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Distortion of atoms around the neutral vacancy in a Si crystal

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Abstract. The single-particle electronic structure of a neutral lattice vacancy in a Si crystal is treated theoretically within the 16-atom supercell using the conventional tight-binding approximation. The physical mechanism leading to a spontaneous symmetric and tetragonal displacement of atoms surrounding a vacancy is discussed in detail. The elastic response of the lattice is calculated using the Keating valence force model applied to the cluster contained 441 atoms. The directions and amplitudes of atomic displacements are strongly symmetry-dependent. The amplitudes decrease with the distance R from the vacancy, approximately, as R^{-2}, independently of the distortion symmetry. The influence of the vacancy defects on the lattice parameter is considered and estimated.

PACS. 61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters – 71.55.Cn Elemental semiconductors

1 Introduction

The isolated lattice vacancy in silicon has been studied extensively [1–10] as a prototype for vacancies in other semiconductors. The properties of vacancy essentially depend on the positions of the nearby atoms. These positions are different from those for the perfect crystal. An example, which demonstrates the importance of relaxation of the nearby atoms is the neutral vacancy defect. There is a competition between the Coulomb interaction of two electrons in the unfilled t_2 level and the interaction of these electrons with the lattice. In the absence of an electron-lattice interaction, the lowest term would be $^3T_1$ with the total spin $S = 1$ since it corresponds to the lowest Coulomb repulsion energy. However, due to the remarkable strength of electron-lattice interaction (the Jahn-Teller tetragonal distortion) the resulting lowest term has the total spin $S = 0$. Since there is no the direct experimental evidence on the position of vacancy neighbors the theoretical studies are of great importance. In reference [3] the tetragonal type distortion was calculated by the Green's function method while in reference [5] this technique was used to determine the breathing type distortion. In references [9,10] the molecular dynamics technique was used to study the vacancy and vacancy-hydrogen defects. There is large difference between the results of references [3,9,10] concerning the amplitude of the tetragonal distortion. Therefore in this paper we present the results of the distortion studies based on the conventional tight binding technique. The method is easy in the application and the physical interpretation is very transparent. Generally, our results are in agreement with those obtained by the molecular dynamics method. We show that both the breathing and the tetragonal distortion are directed outward, with the amplitude of the tetragonal distortion being smaller than that of the breathing distortion. The more distant atoms also move due to the action of the nearest-neighbor interatomic forces. We estimate to which degree the defect-induced distortions influence the measurement of the lattice parameter.

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2 Methodology

To describe the relaxation around the vacancy site quantitatively we apply the Harrison theory [11] for the bonding properties of tetrahedrally coordinated solids. In this theory the total energy is expressed in terms of interaction between pairs of nearest neighbor atoms, *i.e.* in terms of the bond energy. The electronic bond energies of two $sp^3{-}sp^3$ hybrids directed against on two neighboring atoms are given as [11]

$$\varepsilon = \frac{1}{2}\left(\varepsilon_h^\alpha + \varepsilon_h^\beta\right) \pm q\sqrt{V_2^2 + \left(\frac{\varepsilon_h^\alpha - \varepsilon_h^\beta}{2}\right)^2} + \frac{2qV_2^2}{k \mid \varepsilon_h^\alpha + \varepsilon_h^\beta \mid}, \quad (1)$$

where the energy with the minus corresponds to the bonding state. In (1) $q = 2$ is the number of electrons per bond,

$\varepsilon_h^{\alpha,\beta} = (\varepsilon_s^{\alpha,\beta} + 3\varepsilon_p^{\alpha,\beta})/4$, where ε_s and ε_p are the free-atom energies for s and p states [9]. $V_2 = 4.373\hbar^2/md^2$, with m being an electron mass, determines the interaction between two sp^3-sp^3 hybrids [12]. The parameter k is only one fitting coefficient entering this theory. The equilibrium distance d at zero temperature is determined from the minimum of the Helmholtz free energy, *i.e.*, from the bond energy (1) supplemented by the zero-point stretching mode vibration energy for the Si–Si bond. Thus the equation for the determination of d is given as [12]

$$\frac{\partial\varepsilon}{\partial d} + \frac{\hbar}{4\sqrt{\mu}} \frac{\dfrac{\partial^3\varepsilon}{\partial d^3}}{\sqrt{\dfrac{\partial^2\varepsilon}{\partial d^2}}} = 0. \tag{2}$$

The third derivative of ε accounts for the anharmonic effect. From the requirement that calculated and experimental bondlength are equal each other we find $k = 1.455$. From equation (1) one can find the stretching-type vibration of atoms entering the bond. The frequency of the stretching mode is $\omega = \sqrt{k_h/\mu}$, where $k_h = \partial^2\varepsilon/\partial d^2$ is the harmonic force constant and μ is the reduced mass. For the Si bond we have obtained $k_h = 8.37$ eV/Å^2. This value was obtained without involving any adjustable parameters and it will be used later for the determination of the relaxation amplitude around the neutral vacancy. The average vibrational energy is $\hbar\omega = 409$ cm^{-1}.

