Vacancy-related deep levels in *n*-type $Si_{1-x}Ge_x$ strained layers

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Deep-level transient spectroscopy (DLTS) studies of 2-MeV proton-induced defect electronic levels in strained epitaxial $Si_{1-x}Ge_x$, $0 \leq x \leq 0.13$, layers have been performed. It is found that the irradiation results in the formation of a dominant peak in the DLTS spectra for all compositions. Isochronal 20-min annealing studies of the observed deep level have revealed that the peak anneals out at 100–200 °C. This peak is identified as the vacancy-phosphorous (VP) pair. The compositional dependence of the activation enthalpy of the VP pair is nonlinear, with a sharp increase for $x=0.04$ and little variation for higher Ge concentrations. After annealing of the VP pair, the dominating defect level is assigned to the single acceptor state of the divacancy $[V_2(-/0)]$. The double-acceptor state $[V_2(=/-)]$ is observed to be strongly suppressed in the strained $Si_{1-x}Ge_x$ layers. The compositional dependence of the activation enthalpy of $V_2(-/0)$ is relatively weak, with a small decrease in the activation enthalpy. It is found that formation of V_2 in the strained $Si_{1-x}Ge_x$ layers is enhanced with respect to that in Si. This is associated with an increased concentration of vacancies in the strained layer, acting as a sink for vacancies migrating in the substrate.

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I. INTRODUCTION

Vacancy-related defects are fundamental defects in covalent semiconductors. Investigation of these defects provides a basis for understanding atomic diffusion and electronic phenomena in semiconductors. An important manifestation of these defects is deep electronic levels introduced into the energy-band gap. These levels act as carrier traps and recombination centers, and strongly influence the electronic properties of semiconductors. Within the last three decades, vacancy-related defects in silicon, and the associated energy levels, have been actively studied, and a fairly consistent picture of the structure of these defects has emerged. However, further discussion on the exact structure of these defects continues, in particular, on the structure of the doubly negative charge state of the divacancy (V_2) and the value of Jahn-Teller distortion for V_2.[1]

Moreover, in spite of the basic knowledge of the structure of the vacancy-related defects, some fundamental aspects are still far from being understood. One of them is the pinning behavior of the levels introduced by these defects with respect to the band edges. It is not well established how the positions of the levels in the band gap change when the band structure is modified due to either changing temperature or pressure. Information from such studies is crucially needed in testing models of the defects. Van Vechten and Thurmond[2] gave a theoretical estimate of the temperature variation of the free energies for the four charge states of the monovacancy. They found that the donor states of the monovacancy are pinned to the valance-band edge, while the acceptor states are pinned to the conduction-band edge. To the best of our knowledge, no direct experimental proof has been presented for this statement. On the other hand, the pressure dependence of the activation enthalpies for the acceptor levels of the vacancy-phosphorous (VP) pair and the doubly negative state of the divacancy $[V_2(=/-)]$, studied with deep-level transient spectroscopy (DLTS) have been found to be qualitatively different: that of VP increases with pressure, while that of $V_2(=/-)$ decreases.[3] However, the pressure dependence of the free energies for these two acceptor levels remains unclear.

The ability to grow $Si_{1-x}Ge_x$ alloys of high crystalline and electrical quality opens an interesting dimension in the study of the defect levels, when the band structure is gradually modified as a function of the Ge content. A number of DLTS studies on the compositional dependence of the radiation-induced defect electronic levels have been performed up to now. It has been reported that the free activation energy for the acceptor level of the vacancy-antimony (VSb) pair in relaxed $Si_{1-x}Ge_x$ remains constant for Ge concentrations up to 25%, although the activation enthalpy increases.[4] This suggests that the VSb level is pinned to the conduction band, which is consistent with the theoretical predictions by Van Vechten and Thurmond[2] for the acceptor levels of the monovacancy. To the best of our knowledge, there are no similar data reported for the acceptor levels of V_2. Experimental studies on the donor level of $V_2(+/0)$, performed for relaxed *p*-type $Si_{1-x}Ge_x$,[5] demonstrated that the activation enthalpy of the level decreases with Ge content. Although the activation free energy for $V_2(+/0)$ has not been extracted, the compositional dependence of the activation enthalpy indicates that the donor level $V_2(+/0)$, like the acceptor level of VSb, can also be pinned to the conduction band. In fact, this hypothesis can be applied to other deep donor levels irrespective of vacancy or interstitial related origin, since the compositional dependence of the activation enthalpies is similar for V_2, interstitial carbon (C_i) and interstitial boron–substitutional carbon (B_iC_s).[5]

