatively account for the kinetic process involved in reaction (1). This simulation, based on Eq. (4), assumes that the hole capture cross section is not fundamentally affected, as demonstrated previously.

Taking into account all these facts, the extraction of the migration enthalpy $\Delta H_m(x)[\mathrm{Fe}_i^+]$ and the diffusion prefactor D_0 is straightforward. Figure 8 displays the data for all conditions of doping and alloying considered in the present work. The solid line represents a fit of all the data leading to a diffusion barrier and a diffusion prefactor very close to those obtained in silicon by a compilation of a large amount of data collected in the literature.[5] Two points emerging from Fig. 8 are worth mentioning. First, the data corresponding to $x = 3.2\%$ are obtained in the least doped material and, thus, require correction according to the above-developed arguments.[26] As already stated, the time constant of reaction (1), when driven to the left, requires performance of the measurements at higher temperatures as shown by the closed triangles in Fig. 8. The second point worth mentioning is related to the physics of the process. Alloying does not seem to affect the diffusion mechanism, at least up to a Ge content of 10%. It should be noticed, however, that the diffusion data extracted here represent an average over an ensemble of jumps, which might individually be perturbed. The elementary diffusion act, consisting of an atomic jump from one tetrahedral site to the next, through an unstable hexagonal

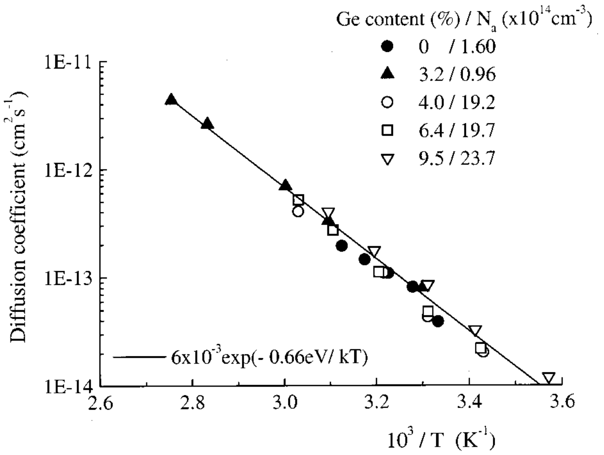

FIG. 8. Diffusion coefficient data for various doping and alloy compositions. The migration of free Fe_i^+ via interstitial mechanism does not seem to be perturbed by alloying Si and Ge at least up to a Ge content of ≈10%.

site, might indeed be locally perturbed by a Ge atom or any related distortion it induces in the lattice. But statistically, the probability for a free Fe_i^+ ion encountering a Ge atom is negligible. Surprisingly, this argument fails if the process of diffusion requires the participation of intrinsic defects as we have demonstrated to be the case for the diffusion of C_i in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy.[27] What is interesting to notice in the latter system is that high Ge content is not required to observe the alloy effect.

C. Alloying effect: Peak broadening and related issues

Compositional fluctuation, one of the main consequences of alloying, is of serious concern whenever microscopic parameters are to be deduced from macroscopic measurements. A local compositional change has two major impacts: (i) it induces a fluctuation in the free energies of one or both types of carriers, directly reflected in a fluctuation of the respective band edges, and (ii) a fluctuation of the atomic arrangement surrounding each individual defect which, depending on the degree of localization of the corresponding wave function, may induce a distribution in defect related-energy levels. When such fluctuations exceed kT, the resulting perturbation is a broadening of the global spectroscopic response due to a distribution of the emission rates given by Eq. (7). In the case of relaxed $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ and for $x<85\%$, the whole fluctuation is taken up by the valence band edge only.[10,22] Thus, a broadening of a signal emerging from electron transitions between a defect and the conduction band would exclusively be due to point (ii). On the other hand, a coupling of points (i) and (ii) may be at the origin of a spectroscopic broadening for a signal emerging from hole transitions between the defect and the valence band as is the case in the present work. Thus, both the free and trapped holes undergo a fluctuation of the energy in this case.

It must be stressed that the global response includes a large ensemble of point defects thus leading to parameters which, by definition, obey the ensemble average. The ultimate issue would of course be to establish a link between collective phenomena and local atomic dispersion. This would help in determining the relationship between the individual and the ensemble. Attempts have already been made to numerically process conventional photoluminescence or DLTS spectra in the case of ternary III–V alloys.[28,29] Recently, a new approach called Laplace DLTS was proposed in order to improve the resolution of the global conventional DLTS response. Although limited to very low alloy compositions, this technique seems to be promising[30,31] in distinguishing between the most abundant atomic configurations of a point defect.

