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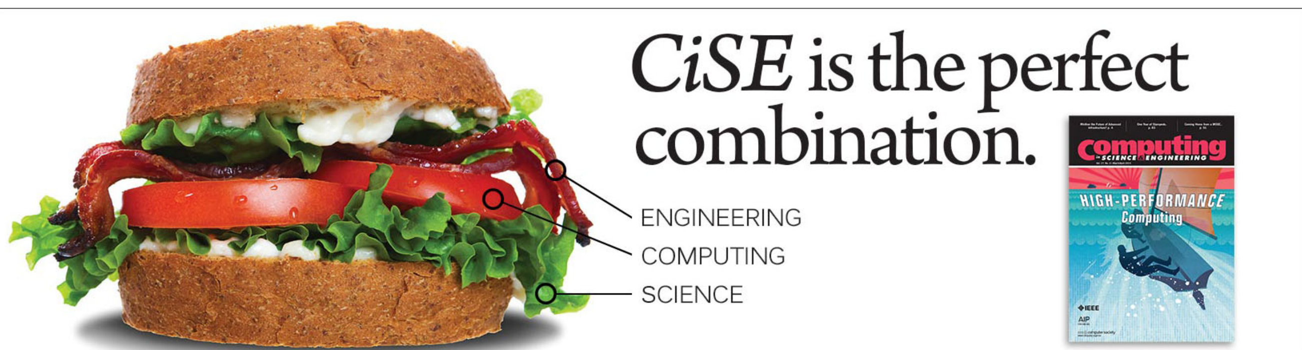


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# Vacancies in SiGe: Jahn–Teller distortion and spin effects

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The electronic structure of a vacancy in silicon-germanium is studied using *ab initio* total-energy minimization methods. The calculations are based on density-functional theory in the local-spin-density approximation. We report ionic relaxations, defect formation energies and ionization levels of Si and Ge vacancies in a zinc blende model structure (SiGe). The Ge vacancy in SiGe is characterized by symmetry-lowering Jahn–Teller (JT) distortions and a negative-effective-$U$ effect, in those respects resembling the vacancy in elemental silicon. For Si vacancy, the exchange-coupling energy is found to overcome the JT energy, and symmetric high-spin ground states are predicted. © *2000 American Institute of Physics.*
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The silicon-germanium ($Si_{1-x}Ge_x$) alloy is an exciting material from both technological and theoretical perspectives.[1] The possibility of band-gap engineering and the integration of fast analog circuits with the standard components using readily available commercial silicon technology is promising. From the point of view of applied theoretical physics, $Si_{1-x}Ge_x$ offers at least as much. The cost in energy of interchanging a Si atom and a Ge atom in $Si_{1-x}Ge_x$ is very small, which makes it an almost perfect random alloy. $Si_{1-x}Ge_x$ exists in many polytypes and the Ge concentration $x$ can be changed over a wide range. This work focuses on the electronic structure of vacancies in zinc blende $Si_{0.5}Ge_{0.5}$ (SiGe). The theory of vacancies in tetrahedrally coordinated covalent semiconductors can be qualitatively formulated in terms of a single-electron orbital model, the linear combination of atomic orbitals (LCAO).[2] Using computational methods described below, we find that the two possible monovacancies in SiGe behave qualitatively differently. The germanium vacancy ($V_{Ge}$) exhibits the negative-effective-$U$ effect, and the silicon vacancy ($V_{Si}$) exists in high-spin states.

Boguslawski and Bernholc[3] have studied segregation effects at vacancies in tetrahedrally coordinated alloys $Al_xGa_{x-1}N$ and $Si_{1-x}Ge_x$. They find that the chemical surrounding of the vacancy has a strong effect on the total energy. Every Ge neighbor decreases the total energy of the vacancy in $Si_{0.5}Ge_{0.5}$ by 0.25 eV, a direct consequence of the different energetic cost of the dangling bonds of Si and Ge. According to Boguslawski and Bernholc, the position of the vacancy triplet level $t_2$ is 0.3 eV above the valence band maximum (VBM), and its position is independent of the number of Ge neighbors to within 0.05 eV.