Besides the effect of composition, $Si_{1-x}Ge_x$ provides the possibility to study the effect of biaxial stress on the deep levels. Varying *x* and *y* independently in $Si_{1-x}Ge_x/Si_{1-y}Ge_y$ heterostructures, one can potentially obtain different magnitudes of compressive or tensile stress. One should remember, however, that there is a natural limitation on the thickness of

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the strained layers which imposes specific requirements for the sample preparation and characterization. In particular, in the case of DLTS studies the doping level should be high enough to confine the space-charge region within the strained layer. Up to now, very few investigations of the elementary defects produced by ion irradiation in strained $Si_{1-x}Ge_x$ have been performed. For *p*-type strained $Si_{1-x}Ge_x$, it has been reported that the activation enthalpies of several unidentified defect levels decrease with Ge content, suggesting that they are pinned to the conduction band.[6] Studies of *n*-type strained $Si_{1-x}Ge_x$ have been performed only for Ge content up to 4%.[7]

Recently we reported on DLTS studies of 2-MeV proton-induced defect levels in Si and strained $Si_{0.87}Ge_{0.13}$ layers.[8] It was found that the irradiation results in formation of a dominant peak in the DLTS spectra that corresponds to deep levels located at 0.44 and 0.53 eV below the conduction band edge in Si and $Si_{0.87}Ge_{0.13}$, respectively. Isochronal 20-min annealing studies of the observed deep level revealed that the peak anneals out at 100–200 °C, giving rise to a peak that corresponds to other levels at 0.44 and 0.42 eV below the conduction-band edge in Si and $Si_{0.87}Ge_{0.13}$, respectively, which remain stable up to 250 °C. These levels have been associated with VP and V_2.

In this paper we report on a DLTS study of the effect of composition and strain on the V_2 and VP electronic levels in phosphorous-doped strained epitaxial $Si_{1-x}Ge_x$ layers with different Ge contents $x=0$, 0.04, 0.07, and 0.13. It was found that a VP pair exhibits a nonlinear dependence on Ge content with a sharp increase of the activation enthalpy for $x=0.04$, and a weak dependence for higher Ge content which is explained by an overpopulation of Ge-perturbed VP pairs at low Ge content. Unlike that of VP pairs, the activation enthalpy of $V_2(-/0)$ decreases slightly in $Si_{1-x}Ge_x$ with respect to that in Si. The formation of V_2 in the strained $Si_{1-x}Ge_x$ layers is found to be enhanced during annealing above 100 °C which is explained by increased concentration of vacancies in the layers since the strained layer acts as a sink for vacancies in the substrate.

II. EXPERIMENT

The growth of the epitaxial $Si_{1-x}Ge_x$ layers was carried out by chemical vapor deposition (CVD) at 650 °C on 100-mm *n*-doped Czochralski (Cz) Si (100) substrates with a resistivity of 0.2–0.5 Ω cm. Each substrate received a 2-min treatment in a H_2 atmosphere at 1190 °C prior to deposition in order to obtain a clean surface. The thickness of the grown layers was 2000–5000 Å for different Ge contents. X-ray-diffraction measurements showed that the $Si_{1-x}Ge_x$ layers remained fully strained after irradiation and subsequent heat treatment. Reciprocal-lattice mapping revealed a uniform Ge concentration over the samples, with an accuracy of 1%. Schottky diodes were prepared by thermal evaporation of gold in a vacuum chamber with a base pressure less than 2×10^{-6} Torr.

Capacitance-voltage measurements were then performed, and the phosphorous doping of the $Si_{1-x}Ge_x$ layers was determined to be $\sim1\times10^{17}\,cm^{-3}$. The built-in voltage of the diodes was found to be ~0.6 V, with a small variation between different samples. The space-charge region reached the substrate at a reverse bias voltage of 2.5–3 V. The extension of the space-charge region in all diodes was from 600 to 1600 Å for the reverse bias from 0 to 2 V used in the DLTS measurements.