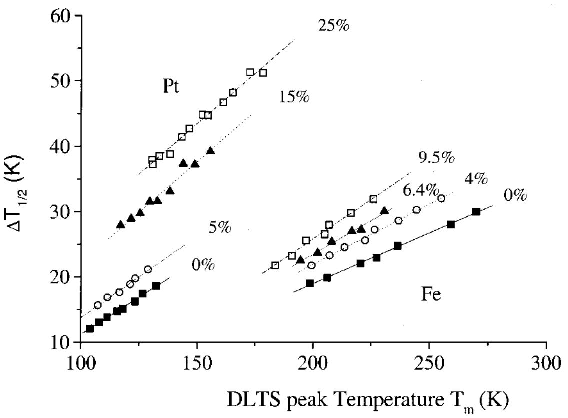

FIG. 9. Absolute thermal broadening $\Delta T_{1/2}$ as a function of the DLTS peak temperature T_m for different alloy compositions. The data are reported for both Fe-donor and Pt-acceptor in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy. The data recorded for Ge content in the range 0–25% correspond to Pt.

However, no matter what technique is used, its intrinsic resolution in an otherwise perfectly ordered environment must be known to enable a link between the alloy effect and the signal broadening. In the case of interstitial iron $\mathrm{Fe}_i^{0/+}$, Fig. 9 shows the DLTS peak half-width, in the following named $\Delta T_{1/2}(x,T_m)$, as a function of the peak temperature T_m for various Ge content x. As is clearly shown, a simple linear relationship links the broadening to T_m, irrespective of the alloy composition. The obvious consequence of such behavior is that a shallower level should exhibit a narrower peak than a deeper one. Accordingly, a given level is better resolved when DLTS analysis is carried out at low emission rates.

Figure 9 also stresses that in alloys the situation may evolve drastically as the compositional fluctuation takes a significant part in the process. To emphasize the necessity of focusing on the relative broadening $\delta(x,T_m) = \Delta T_{1/2}(x,T_m)/\Delta T_{1/2}(0,T_m)$ instead of on the absolute DLTS peak half-width $\Delta T_{1/2}(T_m,x)$, it is instructive to compare the case of $Fe_i^{0/+}$ with our previous findings on $Pt_s^{-/0}$ in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$.[32] The latter species has been investigated in a range of alloy composition of 0–25% as shown in Fig. 9. It is tempting to conclude from the absolute data $\Delta T_{1/2}(x,T_m)$ plotted in Fig. 9 that the alloy fluctuation affects more dramatically the Pt signal than the iron one. But the striking point is that the Pt-related level shifts toward higher temperatures with increasing Ge content,[32] while it is the other way

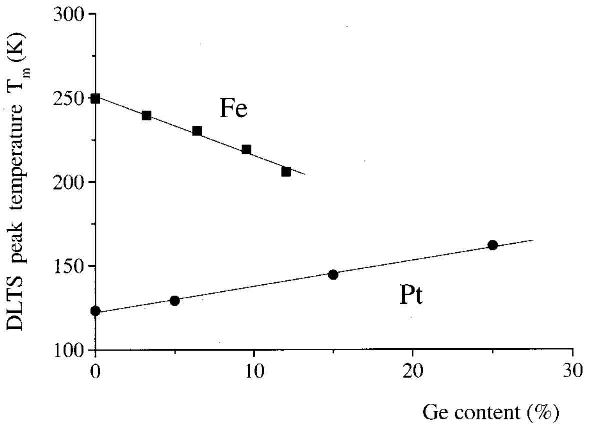

FIG. 10. Plot of the DLTS peak temperature T_m as a function of Ge content. The data were recorded for a rate window of 200 s^{-1}. A simple linear relationship seems to govern the alloy composition dependence of T_m.

around for the Fe-related level. This property, illustrated in Fig. 10 by plotting the DLTS peak temperature T_m as a function of the alloy composition, justifies the choice of Pt for the present purpose. According to the above-mentioned statements, the intrinsic thermal-induced broadening and alloy contribution add up in the case of platinum whereas in the case of iron they tend to balance each other. This is basically the reason for the large difference reported in Fig. 9 between the two metallic species.

