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Pinning behavior of gold-related levels in Si using $Si_{1-x}Ge_x$ alloy layers

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The question as to whether the gold-donor and acceptor levels are pinned either to the conduction band, the valence band, or to neither of them is addressed in the present investigation. The donor and acceptor levels in gold-doped n^+p and p^+n diodes of relaxed, epitaxial $Si_{1-x}Ge_x$ of $0 \leqslant x \leqslant 0.25$ are characterized with deep-level transient spectroscopy (DLTS) and minority-carrier transient spectroscopy (MCTS) and the results are discussed within a thermodynamical model which considers the point defect as a thermodynamic subsystem immersed in the surrounding semiconductor thermostat. It is unambiguously concluded that both levels are pinned to the conduction band. A new effect related to the impact of the statistical distribution of Ge atoms into the lattice on the full width at half maximum of the DLTS or MCTS peaks is clearly observed. Based on these results the so-called entropy-related paradox, i.e., the observation that the entropy change involved in the creation of an electron-hole pair via the gold-acceptor level is significantly larger than that via a direct band-to-band transition, is critically reexamined. It is concluded, however, that the entropy paradox is still unsolved. [S0163-1829(97)00444-X]

I. INTRODUCTION

Since it has been recognized that the very existence of semiconductor technology is based upon the ability to control the purity of the material, point defects in silicon have received the most attention, all kinds of semiconducting systems and types of imperfections included. Today's need for silicon submicrometer scale technology requires even closer attention to the subject. Indeed, some of the fundamental aspects of various imperfections are still far from being understood, if known at all. Among them the pinning behavior of the levels introduced into the gap by specific chemical species or structural defects (vacancy, interstitial, and their related complexes) constitute a major issue. The intensively studied monovacancy defect helps in the understanding of the necessity to master the relationship between a level and the bands with which it interacts. In many of the diffusion issues, the vacancy is the mediating vehicle for dissolving impurities in the matrix. Among its four charge states, the $V^{-/=}$ level, which plays a significant role in diffusion mechanisms,[1] is the closest to the conduction band. Its exact position $[\Delta E = E_c - E(V^{-/=})]$ is not known but only estimated at $\Delta E \geqslant 0.17$ eV.[1] As the diffusion process takes place at high temperature, a gap shrinkage of 200 meV occurring at 800 K would bury the level $E(V^{-/=})$ within the conduction band if it were pinned to the valence band, thus leading to its complete deactivation. Theoretical studies by Van Vechten[2] have shown, however, that this level should remain in the gap shifted by a constant energy ($\Delta E \sim 0.17$ eV) relative to the conduction band, independent of the temperature. No experimental proof, however, has to our knowledge been given for this statement.

The second example, which motivated the present work is concerned with gold-related levels in silicon. This impurity has been discussed at length for many years mainly because of its technological interest, and we believe that the major part of its theoretical and experimental aspects are well known and firmly established.[3–5] However, the question as to whether or not the donor and acceptor levels, two coupled charge states of substitutional gold, are pinned either to the conduction or to the valence band or to neither of them remains open. This controversial issue has been invoked many times. The gold-related levels and the corresponding temperature dependencies of the carrier emission and capture rates have been carefully investigated. A detailed and quantitative discussion of this matter is found in the paper by Lang *et al.*[3] These authors emphasized the most controversial aspect related to the violation of the energy conservation law when a comparison is made between the two possible routes of thermal generation of electron-hole pairs: The generation processes originating from a direct band-to-band transition, or via the gold-acceptor level, located at $E_c - 0.555$ eV, require different amounts of energy. A rigorous investigation of these two possible routes cannot be conducted without an unambiguous determination of the pinning behavior of the acceptor level. So far, three approaches have been followed to answer this question: (i) From fits to the emission rates, Brotherton and Bicknell[6] and Kalyanaram and Kumar[7] came to the conclusion that the level is pinned to the valence band; (ii) from photocapacitance measurements, Engstrom and Grimmeiss[8] came to the opposite conclusion of a pinning to the conduction band; finally, (iii) Samara and Barnes[9] used pressure measurements to find that the acceptor level moves independently of the band edges. It is not surprising, however, that different authors handling such a controversial question end up with discrepancies. The reason is very often related to the difficulty of properly taking into account some ''hidden'' parameters.[10]

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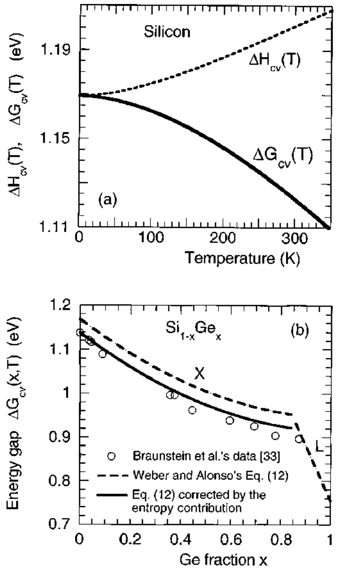

FIG. 1. (a) Gibbs free energy (lower curve) and enthalpy (upper curve) of silicon as a function of temperature. (b) Composition dependence of the energy gap in $Si_{1-x}Ge_x$ alloy as measured at 20 (Ref. 34) and 296 K (Ref. 33). X and L represent the X- and L-conduction band.

To answer the question of the pinning behavior of gold-related levels, we propose to use $Si_{1-x}Ge_x$ alloys rather than pure silicon. $Si_{1-x}Ge_x$ alloys allow for a much more sensitive handling of the gap than is possible for Si either by pressure variation[9] (allowing a gap variation of only 15 meV in the pressure range 0–10 kbar) or by the sole temperature dependence of the gap.[8] The first results obtained by the Aarhus group[11–13] indicate clearly the success of this approach for both gold and irradiation induced defects. Figure 1(a) illustrates the impact of the temperature. An increase from 100 to 300 K reduces the gap, or the Gibbs free energy of electron-hole pair generation, by 40 meV. It is to be noticed, however, that the impact of such a variation is overestimated for two reasons. First, because the study of a typical level involves a considerably narrower temperature range. Second, it is the enthalpy which must be considered in transport measurements and not the Gibbs free energy as we will demonstrate below. Therefore, a simple look at Fig. 1(a) shows that the effect goes in the opposite direction and is much less significant. The consequence is an effective band-gap change of only a few meV. On the other hand, Fig. 1(b) shows that the Ge content x of the alloy will induce a gap shrinkage of 100 meV at any given temperature for x varying from 0% to 25%, thus stressing the advantage of using this alloy to solve the question of the pinning effect.

It is worth pointing out that using $Si_{1-x}Ge_x$ alloys would not have been possible without a significant improvement in the epitaxial growth of this material which has led to a considerable decrease in the dislocation density. This point is crucial as dislocations act as sinks for the metal, thus impeding its electrical activity.[14,15] A very significant reduction of the dislocations and improvement of alloy quality has been accomplished by different groups[16–18] owing to a graded buffer layer grown on the substrate before the epitaxial growth of the $Si_{1-x}Ge_x$ alloy at the nominal composition is started.

The paper is organized as follows. In Sec. II we detail the theoretical background which is composed of two subsections. The first one is devoted to a clarification of the physical meaning of the transport parameters that will be used to interpret the data. To achieve this goal, thermodynamic concepts are used. Then the amphoteric activity of gold is discussed. The transitions and corresponding charge states for each specific level are defined. In Sec. III we give the experimental procedures and sample preparation. Section IV is devided in two parts. First we describe the experimental data of the gold donor and compare our findings to literature data that we consider so far the most relevant. The twofold interactions of the acceptor level with the conduction and valence bands is established in the second part. Section V is devoted to a general discussion of our data motivating a reexamination of various statements in the literature that have come to opposite conclusions or are still controversial.

II. THEORY

A. Thermodynamic concepts

A point defect may be considered as a thermodynamic subsystem immersed into the surrounding semiconductor thermostat. The thermostat and the defect are capable of exchanging free carriers, and phonons in the case of an indirect band gap. This approach, introduced by Thurmond and Van Vechten[2,19] and Engstrom and Alm,[20] has the merit of assigning a clear physical meaning to the quantities describing the carrier-exchange rates between a given level and the allowed bands. One of the main reasons for using the thermodynamic approach is the specific feature of semiconductors that, in contrast to metals, the charge-carrier concentration is a thermodynamic variable. Applying such a concept, the thermostat is defined by its gap or chemical potential for electron-hole pairs generation in the reaction,

$$0 \rightarrow e^- + e^+. \tag{1}$$

The chemical potential may also be defined as the increase in Gibbs free energy $\Delta G_{cv}(T)$ corresponding to an increase by one in the number of electron-hole pairs at constant temperature and pressure,

$$\Delta G_{cv}(T) = \Delta H_{cv}(T) - T\Delta S_{cv}(T), \tag{2}$$

where $\Delta H_{cv}(T)$ is the enthalpy of the process and $\Delta S_{cv}(T)$ is the entropy change resulting from the lattice mode softening in the vicinity of the atom where an electron-hole pair generation occurred. $\Delta S_{cv}(T)$ is positive[2] above $T = 0$ K and according to the thermodynamic definition given by

$$\Delta S_{cv}(T) = -\frac{\partial \Delta G_{cv}(T)}{\partial T}. \tag{3}$$

Experimentally, Varshni[21] and Bludau, Onton, and Heinke[22] extracted semiempirical formulas expressing the Gibbs free energy $\Delta G_{cv}(T)$. If both approaches are similar, the latter is, however, less straightforward to handle. Therefore, in the following we will rely on Varshni's[21] equation expressed as

$$\Delta G_{cv}(T) = \Delta G_{cv0} - \frac{\alpha T^2}{\beta + T}, \tag{4}$$

where $\Delta G_{cv0} = \Delta H_{cv0}$ are the values of ΔG_{cv} and ΔH_{cv} at 0 K and α and β are adjustable parameters, recently reexamined by Alex, Finkbeiner, and Weber[23] who propose $\alpha = (4.9 \pm 0.2) \times 10^{-4}$ eV/K, $\beta = (655 \pm 40)$ K, and ΔG_{cv0} ΔGcv0 = 1.169 eV. Using the three relations (2)–(4), the main functions $\Delta H_{cv}(T)$ and $\Delta S_{cv}(T)$ may now be calculated,

$$\Delta S_{cv}(T) = \frac{\alpha T^2 + 2\alpha\beta T}{(\beta + T)^2}, \tag{5}$$

$$\Delta H_{cv}(T) = \Delta H_{cv0} + \frac{\alpha\beta T^2}{(\beta + T)^2}. \tag{6}$$

Both $\Delta H_{cv}(T)$ and $\Delta G_{cv}(T)$ are plotted in Fig. 1(a) as a function of temperature. Relation (5) shows that the entropy increases with increasing T. This implies a decrease of the Gibbs free energy $\Delta G_{cv}(T)$, expected from the well-established increase in the generated electron—hole pair density with increasing T. However, the enthalpy increase with temperature is less recognized. This increase is essential when evaluating the thermally activated carrier exchanges between the thermostat and a given defect.