To describe the vacancy states in the Si crystal, we use the 16-atom supercell (having the shape of the elementary unit cell) with periodic boundary conditions. We take the matrix elements at the vacancy site and the interaction matrix elements with the nearest neighbors equal to zero. Using a supercell of the same size for the perfect Si crystal, we obtain the electronic levels at the Γ, L, and X points in the Brillouin zone (see right side of Fig. 1) as they result from conventional band-structure calculations. The energy levels of the perfect and imperfect supercell have the same common energy reference.

The electronic states of imperfect cluster were calculated for the perfect crystal atomic positions. However, the system is unstable with respect to a symmetric displacement (the breathing mode Q_A) and at least with respect to one asymmetric displacement (Jahn-Teller distortion) of the neighboring atoms of a vacancy site. The neutral vacancy ground state is an orbital triplet. The possible asymmetric distortions for an orbital triplet have T_2 or E symmetry. The experimental results [1] show that the asymmetric distortion is of E symmetry, and we will therefore only consider this tetragonal distortion mode Q_E which has two components Q_u and Q_v. The driving forces to the new equilibrium position can be obtained by expanding in powers of the normal modes Q_i (*i.e.* Q_A and Q_E) the potential due to the nearest neighbors of a vacancy site. For reasons of symmetry, the symmetric and tetragonal distortions and their effects on the t_2 vacancy electronic state can be represented by the following equivalent operator [14]

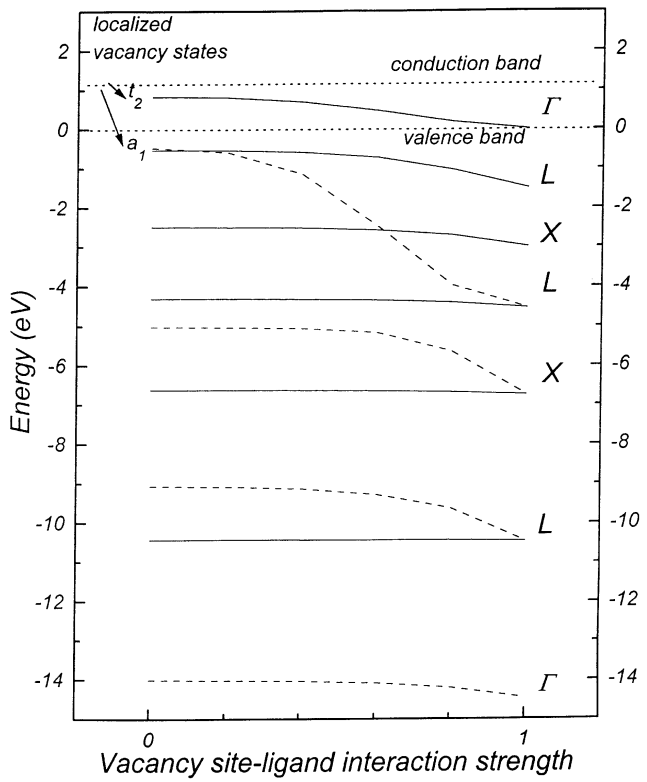

Fig. 1. One-electron energies of the a_1 (dashed) and t_2 (solid) symmetry for a silicon supercell as a function of the vacancy site-ligand interaction strength. The zero on the horizontal axis reflects the situation that all matrix elements on a vacancy site and interaction integrals with nearest neighbors disappear. The one on this axis corresponds to perfect crystal states. We show the corresponding evolution of the perfect crystal states when the strength of interactions between the vacancy site and nearest neighbor is reduced step by step. The vacancy band gap state t_2 occupied by two electrons arises mainly from the state at the point Γ.