Rigorously, the relative broadening $\delta(x,T_m)$, plotted in Fig. 11, reveals without any ambiguity that the compositional fluctuation equally affects both species. Relying on recent LDLTS measurements carried out on the system $Si_{1-x}Ge_x$:Pt,[31] we may conclude that the fluctuations of both the atomic environment of the point defect and the valence band edge [points (i) and (ii) mentioned earlier] affect the DLTS global response. Unfortunately, it is not possible to establish detailed and firm statements on each aspect taken separately as they require at least a scanning of the Ge content in a wider range than is available in the present work. In the case of the FeB pair, consideration of higher alloy composition is of no use since the related band gap level disappears already for $x \geqslant 6.4\%$. It thus remains in the following to give general comments and qualitative indications on the expected relationship between the signal broadening and the valence band edge and or, band gap-level fluctuation, the latter being due to the fluctuating local atomic environment.

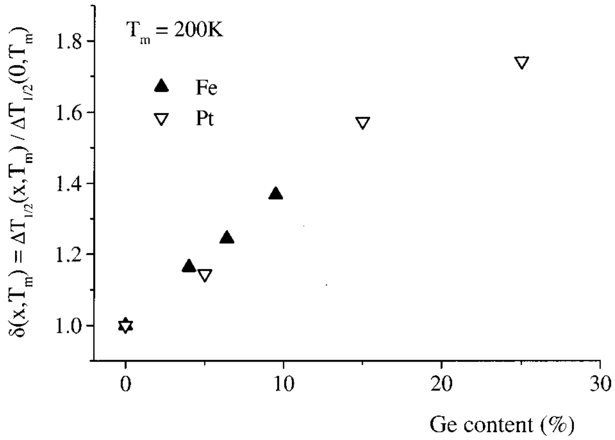

FIG. 11. Normalized line width $\delta(x,T_m)$ for Fe-donor and Pt-acceptor levels showing that the alloying impact is the same for the two species, which is not obvious from the observations of Fig. 9 alone.

The first point worth mentioning is related to the degree of validity of conventional spectra analysis, based on the assumption of a pure exponential, when characterizing point defect in alloys. It seems obvious, indeed, that a broadened level forbids one from assigning a defined time constant to a single thermal transient shot deviating from a simple exponential. This issue has been addressed by Omling *et al.*,[29] who showed that the simple treatment still has a physical meaning, provided the capture rate is temperature independent or alternatively, exponentially dependent on temperature. This restriction has been demonstrated to hold in the present work.

Applying the approach already developed in ternary III–V compounds,[28,29] we may express the alloy broadening $\delta(x,T_m)$, plotted in Fig. 11, by the semiempirical relationship

$$\delta(x,T_m) = 1 + \gamma(x,T_m)\sqrt{x(1-x)}. \tag{8}$$

Equation (8) takes into account the fact that in pure silicon $(x=0)$ and pure germanium $(x=1)$, two homogeneous materials, the x dependence must vanish leaving the intrinsic thermal broadening as the only determining factor. But the most striking implication of Eq. (8) is the physical meaning of the complex factor $\gamma(x,T_m)$ containing the impact of the band gap and defect environmental fluctuations cited previously. An x independent γ would obviously lead us to expect the largest broadening for $x=0.5$.[33] However, this is seldom the case. In fact, owing to the quadratic form of the band gap,[21] and, to a certain degree, the ionization enthalpy of the defect (see Fig. 5), the factor γ contains the derivative $\partial \Delta H_p(x,T)/\partial x$ and is thus at least a linear function of x. As a consequence, a shift of the maximum of the full width at half maximum (FWHM) is to be expected.[34] Unfortunately, a quantitative analysis of the broadening issue is difficult to achieve as it requires one to follow the iron-donor level in a much wider Ge content range than available. We have indeed shown previously that the level merges with the valence band for $x \geqslant 25\%$ (see Fig. 5). This constitutes a serious limitation to a mathematical treatment based on Eq. (8), while the same treatment proved to be valuable in other circumstances.[34]

The second aspect is that alloying does not alter the FWHM only. It may render other simple relationships in homogeneous materials, such as the proportionality between the DLTS peak height and the absolute defect density no longer valid. Instead, an integration of the whole response becomes necessary to account for the ensemble of individual configurations. It is thus intuitive to expect that for a constant concentration of the defect, an increase of the alloy composition increases the broadening and thus decreases the DLTS peak height. But, the conservation law requires that the area under the peak remains constant.[29] In practice, however, and particularly in the present case, it is difficult to keep invariant the concentration of the defect. We know indeed that the density of dislocations increases with the alloy content[35] and we also know that Fe is very much attracted by such dislocations due to the well-known gettering mechanism.[1] Therefore, the rate of gettering of Fe during its diffusion into the substrate cannot be considered independent of the Ge content, restricting us to consider the relative peak heights only.