Since a defect is considered a thermodynamic subsystem, it is defined using the same concepts. This subsystem is not isolated, and the carrier-exchange rates are established at thermal equilibrium, based on the principle of detailed balance, linking the emission and capture rates to the Gibbs free energy by

$$e_{n(p)} = c_{n(p)}(T) N_{c(p)}(T) \exp\left[-\frac{\Delta G_{n(p)}(T)}{kT} \right]. \tag{7}$$

Here c_n and c_p are the temperature-dependent capture coefficients for electrons and holes, respectively, $N_c(N_v)$ is the density of states in the conduction (valence) band, and $\Delta G_{n(p)}(T)$ is expressed by a relation similar to Eq. (2). The common exchanged particles between the subsystem ''defect'' and the thermostat ''semiconductor'' link their respective thermodynamic functions. As far as ΔS_{cv} and $\Delta S_{n(p)}$ are concerned, the microscopic link deserves to be clarified in order to highlight some of the paradoxes encountered when interpreting the experimental results. The former of the two entropies has been defined above as the change in vibrational modes upon an excitation of an electron from the valence band to the conduction band of the host material. The latter, $\Delta S_{n(p)}$, can be defined following thermodynamic concepts as well.[24,25] For electrons ΔS_n is given by

$$\Delta S_n = \Delta S_n^{\text{conf}} + \Delta S_n^{\text{vib}}, \tag{8}$$

where ΔS_n^{conf} corresponds to the statistical change in the configurational entropy of the subsystem connected to any change in the electronic features associated with the defect that occur in the emission process. It is better known as the change in the electronic degeneracy factor g_n of the ground state during the trapping-emission reaction. ΔS_n^{vib} is the vibrational entropy resulting from the change in the frequency spectrum of the lattice upon an electron detrapping. It is worth pointing out that the separation of the two entropy contributions indicated by Eq. (8) is valid only in the absence of a Jahn-Teller effect[26] which is the case in the present investigation. Keeping in mind the clear separation outlined above, we will intentionally simplify the notation by disregarding the superscripts ''conf'' or ''vib.'' A quantitative discussion will require us, however, to take into account this distinction. For instance, the experimentally extracted entropy of electron emission should be reduced by a factor $k \ln(g_n^*/g_n)$, where g_n and g_n^* are, respectively, the degeneracy factors before and after the trap has emitted an electron. From the thermodynamic point of view, the pinning behavior, essential in various thermal processes where defects play a key role, has some consequences on the functions defined above. For instance, if the defect level is pinned to the conduction band it follows immediately that ΔG_n is constant. Therefore, according to definition (3) and to the energy conservation law,

$$\Delta S_n(T) = -\frac{\partial \Delta G_n}{\partial T} = -\frac{\partial[\Delta G_{cv}(T) - \Delta G_p(T)]}{\partial T} = 0, \tag{9}$$

from which it follows that the total entropy change when exciting a hole from the defect-related level to the valence band, $\Delta S_p(T)$, is equal to $\Delta S_{cv}(T)$. The same reasoning can be applied in the opposite case of a pinning to the valence band.

In this context, a reliable use of the Arrhenius treatment of Eq. (7) is possible only when the temperature dependencies of all factors are known. For instance, in the case of a level pinned to the conduction band, the treatment is straightforward if we are probing the transition from the defect level to conduction band, characterized by a constant ΔH_n. However, in the case of hole transition from the level to the valence band, the enthalpy $\Delta H_p(T)$ is given by

$$\Delta H_p(T) = \Delta H_{cv}(T) - \Delta H_n. \tag{10}$$

Using Eq. (6), Eq. (10) becomes

$$\Delta H_p(T) = [\Delta H_{cv0} - \Delta H_n] + \frac{\alpha\beta T^2}{(\beta + T)^2}, \tag{11}$$

where the term in brackets is the hole-emission enthalpy at 0 K, $\Delta H_p(T=0)$. This point being clarified, it remains that in order for the Arrhenius treatment to be valid, the temperature dependencies of the capture cross section and the entropy factor must be known. This requires an independent determination of both functions which is not obvious, particularly for the entropy factor. In addition, the experimental data are often obtained in a narrow temperature range where a semilog plot corresponds always to a linear behavior. This does not provide, therefore, convincing evidence that the observed phenomena are linear.

To overcome all these difficulties, another variable other than temperature is required. The pressure used by some authors is, in principle, a good candidate[9,27–32] as within the reasonable range of 0–10 kbar, the gap shrinkage is equivalent to that which we would expect when the temperature is increased from 200 up to 300 K. However, the resulting energy change of 15 meV is still not significant to firmly establish the pinning behavior. An alternative mean to affect the gap at atmospheric pressure and at a given temperature is to use the $Si_{1-x}Ge_x$ alloy.[33,34] Figure 1(b) shows clearly that an increase of x from 0%–25% shrinks the gap by roughly 100 meV. The dashed curve represents the quadratic fitting of the data as recorded recently by Weber and Alonso[34] from excitonic transitions at 20 K and corresponds to

$$E_g^{(X)}(x,T=20\ \mathrm{K})=1.155-0.43x+0.206x^2\ \mathrm{eV}. \qquad (12)$$

The prefactor of the quadratic term in relation (12), known as the bowing factor, responsible for the deviation from a linear-gap shift, has a strong impact on the hole-emission kinetics. Its role will be discussed later. The superscript (X) stands for the X-conduction band, restricting Eq. (12) to the range $0<x<0.85$, where the Si-like [100] X-conduction band prevails. At $x\approx 0.85$ the crossover to the Ge-like L-conduction band occurs, but as our experimental results concern values far below $x=0.85$, we will disregard this part of the gap.

Below we will use Weber and Alson's semiempirical relation (12) to fit our data. The temperature at which these authors recorded their measurements is low enough for the approximation,

$$E_g^{(X)}(x,T=20\ \mathrm{K})=\Delta G_{cv}(x,T=0)=\Delta H_{cv}(x,T=0) \qquad (13)$$

to be valid. This is seen by putting $x=0$ in Eq. (12) and keeping in mind that 14 meV should be added to the excitonic energies to fit with the total gap.[23] We thus get the expected enthalpy of 1.169 eV, independently extracted by Alex, Finkbeiner, and Weber[23] in pure Si at 0 K. This is also confirmed in Fig. 1(a) where we clearly see that, below 20 K, $\Delta G_{cv}(T)$ is flat, validating thus equality (13). The fact that the data of Braunstein, Moore, and Herman[33] recorded from optical absorption at $T=296$ K and represented by the open circles in Fig. 1(b), are shifted downward highlights the important role of the entropy at high temperature. In such a case, if we modify Eq. (12) by adding the temperature-dependent factor detailed on the right-hand side of Eq. (6), and subtracting the entropy contribution, Eq. (5), due to the increase of T from 20 to 296 K, we get the solid curve which fits the data of Braunstein, Moore, and Herman[33] very well. Moreover, the temperature range $50\ \mathrm{K}<T<300\ \mathrm{K}$ investigated by these authors is convenient for the following reason. In our transport experiments, we handle two variables, namely, the temperature T and the Ge fraction x. Thus, any link between these two variables must be known. The well-established temperature-dependent data of pure silicon and germanium[21,22] and those provided by Braunstein, Moore, and Herman[33] obtained as a function of both temperature and Ge composition, simplifies the analysis of the various thermodynamic functions. Indeed, in the case of thermally activated processes, it is the enthalpy that is measured. Therefore, owing to the pinning effect and the energy conservation, it would, in principle, be possible to link the electron or hole-emission enthalpies $\Delta H_n(x,T)$, respectively, $\Delta H_p(x,T)$, to the total enthalpy of electron-hole pair generation $\Delta H_{cv}(x,T)$ at 0 K. For instance, in the case of a level pinned to the conduction band, ΔH_n is independent on both x and T. We get therefore,

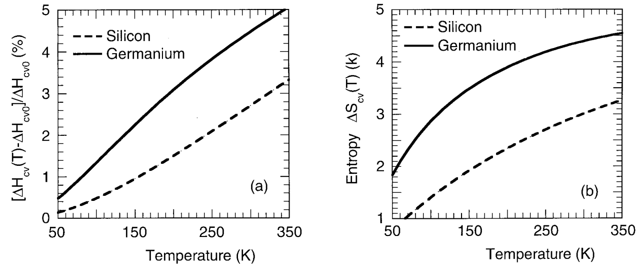

FIG. 2. Variation with temperature of (a) relative enthalpy and (b) entropy of the e^--e^+ pair creation in silicon and germanium.

$$\Delta H_p(x,0)=\Delta H_{cv}(x,0)-\Delta H_n. \qquad (14)$$

In the opposite case of a pinning to the valence band, the subscripts n and p have simply to be transposed. In this relation $\Delta H_{cv}(x,0)$ corresponds to the semiempirical formula (12) derived by Weber and Alonso.[34] At higher temperatures, Braunstein, Moore, and Herman[33] have shown that the general shape of the energy gap versus the temperature dependence remains the same throughout the entire composition range. On the other hand, Fig. 2(a) shows the behavior of the temperature-dependent term of the enthalpy, Eq. (6), where it appears that a value differing by only a few percent differentiates pure Si from pure Ge. Therefore, as we restrict ourselves to compositions $x<30\%$, we can use the temperature-dependent term of $\Delta H_{cv}(x=0,T)$, which is the expression derived for silicon. Under such conditions, the enthalpy of electron-hole pairs generation process in the alloy, expressed as a function of both x and T, is given by

$$\Delta H_{cv}(x,T)=\Delta H_{cv}(x,0)+\frac{\alpha\beta T^2}{(\beta+T)^2}, \qquad (15)$$

where the first term in the right-hand side corresponds to relation (12).