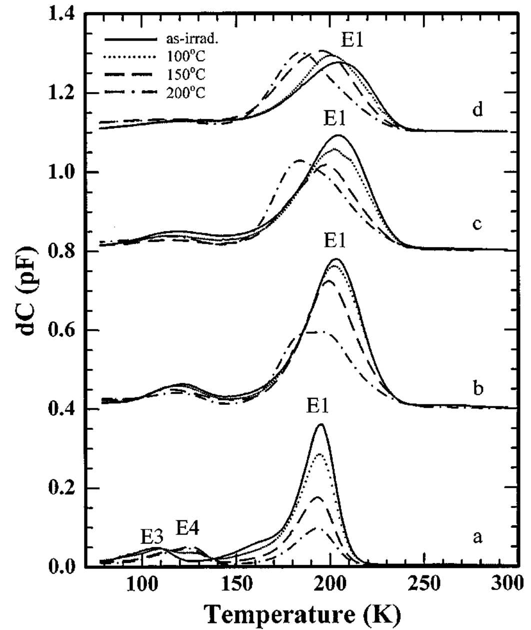

FIG. 1. DLTS spectra of the as-irradiated and 20-min annealed at ≤200 °C $Si_{1-x}Ge_x$ samples with $x=0$ (a), 0.04 (b), 0.07 (c), and 0.13 (d).

The DLTS measurements were performed using a setup described in detail elsewhere.[9] During the measurements the diodes were reversed biased, and no forward bias injection of minority carriers was performed. DLTS measurements of the as-grown samples did not reveal any deep levels with concentrations above $10^{13}\,cm^{-3}$, which corresponds to the detection limit of the measurements.

The diodes were irradiated at room temperature by 2-MeV protons using a current density of about 20 nA/cm^2 and a dose of $1\times10^{14}\,cm^{-2}$. Isochronal anneals with a duration of 20 min were subsequently carried out in the temperature range of 50–300 °C in N_2 flow.

III. RESULTS

A. Heat treatment at ≤200 °C

DLTS spectra of the irradiated $Si_{1-x}Ge_x$ samples, with $x=0$, 0.04, 0.07, and 0.13, are shown in Figs. 1(a), 1(b), 1(c), and 1(d), respectively. After the irradiation the compensation of the carrier concentration in the layers was ≤1%. After the irradiation a dominating peak, labeled *E*1, emerges in the spectra for all the samples. Since the samples have been grown under identical conditions with similar doping concentrations, the *E*1 peak in pure Si and $Si_{1-x}Ge_x$ alloys is expected to be related to the same type of defect. The maximum position of *E*1 for the $Si_{1-x}Ge_x$ layers is shifted to a higher temperature with respect to that for the Si layer. It can be observed that the shift is not gradual with increasing Ge

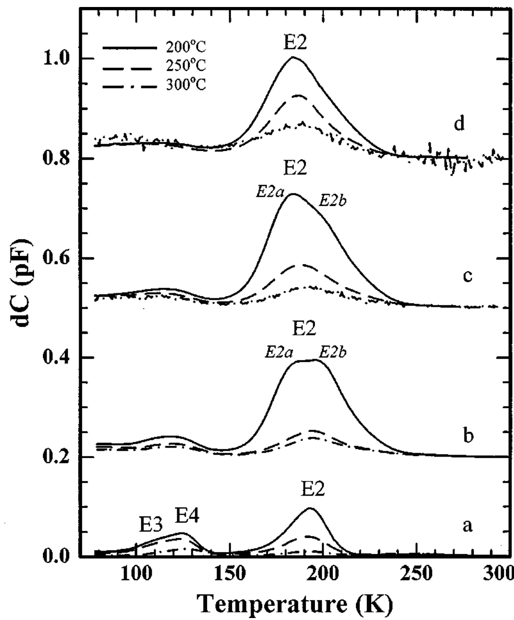

FIG. 2. DLTS spectra of the $Si_{1-x}Ge_x$ samples with $x=0$ (a), 0.04 (b), 0.07 (c), and 0.13 (d) annealed at $\geqslant 200$ °C for 20 min.

content: a strong change in the maximum position (8–9 K) for $x=0.04$, and smaller shifts for $x=0.07(\sim 2\text{ K})$ and $x=0.13(0.5\text{–}1\text{ K})$. Thermal emission studies reveal that $E1$ corresponds to a deep level with activation enthalpies of 0.450, 0.518, 0.534, and 0.532 eV for $x=0$, 0.04, 0.07, and 0.13, respectively, with respect to the conduction-band edge. The experimental error is estimated to be $\sim$0.005 eV using rate windows in the range $(20\text{ ms})^{-1}$–$(3.2\text{ s})^{-1}$. It is observed that the apparent intensity of $E1$ decreases at higher Ge content, and is about a factor of 2 smaller for $x=0.13$ compared to $x=0$. Further, a broadening of $E1$ is observed with increasing Ge content.

