Structure and properties of vacancy-oxygen complexes in Si$_{1-x}$Ge$_x$ alloys

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The electronic properties and structure of vacancy-oxygen (VO) complexes in Czochralski-grown Si$_{1-x}$Ge$_x$ crystals ($0 < x < 0.06$) have been studied by means of capacitance transient techniques and *ab initio* modeling. At least three configurations of the VO centers in SiGe alloys have been identified. The most stable configuration consists of a Si-O-Si unit and a Ge-Si reconstructed bond in a vacancy. This configuration is about 0.2 eV more stable than separated VO and Ge$_s$ defects and possesses an acceptor level which is about 25 meV deeper compared to the level of the VO center without a Ge atom in a nearest-neighbor site. Several configurations with a Ge atom in the second nearest-neighbor shell around an off-center oxygen atom have been found to be stable. One of these configurations has an acceptor level, which is about 15 meV shallower than that for the VO complexes with more remote Ge atoms. The increase of the ionization enthalpy of the VO complexes with the increase in Ge content in Si$_{1-x}$Ge$_x$ crystals is associated with changes in the average Si-Si bond length.

I. INTRODUCTION

SiGe alloys are important materials for the microelectronics industry largely because of the possibilities of band-gap engineering leading to optical and high-speed electronic devices.[1] For the successful fabrication of SiGe-based devices, an understanding of the electronic properties of the most abundant lattice defects is required over the whole composition range of SiGe alloys. There are three types of behavior a defect may exhibit in the SiGe alloy. First, the core of the defect might be occupied with Ge atoms and consequently the properties of the center are quite different from those of the defect in pure Si. Second, the change in lattice parameter can cause the vibrational modes or energy levels to shift often in a linear way for dilute concentrations of Ge, and third, the presence of Ge atoms affect the conduction and valence bands in a way beyond the change in bond lengths and this has an influence on the lattice parameter and other properties. Whereas it is often difficult to distinguish these three effects in the alloy experimentally, we shall show below that theoretical modeling is able to discriminate between them.

The vacancy-oxygen complex (VO or *A* center) is one of the dominant defects induced by irradiation with high-energy particles (electrons, protons, etc.) in Si crystals grown by the Czochralski method,[2,3] where its structure and electronic properties are well understood.[2–4] The VO center is also thought to be one of the main radiation-induced defects in oxygen-rich Ge crystals.[5–9] Here the defect possesses single and double acceptor levels at $(E_v + 0.27)$ eV and $(E_c$

$-0.21)$ eV, respectively.[8,9] However, the situation is not so clear in SiGe alloys although some data has been published recently.[10,11]

Deep level transient spectroscopy (DLTS) has been used to investigate the energy level of VO in *e*- or γ-irradiated bulk Si$_{1-x}$Ge$_x$ crystals ($0 < x \leqslant 0.055$) grown by the Czochralski method.[11] The enthalpy of electron ionization for the single acceptor level of the defect relative to the conduction-band edge, ΔH_n, was found to increase from 0.16 eV to 0.19 eV with x. This shift is much greater than the change in band gap with the increase in Ge content [about $-0.43x$ eV (Ref. 12)]. Moreover, it was argued that the concentration of *A* centers, which have a Ge atom in the first nearest-neighbor shell around an off-center substitutional oxygen, is small after irradiation. This follows from the preference of interstitial oxygen atoms (O$_i$) to bond directly with two Si atoms as Ge-O bonds could not be detected in optical absorption experiments on Czochralski-grown (Cz) SiGe alloys with Ge content up to 77 at. %.[13–16] Moreover the shift of the level with lattice parameter was the same as found by application of hydrostatic pressure to VO in bulk Si.[17] Therefore, the observed change in the energy level of the VO defect was associated with the changes in the lattice parameter in the alloy rather than to any change in the nature of the conduction band caused by the presence of Ge.[11] We shall show here, however, that this interpretation is not completely correct.

While O$_i$ may not bond directly with Ge for concentrations of Ge up to 77 at. %, there is infrared absorption evidence that Ge lies close to VO in SiGe crystals.[10] The domi-

nant local vibrational mode (LVM) at about 830 cm^{-1} in irradiated SiGe alloys was assigned to isolated VO defect as in Ge-lean Si crystals.[2,18] The breadth of this mode prevents a shift due to the change in lattice parameter being resolved. However, two additional lines with weak intensities at 834.6 and 839.2 cm^{-1} (at 300 K) were observed and assigned to VO-Ge complexes. Moreover, upon isochronal annealing of the irradiated samples the 834.6- and 839.2-cm^{-1} lines increase in intensity at the expense of the 830-cm^{-1} band.[10] Thus VO centers with nearby Ge atoms were formed during annealing but their electronic properties are unknown.

In order to obtain more information on the electronic properties and structure of vacancy-oxygen complexes in SiGe alloys a combined capacitance transient spectroscopy and *ab initio* modeling study has been carried out and will be reported in the following sections.

II. EXPERIMENTAL DETAILS

Samples for this study were prepared from *n*-type P-doped Si$_{1-x}$Ge$_x$ crystals, which were grown at the Institute of Crystal Growth (Berlin, Germany) by the Czochralski technique.[19] The phosphorus concentration in the crystals was $(1-3) \times 10^{15}$ cm^{-3}. The concentrations of interstitial oxygen and substitutional carbon atoms measured by optical absorption were found to be $(7-9) \times 10^{17}$ and $(2-3) \times 10^{16}$ cm^{-3}, respectively. The concentration of Ge in the crystals varied from 1.5 to 5.5 at. %. The Ge concentration was determined from x-ray diffraction and Raman-scattering measurements. Ge-free Si samples with similar concentrations of P, O, and C atoms were studied as well. The samples were irradiated at room temperature with 4 MeV electrons or γ rays from a ^{60}Co source. The sample surfaces were cleaned after the irradiation and Schottky barriers were fabricated by thermal evaporation of Au. Electronic levels were characterized with conventional DLTS and high-resolution Laplace DLTS (LDLTS) techniques.[20] Isochronal annealing of the irradiated samples was carried out in the temperature range 100–400 °C with 25 °C increments for 30 min at each step.

III. EXPERIMENTAL RESULTS

It should be noted that in some of the SiGe crystals used in the present study, grown-in defects with energy levels in the range of $[E_c - (0.12-0.16)]$ eV were observed (Fig. 1). The concentration of these defects did not exceed 3×10^{12} cm^{-3}. The grown-in traps are likely to be donors as they exhibited electric-field-enhanced emission. These grown-in traps might be associated with oxygen-related thermal donors,[21,22] but further studies are required to identify their nature properly. The traps can be easily removed by heat treatments in the temperature range 600–700 °C. We have also found that heat treatments in this temperature range are effective for removing hydrogen impurity atoms which were introduced into SiGe during growth or wafer processing. Hydrogen atoms can interact with radiation-induced defects complicating interpretation of defect-impurity interactions in irradiated SiGe crystals. Therefore,
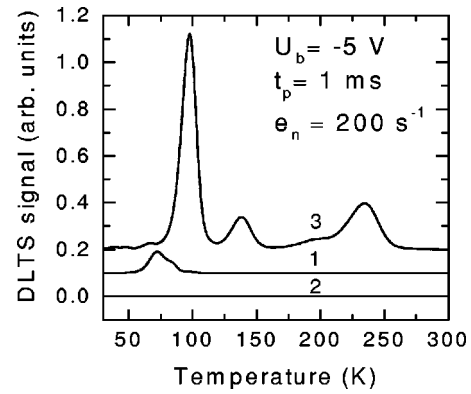

FIG. 1. DLTS spectra for samples from a Si$_{0.985}$Ge$_{0.015}$ crystal: 1—as-grown; 2—after a heat treatment (HT) at 650 °C for 30 min; 3—after an HT at 650 °C for 30 min and following electron irradiation. Irradiation dose was 5×10^{14} cm^{-2}. Measurement parameters are presented in the figure.

some of the samples were subjected to heat treatments in the range of 600–700 °C for 30 min before irradiation in order to remove hydrogen and grown-in defects.