The third and last possible consequence of the alloy induced broadening is reflected in the symmetry of the peak. A sole Gaussian distribution of the energy levels in the band gap around a mean value does not necessarily imply a symmetric DLTS peak. A Gaussian distribution of the corresponding capture cross sections, matching the energy distribution or, alternatively, an energy independent capture cross section, is also required. If this is not the case, a shift and an asymmetry of the DLTS spectrum might show up upon reducing the injection pulse width. The iron donor level ($Fe_i^{0/+}$) does not exhibit any dependency on the injection pulse width, while under similar circumstances involving other point defects, capture cross section induced asymmetry of the DLTS peak has been observed.[36] The situation is, however, unclear for the iron–boron pair for the above-invoked reasons.

V. DISCUSSION

In this study, we have shown that neither the interstitial $Fe_i^{0/+}$ nor the $(Fe_i\text{–}B_s)^{0/+}$ pair follow either of the band edges while they remain at a constant energy from each other when the composition of the alloy is varied. Considered as deep levels, both defects are described by wave functions extending over the entire Brillouin zone, and in this respect the present results are not surprising. As a consequence of the observed inequality,

$$\left.\frac{\partial \Delta H_p(x,T)}{\partial x}\right|_T > \left.\frac{\partial \Delta H_{cv}(x,T)}{\partial x}\right|_T , \tag{9}$$

the $3d$ metals can no longer be used as independent, internal reference levels, in band alignment as is the case for III–V and II–VI compounds semiconductors, a fact already noticed by Nauka and Kamins.[14]

On the other hand, the important shift observed in the present work put a particular emphasis on major technological processes such as the gettering.[1] Whenever point defects play a key role, quantitative assessment may be difficult to achieve without a complete consideration of all the microscopic parameters and their possible changes under various stimuli such as temperature, alloying or stress, etc. Many of these technological processes are carried out at high temperatures involving complex reactions where the charge state dependent branching ratio is fundamental. The normal method is to introduce in the simulator, parameters that are extracted at low temperatures, implicitly assuming their invariance. One of the factors determining the charge state dependent mechanisms is the level position in the band gap of an active point defect. The difficulty is that the population of such a level is implemented by free carriers provided by a reservoir whose characteristics are themselves affected by the above-cited stimuli. If we consider silicon for instance, the band gap or, thermodynamically, the Gibbs free energy for electron–hole pair creation, $\Delta G_{cv}(T)$, is given by

$$\Delta G_{cv}(T) = \Delta H_{cv}(T) - T\Delta S_{cv}(T) = 1.169 - \frac{\alpha T^2}{\beta + T}(\text{eV}), \tag{10}$$

where $\alpha = (4.9 \pm 0.2) \times 10^{-4}$ eV K^{-1} and $\beta = (655 \pm 40)$ K.[20] Therefore, changing the temperature in the range of 0–400 K shrinks the band gap by only about 6%, enabling us to neglect any temperature induced change, as has been done in the present work. Here the range of measurement was even narrower (from 150 to 300 K). The absolute energy reference in the present case can thus, as a first approximation, be assigned to the valence band. This is the case for most of the techniques investigating electronic transitions between a level and the allowed bands, provided the working temperature remains below 400 K. Except for a few cases,[10,37] any impact of the temperature on the electron (n) or hole (p) ionization energy $\Delta G_{n,p}(T)$ can thus barely be detected.

In the range of 400–1100 K, typical for gettering processes for instance, the silicon band gap is reduced however by 30%. If neglected, this fact gives rise to a fundamental misunderstanding. Considering the $Si_{1-x}Ge_x$ alloy as the thermal reservoir, where the Gibbs free energy for electron–hole pair creation $\Delta G_{cv}(x,T)$ is not only dependent on T but also on x, we may expect significant changes from what is observed in silicon. To illustrate this aspect in the framework of the present study, two properties, which are well established in silicon, are revisited in the following.