For the Si layer [Fig. 1(a)], annealing at temperatures from 100 to 200 °C results in a decrease of the intensity of $E1$ without any shift of the peak position, while in the $Si_{1-x}Ge_x$ layers a gradual shift of the dominating peak to lower temperatures is observed during identical heat treatments [Figs. 1(b)–1(d)]. It is also seen that, unlike Si($x=0$), an increase in the peak intensity takes place for $x=0.13$. For $x=0.04$ and 0.07 the peak intensity demonstrates an intermediate behavior relative to $x=0$ and 0.13.

Two minor peaks, labeled $E3(0.22\text{ eV})$ and $E4(0.24\text{ eV})$, are resolved in the low-temperature region of the spectra for the Si epilayers [Fig. 1(a)]. The evolution of these peaks was discussed in Ref. 8, and can also be followed in Fig. 1. In addition, Figs. 1(b)–1(d) reveal a broadening and decrease of the peaks with increasing Ge content, and they cannot be clearly resolved for $x\geqslant 0.07$.

B. Heat treatment at ⩾200 °C

Figure 2 shows the DLTS spectra for the samples after annealing at $\geqslant 200$ °C. In contrast to $E1$ in Fig. 1, the position of peak $E2$ shifts to lower temperatures for the $Si_{1-x}Ge_x$ layers compared to that for the Si layer. It is also observed that, unlike $E1$, the apparent intensity of $E2$ is considerably higher in $Si_{1-x}Ge_x$ than in Si. For $x=0.04$, it is clear that $E2$ consists of at least two peaks, labeled $E2a$ and $E2b$. Fitting of a calculated DLTS spectrum to the experimental one demonstrates that these two peaks are considerably broader then expected theoretically and have activation enthalpies of $\sim$0.40 and $\sim$0.42 eV for $E2a$ and $E2b$, respectively. Also in the spectrum for $x=0.07$ there is an indication of these two peaks, where $E2a$ is the dominant contribution. For $x=0.13$, only a minor contribution from $E2b$ is observed. The activation enthalpies of $E2$ are 0.431, 0.419, and 0.415 eV for $x=0$, 0.07, and 0.13, respectively. In all $Si_{1-x}Ge_x$ samples, independent of Ge concentration, the peaks are broader than theoretically predicted. $E2$ exhibits a similar annealing behavior in the Si and $Si_{1-x}Ge_x$ layers, and anneals out at 250–300 °C. The $E3$ and $E4$ peaks also disappear at 250–300 °C.

IV. DISCUSSION

A. Peak identification

Because of the low concentration of impurities in the CVD-grown layers, the dominating defects in our samples are expected to be of intrinsic and/or phosphorous-related origin. Since all the samples were grown under identical conditions it is also unlikely that the Si and $Si_{1-x}Ge_x$ samples contain different types of contaminations, which could be responsible for a different annealing kinetics of primary defects in Si and $Si_{1-x}Ge_x$. Moreover, since the x-ray measurements did not reveal any strain relaxation in the $Si_{1-x}Ge_x$ layers either before or after irradiation and annealing, it is unlikely that any of the observed levels are caused by extended defects, which are normally detected by DLTS in unirradiated relaxed $Si_{1-x}Ge_x$ layers with very low doping concentration (see Ref. 10, and references therein).

After irradiation of moderately and highly doped n-type float-zone (Fz) Si a dominating defect is the E center consisting of a vacancy-donor pair (a VP pair in the present experiment)[11–13] which gives rise to an acceptor level with an activation enthalpy of $\sim$0.44 eV and anneals out at $\sim$150 °C. The E center is known to overlap strongly with the singly negative divacancy level $[V_2(-/0)]$ located at $\sim$0.42 eV below the conduction-band edge in Si.[14,15] The doubly negative divacancy level $[V_2(=/-)]$, with an activation enthalpy of $\sim$0.23 eV is observed in DLTS spectra at lower temperatures. The ratio between intensities of $V_2(-/0)$ and $V_2(=/-)$ is close to 1:1 in electron and light-ion-irradiated Si.[14–16] It is known that V_2 anneals out at 250–300 °C in Si, with a rate that depends on the purity of Si.[17,18] On the basis of the above consideration, we identify $E1$ as a VP pair and $E2$ as $V_2(-/0)$.[8] The origin of $E2a$ and $E2b$ is discussed in Sec. IV C.