In this work, the electronic structure is calculated using the first-principles plane-wave pseudopotential method based on the density-functional theory. The total energy is minimized with respect to electronic and ionic degrees of freedom without any symmetry restrictions. The exchange-correlation functional of the many-body electron-electron interactions is described with the spin-compensated local-density approximation (LDA) or the local-spin-density approximation (LSDA).[4] For Si we have used carefully tested separable first-principles norm-conserving pseudopotentials with the nonlinear core correction.[5] The Ge pseudopotential was generated with the same procedure as the Si pseudopotential. The $3d$ electrons were incorporated into the pseudopotential core. The converged plane-wave cutoff for Ge pseudopotential was found to be 30 Ry. A 64 atom simple-cubic supercell (SC) is used in all the defect calculations. The Brillouin-zone (BZ) sampling was done using $\Gamma$ and $L$ points with equal weights.[5,6] The use of the periodic boundary conditions (PBC) in the SC approximation results in an artificial Coulomb interaction between a charged defect and its periodic images. The leading order of this contribution ($\Delta E_{PBC}$) decays as $L^{-1}$ with increasing linear dimension $L$ of the supercell. We have followed a scheme introduced by Makov and Payne, and included correction terms up to $O(L^{-5})$.[7] An average potential correction aligning the lowest valence bands ($s$-like states) at the $\Gamma$ point is used in the determination of the valence band maximum $E_{VBM}$ for charged-defect supercells.[8]

The formation energy of the vacancy $\Omega_f(V_i^{(q)})$ as a function of the electron chemical potential $\mu_e$ is calculated from the total energies as

$$\Omega_f(V_i^{(q)}) = E_D(V_i^{(q)}) - E_i^{\text{ref}} + q(\mu_e + E_{\text{VBM}}), \tag{1}$$

where $q$ is the charge state of the defect and $E_D(V_i^{(Q)})$ is the total energy of the supercell containing the vacancy $V_i^{(q)}$ ($i$ =Si,Ge). The reference energy $E_i^{\text{ref}} = E_{\text{SiGe(bulk)}} - \mu_i$ is the total energy of the perfect SiGe supercell minus the chemical potential of the missing atom. Since the calculated heat of formation for SiGe is 0.03 eV, the chemical potentials $\mu_i$ depend on the growth conditions only weakly.[9] All the reported values are calculated assuming Si-rich growth conditions, $\mu_{Si} = \mu_{Si(bulk)}$ and $\mu_{Ge} = \mu_{SiGe(bulk)} - \mu_{Si(bulk)}$.

The calculated local symmetries and the distances between atoms around the vacant site for the minimum energy configurations are shown in Table I. The electronic structure and the relaxation pattern of $V_{Ge}$ follows the Watkins LCAO model,[2,10] with inward breathing ($B$) mode and local sym-

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TABLE I. Formation energies and ionic relaxations of $V_{Si}$ and $V_{Ge}$ in SiGe. The $\Delta E_{PBC}$ is the contribution of the PBC correction in the formation energy $\Omega_f^{(q)}(\mu_e=0)$ (see Ref. 7). The relative volume change $V_{rel}=100(V-V_0)/V_0$ is presented, where $V$ and $V_0$ are the volumes of the tetrahedra formed by the four-next-nearest-neighbor (NNN) atoms of the relaxed and ideal vacancy, respectively. The NNN distances between four atoms surrounding the vacancy are given in the last column. For $D_{2d}$ symmetric configurations, the second entry in the NNN column gives the length of the short bonds between paired atoms, and in the $C_{2v}$ symmetric case, the last two entries give the lengths of inequivalent short bonds. The deviations of $V_{Si}^{(q)}$ from $T_d$ symmetry caused by the dispersion of the defect states are in parenthesis (see Ref. 11). The ideal theoretical NNN distance in SiGe is 3.88 Å.