$$\varepsilon = -V_A Q_A I + \frac{k_A}{2} Q_A^2 + V_E(Q_u U_u + Q_v U_v) + \frac{k_E}{2}(Q_u^2 + Q_v^2), \tag{3}$$

where V_A and V_E are the electron-lattice coupling coefficients and k_A and k_E the force constants entering the elastic energy terms associated with the corresponding distortion. I is a unit matrix while U_u and U_v are electronic operators [14]. Because the operators U_u and U_v are diagonal within the t_2 functions, they are eigenstates of (1) for arbitrary Q_u and Q_v. From equation (3) it follows that the breathing mode distortion reaches a stable energy minimum at $Q_A = V_A/k_A$. The energy gain for this distortion is $E_A = V_A^2/2k_A$. There are three equivalent tetragonal distortions along each of the cubic axes. Contrary to the breathing mode distortion, the tetragonal distortion splits the t_2 triplet into the lower singlet and the upper doublet. In the Q space the stable distortion along

Table 1. Comparison of calculated parameters by Baraff *et al.* [3], Scheffler *et al.* [5], and those in this work for the neutral vacancy in Si. $\varepsilon(t_2)$ is the position of the vacancy level with respect to the valence band, k_A, k_E are the force constants and Q_A, Q_E are the displacement coordinates for the breathing and tetragonal distortion, respectively. Figures in brackets correspond to situation without relaxation of more distant atoms (see text).

Parameter	[3]	[5]	this work
$\varepsilon(t_2)$, [eV]	0.7	0.76	0.74 (0.835)
k_A, [eV/Å^2]	7.5	29±12	7.19 (11.6)
k_E, [eV/Å^2]	14.8	-	26.9 (46.4)
Q_A, [Å]	0.1*	0.11	0.15 (0.093)
Q_E, [Å]	0.3	-	0.031 (0.018)

* Adopted by analogy with the (111) surface.

the z axis is at $Q_u = V_E/k_E$ and $Q_v = 0$. The energy of the singlet at this distortion is reduced by the Jahn-Teller energy $E_{\rm JT} = -V_E^2/2k_E$. When the coupling coefficients $V_{A(E)}$ and the force constants $k_{A(E)}$ are known, it is possible to determine the distortions and the corresponding stabilization energies.

3 Result of calculations

To find the electronic levels of the perfect Si supercell, we use the interaction matrix elements of reference [13] instead the matrix elements expressed in terms of the Harrison universal parameters η. We have slightly changed the interaction matrix element given in [13] to fit better the experimental energies at points Γ, L and X near the region of the forbidden energy gap. They are: $V_{ss} = -9.13$ eV, $V_{sp} = 3.46$ eV, $V_{xx} = 1.7$ eV, and $V_{xy} = 4.7$ eV. Thus the matrix elements partly account for more distant interaction. The diagonal matrix elements entering the corresponding secular equation are the free atomic eigenvalues ($\varepsilon_{3s} = -13.55$ eV and $\varepsilon_{3p} = -6.52$ eV). Figure 1 shows how the vacancy-occupied states arise from perfect crystal states when the corresponding matrix elements are stepwise reduced. The result of our calculation is that the one-electron localized level of t_2 symmetry is produced in the forbidden gap and a level of a_1 symmetry is created near the top of the valence band. The level positions with respect to the valence band for the infinite crystal are $\varepsilon(t_2) = 0.835$ eV and $\varepsilon(a_1) = -0.48$ eV. The respective $\varepsilon(t_2)$ level position calculated in references [3,5] are summarized in Table 1. The wave-function coefficients γ_i^2 for each (111) neighbor nearest to the vacancy are given in Table 2.

It can be seen that the localization of the wave function on the four nearest atoms for the t_2 and a_1 states is 65% and 67%, respectively. It was noted in reference [2] that the γ_x^2, γ_y^2 and γ_z^2 coefficients on a given near-neighbor atom are not equal. If we consider the localized state to be made up of "dangling" orbitals from the neighboring

Table 2. The wave-function coefficients γ_i^2 for each four nearest neighbors of the vacancy.

	a_1	t_{2x}	t_{2y}	t_{2z}
γ_s^2	0.0511	0.0277	0.0277	0.0277
γ_x^2	0.0387	0.1165	0.0097	0.0097
γ_y^2	0.0387	0.0097	0.1165	0.0097
γ_z^2	0.0387	0.0097	0.0097	0.1165

atoms, these orbitals do not point into the center of the vacancy but are rather tilted in a somewhat different direction. This is not in agreement with the usual sp^3 physical chemist's concept. We shall comment on this feature in Section 5.