Figure 1 shows conventional DLTS spectra for a Czochralski grown Si$_{0.985}$Ge$_{0.015}$ crystal in as-grown state, after a heat treatment at 650 °C for 30 min and after following electron irradiation. The irradiation resulted in the introduction of a number of deep level traps into SiGe samples. Qualitatively, the DLTS spectra of irradiated SiGe crystals were similar to those of Ge-free Cz-Si crystals, but the DLTS peaks in SiGe were broader, less intense, and shifted on the temperature scale compared to the corresponding peaks in Si. We have assigned a dominant radiation-induced DLTS peak with maximum in the temperature range 90–110 K to the vacancy-oxygen complex in SiGe crystals. Detailed arguments for such assignment were presented in Ref. 11.

Figure 2 shows dependencies of the *A*-center-related DLTS peak maximum temperature (T_m) and T_m-normalized peak half width ($W_{1/2}/T_m$) on alloy composition. The dependencies can be approximated by linear functions within the
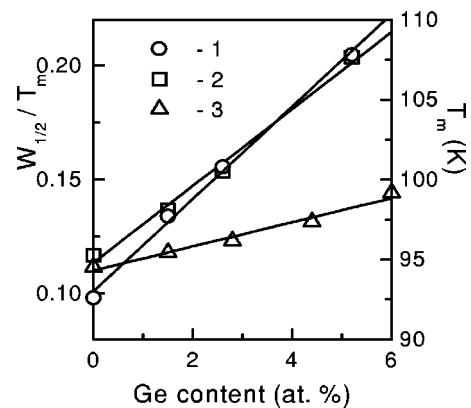

FIG. 2. Dependencies of (1) DLTS peak maximum temperature (T_m) for the VO acceptor level and T_m-normalized DLTS peak half width ($W_{1/2}/T_m$) for (2) the VO acceptor level, and (3) the C$_i$-O$_i$ donor level on Ge content in Si$_{1-x}$Ge$_x$ alloys. The data were recorded for a rate window of 200 s^{-1}.
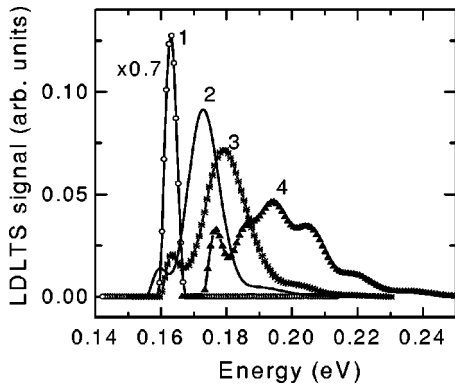
FIG. 3. Laplace DLTS spectra for electron-irradiated Czochralski-grown $Si_{1-x}Ge_x$ crystals with different Ge content, x (at. %): (1) 0.0 at. %, (2) 2.0 at. %, (3) 2.6 at. %, and (4) 5.2 at. %. Irradiation dose was 8×10^{14} cm^{-2}. The spectra were taken at temperatures (1) 105 K, (2) 105 K, (3) 106 K, and (4) 114 K.

FIG. 4. Development of DLTS spectra for (a) a Ge-free Si sample and (b) an electron-irradiated $Si_{0.985}Ge_{0.015}$ sample upon 30-min isochronal annealing with temperature increments of 25 °C. The spectra were measured after anneals at (1) 200°C, (2) 250°C, (3) 300°C, (4) 350°C, and (5) 400°C. Measurement settings were as in Fig. 1.

alloy range studied. DLTS peak broadening is a well-known effect for deep levels in semiconductor alloys and is related mainly to compositional fluctuations of the atomic arrangement surrounding each individual defect.[23–27] Such fluctuations may induce a distribution in defect-related energy levels in alloys. The energy distribution depends on the degree of localization of the appropriate wave function and on the sensitivity of defect-induced energy levels to changes in positions and nature of surrounding lattice atoms. As an example, Fig. 2 shows that alloy-related broadening of the DLTS peak associated to the acceptor level of the vacancy-oxygen center is greater than that for the donor level of interstitial carbon-interstitial oxygen complex (C_iO_i).[28] As a result of the level energy distribution, capacitance transients associated with carrier emission from defects in alloys are nonexponential. More sophisticated treatment of conventional DLTS spectra is usually necessary to obtain correct information on defect parameters and concentrations in alloy materials, but for diluted alloys reliable data on carrier emission rates can be deduced from the conventional "temperature of a DLTS peak maximum" analysis.[23,24]

The resolution of conventional DLTS is rarely sufficient to separate signals from individual defect configurations in alloys. It was shown recently that the application of Laplace DLTS technique, in some cases, allows the most abundant atomic configurations of a point defect in alloys to be resolved.[25,26] We have therefore used Laplace DLTS technique to obtain information about the atomic configurations of the vacancy-oxygen complex in SiGe alloys. Figure 3 shows Laplace DLTS spectra for electron-irradiated SiGe samples. For the sake of clarity the spectra are plotted with emission activation energy on the horizontal axis instead of the conventional emission rate scale. This transformation has been done on the basis of the well-known equation for carrier emission rate:

$$e_n = \sigma_n N_c \langle v_t \rangle \exp(\Delta S_n/kT) \exp(-\Delta H_n/kT)$$
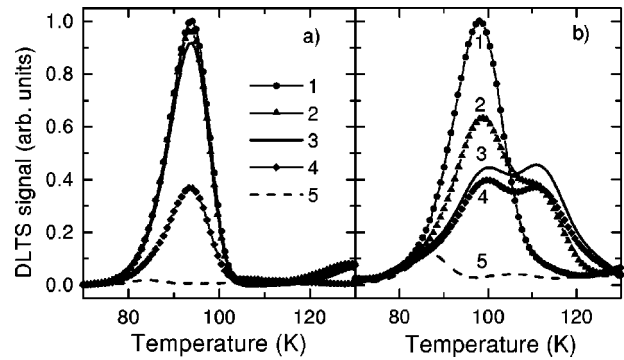
$$= A\, T^2 \exp(-\Delta E_n/kT),$$

with the usual meaning of parameters.[29] Application of this equation to the transformation of the emission rate scale to the energy scale for different samples will be correct only if the value of preexponential factor A is the same for the different samples. It was shown in our previous work that capture cross section and entropy of electron emission for the acceptor level of the VO complex do not depend significantly on Ge content for small x.[11] This finding justifies the above procedure of the horizontal scale transformation of Laplace DLTS spectra for SiGe samples.

The LDLTS spectrum of a Ge-free Si sample consists of one sharp dominant line. This indicates a monoexponential transient related to a single well-defined energy level. In the Laplace DLTS spectra of SiGe samples, dominant lines are much broader with some satellite features on both sides. The dominant lines shift to higher energy with the increase in Ge content. The shifts are consistent with those obtained from the "temperature of a DLTS peak maximum" analysis of conventional DLTS spectra.[11] A well separated (about 0.013 to 0.017 eV) satellite line occurs on the low-energy side of the dominant lines for all SiGe samples. For LDLTS spectra, the area under a peak is proportional to the concentration of the corresponding defect. In order to compare relative concentrations of satellite features in SiGe crystals with different Ge content, all the spectra in Fig. 3 were normalized to the same total area/concentration. The ratio of the area of the low-energy satellite line to the total area increases from 4.2% to 10.8% with the increase in Ge content from 2 to 5.5 at. %. This indicates the involvement of Ge atoms in the defects. It is this perturbation which is responsible for the low-energy satellite line. It was argued in Ref. 11 that the concentration of VO complexes having a Ge atom in the first nearest-neighbor shell should be small in irradiated $Si_{1-x}Ge_x$ crystals with $x < 0.06$. Taking into account those arguments and anticipating the results reported below on the identification of a VO-Ge complex with a Ge atom in the first nearest-neighbor shell, we assign the low-energy satellite feature to VO centers perturbed by Ge atoms in the second-neighbor shell.