This theoretical treatment would not be complete without saying a few words about the entropy of electron-hole pair generation in the alloy. The calculations, according to relation (5), for both silicon and germanium are represented in Fig. 2(b). The constants α and β used in these plots are those refined by Alex, Finkbeiner, and Weber.[23] Because of the lack of recent data for germanium we have used the original data of Varshni.[21] The question as to whether the entropy of the alloy is determined by germanium or silicon or a subtle combination of both is difficult to answer. The only argument that we have in favor of silicon is the fact that we restrict our experimental investigations to $x<30\%$ for which we may reasonably assume that silicon properties are dominating. This assumption seems to hold as the solid curve of Fig. 1(b), which matches the data of Braunstein, Moore, and Herman[33] has been obtained by subtracting from Eq. (12) the entropy contribution of pure silicon.

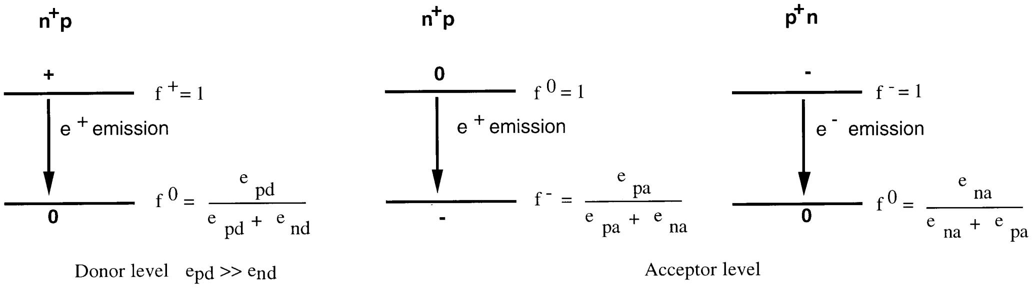

FIG. 3. Schematic diagram showing how the population of the three charge states of Au change relatively to the conductivity of the material. For the acceptor level two cases are to be distinguished, depending upon the conductivity type.

B. The amphoteric activity of gold

To investigate the carrier exchanges between the gold levels and the conduction and valence bands, we use the well-established technique of deep-level transient spectroscopy (DLTS).[35] While this technique is, in principle, able to analyze both majority- and minority-carrier traps in a junction, there are some advantages to restricting it to majority-carrier traps and to using an alternative approach to characterize minority-carrier traps. This alternative approach, called minority-carrier transient spectroscopy (MCTS),[36] uses a subband light source to generate minority carriers in the depletion region. Both techniques are subjected, however, to nonlinear phenomena[37] which must be taken into account.

The achievement of this task first requires the clarification of what is meant by thermal exchanges between the gold levels and the conduction and valence bands. Basically, gold is an amphoteric defect with two coupled levels, the donor and acceptor levels. These two levels differ by their respective charge states. The amphoteric character assigns the same neutral charge state to both levels. The fact that both are coupled may be crucial for some experimental conditions.[38,39] In our context the levels are considered as being disconnected[3] which simplifies the calculations considerably. Figure 3 illustrates the carrier transitions and the resulting charge state variations. To distinguish between the donor (d) and acceptor (a) levels we assign a second subscript to e_n and e_p. The donor level $(0/+)$, located in the lower half of the band gap, acts as a pure hole trap. Thus, its interaction with the conduction band is negligible. The corresponding DLTS signal will therefore not suffer any subtle complication in silicon: it is totally filled with holes when the junction is forward biased and totally emptied during the relaxation under reverse bias. The acceptor state $(0/-)$, however, is a midgap level and thus susceptible to interact simultaneously with both the conduction and the valence band. This double interaction is essential and we believe that it constitutes the main reason for the controversies concerning gold in silicon.[3] In a reverse biased p^+n junction, under the steady-state condition the fraction of the neutral charged state is given by

$$\frac{[\mathrm{Au}]^0}{[\mathrm{Au}]^{\mathrm{tot}}}=\frac{e_{na}}{e_{na}+e_{pa}}, \tag{16}$$

where e_{na} and e_{pa} are defined according to Eq. (7), and $[\mathrm{Au}]^{\mathrm{tot}}$ represents the total electrically active gold concentration. When carrying out DLTS in such an asymmetric p^+n diode, as reported in Fig. 4(a), one single peak is generally observed originating from the sole interaction between the acceptor level and the conduction band. As far as pure silicon is concerned, this is a satisfactory approximation. Since $e_{na}>e_{pa}$, the fraction of gold that switches from the negatively charged state (filled state) to the neutral charge state (empty sate) is very close to unity as expected from Fig. 3. However, this is no longer the case when the gap shrinks significantly. For this reason we consider below the more general situation of a simultaneous interaction with both the conduction and valence bands according to Eq. (16). Taking into account the competition between capture and emission of majority carriers, due to Debye incursion,[37] which introduces the nonlinearity cited above, we obtain the following equation for the resulting capacitance signal:

$$\Delta C(t)=\frac{C_r^3}{(\varepsilon_r S)^2}\frac{[\mathrm{Au}]^{\mathrm{tot}}}{N_d}\frac{e_{na}}{e_{na}+e_{pa}}\exp[-(e_{na}+e_{pa})t]$$
$$\times\int_{W_f-\lambda_t}^{W_r-\lambda_t} x\,\frac{1-\exp\left\{-\frac{t_f}{\tau_{\mathrm{co}}}\left[\frac{n(x)}{N_d}+\eta\right]\right\}}{1+\eta\,\frac{N_d}{n(x)}}\,dx, \tag{17}$$

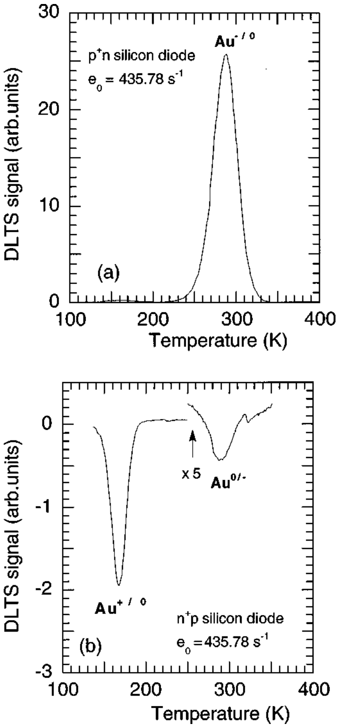

FIG. 4. DLTS spectra obtained from a gold-doped (a) p^+n diode and (b) n^+p diode.

where $\tau_{\text{co}}(=1/c_n N_d)$ is the electron-capture time constant, t_f the DLTS pulse duration, N_d the dopant concentration, and $n(x)$ stands for the free-electron density within a Debye length from the border of the depletion region. $n(x)$ is established to satisfy the neutrality equation within the space-charge region.[37] $\eta=(e_{na}+e_{pa})\times\tau_{\text{co}}$, and λ_t is the so-called transition region or the part of the depletion region, adjacent to the neutral zone, where the trap is below the Fermi level. The deeper the trap the larger λ_t. W_f and W_r represent the space-charge region corresponding, respectively, to forward and reverse bias of the electric pulse. Finally, C_r is the reverse quiescent capacitance, ε_r the dielectric constant, and S is the diode area.

In the case of a simultaneous interaction of the acceptor level with the conduction and valence bands, a separation of electron and hole contributions from the sole emission rates data is impossible as only one time constant $1/\tau=e_{na}+e_{pa}$ is experimentally available from DLTS while we face the two unknowns e_{na} and e_{pa}. Thus, we need a second independent measurable parameter such as, for example, the generation current.[8,40] This requires, however, a special care in preparing the junction. An indication of the double interaction of the acceptor level could have been possible from the shape of the Arrhenius plot $1/\tau$ versus temperature which should, in principle, be nonlinear. But the narrow temperature range accessible by DLTS restricts the significance of this treatment. However, owing to the factor $e_{na}/(e_{na}+e_{pa})$ in relation (17), an alternative is offered by the investigation of the DLTS peak amplitude as a function of the rate window. In pure n-type silicon the condition $e_{na}>e_{pa}$ makes this amplitude constant, provided the experimental rate windows are properly chosen. Under these conditions, it is justified to consider the acceptor level as a pure electron trap.[37] However, in p-type silicon on one hand and $\text{Si}_{1-x}\text{Ge}_x$, for both conductivities, on the other, the peak amplitude will be strongly affected either by the rate window or the Ge fraction x. Numerical adjustments of the DLTS spectra, where both e_{na} and e_{pa} are simultaneously considered, become necessary.

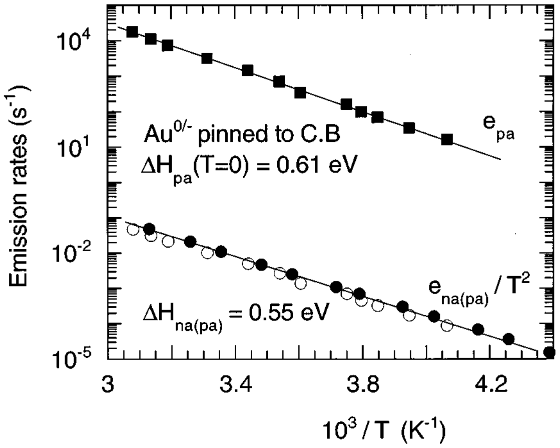

FIG. 5. Thermal activation plots for the gold acceptor in both types of conductivity. The open circles correspond to e_{na}/T^2 as extracted from p^+n junction, while the full circles represent e_{pa}/T^2 as extracted from n^+p junction. e^- and e^+ ionization enthalpies and capture cross sections are assumed to be temperature independent (Ref. 41). The full squares correspond to the acceptor in n^+p diode where both the pinning effect and T dependence of σ_{pa} are taken into account.