| | $\Omega_f^{(q)}(\mu_e=0)$ [eV] | $\Delta E_{PBC}$ [eV] | Spin | Symmetry | $V_{rel}$ | NNN [Å] |
|---|---|---|---|---|---|---|
| $V_{Ge}^{2+}$ | 2.96 | 0.32 | NP | $T_d$ | −3.8 | 3.83 |
| $V_{Ge}^{1+}$ | 3.03 | 0.08 | NP | $D_{2d}$ | −18.1 | 3.68, 3.54 |
| $V_{Ge}^{0}$ | 3.03 | 0.00 | NP | $D_{2d}$ | −36.1 | 3.53, 3.07 |
| $V_{Ge}^{1-}$ | 3.28 | 0.05 | NP | $C_{2v}$ | −41.0 | 3.46, 3.43, 2.64 |
| $V_{Ge}^{2-}$ | 3.68 | 0.25 | NP | $C_{2v}$ | −44.8 | 3.39, 3.38, 2.56 |
| $V_{Si}^{2+}$ | 2.05 | 0.31 | NP | $T_d$ | 2.2 | 3.91 |
| $V_{Si}^{1+}$ | 2.12 | 0.08 | NP | $(T_d)$ | −10.3 | 3.74 (±0.03) |
| $V_{Si}^{0}$ | 2.26 | 0.00 | 1 | $(T_d)$ | −18.3 | 3.63 (±0.03) |
| $V_{Si}^{1-}$ | 2.55 | 0.09 | 3/2 | $T_d$ | −23.8 | 3.55 |
| $V_{Si}^{2-}$ | 3.10 | 0.32 | 1 | $(T_d)$ | −29.5 | 3.46 (±0.06) |
| $V_{Si}^{3-}$ | 3.80 | 0.71 | 1/2 | $(T_d)$ | −33.3 | 3.39 (±0.05) |
| $V_{Si}^{4-}$ | 4.68 | 1.28 | NP | $T_d$ | −36.4 | 3.34 |

metry breaking ($E$) mode relaxations as electrons are added to the defect. The ionization levels for $V_{Ge}$ are shown in Fig. 1. We notice that the charge state changes directly from a doubly positive to neutral at 0.03 eV above the VBM. The Coulomb repulsion $U$ of the electrons in the defect orbitals is exceeded by the gain from the splitting of the $t_2$ triplet and the formation of the pairing mode orbital. The resulting negative-effective-$U$ is given by $U_{eff}=\epsilon_D(0/+)-\epsilon_D(2+/+)=-0.06$ eV.

Unlike $V_{Ge}$, the occupation of the $V_{Si}$ defect follows Hund's rule (Table I). The exchange coupling energy overcomes the symmetry breaking Jahn–Teller (JT) effect, $V_{Si}$ remains $T_d$ symmetric for all the charge states[11,8] and the $t_2$ triplet level is not split. The spin effect is largest for $V_{Si}^{1-}$ with total spin $S=3/2$. The total energy of the spin-polarized (LSDA) calculation is 0.06 eV lower than the spin-compensated (LDA) calculation. The corresponding difference for $S=1$ spin states is 0.02 eV. The ionization level positions in Fig. 1 reflect the compensation of the Coulomb repulsion $U$ by first the breathing mode relaxation ($V_{Si}^{(1+)}$ and $V_{Si}^{(0)}$) and then by the spin alignment ($V_{Si}^{(1-)}$). Since the breathing mode distortion does not change and the energy gain from the spin alignment is small for the remaining charge states, the levels between negative charge states are roughly evenly spaced.