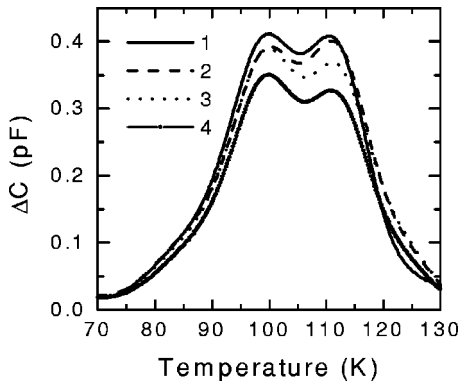Figure 4 shows the development of conventional DLTS

FIG. 5. Development of DLTS spectra for an electron-irradiated $Si_{0.985}Ge_{0.015}$ sample upon 30-min isochronal annealing with temperature increments of 25 °C. The spectra were measured after anneals at (1) 275°C, (2) 300°C, (3) 325°C, and (4) 350°C. Measurement settings were as in Fig. 1.

spectra in the range of the *A*-center-related peak for a Ge-free Si sample and a $Si_{0.985}Ge_{0.015}$ sample upon isochronal annealing in the temperature range of 200–400 °C. The processes of the *A*-center elimination differ significantly in these samples. VO centers in the Ge-free sample anneal out upon heat treatments in the range of 300–400 °C without the appearance of other electrically active defects with comparable concentrations. In the $Si_{0.985}Ge_{0.015}$ sample, the VO-related DLTS peak started to decrease upon annealing at temperatures higher than 200 °C. The decrease in the concentration of *A* centers upon heat treatments in the range of 200–275 °C was accompanied by a simultaneous appearance of another DLTS peak with a maximum at higher temperatures compared to that for the original VO-related peak. Analysis showed an approximate 1 to 1 anticorrelation in changes of magnitude of the annihilated and newly formed DLTS peaks. Upon annealing in the temperature range of 300–325 °C only small variations in intensity of both peaks were observed (Fig. 5). Both peaks disappeared simultaneously upon further annealing at temperatures higher than 350 °C. Figure 6 shows Arrhenius plots of T^2-corrected electron emission rates from dominant traps responsible for the DLTS peaks, which were observed in a $Si_{0.985}Ge_{0.015}$ sample after annealing at 300 °C. The ionization enthalpy of the trap, which appeared upon annealing, is about 25 meV higher compared to the value of ionization enthalpy for the original trap. Similar transformations of the *A*-center-related DLTS peak occurred upon isochronal annealing in all electron-irradiated $Si_{1-x}Ge_x$ samples $(0.015 \leq x \leq 0.055)$, which were studied (Fig. 7).

In the Laplace DLTS spectra, an increasing number of components have been observed upon isochronal annealing of irradiated SiGe samples. The increase in the number of components results in a decrease in the reliability of LDLTS analysis. So, the results of isochronal annealing study are based mainly on the analysis of conventional DLTS spectra.

Our results on the *A*-center elimination in Ge-free Cz-Si samples are consistent with published results.[30–32] It is thought that the main mechanism of disappearance of the *A* center in Cz-Si samples upon heat treatments in the tempera-
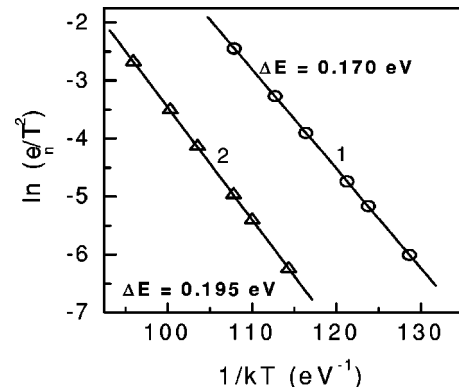
FIG. 6. Arrhenius plots of T^2-corrected electron emission rate from two dominant traps in an electron-irradiated $Si_{0.985}Ge_{0.015}$ sample, which was annealed at 300 °C. Data (1) corresponds to a trap responsible for a peak with maximum at about 100 K in DLTS spectra of Fig. 5 and data (2) to a trap responsible for a peak with maximum at about 110 K in DLTS spectra of Fig. 5. The data were obtained from deconvolution of conventional DLTS spectra and application of the "temperature of a DLTS peak maximum" analysis.

ture range of 300–400 °C is associated with VO migration and its interaction with interstitial oxygen atoms. This leads to the formation of a complex, which consists of two oxygen atoms in a vacancy (VO_2). The VO_2 complex is electrically inert and does not introduce any energy levels into the band gap.[4,33]

The above results on *A*-center elimination in electron-irradiated SiGe samples are consistent with the results of infrared absorption measurements, where upon isochronal annealing of irradiated $Si_{1-x}Ge_x$ samples $(x<0.15)$ a transformation of VO complexes, which are responsible for a LVM line at 830 cm^{-1}, to other centers with LVM lines at 834.6 and 839.2 cm^{-1} was observed.[10] It was suggested in Ref. 10 that Ge atoms could be effective traps for migrating VO centers and the observed LVM's at 834.6 and 839.2 cm^{-1} were associated with VO centers perturbed by Ge atoms in the nearest-neighbor shells. It is reasonable to suggest that the DLTS peak with maximum at about 110–115 K (see Figs. 4, 5, and 7), which appeared upon isochronal

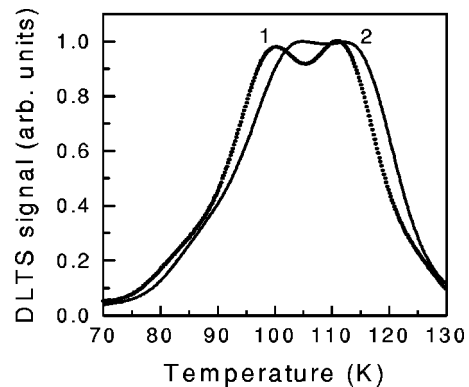FIG. 7. DLTS spectra for electron-irradiated $Si_{1-x}Ge_x$ samples with *x* values of (1) −0.015 and (2) −0.026. The samples have been annealed after irradiation (1) for 30 min at 300 °C and (2) for 90 min at 225 °C. Measurement settings were as in Fig. 1.

annealing of irradiated SiGe samples, is also related to the VO centers perturbed by Ge atoms in the nearest-neighbor shell.

Comparable concentrations of the two DLTS peaks after anneals in the temperature range 300–350 °C (Fig. 5) suggest that the value of binding energy of VO-Ge complex is not high and dynamic equilibrium between VO-Ge complexes and separated VO and Ge_s centers occurs in this temperature range. It is possible to roughly estimate the binding energy of the VO-Ge complexes taking into account close concentrations of Ge bound and separated VO complexes in the temperature range 300–325 °C. We have carried out a simple analysis considering only one type of Ge-bound VO complexes. All other configurations are treated as separated ones. This can be justified by the fact that in conventional DLTS spectra signals from the VO complexes with a Ge atom in the second-nearest-neighbor shell and with more remote Ge atoms cannot be separated and are treated as one DLTS signal. Dissociation of VO complexes followed by formation of other defects is neglected due to the fact that changes in magnitudes of the appropriate DLTS peaks are small in the temperature range 300–325 °C.