Let us first consider pure silicon. When DLTS measurements are carried out using a n^+p junction, one observes the donor level and also a small but significant peak at around 250 K as shown in Fig. 4(b). For the donor level, the situation is very simple as this level acts exclusively as a hole trap. Therefore, the DLTS signal is still given by relation (17) where the subscript a in the fraction $e_{na}/(e_{na}+e_{pa})$ must be replaced by d with the supplement condition $e_{pd}\gg e_{nd}$. N_d and $n(x)$ must also be replaced by the corresponding hole functions N_a and $p(x)$. The deeper peak at ~ 250 K has been interpreted by Brotherton and Lowther[41] as a small relaxation in occupancy taking place at the gold acceptor. This interpretation deserves, however, some clarification. As depicted in Fig. 3, when the DLTS analysis is carried out using a p^+n junction the acceptor related signal corresponds to the transition from the negative charge state to the neutral charge state, emitting an electron. On the other hand, the small peak at ~ 250 K appearing in a n^+p diode corresponds to the opposite transition from neutral charge state to the negative one emitting a hole. This explains why the signal amplitude is much higher in the former than in the latter case. Such a fundamental behavior in the dynamics of the acceptor, whether it is analyzed in n or p type, may induce confusion if not properly taken into account. Indeed, by using a simple Arrhenius treatment, Brotherton and Lowther[41] found that the signature of the gold acceptor does not depend on the type of conductivity of the material. However, these authors did not take into account either the thermal pinning effect nor the temperature-dependent hole capture cross section. If we consider the conclusion by Engstrom and Grimmeiss[8] that the acceptor level is pinned to the conduction band (an assertion that will be confirmed in this work) and following the thermodynamic concepts developed above, the electron and emission rates are, respectively, given by

$$e_n=\sigma_n v_n(T) N_c(T)\exp\left[\frac{\Delta S_n(T)}{k}\right]\exp\left[-\frac{\Delta H_n}{kT}\right], \tag{18}$$

where the pinning to the conduction band implies for ΔH_n to be temperature independent. The hole-emission rate obeys

$$e_p=\sigma_p(T) v_p(T) N_v(T)\exp\left[\frac{\Delta S_p(T)}{k}\right]\exp\left[-\frac{\Delta H_p(T)}{kT}\right]. \tag{19}$$

In both Eqs. (18) and (19) $v_{n(p)}(T)$ and $\sigma_{n(p)}(T)$ represent, respectively, the electron and hole thermal velocities and capture cross sections. $N_{c(p)}(T)$ were defined in the previous section. We consider as a first approximation that $\Delta S_n(T)$ and $\Delta S_p(T)$ are constant. Taking for $\sigma_p(T)$ the data of Engstrom and Grimmeiss and knowing that σ_n is temperature independent,[3,37] we are able to reexamine the Arrhenius plot of the emission data. The results are plotted in Fig. 5 where it clearly appears that the sum $\Delta H_n+\Delta H_p(T=0)=1.160$ eV which is very close the total enthalpy required to create a electron-hole pair via the gold-acceptor level at 0 K $[\Delta H_{cv}(T=0\text{ K})=1.169\text{ eV}]$. This result is clearly inconsistent with the value of 1.11 eV given by Brotherton and

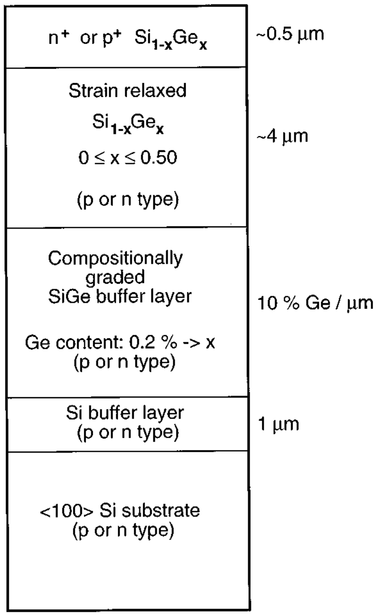

FIG. 6. Schematic structure of an epitaxially grown, strain-relaxed $Si_{1-x}Ge_x$ sample.

Lowter.[41] It corresponds to twice the value of 0.55 eV as extracted from the data of Fig. 5 based on two assumptions. First that the electron and hole emission rates are similar, and second that both ionization enthalpies, ΔH_n and ΔH_p, are supposed to be temperature independent, ignoring any pinning effect.

III. EXPERIMENTAL CONDITIONS

Relaxed $Si_{1-x}Ge_x$ layers with x varying from 0% to 25% were grown by molecular-beam epitaxy (MBE) on (100) Si substrates using the compositional grading technique as described elsewhere.[16,17] The silicon substrates were either p- or n-type doped to $\sim 1\times 10^{19}$ cm^{-3} of B or Sb, respectively. A silicon buffer layer of thickness 1 μm was first grown followed by the growth of the compositionally graded buffer layer with a starting Ge content of $\sim 0\%$ and a grading rate of 10% Ge/μm. A growth rate of 5 Å/s was maintained throughout the growth procedure and all wafers were processed with a substrate temperature of 800 °C. Then the top uniform layer of thickness 4 μm and the nominal Ge content was grown. These epitaxial layers were uniformely doped to the same conductivity as the substrate with either B or Sb to a concentration of $(2-5)\times 10^{15}$ cm^{-3}. On top of this structure was added a highly doped ($\sim 10^{19}$ cm^{-3}), 0.5-μm-thick layer of the same composition as the uniform top layer but of opposite conductivity type. This allows us to have the final n^+p or p^+n junction for electrical characterization. The whole structure is shown in Fig. 6.

The quality of relaxed $Si_{1-x}Ge_x$ layers grown on this MBE instrument and under identical conditions to those mentioned above has previously been characterized by structural Rutherford backscattering spectrometry channeling, transmission electron microscopy, atomic force microscopy, and photoluminescence methods. The growth procedure has been demonstrated to result in fully relaxed layers of high crystalline quality, with a threading dislocation density $\leqslant 5 \times 10^5$ cm^{-2}, and strong near-band-gap photoluminescence typical of bulk material.[17] The compositions of the layers were determined by Rutherford backscattering spectrometry to an absolute uncertainty of less than 5%.

Mesa diodes were formed from these MBE grown structures by chemical etching of photolithography-defined areas. Subsequently, gold was diffused into the mesa diodes from thin (~ 0.1 μm) aligned gold layers deposited on top of the mesa diodes. Different diffusion temperatures between 600 and 800 °C were used with a diffusion time of 24 h. Diodes without gold layers, but having undergone the same high-temperature heat treatment, did not indicate any process-induced defects. Finally, an In-Ga alloy layer was deposited on the back of the structure acting as an Ohmic contact.

DLTS spectra were recorded with two commercial systems. The first one is a Semitrap spectrometer using the lock-in principle to process the capacitance transient signal,[11–13] while the second, used also for MCTS, is a Biorad setup, based on the hypothesis of a pure exponential transient for which an electronic sampling at two distant points in time scale are enough to reproduce the observed time constant.[35,37] The carrier-capture cross sections are measured according to the pulse variation procedure[35] where the nonlinear contributions are taken into account.[37]

IV. EXPERIMENTAL RESULTS

A. The gold-donor level

Plots of conventional DLTS and MCTS spectra as obtained, respectively, from gold-doped n^+p and p^+n diodes are shown in Figs. 7(a) and 7(b). For the sake of clarity, the temperature range is deliberately restricted to values lower than 200 K, where only the donor trapping level is observed. It should be noticed, in the case of MCTS, that despite the large capture cross section of the gold-donor level,[3,41,42] its saturation with the optically generated holes is not attained. This is a consequence of the low injection regime available and the measurements conditions.[37]

Two features of Figs. 7(a) and 7(b) are quite striking; First, the increase in the full width at half maximum (FWHM) of the peaks for increasing Ge composition. Neither the type of conductivity nor the measurement technique used could explain the enlargement observed. This point deserves a separate discussion which will be postponed to Sec. V C. Second, the shift of the gold-donor level toward lower temperatures with increasing x. The preliminary measurements presented in Ref. 11 revealed a corresponding decrease in the activation energy for the hole exchange rate. Qualitatively, this indicates that the level is at least partially pinned to the conduction band. Quantitatively, the observed shift can be described very simply as resulting from a gold-donor level that behaves as a pure trap, interacting exclusively with the valence band. Therefore, the electron emission rate e_{nd} is negligible compared to the hole-emission rate e_{pd}, thus allowing the factor $e_{pd}/(e_{pd}+e_{nd})$ to be replaced in relation (17) by unity. This has two consequences. First, for a given rate window, the DLTS or MCTS peak heights do not depend upon the Ge fraction x. Second, the DLTS signal magnitude corresponding to a given x is not influ-

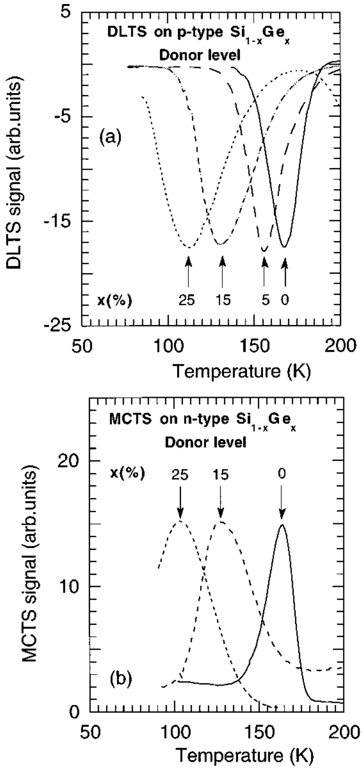

FIG. 7. DLTS (a) and MCTS (b) spectra as obtained, respectively, from gold doped n^+p and p^+n $Si_{1-x}Ge_x$ diodes. The MCTS spectra were recorded with a pulse duration of 4 ms and a photocurrent density of 77 μA/cm^2. For both techniques the reverse voltage was -3 V, while for DLTS the pulse height was 3 V. Notice the enlargement of the peaks for increasing x.

enced by the experimental rate window in the case of the boxcar treatment so long as the ratio of the sampling times t_2/t_1 is constant.[37]

The relatively high doping level of the alloy layers used $[(2-5)\times10^{15}\ \mathrm{cm}^{-3}]$ does not allow for measuring the hole capture cross section. The large value of $\sigma_{pd}\sim5\times10^{15}\ \mathrm{cm}^2$, found in silicon,[42] necessitates pulse durations below 10 ns which is not attainable with our setup. But, if we rely on the "gap rule" model,[43] which gives a fairly satisfactory description of the carrier trapping mechanisms in the case of a weak carrier-phonon coupling behavior, the expected capture cross sections for $x>0$ are higher than in pure silicon ($x=0$). In this model $\sigma_{n(p)}$ are expressed by

$$\sigma_{n(p)}(\Delta H_{n(p)})=\sigma_{n(p)}(0)\exp(-\alpha\Delta H_{n(p)}), \tag{20}$$

where α is correlated to the Huang Rhys factor.[43] The main implication of this model, restricted to centers being neutral before capture, is that the hole capture cross section is determined only by the energy position $\Delta H_{n,p}$ of the level, which might be slightly temperature dependent according to the pinning behavior. Figure 8 illustrates the appropriateness of this "gap rule" model for some defects belonging to such a weak carrier-phonon coupling class. The data for both gold levels are represented by the full circles.