We first consider the process of gettering by segregation due to highly p-doped silicon-based materials, an interesting alternative for today's device processing. In this process, spatially localized high solubility of impurities can be generated through the Fermi level effect and ion pairing.[38] This aspect, which has been addressed in silicon by Gilles *et al.*[39] and McHugo *et al.*,[40] can be extended to the present work through the role of the additional and very significant alloying band gap shrinkage in the $Si_{1-x}Ge_x$ material. These authors observed a significant decrease of the iron segregation efficiency at high temperature in highly boron-doped silicon, than expected if the iron level were invariant in the band gap. This led them to fit the temperature-dependent Fe solubility with the ionization Gibbs free energy $\Delta G_p(T)$ of $Fe_i^{0/+}$ taken as a free parameter. The result was a significant decrease of $\Delta G_p(T)$ above 900 K necessary to account for the experimental observations. The extension to $Si_{1-x}Ge_x$ alloy raises the obvious question of the alloy-induced energy shift of the Fe-donor level and its impact on the segregation gettering efficiency even at low temperature where the thermal-induced shift is negligible. We assume that the independence of the two variables, x and T, demonstrated below room temperature,[41] can be extended to higher values, thus validating the use of the thermal-induced shift determined in silicon by Gilles *et al.*[39] This leads to a straightforward determination of the total Fe solubility as a function of the dopant concentration at a given temperature for various alloy compositions. It is simply given by the sum of the following three contributions:

$$[\mathrm{Fe}]_{\mathrm{total}} = [\mathrm{Fe}_i^0] + [\mathrm{Fe}_i^+] + [\mathrm{Fe}_i^+\mathrm{B}_s^-], \tag{11}$$

where the first term on the right-hand side is the neutral iron concentration, the second term expresses the positively charged free iron, due to the Fermi level effect, and the third term is the amount of paired iron. It is extracted from the detailed balance of reaction (1) and given by[38]

$$[\mathrm{Fe}_i^+\mathrm{B}_s^-] = [\mathrm{Fe}_i^+][\mathrm{B}_s^-]\Omega(T), \tag{12}$$

where $[\mathrm{B}_s]$ is the boron concentration and $\Omega(T)$ is the equilibrium constant[38] given by

$$\Omega(T) = \frac{Z}{N}\exp\left(\frac{E_b}{kT}\right). \tag{13}$$

In Eq. (13) Z is the number of pair configurations (4 for the tetrahedral site), N is the lattice site density in Si or $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ (5×10^{22} cm^{-3}), and E_b is the binding energy of the pair ($E_b = 0.65$ eV),[16] considered in the following as independent of Ge content. It is obvious from relation (11) that the heavy boron-doping of a part of the substrate will contribute to a significant increase of iron in that part. Combining Eqs. (11)–(13) and (4), we obtain for the total extrinsic Fe solubility, normalized to the intrinsic value,

$$\frac{[\mathrm{Fe}]_{\mathrm{tot}}^{\mathrm{ext}}}{[\mathrm{Fe}]_{\mathrm{tot}}^{\mathrm{int}}} = f_{\mathrm{int}}^0\left\{1 + \frac{f^+}{1-f^+}[1+[\mathrm{B}_s]\Omega(T)]\right\}. \tag{14}$$

In Eq. (14), f^+ is given by relation (4) and f_{int}^0 is the fraction of neutral iron in intrinsic material.[40] Taking into account the Ge content dependent Gibbs free energy, $\Delta G_{cv}(x,T)$ [see Eq. (10) and Ref. 21] and $\Delta H_p(x,T)$ displayed in Fig. 5 leads to the curves plotted in Fig. 12. We can see that for a boron concentration of 2×10^{18} cm^{-3}, the relative concentration of iron driven to the highly boron-doped area drops by an order of magnitude in $\mathrm{Si}_{0.8}\mathrm{Ge}_{0.2}$. This is the first demonstration that the gettering by segregation, considered as a possible alternative in silicon technology, is totally inefficient in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy for $x \geqslant 20\%$.