The formation and dissociation of the bound VO-Ge complexes can be described then by the following reaction and kinetic equations:

$$VO + Ge \Leftrightarrow VO\text{-}Ge, \tag{1}$$
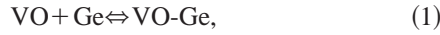
and

$$\frac{dN_{VO\text{-}Ge}}{dt} = k_f N_{VO} N_{Ge} - k_d N_{VO\text{-}Ge},$$

where k_f and k_d are the rate constants for formation and dissociation, N_{VO}, N_{Ge}, and $N_{VO\text{-}Ge}$ are the concentrations of the appropriate defects. The rate constants for the formation and dissociation can be expressed as[34]

$$k_f = 4\pi r_c D_{VO},$$

$$k_d = k_f \frac{g_{Ge} g_{VO}}{g_{VO\text{-}Ge}} \frac{1}{\Omega} \exp\left(-\frac{E_b}{kT}\right),$$

where r_c is the capture radius of a mobile VO center by a Ge atom, D_{VO} is the diffusion coefficient of the vacancy-oxygen complex, g_{VO}, g_{Ge}, and $g_{VO\text{-}Ge}$ are the numbers of possible minimum-energy positions for an appropriate defect in each unit cell of volume Ω, of the silicon lattice; E_b is the binding energy of the VO-Ge complex. If only reaction 1 occurs upon annealing, the total concentration of A centers $N_{\Sigma VO}$ should be constant, i.e., $N_{VO\text{-}Ge} + N_{VO} = N_{\Sigma VO}$, and the equilibrium concentration of VO-Ge complexes can be described by a following equation:[35]

$$N_{VO\text{-}Ge}^{eq} = \frac{N_{Ge} N_{\Sigma VO}}{N_{Ge} + \frac{g_{VO}}{g_{VO\text{-}Ge}} N_s \exp\left(-\frac{E_b}{kT}\right)}, \tag{2}$$

where N_s is the number of substitutional sites per unit volume in silicon ($N_s = 5 \times 10^{22}$ cm^{-3}) respectively.
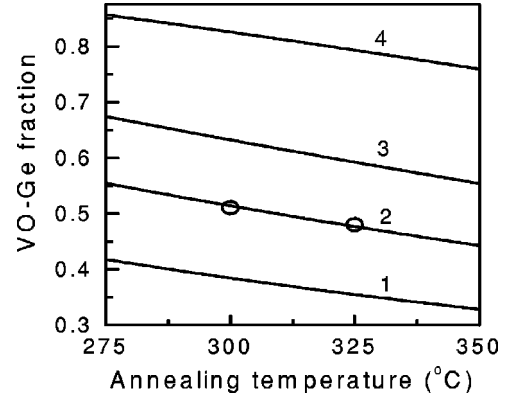

FIG. 8. Temperature dependencies of the equilibrium fraction of bound VO-Ge complexes in a SiGe crystal for different values of the VO-Ge binding energy 1—0.15 eV, 2—0.176 eV, 3—0.20 eV, and 4—0.25 eV. The dependencies were calculated in accordance with Eq. (2) for $N_{Ge} = 7.5 \times 10^{20}$ cm^{-3} and $g_{VO}/g_{VO\text{-}Ge} = 0.5$. Open circles represent values of ratio of the magnitude of the DLTS peak with maximum at about 110 K to the sum of magnitudes of this peak and the one with maximum at about 100 K in Figs. 4 and 5.

Dependencies of normalized equilibrium VO-Ge fraction ($N_{VO\text{-}Ge}^{eq}/N_{\Sigma VO}$) versus temperature calculated in accordance with Eq. (2) for different values of binding energy are presented in Fig. 8. The Ge concentration was taken as $N_{Ge} = 7.5 \times 10^{20}$ cm^{-3} and $g_{VO}/g_{VO\text{-}Ge} = 0.5$.[36] Points in Fig. 8 represent experimental values of normalized equilibrium VO-Ge fraction derived from the analysis of the DLTS spectra shown in Fig. 5. The value of binding energy of about 0.18 eV is consistent with the close fractions of Ge-bound and separated VO centers in the temperature range 300–325 °C for a $Si_{0.985}Ge_{0.015}$ sample. Binding-energy values in the range of 0.15–0.20 eV have been obtained from the analysis of isochronal annealing-induced transformations of the VO-related DLTS peak in four $Si_{1-x}Ge_x$ samples with Ge content 1.5 and 2.5 at. %. It should be noted, however, that more precise determination of the binding energy of VO-Ge complex requires a study of kinetics of transformations of the VO centers upon isothermal annealing of irradiated SiGe samples with different Ge content. Such a study is in progress now. This allows us also to investigate the effect of Ge content on the diffusivity of the VO center.

IV. THEORETICAL MODELING

We use an *ab initio* density-functional code[37] (AIMPRO), along with the parametrization for the local-exchange correlation by Perdew and Wang.[38] Norm-conserving pseudopotentials by Bachelet, Hammann, and Schlüter are employed,[39] and Cartesian-Gaussian *s*-, *p*-, and *d*-type basis functions are placed on each atom. Basis sets for Si, Ge, and O are (4,4,2), (4,4,2), and (6,6,3), with the triplets (n_s, n_p, n_d) representing the minimum number of *s*-, *p*-, and *d*-like functions, respectively. The charge density and potential terms are expanded in plane waves with energy of 150 Ry. Defects were placed in large cubic supercells with 216 Si atoms, and the Brillouin zone was sampled with eight Monkhorst-Pack **k** points,[40] referred to as MP-2^3 special **k**

point set. For this **k**-point sampling level and basis, we obtained converged results, with energy differences (electrical levels, binding energies, etc.), differing by less than 0.1 eV from those using Γ and a larger basis.

Optimized exponents associated with the basis functions were found using bulk Si, Ge, and SiO_2 with experimental lattice parameters. Relaxing the cells with the optimized basis gave $a_0 = 5.388$ Å ($a_0 = 5.623$ Å) for Si (Ge). The Murnaghan equation of state,[41]

$$P = \frac{B}{B'}\left[\left(\frac{V_0}{V}\right)^{B'} - 1\right],$$

can then be used to determine the bulk modulus. This gave $B = 98$ and 74 GPa for Si and Ge, respectively. These values are similar to earlier calculations using a different basis[4] and agree well with the measured values $a_0 = 5.431$ Å ($a_0 = 5.658$ Å) and bulk modulus $B = 97.9$ GPa ($B = 77.2$ GPa), for Si (Ge), respectively.[42,43]

The basis set for oxygen was found in a α-quartz crystal. The equilibrium crystalline structure was found by relaxing the atomic coordinates as well as the lattice vectors. During the later process a conjugate gradient algorithm was used, with all atoms locked to their internal coordinates. Atomic and lattice relaxation were performed sequentially until the energy change was negligible. The equilibrium lattice parameters for SiO_2 were found to be $a = 4.902$ Å and $c = 5.395$ Å. These agree well with the measured $a = 4.9136$ Å and $c = 5.4051$ Å.[44] According to the Murnaghan equation of state, $B = 40$ GPa and $B' = 7$, reproducing well the measured $B = 37.1$ GPa and $B' = 6.0$.[45]

The electrical activity of VO defects is of primary interest here. The energy levels of the defects were found using the marker method.[46,47] Accordingly, the $(-/0)$ level of a defect relative to the $(-/0)$ level of a *marker* is calculated using the same calculational parameters. In other terms, we compare electron affinities $A_m = E_m(0) - E_m(-)$ and $A_d = E_d(0) - E_d(-)$ of supercells containing the marker and the defect of interest, respectively. The difference $A_d - A_m$ is then offset to the experimental location of the acceptor state of the marker. The marker defect should possess a well established $(-/0)$ level in the gap, and its acceptor wave function should ideally have the same symmetry and range as that of the defect under investigation. In the present work we are interested in the VO defect in Si possessing a neighboring substitutional Ge atom. The VO complex in Si, possessing an acceptor state at $(E_c - 0.17)$ eV,[2] is the obvious choice for the marker.