Taking into account the T^2 dependence of the product $v_p(T)N_v(T)$, where the hole effective mass is essentially determined by its value in silicon,[44] and provided $\Delta S_{pd}(x,T)$

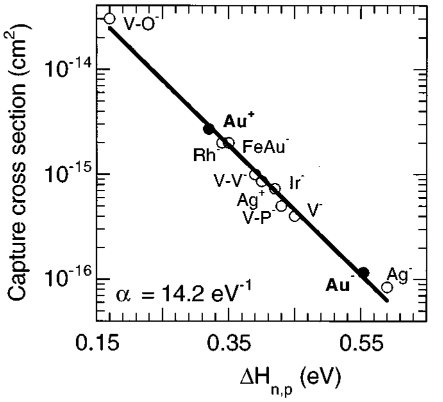

FIG. 8. The "gap rule" model applied to levels involving smoothly varying process of energy dissipation. The data of defects other than gold are taken from Graff (Ref. 60).

is known, the Arrhenius treatment of Eq. (19) is straightforward. Using Eqs. (14) and (15) we get

$$\frac{e_0\exp\left(\frac{f(T_m)}{kT_m}\right)}{T_m^2\exp\left(\frac{\Delta S_{pd}(x,T_m)}{k}\right)}=C\ \exp\left(-\frac{\Delta H_{pd}(x,0)}{kT_m}\right), \tag{21}$$

where the T_m's are the temperatures corresponding to the maxima of the DLTS or MCTS peaks, recorded at different experimental rate windows e_0; $f(T_m)$ is the temperature-dependent function detailed on the right-hand side of Eq. (6); the preexponential factor C at the right-hand side of Eq. (21) is a temperature-independent constant including $\sigma_{pd}(x)$ and the configurational entropy, $\Delta S^{pd}_{\mathrm{conf}}$. Therefore, the remaining of $\Delta S_{pd}(x,T_m)$ displayed in the relation above stands for the vibrational part of the total entropy, normally represented by $\Delta S^{\mathrm{vib}}_{pd}(T)$, but where we have dropped the superscript "vib." Equation (21) assumes that the gold-donor level is pinned to the conduction band as expected from Fig. 7. On the other hand, to satisfy the thermodynamic condition expressed through Eq. (9), $\Delta S_{pd}(x,T_m)$ is taken to be equal to $\Delta S_{cv}(0,T_m)$, the contribution of pure silicon. The extracted hole-emission enthalpies at 0 K, $\Delta H_{pd}(x,T=0)$, allow us to get the Ge composition-dependent differential quantity,

$$\partial_{pd}(x,T=0)=\Delta H_{pd}(x,T=0)-\Delta H_{pd}(x=0,T=0), \tag{22}$$

where $\Delta H_{pd}(x=0,T=0)$ is the hole-emission enthalpy in pure silicon at 0 K. Equation (22) predicts that in the case of a pinning to the conduction band, the plot of $\partial_{pd}(x,T=0)$ versus x will coincide with the gap shrinkage. Figure 9 shows indeed that the hole-emission enthalpy follows entirely the gap decrease at 0 K, independently determined by Weber and Alonso[34] and expressed by the x-dependent quantity of the right-hand side of Eq. (12). This result allows us to unambiguously state that the gold–donor level is totally pinned to the conduction band, thus supporting the conclusions drawn by Wong and Penchina[45] from a transport analysis carried out in pure silicon.

Two striking features, resulting from the above considerations and the data displayed in Fig. 9, deserve comments.

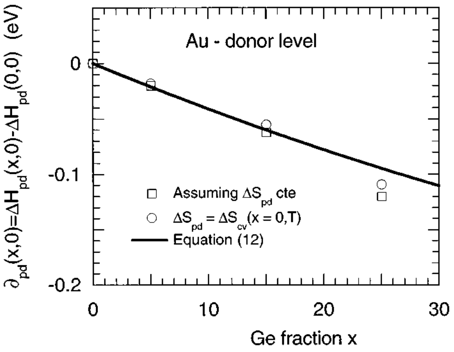

FIG. 9. Decrease of the hole ionization enthalpy at 0 K of the donor level, as a function of Ge fraction x. The solid curve represent the gap shrinkage as determined by Weber and Alonso (Ref. 34).

First, our previous assumption that the vibrational entropy $\Delta S_{pd}(x,T)$ corresponds simply to $\Delta S_{cv}(0,T)$ is a good approximation at least up to 25%. When the Ge fraction approaches this value or becomes higher, the equality $\Delta S_{pd}(x,T)=\Delta S_{cv}(0,T)$ might cease to be valid. Indeed, whether the slight deviation observed for $x=25\%$ is due to experimental uncertainties or is linked to the assumption that the entropy of the alloy is entirely determined by silicon, remains to be clarified. Another more fundamental reason may be invoked to explain this discrepancy. It emerges from a careful observation of Fig. 1(b), where it appears that an increase in x leads to serious deviation of the energy gap from a linear combination of both Si and Ge fractions. This deviation, related to the disorder in Si and Ge distribution, is linked to the so-called ''bowing'' factor[34,46] expressed by the quadratic term in Eq. (12). In such a context, if a correlation exists between the Au and Ge distributions, the analyzed emission rate becomes significantly higher than expected from the averaged x value. In that case, the discrepancy observed for $x=25\%$ should even increase up to 50% before it starts to decrease for $x>50\%$. Thus, it would be worthwhile to investigate alloys with higher Ge composition. The second point to be noticed concerns the entropy factor. Whether ΔS_{pd} is considered to be temperature independent or not, the differential Eq. (22) gives almost the same result. This is inconsistent with the third thermodynamic law which states that the entropy of a thermally activated process decreases with the temperature until it reaches zero at $T=0\,\mathrm{K}$, as shown in Fig. 2(b). From this figure it clearly appears that within the temperature range considered in the present work, and by all authors dealing with the same kind of transport measurements, $\Delta S_{cv}(T)$ should not be taken as a constant. Table I summarizes the absolute values of $\Delta H_{pd}(x,T)$ extracted assuming ΔS_{pd} either to be constant or, more rigorously, to be temperature dependent as it should be. Even though a good agreement with data in the literature is obtained in the former case, we believe that the values having a physical meaning are those which are extracted in agreement with the thermodynamic laws, required to handle such transport measurements.

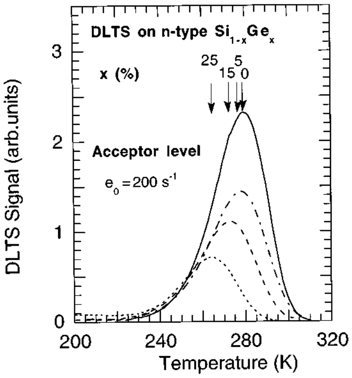

FIG. 10. DLTS spectra as obtained from gold-doped p^+n $Si_{1-x}Ge_x$ diodes for different x.

B. The gold-acceptor level: Interaction with the conduction band

DTLS spectra from $Si_{1-x}Ge_x$ alloy layers on p^+n diodes are shown in Fig. 10. Here, in principle, we probe the electron transition from the acceptor level to the conduction band. Therefore, the observed shift toward lower temperatures of the DLTS peaks, for increasing Ge fraction x, could correspond to an increase in the electron-emission rate. As electron emission is a thermally activated process, the shift would be a consequence of a decrease in the electron-emission enthalpy, thus excluding any pinning of the accep-

TABLE I. Emission enthalpy data relative to the gold donor in Si and $Si_{1-x}Ge_x$.

	$\Delta S_p^{\mathrm{vib}}$ constant			$\Delta S_p^{\mathrm{vib}}=\Delta S_{cv}(x=0,T)$		
	Interaction with V.B.[a]		Interaction with C.B.[b]	Interaction with V.B.		Interaction with C.B.
$x(\%)$	$\Delta H_p(T=0\,\mathrm{K})$ (eV)	$\Delta H_p(T=90\,\mathrm{K})$ (eV)	$\Delta H_n=cte$ (eV)	$\Delta H_p(T=0\,\mathrm{K})$ (eV)	$\Delta H_p(T=90\,\mathrm{K})$(eV)	$\Delta H_n=cte$ (eV)
0	0.322	0.328	0.847	0.302	0.306	0.867
	0.321–0.325[c]	0.345[d]	0.841–0.845[d]			
5	0.303		0.845	0.284		0.864
15	0.262		0.847	0.247		0.862
25	0.204		0.870	0.192		0.882

[a] Valence band.
[b] Conduction band.
[c] Wong and Penchina (Ref. 45).
[d] Braun and Grimmeiss (Ref. 47).

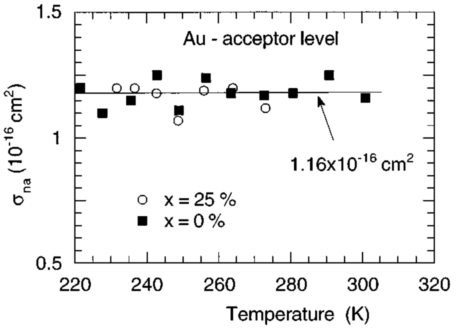

FIG. 11. The electron capture cross section σ_{na} of gold acceptor level as measured in p^+n $\mathrm{Si}_{1-x}\mathrm{Ge}_x$. The data show that σ_{na} is both x and T independent.

tor level to the conduction band. The decrease by 50 meV of ΔH_{na} in the alloy $\mathrm{Si}_{0.75}\mathrm{Ge}_{0.25}$ corresponds to the half of the induced band-gap shrinkage as shown in Fig. 1(b). Qualitatively, the feature is similar to the observations made by Samara and Barnes[9] who carried out pressure measurements. Their conclusion was that the level is neither pinned to the conduction band nor to the valence band.