The Harrison theory predicts that matrix elements depend on the interatomic distance as $1/d^2$. Imposing the Q_A distortion on the four vacancy neighbors we find that t_2 gap level depends linearly on displacement. Hence, the vacancy neighbors will move from their perfect crystal equilibrium position. Imposing the same distortion on the perfect supercell we find that s and p states at the point Γ do not exhibit linear dependence on Q_A. This is so because they are average of the electronic interaction energy taken with the same weight over all pairs of atoms in the supercell. Due to the distortion Q_A some of the bondlength elongates and some of them shortens and the energy terms linear in displacements cancel each other. Thus the vacancy states originated from the states at the point Γ can be used for the calculation of the electron-lattice coupling coefficients V_A. Taking into account that the t_2 defect level is occupied by 2 electrons we find from the slope of the average electronic energies $V_A = 1.08$ eV/Å. The breathing mode force constant is given as $k_A = 4k_h/3 = 11.6$ eV/Å^2. From equation (3) we find the radial displacement of the vacancy neighbor equals to 0.093 Å.

Contrary to the symmetric distortion Q_A, the tetragonal distortion Q_E influences only the p-type Γ state. The t_2 defect state is split by the tetragonal distortion into a lower energy a_1 state and a higher doublet e. We determined the slope V_E of the a_1 state with respect to the average energies of the a_1 and e states to ensure that the trace of tetragonal distortion is equal zero. We found that $V_E = -0.84$ eV/Å. The force constant for the tetragonal mode is $k_E = 16k_h/3 = 46.4$ eV/Å^2. This leads to the equilibrium geometry for the tetragonal distortion along the z-axis at $Q_u = 0.018$ Å and $Q_v = 0$.

As it was already demonstrated in reference [3] the inclusion of the relaxation of more distant atoms reduces the k_A and k_E force constants and, hence, affects the equilibrium position of four vacancy neighbors. In reference [3] k_A and k_E were determined using the Keating valence-force model [3,15] in which all interatomic forces are resolved into nearest neighbor bond-stretching and bond-bending forces. Two parameters entering this model are the bond-stretching force constant ($\alpha = k_h/3 = 2.9$ eV/Å^2) and the bond-bending force constant $\beta = 0.72$ eV/Å^2. We determined the β from the fit to the phonon LA and LO

dispersion curves (direction $\Gamma - X$). To obtain k_A, the distortion Q_A was imposed on the four neighbor atoms nearest to the vacancy. The other atoms were allowed to relax freely until the elastic energy E_t reaches the minimum. Then the force constant is determined as $k_A = 2E_t/Q_A^2$. In their calculation Baraff *et al.* [3] use a cluster containing a vacancy site and up to 10 atomic shells (99 atoms) around the vacancy. We repeated their calculations taking a cluster containing a vacancy site and 21 atomic shells (441 atoms). We obtained that k_A is reduced due to relaxation by 38% and, thus the radial displacement of vacancy neighbors increases up to 0.15 Å. The force constant for the tetragonal mode with account for relaxation is reduced by 42% and the corresponding equilibrium distortion is $Q_u = 0.031$ and $Q_v = 0$ Å.

In Table 1 we compare the results of this calculation with those in references [3,5]. In reference [5] the gradient of the total energy on the four nearest neighbors of the Si vacancy as a function of the breathing distortion was calculated by self-consistent method. The long-range deformation energy was included *via* a semiempirical model with parameters taken from reference [3]. Only the breathing mode distortion was determined. In reference [3], the breathing distortion was not determined. In analogy to the Si(111) surface, an outward distortion of 0.1 Å was assumed for the neutral vacancy. The tetragonal mode distortion was directly calculated there by self-consistent Green's-function technique.

In recent molecular dynamic study of the vacancy-hydrogen complexes in Si crystals [9,10] was calculated the position of the four neighbors to the vacancy site using 64 atoms supercell. The determined there directly net displacement of each Si atoms was 0.12 Å. Since vectors of the breathing and tetragonal mode displacements are perpendicular to each other and, in the linear electron-lattice coupling approximation, the symmetric and the asymmetric distortion takes place independently of each other and simultaneously the net displacement is given as $Q = \sqrt{Q_A^2 + Q_E^2}$. Thus net displacement calculated in references [9,10] is between our value $Q = 0.095$ Å when only four atoms relax and the value 0.153 Å for the case when relaxation of more distant is account for.