A. Modeling the alloy

The procedure described above yields a defect level which is independent of the Ge concentration x. However, the lattice parameter increases with x and this by itself can influence the level position.[48]

X-ray measurements reveal that the changes of the lattice parameter with Ge concentration x obeys Vegard's law

$$\delta a = a - a_{Si} = (a_{Ge} - a_{Si}) x. \tag{3}$$

This does not, however, imply that the average Si-Si, Si-Ge, and Ge-Ge bond lengths scale in the same way. According to x-ray absorption fine structure (XAFS) measurements, although the average Si-Ge and Ge-Ge bonds change in a linear way, the gradients are much smaller than expected from using Eq. (3).[49,50] To see the effect of this, we compare the measured asymmetric stretch mode of O_i in SiGe alloys[13] ($0.0 < x < 0.77$) with that in Si under hydrostatic pressure.[51] The pressure induced shift of the mode has been measured as $\Delta = -2.3$ cm^{-1}GPa^{-1}, whereas its variation with Ge content x in SiGe alloys is about $-18x$ cm^{-1}. If the lattice parameter a varies according to Vegard's law above, we conclude that the $-18x$ cm^{-1} shift rate in SiGe alloys corresponds $\Delta = -1.41$ cm^{-1}GPa^{-1}. This is about half of that found in the hydrostatic pressure measurements. The explanation is that the Si-Si bond length change is much less than that of the lattice parameter and this is supported by previous modeling studies.[52,53] We checked this result by finding the change in lattice parameter and average Si-Si bond length in cells containing 0, 1, and 7 well separated Ge substitutional atoms in $Si_{216}Ge_0$, $Si_{215}Ge_1$, and $Si_{209}Ge_7$ supercells. We find, that the change in lattice parameter in these ordered alloys is $\delta a = (0.25 \pm 0.05)x$ Å which is close to Vegard's law given above where δa is $0.21x$ Å. However, the change in average Si-Si bond length is $\delta r = (0.062 \pm 0.006) x$ Å which is considerably less than that found by scaling the lattice parameter change.

If the VO defects are remote from Ge atoms, the variation of the $(-/0)$ level with Ge concentration can be found by assuming that the average Si-Si bond length in a large cell varies as $0.062x$ and such a variation arises if we place the defect in a Si cell with a lattice parameter given by (in Å)

$$\delta a = 4 \, \delta r / \sqrt{3} = 0.143x. \tag{4}$$

The assumption here is that the bond angle variation at Si sites remote from Ge is unimportant.

All the atoms in Si supercells with the above lattice constants, and containing a VO defect, are fully relaxed, and their electron affinities compared with those of the interstitial carbon defect (C_i) found in similar cell with the same lattice constant. C_i is now chosen as the marker because the variation of the $C_i(-/0)$ level has been measured for $0 \leq x \leq 0.5$.[54,55] The continuous variation in the C_i level with x implies that this defect does not possess Ge atoms within its core.

This approach ignores the effect of Ge atoms on the band structure over and above the effect of a Si-Si bond length change. Clearly, one effect of this is to correct the lattice parameter. To take this effect into account, we insert VO and C_i defects in the $Si_{215}Ge_1$ and $Si_{209}Ge_7$ supercells described above whose volumes had been previously relaxed. The lattice parameters are then almost given by Vegard's law. The $(-/0)$ level of VO was then obtained and compared with the level found in the same sized cell, with the same Ge atoms, and containing C_i.

The Mulliken bond populations of gap states were found using MP-2[3] **k**-point sampling. The populations describe the localization of gap states as discussed previously.[56]
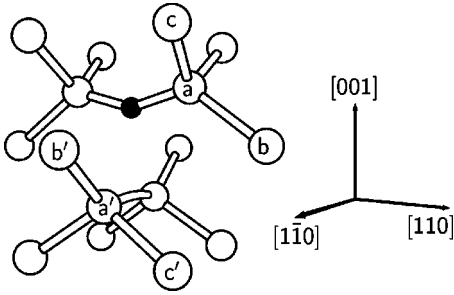
FIG. 9. Structure of the VO complex in silicon. The VO-Ge complexes considered here result from substituting first- or second-neighboring Si atoms by Ge. These structures are labeled with letters from a to c and a' to c'.

The oxygen related local vibrational mode frequencies of VO complexes in Si and $Si_{1-x}Ge_x$ alloys were also investigated. Second derivatives of the energy were evaluated by displacing atoms forming the Si-O-Si unit along all six Cartesian coordinates.[57] The contribution from more remote atoms was taken into account by using a Musgrave-Pople interatomic potential derived earlier.[58]

B. Defect structure

VO defects containing a core Ge atom (one of the neighbors or next neighbors of the vacancy) are referred to as VO-Ge complexes. The structures investigated are shown in Fig. 9. These VO-Ge complexes are labeled with letters from a to c and a' to c', representing sites for Ge substitution. For example, a VO defect with a Ge atom on site b' will be referred as VO-Ge$_{b'}$.

First we study VO-Ge complexes in bulk Si using the bulk Si lattice parameter. Relative energies of neutral and negatively charged defects [$E_r(0)$ and $E_r(-)$, respectively] are shown in Table I. Two main factors determine the stability of these complexes. These are (i) the existence of sites in the open part of the lattice which can accommodate a large Ge atom and (ii) bonding effects due to the Ge-O chemistry. The first is more relevant in VO-Ge$_{a'}$ or in VO-Ge$_b$ and

VO-Ge$_{b'}$. Sites b and b' lie in expanded Si-110 chains, and this is due to the tensile character of the Si-O-Si unit and Si-Si reconstruction. Finally, VO-Ge$_c$ and VO-Ge$_{c'}$ have no apparent reason for having a strong binding energy and they are somewhat closer to the isolated VO complex in Si. We note that all complexes without a Ge-O bond possess four Si-Ge bonds.

Table I also gives structural details and binding energies of VO-Ge complexes. The binding energies reflect the energy released following a $VO + Ge_s \rightarrow VO\text{-}Ge$ reaction. They are found by calculating the energies of neutral VO and Ge$_s$ defects in separate supercells. From Table I we conclude that the formation of VO-Ge$_a$ is energetically unlikely as the binding energy is negative. This is supported by the much lower formation enthalpy of SiO$_2$ (α-quartz), $\Delta H_f^0 = -910.7$ kJ/mol, than that of GeO$_2$ at -580.0 kJ/mol of GeO$_2$ (rutile).[44] Thus we argue that in VO-Ge the formation of the Si-O-Si bridge is strongly favored over a direct Ge-O-Si unit due to bond energetics.

As stated above, sites b and b' give low-energy metastable structures, whereas VO-Ge$_{a'}$ represents the most stable state. The available free space accommodating site a' is responsible for the stability of the complex. Note that Ge makes three Ge-Si bonds of length ~ 2.4 Å and a long ~ 3.0 Å Si-Ge reconstruction bond. These lengths are to be compared with the 2.369 Å Si-Ge bond length in substitutional Ge and with the 3.094 Å for the Si-Si reconstruction in the VO complex in Si. Structures c and c' are not bound (or are marginally bound) since the Ge atom is now close to the [001] symmetry axis of VO, and it is known that the defect is compressive along this axis.[2,4]

The low binding energies of a', b, and b' are in line with the results of both electrical and Fourier transform infrared (FTIR) measurements.[10] Moreover, the 0.19 eV binding energy of VO-Ge$_{a'}$ is in excellent agreement with the 0.15–0.20 eV found experimentally for the VO-Ge defect possessing the deepest level. Accordingly, in $Si_{1-x}Ge_x$ alloys and at $\sim 250 °C$, VO defects become mobile and are likely to be trapped by Ge atoms. This will lower their energy by ~ 0.1–0.2 eV, but at 350 °C they disappear through dissociation or by interaction with other defects in the alloy.

C. Energy levels of VO-Ge defects

In Table I we also report the calculated acceptor levels for the several VO-Ge defects. These were obtained by using VO in Si as marker using the bulk Si lattice parameter. All stable VO-Ge complexes produce an acceptor state very close to that of VO, but only VO-Ge$_{a'}$ has a deeper level, i.e., 20 meV deeper than VO($-$/0). Although the method usually is affected by errors of about 0.2 eV, when the marker and defect being studied produce similar gap states the errors may decrease below 0.1 eV.[47] Therefore, and considering that the a' structure is energetically favored, we assign the deepest VO-Ge electron trap [25 meV deeper than VO($-$/0)], to VO-Ge$_{a'}$. We note that VO-Ge$_b$ and VO-Ge$_{b'}$ have shallower acceptor levels [about 30 and 70 meV above VO($-$/0)]. Considering that these structures possess a posi-

TABLE I. Relative energies of neutral and negative defects [$E_r(0)$ and $E_r(-)$, respectively], structural details (bond lengths for neutral defects), binding energies (E_b), and acceptor level location [$E_c - E(-/0)$], for the several VO-Ge complexes. All energies and bond lengths are given in eV and Å, respectively. Labeling is according to Fig. 9. X-O (Si-X) stands for Si-O (Si-Si reconstruction) distance except for VO-Ge$_a$ (VO-Ge$_{a'}$) where it stands for Ge-O (Si-Ge reconstruction) distance, respectively.