As long as we consider the acceptor level as a pure electron trap, thus ignoring the particularity originating from its location at the middle of the band gap, our observations of Fig. 10 seem in favor of the conclusion drawn by Samara and Barnes.[9] However, the recombination-generation character of the gold-acceptor level suggests its interaction with both allowed bands. Such a possibility is to be excluded in pure silicon, because $e_{na} \gg e_{pa}$. In $\mathrm{Si}_{1-x}\mathrm{G}_x$, however, this inequality is no longer valid as soon as the Ge fraction becomes significant, indicating a non-negligible gap shrinkage. But, if this condition is necessary it is not sufficient. Indeed, the double interaction of the gold acceptor with both the valence and the conduction band needs a pinning to the conduction band. Then, the increase of e_{pa} with x implies both a shift toward lower temperatures of the DLTS peaks and a decrease of the peak heights according to the factor $e_{na}/(e_{na}+e_{pa})$ of Eq. (17). This is clearly shown in Fig. 10. Therefore, both the shift and the reduction of the peak height result from a simultaneous interaction of the gold acceptor with both bands. In the other cases of a pinning to the valence band on to neither of the allowed bands, but with the condition,

$$\left|\frac{\partial \Delta H_{pa}(x,T)}{\partial x}\right|_{T=cte} > \left|\frac{\partial \Delta H_{na}(x,T)}{\partial x}\right|_{T=cte}, \qquad (23)$$

indicating that the level remains more distant from the valence band than from the conduction band, as claimed by Barnes and Samara,[9] e_{na} would remain much higher than e_{pa} for any x. In Eq. (23) the vertical bars indicate absolute values. Thus, the shift would still be observed, as a consequence of the reduction of ΔH_{na}, but no decrease of the height of the DLTS peaks would have been detected as the factor $e_{na}/(e_{na}+e_{pa})$ would not deviate from unity.

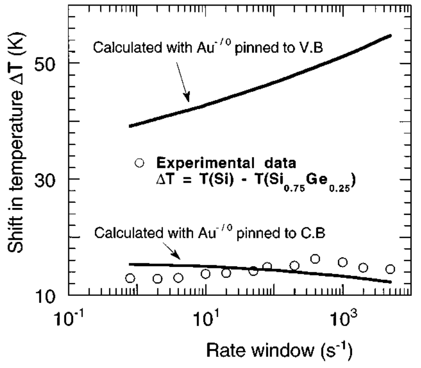

FIG. 12. The temperature shift of DLTS peak maxima ΔT as a function of the rate windows, obtained from pure Si and $\mathrm{Si}_{0.75}\mathrm{Ge}_{0.25}$. The curves represent the calculations based on relation (17), considering both cases of pinning.

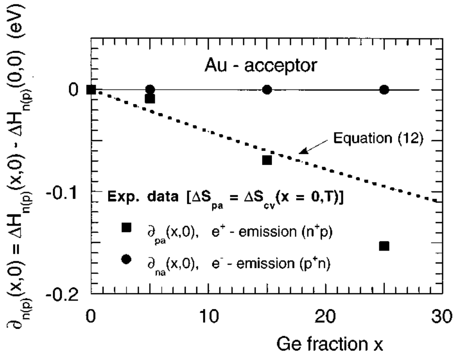

FIG. 13. Decrease of the hole ionization enthalpy at 0 K of the acceptor level, as a function of Ge fraction x. The dashed curve represents the gap shrinkage as determined by Weber and Alonso (Ref. 34).

As in the case of the gold donor, the electron-capture cross section for the acceptor level plays a key role in these experiments. If there is a general consensus that the electron-capture cross section is temperature independent, its absolute value has been found to vary greatly. This led Lang *et al.*[3] to classify it according to the ratio of gold to dopant concentrations and to suggest a physical interpretation of the nature of the acceptor level. In this work the electron-capture cross section of the acceptor level was measured for both Si and $\mathrm{Si}_{0.75}\mathrm{Ge}_{0.25}$ according to the procedure described elsewhere,[37] where the nonlinear contribution, due to the so called Debye incursion has been taken into account. Figure 11 displays the results for $x=0$ and 25 % and the extracted mean value of σ_{na} is represented in Fig. 8 according to the ''gap rule'' model. The resulting average electron ionization entropy is found to be $\Delta S_{na}=3.26\,k$. In this capture mechanism, involving a smoothly varying process of energy dissipation, the fact that σ_{na} is independent of x, is a serious indication that ΔH_n does not change as expected from Eq. (20). This statement is confirmed in Fig. 12 where we plot the temperature shift ΔT as a function of the experimental rate window. In the same figure we report a theoretical simulation based on the assumption $\Delta S_{pa}(x,T)=\Delta S_{cv}(0,T)$ and $\sigma_{pa}(x,T)=\sigma_{pa}(0,T)=6.3\times10^{-9}\ \mathrm{T}^{-2}\ \mathrm{cm}^2$ as given for pure silicon.[48] The value for σ_{pa} was found to be roughly the same for pure Si and Ge.[49] Therefore, it is reasonable to assume a similar value for $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy. The comparison

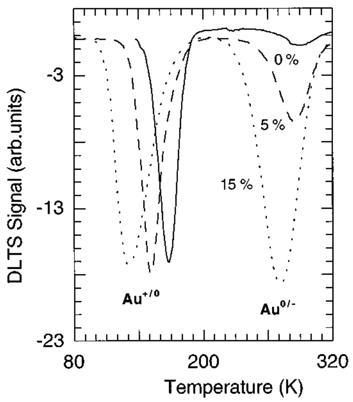

FIG. 14. DLTS spectra as obtained from gold-doped n^+p $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ diodes. Notice the considerable increase of the acceptor signal for increasing x.

of the simulations, based on Eq. (17) with the experimental data clearly favors a pinning to the conduction band.

In addition, it should be noticed that the spectra in Fig. 10 show no degradation of the FWHM, in contrast to that which is observed for the donor level. This is also a consequence of the pinning of the acceptor level to the conduction band as we will see in Sec. V C.

C. The gold-acceptor level: Interaction with the valence band

The transition from the acceptor level to the valence band is still controlled by Eq. (17), where e_{na} is replaced by e_{pa} and vice versa. Based on the same assumptions and constants used for the calculations of Fig. 12, the data $\partial_{pa}(x,0)$, describing the decrease of the hole-emission enthalpy $\Delta H_{pa}(x,0)$, are plotted in Fig. 13. The dashed curve represents the gap shrinkage as predicted by Eq. (12). We show only the data extracted assuming $\Delta S_{pa}(x,T)=\Delta S_{cv}(0,T)$, but the same comments as for the gold donor can be made here. Again a deviation is observed for the $\mathrm{Si}_{0.75}\mathrm{Ge}_{0.25}$ alloy and it is even more pronounced than for the donor level. This anomaly cannot be understood without extending the analysis to $x>25\%$. Nevertheless, the behavior observed in Fig. 13 strongly supports the pinning of the gold-acceptor level to the conduction band. The full circles representing the electron-emission enthalpy ΔH_{na}, plotted after having taken into account the double interaction of the acceptor level, confirm this statement.

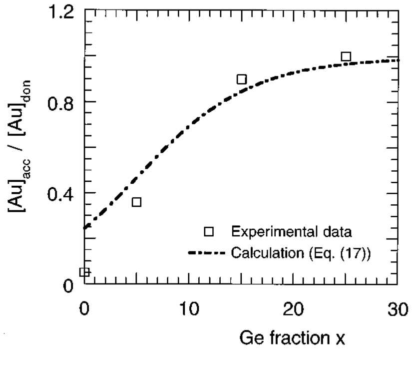

FIG. 15. The concentration ratio $[\mathrm{Au}]_{\mathrm{don}} \backslash [\mathrm{Au}]_{\mathrm{acc}}$ as a function of Ge fraction in the alloy.

The consequence of this result is the tremendous increase in the corresponding DLTS signal in p-type alloys, so far considered as a small relaxation in pure silicon. DLTS plots obtained for three Ge fractions are displayed in Fig. 14. It is very simple to see that the increase in hole transition magnitude, taking place at the acceptor level, is related to the ratio $e_{pa}/(e_{pa}+e_{na})$. At a constant temperature, e_{na} remains unaffected by changing x, while because of the shrinkage of $\Delta H_{pa}(x,T)$, e_{pa} increases dramatically. Therefore, the signal given by relation (17) increases accordingly. Calculations of the ratio $[\mathrm{Au}_a]/[\mathrm{Au}_d]$, where $[\mathrm{Au}_a]$ and $[\mathrm{Au}_d]$ stand, respectively, for the acceptor and donor DLTS signal heights, performed at the rate window of 200 s^{-1} are plotted in Fig. 15 as a function of Ge fraction x and compared to the data. In the calculations we take into account the impact of the transition region, expressed as λ_t in Eq. (17), which is not the same for the donor and the acceptor levels. The result shown in Fig. 15 is a striking illustration that the acceptor level can no longer be assumed to be a pure trap in the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy, even for small Ge fractions.

V. DISCUSSION

The DLTS measurements carried out in this work, interpreted by the well-established thermodynamic concepts, indicate that both the donor and acceptor gold-related levels are pinned to the conduction band. As to the donor level, this is consistent with the results obtained by Wong and Penchina[45] for pure silicon using different types of experimental approaches, such as photocapacitance, resistivity, and Hall effect. The level is fixed in energy 0.84 eV below the conduction-band edge, independent of the temperature and Ge content.