Interestingly, the findings of Gilles *et al.*[39] and McHugo *et al.*[40] implied a change in the structure of the point defect when the temperature is higher than 900 K. The former authors motivated their statement by considering the fact that a decrease in the ionization Gibbs free energy at high temperatures corresponds to an increase in the corresponding entropy according to the universal relationship

$$\Delta S_p(T) = -\frac{\Delta G_p(T)}{\partial T}. \tag{15}$$

Equation (15) mainly describes the vibrational part of the ionization entropy which was revealed to be negligible in the temperature range over which the DLTS measurements were carried out, leaving only the electronic configurational contribution.[11] A simple estimation led Gilles *et al.*[39] to suggest a huge increase of the accompanying entropy ($\Delta S_p \approx 13$ k for $T > 900$ K). Again, it is a simple matter to show that such an increase of $\Delta S_p(T)$ must necessarily be followed in parallel by an increase of the ionization enthalpy $\Delta H_p(T)$, otherwise we would face a negative Gibbs free energy $\Delta G_p(T)$, which has no physical meaning. It is interesting to notice that this is not the first instance of raising such a compensating effect between the entropy and the enthalpy of a thermally activated process. The migration of the vacancy in silicon, playing a key role in dopant diffusion, exhibits a very similar behavior.[42] All these observations are, indeed, as suggested by Gilles *et al.*,[39] in favor of a change in the structure of the defect at high temperature, an important point which remains to be clarified.

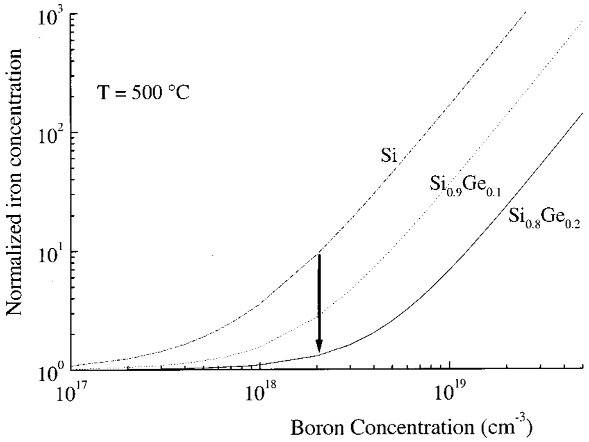

FIG. 12. Normalized iron concentration as a function of boron concentration for different Ge contents. The fact that it is higher than unity stems for the expected increase of the solubility by segregation [Eq. (14)]. Here, we show that the efficiency of such a mechanism decreases in the alloy as a consequence of the energy shift discussed in the text. The arrow shows the drop in the solubility from Si to $\mathrm{Si}_{0.8}\mathrm{Ge}_{0.2}$ while the doping level is kept unchanged at 2×10^{18} cm^{-3}.

The second major consequence of the energy shift shown in Fig. 5 is related to the so-called carrier-emission-limited drift in reverse biased junctions.[4] This effect, first demonstrated for free iron in *n*-type silicon, may concern any species introducing a level in the band gap and having a reasonable charge state dependent mobility. Basically, in a high-field region of a reverse biased junction, where no carrier capture occurs, the charge state of the level is determined by the competition between electron and hole emission processes. According to the Shockley–Read–Hall statistics, the average fraction of positively ionized iron, adapted to the *n*-type $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy by introducing the variable *x*, is given by

$$f^+(x,T)|_{\mathrm{hf}} = \frac{e_n(x,T)}{e_n(x,T)+e_p(x,T)}, \tag{16}$$

where $e_n(x,T)$ and $e_p(x,T)$ are the electron and hole emission rates, respectively, in the high field region (hf), the latter being given by Eq. (7). Relation (16), expressing a situation

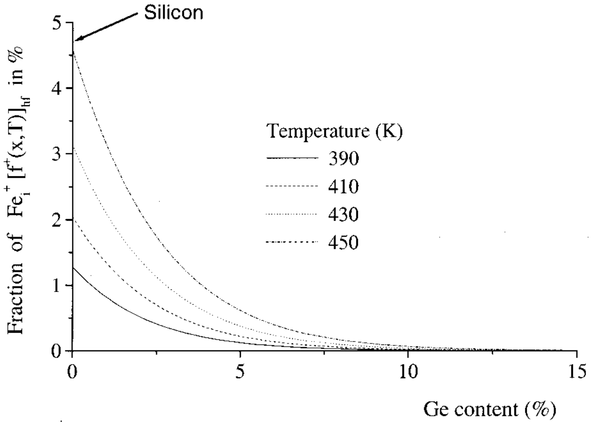

FIG. 13. Nonequilibrium fraction of positively charged Fe in a reverse biased *n*-type $Si_{1-x}Ge_x$-based device. The rapid decrease of this fraction for increasing Ge content impedes the field-induced drift of Fe_i^+ out of the active area whereas this process was demonstrated to be very efficient in *n*-type silicon (Ref. 4).