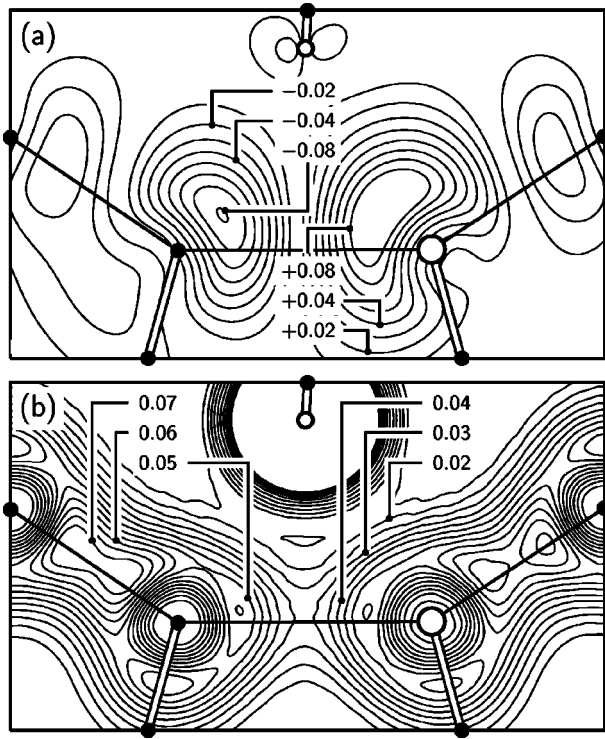| Structure	a	b	c	a'	b'	c'
$E_r(0)$	0.733	0.117	0.196	0.000	0.098	0.201
$E_r(-)$	0.839	0.166	0.245	0.000	0.189	0.264
X-O	1.912	1.685	1.692	1.687	1.689	1.689
O-Si	1.686	1.683	1.688	1.687	1.689	1.688
Si-X	2.979	3.049	3.070	3.056	2.896	3.038
E_b	-0.54	0.07	-0.01	0.19	0.09	-0.01
$E_c - E(-/0)$	0.09	0.14	0.14	0.19	0.10	0.13

FIG. 10. Wave function of highest occupied state of VO-Ge$_{a'}$ at Γ plotted in the (110) plane (a), and charge density (a.u.$^{-3}$) normalized to the number of electrons in the supercell (b). Si, Ge, and O atoms are represented as closed, large open, and small open circles, respectively.

FIG. 11. Effects of lattice-parameter change (closed symbols) and the presence of Ge (open symbols) on the electron affinity (A) of C$_i$ and VO defects. Open squares (triangles) show A for VO (C$_i$) in volume relaxed Si$_{214}$GeO (Si$_{215}$GeC) and Si$_{208}$Ge$_7$O (Si$_{209}$Ge$_7$C) supercells.

Figure 10(b) shows the charge density on the (110) symmetry plane of the VO-Ge$_{a'}$ defect. Clearly, the charge density is slightly peaked on the Si atom in the reconstructed Si-Ge bond. This mirrors the small ionic character of the Si-Ge bond: bonding states are more localized on the cation (Si), and antibonding states (in this case the acceptor state) prefer the anion (Ge) sites. This small ionic character can also be found in the bonds between Ge and its nearest Si neighbor on the (110) plane (see Fig. 10).

tive binding energy, they are assigned to the shallower VO-Ge trap [about 15 meV above VO($-$/0)].

The band structure found from supercells containing VO-Ge$_{a'}$, VO-Ge$_{b'}$, and VO-Ge$_b$ are *similar* to the isolated VO defect in Si, i.e., these possess an empty band detached from the bottom of the conduction states. This suggests that all these complexes produce close-by electrical levels within the gap. Figure 10(a) depicts the wave function for the highest occupied state of the stable VO-Ge$_{a'}$ complex at $\mathbf{k}=\Gamma$. Clearly the wave function is slightly peaked near the Ge atom. The behavior of the wave function near the Si atom is almost identical to that found for VO in Si. This suggests that the acceptor state is more localized in VO-Ge$_a$ than in VO. A Mulliken analysis of this state is almost identical for VO-Ge$_{a'}$ and VO. In VO-Ge$_{a'}$ about 17% and 19% of the spin density is localized on the Si and Ge atoms, respectively. This is to be compared with the 17% calculated for VO. The angular momentum character of the state is however different. In VO-Ge$_{a'}$ the wave function on Ge has about 37% and 57% of s and p character, whereas it is 28% and 67% s like and p like on Si for both VO-Ge and VO complexes. These figures are to be compared with the ^{29}Si hyperfine data from electron paramagnetic resonance on VO$^-$ in Si,[2] which gives 18%, 40%, and 60% of localization, s- and p-like character at the analogous Si atom, respectively. In summary, the acceptor state of VO-Ge is more localized than that of VO, and the wave function on Ge is more isotropic than in Si.
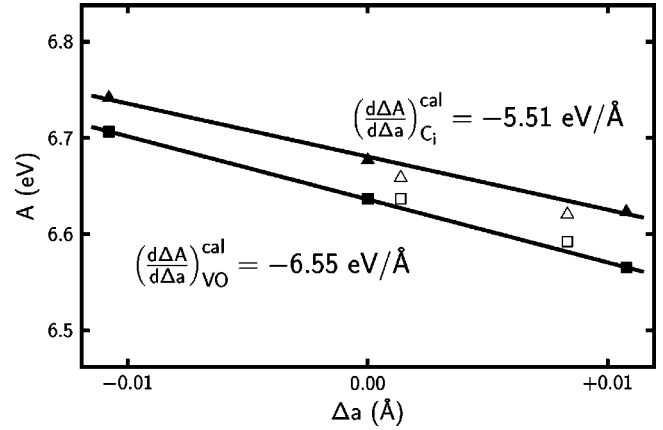
D. Effect of Si-Si bond length variation on energy level of VO

To investigate the effect of the Si-Si bond-length variation on $E_c-E(-/0)$, we found A_m and A_d as the lattice parameter was varied according to Eq. (4) above. As discussed in Sec. IV, the marker was chosen to be the ($-$/0) level of C$_i$ whose variation is known for $0 \leqslant x \leqslant 0.5$.[55] From Ref. 55 we find the variation in the level of C$_i$ with x to be $E_c - C_i(-/0) \sim (0.1 + 0.3 x)$ eV.

Figure 11 shows the calculated electron affinities of C$_i$ and VO complexes, for volume contracted and expanded supercells, as well as the equilibrium a_0 of Si. The effect of the volume expansion is to increase C$_i(-/0) - VO(-/0)$ at an approximate linear rate of $6.55 - 5.51 = 1.04$ eV/Å. Considering Eq. (4), this rate corresponds to $0.15 x$ eV. If we offset this value by the measured $0.3 x$ eV shift rate of C$_i(-/0)$, we end with a $0.45 x$ eV shift rate for VO. This is very close to the measured $0.56 x$ eV shift rate of VO in SiGe alloys,[11] and explains the gradual increase in the ionization enthalpy of VO($-$/0) as a consequence of an increase of the Ge content.

The effect of adding remote and separated Ge atoms to the supercell was also considered. Here we formed ordered alloys with one and seven substitutional Ge atoms, forming Si$_{214}$GeO and Si$_{208}$Ge$_7$O supercells. As stated above, the relaxed volume of these cells is close to Vegard's law in Eq. (3) while the average Si-Si bond length are close to results found in previous calculations. Electron affinities of VO under these conditions are plotted in Fig. 11 as open squares. Both values lie only 0.02 eV above (or 0.002 Å to the right

TABLE II. Calculated asymmetric and symmetric local vibrational mode frequencies (v_a and v_s, respectively) for structures a', b', and b. Experimental frequencies (Expt.) are also shown. All values are given in cm^{-1}.