For the acceptor level, more widely investigated than the donor level, the situation is more complex. Our results are in agreement with detailed series of photocapacitance experiments also carried out in pure silicon by Engstrom and Grimmeiss.[8] However, they disagree with those of Brotherton and Bicknell[6] and Kalyanaraman and Kumar[7] obtained from fits to the electron-emissions rates. This procedure consisted in fitting Eq. (18) to their electron-emission rates replacing ΔH_{na} by some activation energy $E_t(T)$ and the entropy term $\exp(\Delta S_{na}(T)/k)$ by the so-called degeneracy factor g_{na}, to which these authors attributed the major role. Assuming all other factors of Eq. (18) as firmly established and $e_{na}(T)$ experimentally known, they tried to extract the temperature dependence of $E_t(T)$ for different values of g_{na} and to compare the result to $\Delta G_{cv}(T)$. Two values of the degeneracy factor were considered, namely 2/3 and 4, as derived by Ralph[50] from a simple bonding model. The agreement between $E_t(T)$ and $\Delta G_{cv}(T)$ found for $g_{na}=4$ led Brotherton and Bicknell[6] and Kalyanaraman and Kumar[7] to conclude the pinning of the gold-acceptor level to the valence band. Their approach, however, is subject to the following criticism: (i) the scatter in the data[6,7] induce a nonnegligible uncertainty in the extracted activation energy; (ii) if the temperature shape of $E_t(T)$ is strongly influenced by a slight variation of g_{na} as the authors claimed, then it must also be influenced by a slight variation of the capture cross section σ_{na}, which is generally known to only within a factor of 2–5; (iii) the value of $g_{na}=4$ (which led to the conclusion of the pinning to the valence band) is very low compared to what is known from a compilation of data in the literature.[3] Moreover, the value of $\Delta S_{na}=3.26k$ found in this work excludes the simple bonding model of Ralph.[50] But, the most severe drawback of the fitting approach is the lack of a clear and reliable definition of $E_t(T)$. Indeed, if we compare the relation of the emission rate used by Brotherton and Bicknell[6] and Kalyanaraman and Kumar[7] and Eq. (18) established from thermodynamic considerations, $E_t(T)$ corresponds to $\Delta H_{na}-T\Delta S_{na}^{\mathrm{vib}}$ which is in fact $\Delta G_{na}(T)+T\Delta S_{na}^{\mathrm{conf}}$, and not $\Delta G_{na}(T)$ as implicitely assumed by these authors. Therefore, even though the acceptor level is pinned to the conduction band as proved in this work, the activation energy $E_t(T)$ as defined by the authors above remains a linear function of T in the form $a-bT$, where a and b are some positive constants. Moreover, provided we restrict the analysis to the range 200–300 K, $\Delta G_{cv}(T)$, represented by Eq. (4) and displayed in Fig. 1(a), may easily be approximated by a linear function of T as well. Thus, it is not surprising that Brotherton and Bicknell[6] and Kalyanaraman and Kumar[7] found a similarity in the shapes of $E_t(T)$ and $\Delta G_{cv}(T)$ leading them to conclude for a pinning to the valence band. Therefore, based on the fitting procedure of $e_{na}(T)$, we cannot conclusively decide for the pinning effect.

However, the most questionable results are those concerning the hydrostatic pressure measurements carried out by Samara and Barnes,[9] who came to the conclusion that the acceptor level is neither pinned to the conduction nor to the valence band. A quantitative reexamination of this approach is detailed below. Then, we briefly discuss the most difficult aspect of the present work, related to the entropy paradox. This important thermodynamic function has some impact when we try to evaluate the energy required to create an electron-hole pair either directly, that is band-to-band, or indirectly, via the acceptor level. As long as an independent determination of this function is unavailable, the question remains open, leading to speculation only.

A. Hydrostatic pressure measurements

As we have already mentioned in the Introduction, the temperature and the hydrostatic pressure are the two intensive thermodynamic variables which have been used so far to probe the pinning effect in pure silicon. However, in practice, both variables allow only for a very narrow-band-gap variation. Despite this limitation, Engstrom and Grimmeiss[8] have established in a very rigourous manner the pinning character of the gold-acceptor level in the temperature range of 90–242 K. On the other hand, Samara and Barnes[9] have investigated the alternative offered by the hydrostatic pressure to study the behavior of the emission rate of the same midgap level. They unfortunately came to a different conclusion, namely, that the acceptor level is neither pinned to the conduction band nor to the valence band. To interpret their data, Samara and Barnes took the partial derivative of e_{na}, expressed in Eq. (18), with respect to the pressure at constant temperature. In doing so, several parameters are, in principle, involved. But, these authors have shown that the mathematical treatment is considerably simplified by the fact that the pressure dependence of the thermal velocity and the density of states, via the effective mass and the conduction-band minima, cancel each other. They have also shown that the electron-capture cross section is pressure independent and this has since been confirmed.[30] Taking into account all these considerations, the link between the pressure-dependent emission rate and the associated Gibbs free energy is given by

$$\left(\frac{\partial\ \ln(e_{na})}{\partial P}\right)_T=-\frac{1}{kT}\left(\frac{\partial\Delta G_{na}}{\partial P}\right)_T. \qquad (24)$$

This equation gives a straightforward estimation of the quantity $(\partial\Delta G_{na}/\partial P)_T$ which represents the slope of the pressure dependence of the emission rate. Moreover, as the Arrhenius plot of the temperature-dependent emission rate only gives the enthalpy, a pressure derivation of Eq. (2) allows us to obtain the pressure dependence of the entropy function. To achieve this task, Barnes and Samara used for the pressure-induced shrinkage of the indirect silicon band gap[51] the value,

$$\left(\frac{\partial\Delta G_{cv}}{\partial P}\right)_T=-1.5\ \ \mathrm{meV/kbar}. \qquad (25)$$

Assuming that this reduction is only weakly influenced by the temperature, relations (4) and (25) give

$$\Delta G_{cv}(P,T)=\Delta G_{cv}(0,T)-\left(\frac{\partial\Delta G_{cv}}{\partial P}\right)_T P. \qquad (26)$$

Applying all these considerations to gold-doped silicon, Samara and Barnes[9] demonstrated a shift of the acceptor level larger than the total gap shift, that is $(\partial\Delta G_{na}/\partial P)_T=-1.9$ meV/kbar at 250 K. This value and relation (25) allow us to calculate the value of $(\partial\Delta G_{pa}/\partial P)_T=+0.4$ meV/kbar. The result clearly indicates that the gold-acceptor level is pinned neither to the conduction band nor to the valence band, but also that the level moves away from the valence band. This would imply that at high pressure the recombination-generation character of the acceptor level reduces considerably favoring the pure trap character. Thus, the small relaxation peak observed in p-type silicon [see Fig. 4(b)] would disappear. However, here also the findings are subject to the following criticisms: (i) as shown by Pfeiffer, Prescha, and Weber[52] a correction to the experimental data is necessary to account for the hydrostatic pressure influence on the temperature sensor. With this correction, Pfeiffer, Prescha, and Weber[52] found $(\partial\Delta G_{na}/\partial P)_T=-0.9$ meV/kbar at 250 K which is significantly lower than the total gap shrinkage and to the value found by Samara and Barnes;[9] (ii) the hydrostatic pressure measurements carried out by Nathan and Paul[27] on gold-doped p-type silicon rule out the hypothesis of a pure trap character as they found a non-negligible interaction with the valence band. Therefore, a correction related to the simultaneous interaction of the level with both allowed bands, might have to be applied: such a correction is useless if a shift of the acceptor level toward the conduction band is stronger than to the valence band, because $e_{na}\gg e_{pa}$ would still hold. But in the opposite case, the interaction with the valence band can no longer be neglected. We have seen how dramatic this effect can be in p-type $\mathrm{Si}_{1-x}\mathrm{Ge}_x$. A simple simulation might help to elucidate this point. Assuming that the acceptor level is pinned to the conduction band and that the total pressure shift of the gap is taken up by the valence band, the Eqs. (17) and (26) allow for an estimate of the corresponding DLTS response. In these simulations, we have assumed of course that neither of the products $\sigma_{na}\exp(\Delta S_{na}(T)/k)$ nor $\sigma_{pa}(T)\exp(\Delta S_{pa}(T)/k)$ are affected by the pressure. The temperatures extracted at the maxima of the DLTS peaks for different experimental rate windows are then used to treat the data as if the level was a pure electron trap. This approach results in an apparent shift $(\partial\Delta G_{na}/\partial P)_T = -0.4$ meV/kbar. As a consequence, the acceptor level moves closer to the valence-band edge by 1.1 meV/kbar. Even though not firmly in favor of a pinning to the conduction band, this estimation moderates significantly the conclusions drawn from the hydrostatic pressure data.[9,52]

The most questionable result, related to the pressure measurement, is, however, the finding that the gold donor, which is a pure hole trap, and therefore not suffering the double interaction, is pinned to the valence band.[27,52] For this level Pfeiffer, Prescha, and Weber[52] and Nathan and Paul[27] found a very low-pressure coefficient, $(\partial\Delta G_{pd}/\partial P)_T = -0.1$ meV/kbar at 250 K, allowing a large shift of the level position toward the conduction band. There is definitely a discrepancy between the present work and the results of Wong and Penchina[45] on the one hand and the pressure results[27,52] on the other.

As a final comment on this matter, another point is worth mentioning. We have seen that the ‘‘gap rule,’’ states that the capture cross section of neutral centers only depends on the position of the level. If this is correct, and there is *a priori* no reason for not being so, a shift toward the conduction band will have an effect on the absolute value of the capture cross section. But this parameter has been found to not be affected by the hydrostatic pressure,[9,30,32,52] bringing also the ‘‘gap rule’’ and the pressure data into contradiction. This critical reexamination of the impact of the hydrostatic pressure stresses the great care that must be taken in considering independently T,P, or the Ge fraction x as a mean to reduce the gap. Clearly, the pressure does not shrink the band gap only, it affects the microscopic structure of the defect as well. On the other hand, for high Ge fraction, say $x > 50\%$, the structural environment might need to be taken into account.

B. Entropy paradox

We have seen in this work that thermodynamic concepts cannot be bypassed when we deal with transport measurements as has already been stressed by other authors.[2,19,20] Our main motivation for underlining this point is the entropy-related paradox and its consequences on the interpretation of the recombination-generation kinetics taking place at the gold center. This point has been discussed by Lang *et al.*[3] for pure silicon. Apparently, substituting Si by $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy did not help to elucidate the paradox. Therefore, only a brief comment on this matter is given below.

Starting with the gold donor level, we have found a fairly good agreement between Eq. (22), extracted on the basis of a pinning to the conduction band, and Weber and Alonso's gap enthalpy Eq. (12). This means that vibrational related entropy involved in electron emission is negligible, i.e., $\Delta S_{nd} \approx 0$. But as far as the condition $e_{pd} \gg e_{nd}$ is satisfied, as shown above, the electron emission related entropy has no impact either from a mathematical or physical point of view. Thus, to make the proposition of the donor level being pinned to the conduction-band coherent with thermodynamic requirements, particularly the third law, ΔS_{pd} must be equal to the entropy $\Delta S_{cv}(x,T)$ of the alloy. The consequence of not applying this law would lead to an overestimation of the hole-emission enthalpy of the gold donor as shown in Table I. Finally, the entropy accompanying a band-to-band electron-hole pair generation in a $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy is problematic. But we can make the plausible assumption that for $x < 30\%$, $\Delta S_{cv}(x,T)$ is entirely determined by pure silicon $(x=0)$.

