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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 (Si1-xGe 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, Si1-xGe x offers at least as much. The cost in energy of interchanging a Si atom and a Ge atom in Si1-xGe x is very small, which makes it an almost perfect random alloy. Si1-xGe x exists in many polymorphs and the Ge concentration x can be changed over a wide range. This work focuses on the electronic structure of vacancies in zinc blende Si0.5Ge0.5 (SiGe). The theory of vacancies in tetrahedrally coordinated alloys 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 (VGe) exhibits the negative-effective-U effect, and the silicon vacancy (VSi) exists in high-spin states.

Boguslawski and Bernholc3 have studied segregation effects at vacancies in tetrahedrally coordinated alloys AlxGa1-xN and SixGe1-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 Si0.5Ge0.5 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 t2 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 Γ 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 (∆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 Γ point is used in the determination of the valence band maximum E_{VBM} for charged-defect supercells.8

The formation energy of the vacancy Ω ∆(V^{(q)}_i) as a function of the electron chemical potential μ_e is calculated from the total energies as

$$\Omega_i^{(q)} = E_i^{(q)} - E_i^{ref} + q(\mu_e + E_{VBM}).$$

where q is the charge state of the defect and E_i^{(q)} is the total energy of the supercell containing the vacancy V^{(q)}_i (i = Si,Ge). The reference energy E_i^{ref} = E_{SiGe(bulk)} - μ_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 μ_i depend on the growth conditions only weakly.9 All the reported values are calculated assuming Si-rich growth conditions, μ_{Si} = μ_{Si(bulk)} and μ_{Ge} = μ_{Ge(bulk)} - μ_{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 VGe follows the Watkins LCAO model,2,10 with inward breathing (B) mode and local sym-
symmetry breaking ($E$) mode relaxations as electrons are added to the defect. The ionization levels for $V_{\text{Ge}}$ 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 $U_{\text{eff}} = \epsilon_D(0/-) - \epsilon_D(2+/+) = -0.06$ eV.

Unlike $V_{\text{Ge}}$, the occupation of the $V_{\text{Si}}$ defect follows Hund’s rule (Table I). The exchange coupling energy overcomes the symmetry breaking Jahn–Teller (JT) effect, $V_{\text{Si}}$ 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 $V_{\text{Si}}^{1/2}$ 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 ($V_{\text{Si}}^{1+}$) and $V_{\text{Si}}^{0}$) and then by the spin alignment ($V_{\text{Si}}^{1-}$). 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.

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 $E_{\text{JT}} = V_{\text{JT}}^2/2E_F$, where the electron-phonon coupling $E_F = -\partial^2E/\partial Q^2$ describes how the energy of the pairing orbital $Q$ changes as a function of the generalized coordinate $Q_F$. The corresponding force constant $k_F$ 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 $V_{\text{Si}}$ 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 $\epsilon = \epsilon(Q_{F} = 0) \propto -E_P e^{-d_{ij}/R_{\text{orb}}}$.$^{17}$ Here $R_{\text{orb}}$ is some relevant length scale accounting for the size of the dangling $s^3$ orbitals, and $E_P$ 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, $E_F \propto E_P/R_{\text{orb}}$, and thus a larger driving force towards the JT distortion for $V_{\text{Ge}}$ compared to $V_{\text{Si}}$. Moreover, the next-nearest-neighbor (NNN) distance between the Si atoms around $V_{\text{Ge}}$ is smaller as compared to the atomic arrangement in a monovacancy in pure Si.$^{5}$ In particular, the 2 +
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 vacancy in SiGe as compared to the vacancy in pure Si. This results in the higher electronic charge located inside the Si vacancy, surrounded by four Si atoms, is found to closely resemble the vacancy in Si. The germanium vacancy, surrounded by four Si atoms, is found to closely resemble the vacancy in Si. Therefore, we have rationalized our results in terms of a simplified model of the valence band. The description for $V_{\text{Si}}$ is qualitatively different. The electron-phonon coupling for the vacancy is $V_{\text{Si}}$ and the exchange-coupling energy overcomes the Jahn–Teller energy. It follows that the defect orbitals are filled according to Hund’s rule.

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 $V_{\text{Si}}$ is qualitatively different. The electron-phonon coupling for the vacancy is smaller for $V_{\text{Si}}$, 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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7. G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995). For completeness, we report the values of parameters used in this work in connection with Eq. (17) in the reference. The static dielectric constant $\varepsilon = e^{4\pi \hbar}$ is 15.0, the Madelung constant $a$ for simple-cubic SC is 1.419 and the linear dimension $L$ of the supercell is 10.98 Å.
11. In supercell defect calculations the orbitals for the different $k$ points have usually the same fill factors assuming implicitly that the defect state does not present dispersion in $k$ space. In that sense, the perfect point. This will remain unchanged.