At least two peaks ($E3$ and $E4$), which can be assigned to $V_2(=/-)$, are observed in the DLTS spectra of as-irradiated Si [Fig. 1(a)] and after annealing at 200 °C [Fig. 2(a)], when the VP pair anneals out and only V_2 should remain. It can also be seen that after annealing at 200 °C the intensity of both $E3$ and $E4$ is considerably lower than that of $E2$, while

the ratio between $V_2(-/0)$ and $V_2(=/-)$ is expected to be close to 1:1. Possible variants of $E3$ and $E4$ identification can be divided into two groups: (a) one level is $V_2(=/-)$ while the other is an impurity-related complex, and (b) both $E3$ and $E4$ are related to $V_2(=/-)$.

It cannot be excluded that a small amount of impurities, such as C or H, is present in the layers and involved in formation of minor defect complexes. At this stage we cannot conclusively identify $E3$ or $E4$ as a certain impurity-related complex. One possible candidate for $E3$ or $E4$ can be the substitutional P interestitial C (P_sC_i) complex.[19,20] However, with variant (a) it is difficult to explain why $E3$ and $E4$ are similarly suppressed and broadened in $Si_{1-x}Ge_x$ (Figs. 1 and 2) although they are of different origin.

Identification (b), seemingly paradoxical, can be consistent with previously reported data. At least two known phenomena can provide arguments for the nature of $E3$ and $E4$ and the suppression of $E3$ and $E4$ in $Si_{1-x}Ge_x$.

First, it was argued that, for doping of $\sim 8\times 10^{16}$ P/cm^3, the intercenter charge transfer between P donor levels and deep levels can play a significant role in the carrier capture-emission kinetics that is beyond the framework of the standard Shockley-Read-Hall (SRH) model.[21] In the present investigation with the layers doped at $\sim 1\times 10^{17}$ P/cm^3, the charge transfer between P donor level and $V_2(=/-)$ can be important as well. This can perturb the DLTS signature of $V_2(=/-)$ that is defined within the SRH approximation.

Second, in Si implanted with heavy ions, the intensity of the DLTS peak corresponding to $V_2(=/-)$ is known to be suppressed with respect to the peak from $V_2(-/0)$.[16,22] This effect is normally explained by presence of local lattice distortion and strain in the damage peak region, which retards the motional averaging of V_2 and strongly affects $V_2(=/-)$. In the studied CVD-grown Si layers, the local lattice distortion can be due to (i) electrically inactive intrinsic defects that can form during CVD growth at 650 °C; (ii) as-grown electrically inactive dopant-related defect complexes, such as P dimers, which are believed to form on the growing surface during CVD growth and can be ''frozen'' into the material since the growth temperature was relatively low (650 °C) (Ref. 23); or (iii) radiation-induced electrically inactive complexes, which can have considerable concentration since the layers were relatively highly doped and irradiated with relatively high dose. Thus an assignment of $E3$ and $E4$ to distorted and undistorted $V_2(=/-)$ can be suggested. In the $Si_{1-x}Ge_x$ layers, the lattice strain is present due to Ge atoms and is higher with higher Ge concentration, consistent with the stronger suppression of $E3$ and $E4$ in $Si_{1-x}Ge_x$ (Figs. 1 and 2). It is necessary to point out that the relation between $E3$, $E4$, and $V_2(=/-)$ has to be further investigated in detail. It also should be mentioned that uniaxial stress in Si considerably effects $V_2(=/-)$ resulting in splitting of the peak.[24] In the following the discussion of the V_2 properties will focus on $V_2(-/0)$.

B. Strain and composition effects on the E-center

The effect of composition on the VP level position in strained $Si_{1-x}Ge_x$ is illustrated in Fig. 3. The activation enthalpy of $E1(H_{E1})$ is compared with the activation enthalpy of the VSb level (H_{VSb}) in low dislocation density-molecular-beam-epitaxy- (MBE)-grown relaxed $Si_{1-x}Ge_x$.[4] A considerable difference between the monotonous increase of H_{VSb} and the sharp increase of H_{E1} for $x=0.04$, with an almost constant value for higher Ge content, is observed.