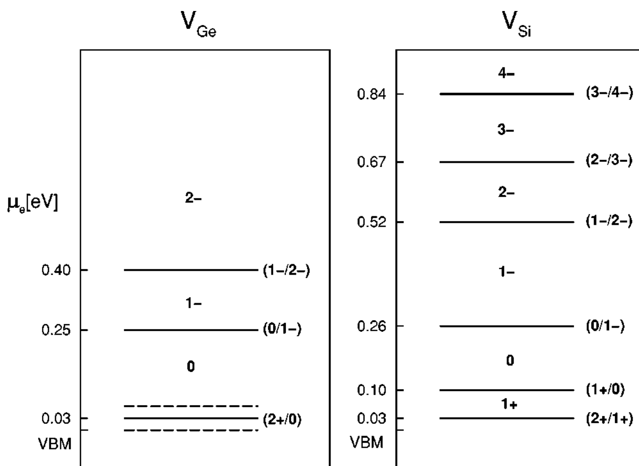


FIG. 1. Ionization levels $\epsilon_D(q/q')$ of $V_{Si}$ and $V_{Ge}$ with respect to the VBM in SiGe. Transition energies $\epsilon_D(0/+)$ and $\epsilon_D(2+/+)$ defining $U_{eff}$ are shown with dashed lines. The LDA eigenvalue gap for SiGe is 0.44 eV.

It is interesting to compare the present results with the recent calculations for the vacancy defects in SiC[8,12] and with the vacancies in elemental tetrahedrally coordinated materials C, Si, and Ge.[5,13,14] Let us use the simple version of the Schlüter model in order to estimate the relative magnitude of the pairing-mode JT distortion.[15] Following their notation, the JT energy associated with the pairing mode distortion $E$ is given by $E_{JT}=V_E^2/2k_E$, where the electron-phonon coupling $V_E=-\partial\epsilon/\partial Q_E$ describes how the energy of the pairing orbital $\epsilon$ changes as a function of the generalized coordinate $Q_E$. The corresponding force constant $k_E$ can be estimated from phonon frequency calculations.[16] The elastic constants for diamond carbon are roughly three times larger than for Si. That prevents the distortion for the $V_{Si}$ in SiC. However, the elastic constants of Si and Ge are nearly equal, and the argument given for vacancies in SiC does not suffice for vacancies in SiGe.

We can consider, for the purposes of the discussion, that the orbital energy of the pairing bond, in the attractive region of the potential, is essentially proportional to the overlap of the dangling bond orbitals $\epsilon-\epsilon(Q_E=0)\propto -E_b e^{-d_{ij}/R_{orb}}$.[17] Here $R_{orb}$ is some relevant length scale accounting for the size of the dangling $sp^3$ orbitals, and $E_b$ some energy scale related to the binding energy. The interatomic distance $d_{ij}$ is determined from the breathing and pairing distortions. We notice that the Si orbitals are more localized than the Ge orbitals, and the former have a larger binding energy than the latter. That implies a larger electron-phonon coupling, $V_E \propto E_b/R_{orb}$, and thus a larger driving force towards the JT distortion for $V_{Ge}$ compared to $V_{Si}$. Moreover, the next-nearest-neighbor (NNN) distance between the Si atoms around $V_{Ge}$ is smaller as compared to the atomic arrangement in a monovacancy in pure Si.[5] In particular, the 2+

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state exhibits a larger breathing mode distortion (NNN distance 3.92 Å) in pure Si than in SiGe (NNN distance 3.83 Å). This is in contrast to the larger lattice constant for SiGe. Although this could partly be a side effect due to the finite size of the supercell, we have noticed that the Si-Ge bonds are more polarized towards the $V_{Ge}$ as compared to the $V_{Si}$. This results in the higher electronic charge located inside the former by $\sim 0.25e$ for the $2+$ configuration, thus reducing its size. In any case, the direct consequence of the larger inward breathing mode relaxation is to enhance the formation of pairing bonds, which results in a larger JT energy.

In summary, we have characterized the vacancies in zinc blende SiGe lattice using *ab initio* total energy methods. We have rationalized our results in terms of a simplified model for vacancies. The germanium vacancy, surrounded by four silicon atoms, is found to closely resemble the vacancy in elemental silicon. It is an Anderson negative-effective-$U$ system, with the $(2+/0)$ transition located at 0.03 eV above the valence band. The description for $V_{Si}$ is qualitatively different. The electron-phonon coupling for the vacancy is smaller for $V_{Si}$, and the exchange-coupling energy overcomes the Jahn–Teller energy. It follows that the defect orbitals are filled according to Hund's rule.

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