4 Defect-related relaxation and the lattice parameter

A finite amount of energy is required to form a vacancy so that a solid with vacancies has a higher internal energy than one without. One would therefore expect that, in equilibrium, a solid would tend to become vacancy-free. This is not so due to the "action" of entropy. At a finite temperature T, the equilibrium state of a crystal is determined by minimizing the Gibbs free energy $F = H - TS$, where H is the vacancy formation enthalpy and S is the vacancy formation entropy. At equilibrium, the vacancy concentration N_{V} in the crystal is given by the expression

$$N_{\mathrm{V}} = N_{\mathrm{Si}} \mathrm{e}^{S/k - H/kT}, \tag{4}$$

where $N_{\mathrm{Si}} = 5.43 \times 10^{22}$ cm^{-3} is the density of lattice sites in Si and k is the Boltzmann constant. The vacancy concentration increases as the temperature increases. This is due to the fact that the vacancies increase the disorder (the number of ways of selecting which atomic site will be vacant). The increase in internal energy due to vacancies is compensated for by the associated increase in entropy. In reference [17], the formation enthalpy of the neutral vacancy was determined from positron annihilation measurements $H = 3.6 \pm 0.2$ eV, and very rough estimations yielded S/k in the range from 6 to 10. Using these values ($S/k = 6$), equation (4) yields $N_{\mathrm{V}} \approx 7 \times 10^{-36}$ cm^{-3} at $T = 300$ K and $N_{\mathrm{V}} \approx 2 \times 10^{13}$ cm^{-3} at $T = 1500$ K. These estimations furnish remarkably smaller N_{V} than a detectable concentration of vacancies which was estimated [18] to be of the order of 5×10^{15} cm^{-3} at $T = 1220$ K. The vacancy concentration predicted on thermodynamics base is smaller than the vacancy concentration caused by the technological process.

The knowledge of vacancy-induced lattice distortions is very important for a more accurate determination of the Avogadro constant from Si crystal properties. This opens up possibilities of a new definition of the unit of mass, the kilogram [19]. The Avogadro constant N_{A} is expressed as $N_{\mathrm{A}} = M/\rho v$, where M is the molar mass, ρ the crystal density and v the atomic volume. Each of these values is determined by an independent measurement. Therefore the knowledge of the atomic volume (hence a lattice parameter) is crucial for the determination of N_{A}.

The electron-lattice interaction causes the volume change of the atom cage around the vacancy site and it influences the positions of more distant atoms. Figures 2 and 3 show the relative displacement amplitudes for the breathing and for the tetragonal distortion modes, respectively, as it was determined in Section 3. The displacement amplitudes decay "radially", approximately, as $1/R^2$. The relaxation around the defect plays a similar role as electronic screening around a charged defect. The screening effect reduces the extent of the electric field and similarly the relaxation reduces the displacements of distant atoms around the defect. The symmetric distortion mainly propagates along zig-zag atomic chains. If the displacement of each atom in the first shell is, say 0.1 Å then, as it is seen in Figure 2, each atom in the second shell (atoms 6 to 17) experiences displacement 0.4×0.1 Å $= 0.04$ Å in a direction other than that of the first neighbors. The change of the interatomic distance between atoms from the second and the third shell is smaller than $0.1 - 0.04 = 0.096$ Å because the amplitudes should be projected along the line connecting the particular atoms. In the case of the tetragonal distortion, the particular atoms in a given shell can show the different displacement amplitudes.

The influence of defects on the lattice parameter can be measured in the X-ray lattice spacing comparator, where the lattice parameter of unknown samples is measured with respect to a reference crystal. When both sample have a different interatomic distance d, the angular variation of the diffraction lines can be observed. The ratio $\Delta d/d$ can thus be measured with an accuracy of up to