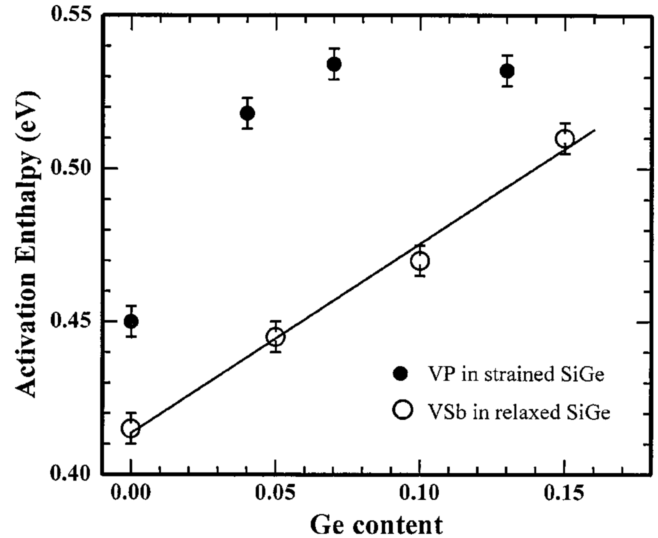

FIG. 3. The effect of composition on the VP level in strained $Si_{1-x}Ge_x$ as compared with data for the VSb level in relaxed $Si_{1-x}Ge_x$ (Ref. 4).

The difference in compositional dependence of H_{E1} (primarily attributed to a VP pair) in strained $Si_{1-x}Ge_x$ and H_{VSb} in relaxed $Si_{1-x}Ge_x$ cannot be explained by the effect of biaxial strain alone. It is known that a hydrostatic pressure of 10 kbar results in a change of the activation enthalpies of both the E center (increase) and the divacancy (decrease) by $\sim$15 meV in Si[3]. For $x=0.04$, the biaxial compression in the layer can be roughly estimated as corresponding to a pressure of about 3 kbar that can result in, at most, 5 meV of the level shift, which is evidently much smaller then the observed sharp increase of $\sim$0.1 eV, though it acts in the same direction.

Two possibilities can be suggested to explain the difference in compositional behavior of H_{E1} and H_{VSb}: (a) in the strained $Si_{1-x}Ge_x$ layers there is a defect complex different from the VP pair and not present in the Si layers that contributes to $E1$ and influences H_{E1}; and (b) an abnormally large fraction of the VP centers, compared to VSb centers has a nearest-neighbor Ge atom which perturbs H_{E1}. Again, since all the layers were grown under the same conditions, it is unlikely that the $Si_{1-x}Ge_x$ layers contain an impurity or a defect complex not present in the Si layers. Because of the fact that the main difference between the Si and $Si_{1-x}Ge_x$ layers is the presence of Ge atoms, it is believed that an overpopulation of Ge-perturbed VP pairs is responsible for the nonmonotonic behavior of the activation enthalpy. The phenomenon of an overpopulation of Ge-perturbed sites is reported for Au and Pt in $Si_{1-x}Ge_x$.[25]

At least two factors can be suggested to cause the proposed overpopulation of Ge-perturbed VP pairs, compared to VSb pairs (i) the difference between the covalent radii of P

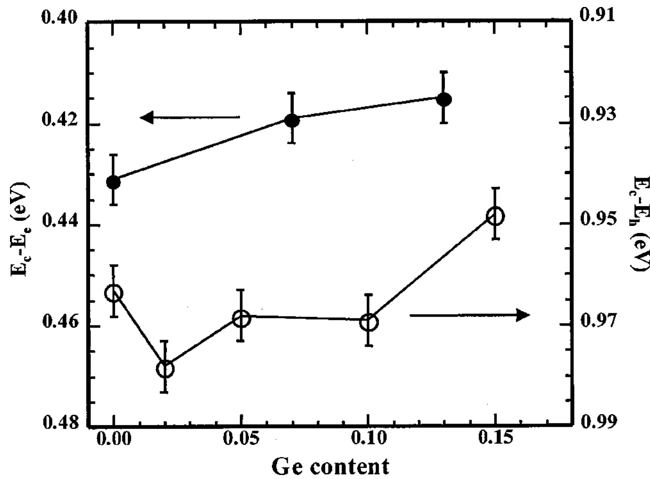

FIG. 4. The energy position of the electron trap $V_2(-/0)$ level E_e in n-type strained $Si_{1-x}Ge_x$ (solid circles) and the hole trap $V_2(+/0)$ level E_h in p-type relaxed $Si_{1-x}Ge_x$ (open circle) with respect to the conduction-band edge E_c vs Ge content.

and Sb, and (ii) the difference between the growth techniques for the strained (CVD) and relaxed layers (MBE).