Structure	VO	a'	b'	b
v_a	832	854	852	852
v_s	565	565	565	560
Expt.[a]	830	839.2	834.6	834.6

[a]Reference 10.

of) the line representing VO($-$/0) and show the same volume shift as in Ge free supercells. An analogous trend is obtained for C_i with Ge atoms at remote positions (open triangles in Fig. 11). When using the bulk Si lattice constant to evaluate the VO($-$/0) state in Si$_{214}$GeO and Si$_{208}$Ge$_7$O supercells the levels differ by only 0.01 eV. Therefore we conclude that the measured shift of the acceptor state of VO with x is almost entirely due to an expansion of the Si-Si bond lengths in SiGe alloys at least for $x < 0.05$.

E. LVM frequencies

Local vibrational modes for the most stable a', b', and b forms are reported in Table II. These were calculated in 216 atom cells with the bulk Si lattice parameter and using the MP-2^3 special **k** points to sample the Brillouin zone.

On the left-hand side of Table II we show LVM frequencies for VO in Si, here chosen as a reference. In agreement with the measurements, all defects (a', b', and b) give rise to LVM frequencies above that of VO. From the FTIR measurements we know that the 839.2-cm^{-1} band grows at the expense of the 834.6-cm^{-1} band, both of them lying *above* the main band of VO at 830 cm^{-1}.[10] Therefore we assign the 839.2-cm^{-1} band to VO-Ge$_{a'}$, and the 834.6-cm^{-1} band to VO-Ge$_{b'}$ and/or VO-Ge$_b$ defect forms. Despite the error associated with the absolute LVM frequencies (~ 20 cm^{-1}) being larger than their relative differences, this assignment is also supported by the relative defect stability and respective electric levels.

The variation of the Si-O-Si stretch frequency with lattice expansion has also been investigated. The shift Δ of the LVM frequency under an isotropic deformation is given by $\Delta = 3 B \mathrm{Tr}(A) \epsilon$ where the strain tensor is given by $\epsilon_{ij} = \epsilon \delta_{ij}$. Here B is the bulk modulus of Si and A is the piezospectroscopic strain tensor.[59] For strain values between 0.001 and 0.002, the 832 cm^{-1} mode of VO shifts linearly at a rate corresponding to $\mathrm{Tr}(A) = -3.1$ cm^{-1}/GPa. This means that lattice expansion ($\epsilon > 0$) lowers the asymmetric stretch frequency of VO. This value reproduces qualitatively the -6.7 cm^{-1}/GPa from the dispersive IR measurements by Bosomworth *et al.*,[60,61] and agrees well with the -2.8 cm^{-1}/GPa arriving from a more precise FTIR data by Pajot *et al.*[61,62] Using Eq. (4) we can convert the shift to $\Delta = -24 x$ cm^{-1}. The shift of the 830-cm^{-1} absorption band in SiGe alloys (for $0.035 \leq x \leq 0.15$) was not reported in Ref. 10. This range of composition corresponds to $-3.6 \leq \Delta \leq -0.8$ cm^{-1} but this effect may be hidden by band broad-

ening. Finally we note that using the ordered alloy method the 832 cm^{-1} mode was shifted by -2 and 4 cm^{-1} for the volume relaxed Si$_{214}$GeO and Si$_{208}$Ge$_7$O supercells, respectively. The upward shift for Si$_{208}$Ge$_7$O is likely to be a consequence of the local strain, which among other contributions is also responsible for the band broadening.

V. CONCLUSIONS

We have found from the DLTS studies at least three configurations of VO centers with distinct levels. In as-irradiated material, one has an energy level shifted upward by about 15 meV from the level of the dominant configuration. Upon isochronal annealing in the temperature range of 200–300 °C, the dominant VO defect transforms into another one whose level is about 25 meV deeper. The binding energy of the deeper VO-Ge complex compared to separated VO and Ge$_s$ defects is found experimentally to be about 0.18 eV.

From a theoretical point of view there are three effects on the energy levels of defects found in Si caused by alloying with Ge. The first leads to defects having Ge atoms in their cores, the second arises from the increase in average Si-Si bond lengths caused by the presence of remote Ge atoms. However, this increase is only about half that expected from a uniform scaling of Si bonds in a cell whose lattice parameter obeys Vegard's law. Thus, this effect is not numerically identical to the effect of a hydrostatic pressure on the lattice parameter. The third effect comes from the changes to the electronic structure caused by the presence of Ge over and above the bond length changes. This effect must correct the lattice parameter.

From the *ab initio* modeling studies we were able to investigate all the effects of alloying. We found three bound VO-Ge structures referred to as a', b, and b', respectively (see Fig. 9) where Ge atoms lay at different sites within the core of the defect. Structure a' is the ground state, and possesses a Ge atom on the first-neighboring shell of the VO complex, making a direct but weak reconstructed bond with a Si atom. Defects b and b' are metastable by ~ 0.1 eV, and Ge lies on a second-neighboring shell along tensile $\langle 110 \rangle$ Si chains. Analysis of their electrical activity found acceptor states close to that of VO in Si. The VO-Ge$_{a'}$($-$/0) level is deeper [($E_c - 0.19$) eV], and the gap state more localized than that of VO. This is a consequence of the slightly ionic character of the Si-Ge reconstructed bond in VO-Ge$_{a'}$. On the other hand, the ($-$/0) levels of VO-Ge$_{b'}$ and VO-Ge$_b$ are shallower than VO($-$/0). Their relative stability, binding energies, and level location allows us to assign VO-Ge$_{a'}$ to the electron trap 25 meV deeper than VO($-$/0), and VO-Ge$_b$ and/or VO-Ge$_{b'}$ to the shallower precursor that appears in as-irradiated Si$_{1-x}$Ge$_x$ samples.

The second effect of alloying is illustrated by the change in the level of an isolated VO($-$/0) defect with Si-Si bond expansion. Here the variation in bond angles in the alloy is ignored. The third effect arises from the presence of Ge atoms within the supercell over the Si-Si bond expansion. This, as we have shown, leads to the observed lattice-parameter change. We have also shown, perhaps surprisingly,

that the last effect has a small influence on the VO($-/0$) level. We found that the level deepens with x at a rate of $0.45\,x$ eV and is almost entirely due to the variation in average Si bond lengths. The calculated rate is in good agreement with the measured $0.56\,x$ eV.[11]

The local vibrational modes of VO-Ge defects were also investigated. For defects a', b', and b we obtain antisymmetric Si-O-Si stretch modes at 854, 852, and 852 cm^{-1}, respectively. These lie above that of VO (832 cm^{-1}). Hence, VO-Ge$_{a'}$ is assigned to 839.2-cm^{-1} IR band, whereas VO-Ge$_{b'}$ and/or VO-Ge$_b$ are again very similar, being assigned to the 834.6-cm^{-1} band. The 839.2-cm^{-1} band is known to arise from a more stable complex,[10] further supporting our assignment.

The trace of the piezospectroscopic strain tensor A of the asymmetric stretch mode of VO in Si is estimated as $\text{Tr}(A) = -3.1$ cm^{-1}/GPa. This agrees well with the -2.8 cm^{-1}/GPa from FTIR data and suggests that the 830 cm^{-1} band of VO in Si$_{1-x}$Ge$_x$ shifts at a rate of $-24\,x$ cm^{-1} in the alloy. This shift has not been measured so far.

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[1] H.G. Grimmeiss, Semiconductors **33**, 939 (1999).

[2] G.D. Watkins and J.W. Corbett, Phys. Rev. **121**, 1001 (1961); J.W. Corbett, G.D. Watkins, R.M. Chrenko, and R.G. McDonald, *ibid.* **121**, 1015 (1961).

[3] S.D. Brotherton and P. Bradley, J. Appl. Phys. **53**, 5720 (1982).

[4] J. Coutinho, R. Jones, P.R. Briddon, and S. Öberg, Phys. Rev. B **62**, 10 824 (2000).

[5] R.E. Whan, Appl. Phys. Lett. **6**, 221 (1965); Phys. Rev. **140**, A690 (1965).