out of equilibrium, is clearly different from relationship (4), which is valid under equilibrium conditions only. Now the peculiarity for iron having a distinct diffusion coefficient for each charge state, with $D(Fe_i^+) > D(Fe_i^0)$,[4] leads to a much faster decrease in the concentration of Fe in the depletion region compared to the neutral zone. Due to equilibrium, a neutral charge state prevails all the time in the later region. In operating bipolar power devices, a strong electric field and moderate temperature are easily achieved. Therefore, *a prior* iron contamination, whether intentional or not, is expected to lead to an accumulation of the metallic species in the *p*-type region, according to the direction of the applied field. In $Si_{1-x}Ge_x$-based devices the evaluation of relation (16), based on all the above-mentioned findings and the considerations developed in Ref. 4 leads to the behavior displayed in Fig. 13. It is again straightforward to predict that in the alloy, the carrier-emission-limited drift mechanism vanishes already for low Ge content impeding iron from escaping the depletion region, thus leading to the near absence of field-induced, outdiffusion in the alloy.

It is noteworthy to ask whether the above-noted conclusions for the relaxed $Si_{1-x}Ge_x$ alloy are equally valid in the strained material, especially important for the heterobipolar transistor. The answer to this question is found in the results of Nauka and Kamins.[14] These authors investigated in some detail the strained material and also found an important shift of the Fe_i donor level toward the valence band with increasing alloy composition. However, while in the relaxed material the level is predicted to merge within the valence band for $x \approx 25\%$, a value of 40% is needed in the strained material. Therefore, although less stringent, the same conclusions can be drawn for the strained material.

Finally, an interesting aspect deserving attention in this context refers to the simple charge-state-driven bistability of the Fe–A pair (where A≡B, Al, Ga or In), firmly established many years ago.[3] This mechanism consists of two configurations of the pair in which the free interstitial Fe can flip from the first stable tetrahedral site along the ⟨111⟩ direction to the second metastable hexagonal site along the ⟨100⟩ direction. Each configuration leads to a level in the gap and the conversion from one configuration to the other has been quantitatively analyzed. Surprisingly, in Al doped *p*-type silicon the trivial two-point charge model, known as the Coulombic model, accounts perfectly for all the observations. It is our belief that in this context the *p*-type $Si_{1-x}Ge_x$:Al+Fe system offers a unique opportunity to test how the additional short-range elastic forces due to alloying compete with the electrostatic ones in controlling the bistability and thus the iron-acceptor pairing formation and stability.

VI. CONCLUSION

Tuning the band gap of $Si_{1-x}Ge_x$ alloy by varying the Ge content is a valuable tool to affect the thermodynamic properties of point defects. Although this approach has been widely applied in the study of other binary and higher order alloys, the increasing interest in IV–IV-based materials allowed only recently some technologically relevant defect engineering issues to be solved. This would not have been possible without a refinement of the crystal growth technique leading to a considerable reduction in the density of extended defects. In this work we demonstrate that new variables such as the band gap or alloy disordering become accessible. In this context the case of iron is particularly interesting: the concepts developed for modeling electrical and thermodynamic properties, transport behavior, precipitation, and gettering phenomena may be tested using iron as a probe. We have shown that the band gap shrinkage following an increase in the Ge content results in the iron-related electrically active levels shifting downwards. The shift is shown to occur much faster than the gap reduction. Consequently, the FeB pair-related donor level merges within the valence band already at an alloy composition of about 7%. Above this value, the only remaining electrically active level is due to the interstitial $Fe_i^{0/+}$. This level is expected to merge within the valence band edge for $x \geqslant 25\%$. It thus becomes difficult for this species to be ionized in moderately boron-doped $Si_{1-x}Ge_x$ alloys. Consequently, gettering by segregation, routinely used in silicon technology, becomes inefficient in these materials. Diffusion is also of main concern for the simulation of device performances. We have shown that the diffusion properties of the positively charged interstitial iron remain unaffected neither by the band gap reduction nor by the alloying-induced disorder. This is not always the case since other species have been found to be strongly sensitive to the atomic environment. Finally, we believe that a local, alloying-induced stress, offers a unique opportunity to investigate other mechanisms governing reactions at the atomic scale. The electronic bistability of the iron-acceptor complex, where the acceptor nature plays a key role, deserves in this respect special attention.

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