Since P and Sb belong to the same group V in the Periodic Table, and both are hydrogenlike single donors in Si and $Si_{1-x}Ge_x$, the difference in their interaction with impurities and defects is associated with the difference in their covalent radii, i.e., different stress fields around P and Sb. It is established that doping with P causes a contraction of the silicon lattice, while doping with Sb results in an expansion.[26,27] Taking into account that Ge causes an expansion of the lattice, one can speculate that it is more energetically favorable for a P atom than for a Sb atom to be located next to a Ge atom. This may result in a larger fraction of P atoms with a nearest-neighbor Ge atom than that of Sb atoms. In addition, similar to the above speculation, it can be more energetically favorable for the VP center to form next to a Ge atom than for the VSb center to do so. However, numerical calculations are required to support this speculation.

The difference between the growth techniques for the strained (CVD) and relaxed (MBE) layers can also be an important factor. It is known that the presence of Ge enhances P incorporation during CVD growth because of chemical effects.[23] Thus one can suspect that P atoms incorporate preferably nearby Ge atoms, and hence an increase in the percentage of the VP centers next to Ge atoms. Also, the growth temperatures for the strained (650 °C) and relaxed (850 °C) layers were different and may result in different arrangement of the dopants.

C. Strain and composition effects on V_2

To the best of our knowledge, there are no previously reported data on composition effect on the divacancy levels in n-type strained or relaxed $Si_{1-x}Ge_x$. However, one can compare the data for V_2 in p-type relaxed $Si_{1-x}Ge_x$.[5] Figure 4 demonstrates the energy position of the V_2 levels in n-type strained and p-type relaxed $Si_{1-x}Ge_x$ as a function of Ge content. Although the activation enthalpy of the hole trap $V_2(+/0)$ level in p-type $Si_{1-x}Ge_x$ exhibits a considerable composition dependence, the position of the level relative to the conduction-band edge has a relatively small variation with composition (Fig. 4), given the fact that the change of the band gap in $Si_{1-x}Ge_x$ is mostly due to the valence-band offset. The position of the electron trap level relative to the conduction band also exhibits a relatively weak composition dependence for $x=0.07$ and 0.13.

For $x=0.04$, several suggestions on the nature of $E2a$ and $E2b$ (Fig. 2) can be made: (a) one of the levels is due to V_2, while the other, not present in the Si layers, originates from a complex different from both V_2 and the VP pair; (b) $E2a$ is due to V_2, while $E2b$ is caused by the remaining VP centers; and (c) $E2a$ and $E2b$ are V_2 levels perturbed and unperturbed, respectively, by Ge atoms. Again, since all the layers were grown at the same conditions it is unlikely that the $Si_{1-x}Ge_x$ layers contain an impurity or a defect complex not present in the Si layers.

Suggestion (b) is not supported by the fact that the maximum position of $E2b$ does not coincide with that of $E1$ (the VP pair) in the $Si_{1-x}Ge_x$ layers [Figs. 1(b)–1(d)], strongly indicating that they have different origin.

The identification of $E2a$ and $E2b$ as V_2 levels perturbed and unperturbed by Ge atoms appears to be the most likely one, and is consistent with the experimental observations. $E2b$, unperturbed V_2, has a significantly lower intensity for $x=0.07$ compared to $x=0.04$, and there is only a very small sign of $E2b$ for $x=0.13$. The position of $E2b$ coincides with the position of V_2 in $Si(x=0)$.

D. Comparison of the Ge effect on V_2 and the E center

For low Ge concentrations such as $x=0.04$, when the band structure of $Si_{1-x}Ge_x$ is essentially that of Si and the biaxial strain in the $Si_{1-x}Ge_x$ layers is relatively small, it is likely that the effect of Ge content on the electronic levels is mainly determined by individual Ge atoms close to the localized defects. Two mechanisms of the influence by a Ge atom on a localized defect can be suggested: (a) a perturbation caused by different electron binding energies for Si and Ge atoms, and (b) a local microscopic stress caused by the difference in size of Si and Ge atoms.

Mechanism (a), however, appears to be unlikely, since the ionization energies of the first electron, which characterize the outer shell electron energetics, are identical within 4% (789 kJ/mol for Si and 762 kJ/mol for Ge), while the observed difference between H_{E1} in $x=0$ and 0.04 (Fig. 3) is about 20% ($\sim$0.1 eV). Moreover, this mechanism cannot explain the opposite behavior of the $V_2(-/0)$ and VP levels: that of the VP pair becomes deeper while that of $V_2(-/0)$ becomes shallower in $Si_{1-x}Ge_x$ compared with the corresponding levels in $Si(x=0)$. This can be readily explained using hypothesis (b). Indeed, a similar observation of strain-dependent activation enthalpies was made in Si under hydrostatic pressure: the activation enthalpies of the VP pair and $V_2(=/-)$ were reported to increase and decrease with increasing pressure, respectively.[3] The difference was explained in terms of lattice relaxation at electron emission

from these defects: for VP the lattice relaxes outward, which reflects its bonding character, and for $V_2(=/-)$ inward, as for an antibonding level. It has been suggested that V_2 $(-/0)$ and $V_2(=/-)$ should demonstrate a similar behavior under hydrostatic pressure since both of them are antibonding states.[3]