[6] J. Fage-Pedersen, A. Nylandsted Larsen, and A. Mesli Phys. Rev. B **62**, 10 116 (2000).

[7] P. Vanmeerbeek and P. Clauws, Phys. Rev. B **64**, 245201 (2001).

[8] V.P. Markevich, I.D. Hawkins, A.R. Peaker, V.V. Litvinov, L.I. Murin, L. Dobaczewski, and J.L. Lindström, Appl. Phys. Lett. **81**, 1821 (2002).

[9] V.P. Markevich, V.V. Litvinov, L. Dobaczewski, J.L. Lindström, L.I. Murin, and A.R. Peaker, Phys. Status Solidi C **0**, 702 (2003).

[10] Yu.V. Pomozov, M.G. Sosnin, L.I. Khirunenko, V.I. Yashnik, N.V. Abrosimov, W. Schröder, and M. Höhne, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **34**, 1030 (2000); Semiconductors **34**, 989 (2000).

[11] V.P. Markevich, A.R. Peaker, L.I. Murin, and N.V. Abrosimov, Appl. Phys. Lett. **82**, 2652 (2003).

[12] J. Weber and M.I. Alonso, Phys. Rev. B **40**, 5683 (1989).

[13] I. Yonenaga, M. Nonaka, and N. Fukata, Physica B **308-310**, 539 (2001).

[14] H. Yamada-Kaneta, C. Kaneta, and T. Ogawa, Phys. Rev. B **47**, 9338 (1993).

[15] D. Wauters and P. Clauws, Mater. Sci. Forum **258-263**, 103 (1997).

[16] L.I. Khirunenko, Yu.V. Pomozov, M.G. Sosnin, N.V. Abrosimov, M. Höhne, and W. Shröder, Physica B **273-274**, 305 (1999).

[17] G.A. Samara, Phys. Rev. B **36**, 4841 (1987).

[18] J.L. Lindström, L.I. Murin, V.P. Markevich, T. Hallberg, and B.G. Svensson, Physica B **273-274**, 291 (1999).

[19] N.V. Abrosimov, S.N. Rossolenko, V. Alex, A. Gerhardt, and W. Shröder, J. Cryst. Growth **166**, 657 (1996).

[20] L. Dobaczewski, P. Kaczor, I.D. Hawkins, and A.R. Peaker, J. Appl. Phys. **76**, 194 (1994).

[21] P. Wagner and J. Hage, Appl. Phys. A: Solids Surf. **49**, 123 (1983).

[22] E. Hild, P. Gavorzewski, M. Franz, and K. Pressel, Appl. Phys. Lett. **72**, 1362 (1998).

[23] P. Omling, L. Samuelson, and H.G. Grimmeiss, J. Appl. Phys. **54**, 5117 (1983).

[24] A. Das, V.A. Singh, and D.V. Lang, Semicond. Sci. Technol. **3**, 1177 (1988).

[25] L. Dobaczewski, K. Gościński, K. Bonde Nielsen, A. Nylandsted Larsen, J. Lundsgaard Hansen, and A.R. Peaker, Phys. Rev. Lett. **83**, 4582 (1999).

[26] K. Gościński, L. Dobaczewski, K. Bonde Nielsen, A. Nylandsted Larsen, and A.R. Peaker, Phys. Rev. B **63**, 235309 (2001).

[27] A. Mesli, B. Vileno, C. Eckert, A. Slaoui, C. Pedersen, A. Nyladsted Larsen, and N.V. Abrosimov, Phys. Rev. B **66**, 045206 (2002).

[28] V.P. Markevich, A.R. Peaker, L.I. Murin, and N.V. Abrosimov, J. Phys.: Condens. Matter **15**, S2835 (2003).

[29] P. Blood and J. W. Orton, *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States* (Academic Press, London, 1992).

[30] J.W. Corbett, G.D. Watkins, and R.S. McDonald, Phys. Rev. **135**, A1381 (1964).

[31] B.G. Svensson and J.L. Lindström, Phys. Rev. B **34**, 8709 (1986).

[32] V.P. Markevich and L.I. Murin, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **25**, 1737 (1991) [Sov. Phys. Semicond. **25**, 1045 (1991)].

[33] M. Pesola, J. von Boehm, T. Mattila, and R.M. Nieminen, Phys. Rev. B **60**, 11 449 (1999).

[34] C. Herring and N. M. Johnson, in *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34, edited by R. K. Willardson and A. C. Beer (Academic, San Diego, 1991), Chap. 10.

[35] V.P. Markevich and M. Suezawa, J. Appl. Phys. **83**, 2988 (1998).

[36] The number of possible minimum-energy states in a two atom Si unit cell is 8 for the VO center and 16 for the ground-state VO-Ge defect reported in the theoretical modeling section.

[37] P.R. Briddon and R. Jones, Phys. Status Solidi B **207**, 131 (2000).

[38] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[39] G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[40] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[41] F.D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **3**, 224 (1944).

[42] Jasprit Singh, *Physics of Semiconductors and Their Heterostructures* (McGraw-Hill, New York, 1993).

[43] P.J. Mohr and B.N. Taylor, Rev. Mod. Phys. **72**, 351 (2000).

[44] *CRC Handbook of Chemistry and Physics*, 81st ed., edited by D. R. Lide (CRC Press LLC, Boca Raton 2000).

[45] J.D. Bass, R.C. Libermann, D.J. Widner, and S.J. Finch, Phys. Earth Planet. Inter. **25**, 140 (1981).

[46] A. Resende, R. Jones, S. Öberg, and P.R. Briddon, Phys. Rev. Lett. **82**, 2111 (1999).

[47] J. Coutinho, V.J.B. Torres, R. Jones, and P.R. Briddon, Phys. Rev. B **67**, 035205 (2003).

[48] J.P. Dismukes, L. Ekstrom, and R.J. Paff, J. Phys. Chem. **68**, 3021 (1964).

[49] J.C. Aubry, T. Tyliszczak, A.P. Hitchcock, J.M. Baribeau, and T.E. Jackman, Phys. Rev. B **59**, 12 872 (1999).

[50] I. Yonenaga and M. Sakurai, Phys. Rev. B **64**, 113206 (2001).

[51] M.D. McCluskey and E.E. Haller, Phys. Rev. B **56**, 9520 (1997).

[52] M.H.F. Sluiter and Y. Kawazou, Mater. Trans., JIM **42**, 2201 (2001).

[53] P. Venezuela, G.M. Dalpian, A.J.R. da Silva, and A. Fazzio, Phys. Rev. B **64**, 193202 (2001).

[54] T.P. Leervad Padersen, A. Nylandsted Larsen, and A. Mesli, Appl. Phys. Lett. **75**, 4085 (1999).

[55] A. Nylandsted Larsen, A. Bro Hansen, D. Reitze, J.-J. Goubet, J. Fage-Pedersen, and A. Mesli, Phys. Rev. B **64**, 233202 (2001).

[56] J. Coutinho, R. Jones, P.R. Briddon, S. Öberg, L.I. Murin, V.P. Markevich, and J.L. Lindström, Phys. Rev. B **65**, 014109 (2002).

[57] R. Jones and P. R. Briddon, in *Identification of Defects in Semiconductors*, edited by M. Stavola, Semiconductors and Semimetals Vol. 51A (Academic, New York, 1998), p. 287.

[58] M.J.P. Musgrave and J.A. Pople, Proc. R. Soc. London, Ser. A **268**, 474 (1962).

[59] A.A. Kaplyanskii, Opt. Spectrosc. **16**, 329 (1964).

[60] D.R. Bosomworth, W. Hayes, A.R.L. Spray, and G.D. Watkins, Proc. R. Soc. London, Ser. A **317**, 133 (1970).

[61] In this work we follow the convention where a positive stress is tensile. However, in Refs. 60 and 62 the authors opted to use positive values for compressive stress, and therefore their values for Tr(A) are reported here with opposite sign.

[62] B. Pajot, S. McQuaid, R.C. Newman, C. Song, and R. Rahbi, Mater. Sci. Forum **143-147**, 969 (1994).