The case of the gold acceptor level is much more complicated, simply because it is a recombination-generation center, thus interacting with both the conduction and the valence bands. The electron-emission rate analysis leaves us with the paradox stemming from the enormous entropy factor $X_{na} = \exp(\Delta S_{na}/k)$ as deduced from Eq. (18). The value of 26.2 found for this factor, which is insensitive to the Ge fraction, leads to an averaged ionization entropy $\Delta S_{na} = 3.26k$. This strongly contrasts with the thermodynamic law in Eq. (9) stating that the pinning of the acceptor level to the conduction band implies $\Delta S_{na} = 0$. It is worth pointing out that, as for the donor level, if the value of $3.26k$ for ΔS_{na} has a physical meaning at all, it must decrease with temperature to satisfy the third law of thermodynamics. Therefore, all literature-quoted values of ΔS_{na}, including ours, must be taken with great care. The justification of this is given in Fig. 2(b) which shows clearly that in the investigated temperature range, 190–320 K, the entropy function is far from being constant.

Now, if we consider the acceptor level as being definitely pinned to the conduction band, $\Delta S_{pa}(T)$ must necessarely be equal to the entropy of electron-hole pair generation in the alloy, $\Delta S_{cv}(x,T)$, still considered here to be determined by pure silicon $(x=0)$. The consequence of the paradox outlined above is that the total entropy to create an electron-hole pair via the gold-acceptor level, $\Delta S_{na}(T) + \Delta S_{pa}(T)$, is more than twice as large as that associated with a direct or band-to-band creation, $\Delta S_{cv}(T)$. As a consequence, we end up with a deficit of 63 meV in the Gibbs free energy when we evaluate both routes of electron-hole pair generation; namely, the band-to-band transition or via the gold-acceptor level. The latter requiring less energy than the former. In order to give a physical meaning to this paradox, Lang *et al.*[3] considered three possibilities: (i) a field effect which may forbid the use of the detailed balance relationship Eq. (7); (ii) a possible temperature-dependent electron-capture cross section which might, if ignored, be responsible for an overestimation of ΔS_{na}; and finally, (iii) a structural reason, e.g., that the gold defect could be a complex (involving a vacancy) rather than a simple substitutional imperfection. This last possibility, suggested by Van Vechten and Thurmond,[2] is of vital importance as it raises the question as to whether a substantial relaxation of the lattice equilibrium position takes place near the atomic gold after the electronic state is changed, due to capture or release of a charge carrier. In their model, the authors above proposed that gold is no longer a substitutional atom but rather a complex $\mathrm{Au_1}^{+}\mathrm{V_{Si}}^{-}$. Thus, in the process of capture—release of an electron, ΔS_{na} is taken up by the vacancy. In other words, it is the entropy of ionization of the doubly charged vacancy, $\Delta S_n(\mathrm{V_{Si}}^{2-})$, that should account for all the experimental observations. This model requires, however, as claimed by Lang *et al.*[3] that the complex relaxes to a lower state with additional energy to account for the energy deficit of 63 meV. But simultaneous optical and thermal studies carried out in pure silicon led Braun and Grimmeiss[47] to conclude a negligible relaxation if any at all. Moreover, from Zeeman studies of both electron and hole excitation spectra,[53,54] Watkins and William[5] have shown that the ground state of the neutral defect has C_{2v} symmetry, and its ease of reorientation at $T < 4$ K established unambiguously that gold is an isolated atom, not a complex. Further strong evidence that the defect arises from isolated substitutional gold comes from DLTS studies[55] carried out in silicon doped with radioactive ^{195}Au decaying to ^{195}Pt. The latter being known as a pure substitutional defect. Therefore, Van Vechten and Thurmond's model is not the appropriate one.

The two other possibilities mentioned above as being likely responsible for the enormous entropy of electron emission from the gold-acceptor level must also be rejected for the following reasons. First, it is now well established that neither the electron nor the hole-emission process are field dependent,[37,56] in contrast to what was claimed previously,[57] particularly for the electron emission. The reason is that the potential involved is likely to be of the polarization type. This potential has no excited states[58] and thus cannot be sensitive to an external field, at least up to 10^5 V/cm. Above this value, the tunneling effect cannot be excluded. Second, a possible T dependence of the electron-capture cross section has also to be excluded. The gold-acceptor level is one of the most studied in this respect and to our knowledge, except for one work,[59] no temperature dependence has been reported for σ_{na} at least in the temperature range of interest of 200–300 K. Thus, this critical reexamination leaves us with the entropy paradox still unsolved.

C. The impact of Ge fluctuation

Besides the pinning effect, revealed by a shift in the DLTS and MCTS signals, an interesting feature appears when using a $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloy in studying deep levels to allowed-band transitions. This feature is related to the degradation of the full width at half maximum (FWHM) of the peaks with increasing Ge content. For both characterizing techniques used in the present investigation, an increase of the FWHM of the donor related peak is clearly visible in Figs. 7(a) and 7(b); however, the width of the DLTS signal of the acceptor related peak extracted from n-type material remains unchanged (Fig. 10). Figure 16 reports the behavior of the FWHM in all possible configurations, including the hole transition from the acceptor level.[11] The first observation to be made is that the degradation of the FWHM appears only when probing hole transitions. The electron transition from the acceptor level (full circles in Fig. 16) does not exhibit any change in the FWHM.

We believe that this effect stems from a local Ge fluctuation or disorder in the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys. The occupation of the substitutional lattice sites by Si or Ge is assumed to be purely statistical; hence there will be Ge atoms having one, two, three, or four Ge atoms as nearest neighbors with a distribution depending on the Ge content. The main effect of the resulting distribution is a variation in band-gap energy around an averaged value, produced by local fluctuations in the alloy composition x; this has already been reported by Alferov, Portnoi, and Rogachev[61] and discussed by Weber and Alonso[34] in relation to the linewidths in photoluminescence spectra. To go further, we must take into account the experimentally[62] and theoretically[63] established fact that the variation of the gap in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys is entirely taken up by the valence band.

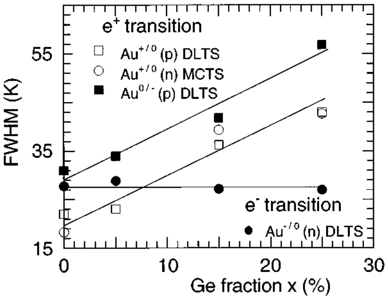

FIG. 16. Full width at half maximum of the different transitions corresponding to gold levels.

A quantitative analysis of this effect, illustrated in Fig. 16, is beyond the scope of this work. Therefore, we restrict ourselves to a qualitative description only. The mechanism underlying the hole-to-valence band transition from a level pinned to the conduction band is schematically shown in the left part of Fig. 17, the right part describes the case of a level pinned to the valence band. It is clear that the fluctuation of the valence band on the one hand and the pinning to either one of the allowed bands on the other hand has a direct impact on the FWHM of the transition that is probed. The corresponding electron or hole-emission rate should obey the integral relation,[64]

$$e_p = \int_{E_v(\mathrm{Ge})}^{\infty} e_p(E) N(E)(1-f\,)dE, \tag{27}$$

where $E_v(\mathrm{Ge})$ represents the variation of the top of the valence band due to Ge fluctuation. The consequence of this fluctuation is that for a level pinned to the conduction band, e_n is given by Eq. (18) and e_p is described by integral (27); for a level pinned to the valence band the opposite holds but in Eq. (27) we must now consider that the energy fluctuation is virtually taken up by the conduction band. It is easy to see from Fig. 17 that transitions (1) and (4) should not exhibit

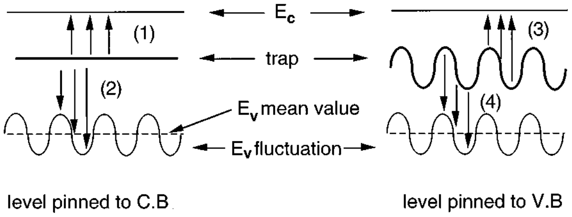

FIG. 17. A schematic representation of the consequence of the pinning effect and Ge fluctuation on the FWHM of the DLTS or MCTS peaks.

any degradation of the FWHM, while transitions (2) and (3) should. A detailed and quantitative study on this matter also involving other impurities is being undertaken.

VI. CONCLUSION

The improvement of the epitaxial growth of relaxed $Si_{1-x}Ge_x$, leading to a considerable reduction in the density of threading dislocations, allows for a controlled doping with metal impurities, such as gold, without perturbation from the dislocation. This opens up a different approach in the study of the pinning behavior of the energy levels in the band gap related to these impurities, as the band gap changes as much as 100 meV resulting from a change of the Ge content from 0% to 25%. This effect is thus more efficient and easier to handle, in practice, than the variation of the thermodynamic variables, pressure and temperature, commonly used to reduce the band gap.

In the present investigation we have used this approach to study the pinning behavior of gold-related donor and acceptor states in Si. It is demonstrated that both gold donor and acceptor levels are pinned to the conduction band; this is in agreement with previously published results from transport experiments carried out in pure silicon but, in the case of the acceptor, in disagreement with previously published results from hydrostatic pressure measurements.

We have demonstrated that the treatment of the acceptor level has to be done with great care as this level possesses the important and well-established property of being a recombination-generation center. This makes this level interact simultaneously with both the conduction and the valence bands. In the case of n-type silicon the interaction is almost entirely with the conduction band justifying the use of a pure trap model. However, when the band gap is gradually reduced, as in the present case by changing the Ge content in the $Si_{1-x}Ge_x$ alloys from 0% to 25%, and the level is pinned to the conduction band, the importance of the interaction with the valence band becomes gradually more and more important. If not properly taken into account, the recombination-generation property will then give rise to conflicting results.

An interesting phenomenon has been observed related to the FWHM of the DLTS and MCTS peaks. The FWHM was found to increase with increasing Ge content when probing hole transition to the valence band but not when probing electron transition to the conduction band. This is suggested to be an effect of the statistical nature of the occupation of the substitutional lattice site by Si and Ge together with the previously reported experimental observation that the variation of the energy gap in the $Si_{1-x}Ge_x$ with varying x is entirely taken up by the valence band.

Based on the result of the present investigation the so-called entropy-related paradox has been critically reexamined. This paradox is related to the observation that the entropy change involved in the creation of an electron-hole pair via the gold-acceptor level is significantly larger than that via a direct band-to-band transition. It is concluded, however, that the entropy paradox is still unsolved.

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