Taking into account that the difference between the Si and Ge lattice constants is relatively large (~4%), and applying the above considerations to the defect complexes in $Si_{1-x}Ge_x$, one can speculate that the effect of Ge on the electronic levels is due to a high local stress caused by Ge atoms located close to the defects. The local strain changes the level position in the band gap in a way similar to what is caused by hydrostatic pressure. One can make a rough estimate that, if a pressure of 10 kbar causes an increase in the activation energy of a VP pair by ~15 meV,[3] then a pressure of about 70 kbar (equivalent to a ~3% strain) is necessary to provide a 0.1 -eV shift of the VP level. Additionally, the local stress induced by Ge atoms can influence the magnitude of the Jahn-Teller distortion, which can also lead to a change in the level positions.

Within this ''local strain'' model it is possible to account for the difference in the magnitude of the Ge effect on V_2 $(-/0)$ and the VP pair. Since V_2 is a more extended defect than the VP pair (V_2 has six nearest-neighbor atoms, while the VP pair has four) and the Ge-induced stress is localized mainly within the nearest-neighbor sphere, the energy levels of V_2 are influenced to a smaller extend than that of the VP pair.

E. Formation of V_2 and the VP pair

It is found that in $Si_{1-x}Ge_x$ the apparent intensity of the VP pair decreases with respect to that in pure Si (Fig. 1). This effect was observed previously in relaxed $Si_{1-x}Ge_x$,[4] and can be explained by (i) a reduced formation rate of VP pair in $Si_{1-x}Ge_x$, (ii) an interaction between the VP pair and the valence band;[28–30] (iii) the alloy effect, where a random number of neighboring Ge atoms can lead to an increase in the peak width and to a decrease in the peak maximum with a constant integral of the peak; and (iv) for strained layers, a strain-induced splitting of the level which manifests itself similarly to the alloy effect. It appears that the alloy effect and/or the strain-induced splitting dominate, since the integrals of $E1$ in Si and $Si_{0.87}Ge_{0.13}$ are equal within an accuracy of 10%.

In contrast to the VP pair, the intensity of $V_2(-/0)$ in the $Si_{1-x}Ge_x$ layers after annealing at 200 °C is considerably higher than that in Si (Fig. 2). The effect of the high purity of the films (V_2 is known to be more stable in high-purity Si)[17,18] can be ruled out, since all the layers were grown under the same conditions. At the present stage, the enhanced formation of V_2 in $Si_{1-x}Ge_x$ during annealing is attributed to a thermodynamic driving force, where the strained $Si_{1-x}Ge_x$ film acts as a sink for migrating vacancies in the silicon substrate in order to lower the strain energy stored in the film. Hence the vacancy concentration in the $Si_{1-x}Ge_x$ layers is increased during annealing and the formation of V_2 is promoted.

V. CONCLUSIONS

DLTS studies of electronic levels in CVD-grown strained epitaxial $Si_{1-x}Ge_x$, $0 \leqslant x \leqslant 0.13$, layers, irradiated with 2-MeV protons, have been performed. Two major levels assigned to VP and $V_2(-/0)$ centers have been observed. It has been found that the VP level exhibits a nonlinear dependence on Ge content with a sharp increase of the activation enthalpy for $x=0.04$ and a weak dependence for higher Ge content. This dependence is explained by an overpopulation of Ge-perturbed VP pairs. Unlike VP, the activation enthalpy of $V_2(-/0)$ decreases slightly in $Si_{1-x}Ge_x$ with respect to that in Si. It is suggested that for low Ge content the effect on the deep levels is mainly determined by local strain from individual Ge atoms situated close to the defects. A decrease in the apparent intensity of the VP level and an increase of the peak width have been observed in $Si_{1-x}Ge_x$ layers compared to that in Si, and are attributed to the alloy effect or/and splitting of the level due to biaxial strain. The formation of V_2 in the strained $Si_{1-x}Ge_x$ layers is found to be enhanced during annealing above 100 °C which is associated with an increased concentration of vacancies in the layers, since the strained layer acts as a sink for migrating vacancies in the substrate.

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