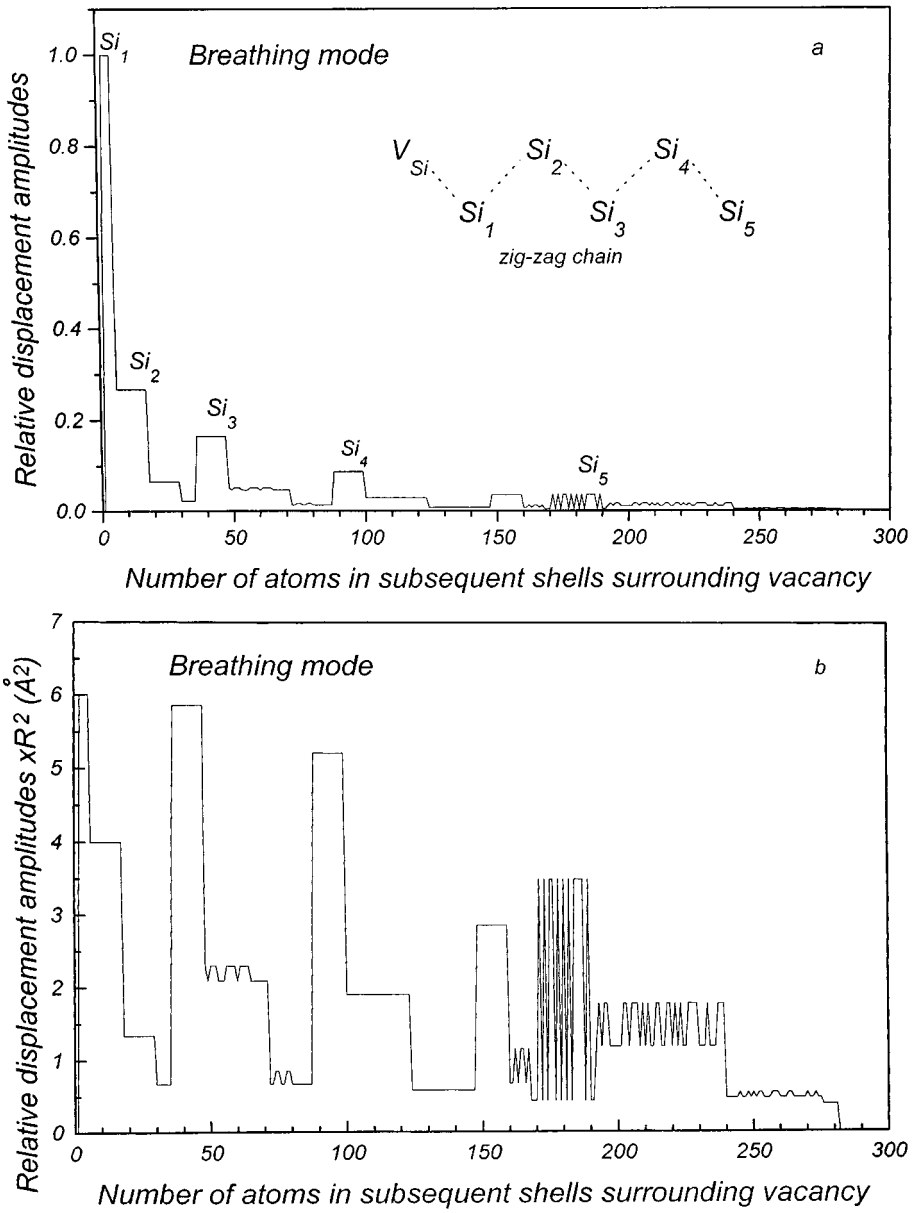

Fig. 2. (a) Relative displacement amplitudes of atoms in successive shells surrounding a vacancy. A breathing mode distortion of amplitude 1 is imposed onto the four nearest neighbors, *i.e.* the (111) shells. All other atoms are allowed to relax freely within the Keating force model with force constants $\alpha = 2.9$ eV/Å^2 and $\beta = 0.72$ eV/Å^2. The largest displacement amplitude is along zig-zag chains. (b) Relative relaxation amplitudes multiplied by R^2, where R is the distance of the atoms from the vacancy. The amplitudes decrease faster than R^{-2}.

1.0×10^{-9} [20]. The Si crystal containing the point defects (vacancies, impurities) can be considered as a strongly dilute alloy of foreign constituents among Si atoms. An example of this is Ge_xSi_{1-x}, where x is the concentration of the dissolved Ge atoms. The Bragg X-ray diffraction averages the influence of foreign atoms on the lattice constant over many diffraction surfaces. The average interatomic distance $d_{\rm av}$ between two atoms in alloy can be determined statistically as

$$d_{\rm av} = x^2 d_1 + 2x(1-x)d_{12} + (1-x)^2 d_2, \qquad (5)$$

where x^2 is the probability that two nearest lattice sites are occupied by Ge atoms. Similarly, $2x(1-x)$ is the probability that two neighboring sites are pair Ge–Si or Si–Ge atoms. Here, in the nearest-neighbor approximation, the d_1 is the equilibrium distance between Ge–Ge pairs in the perfect Ge crystal and d_2 is the distance between Si–Si pairs in perfect Si crystal. d_{12} is the unknown distance between Ge–Si pairs in alloy. Taking into account that $x = N_1/N$, where N_1 is the number of Ge atoms distributed among N lattice sites in the Si crystal, the above

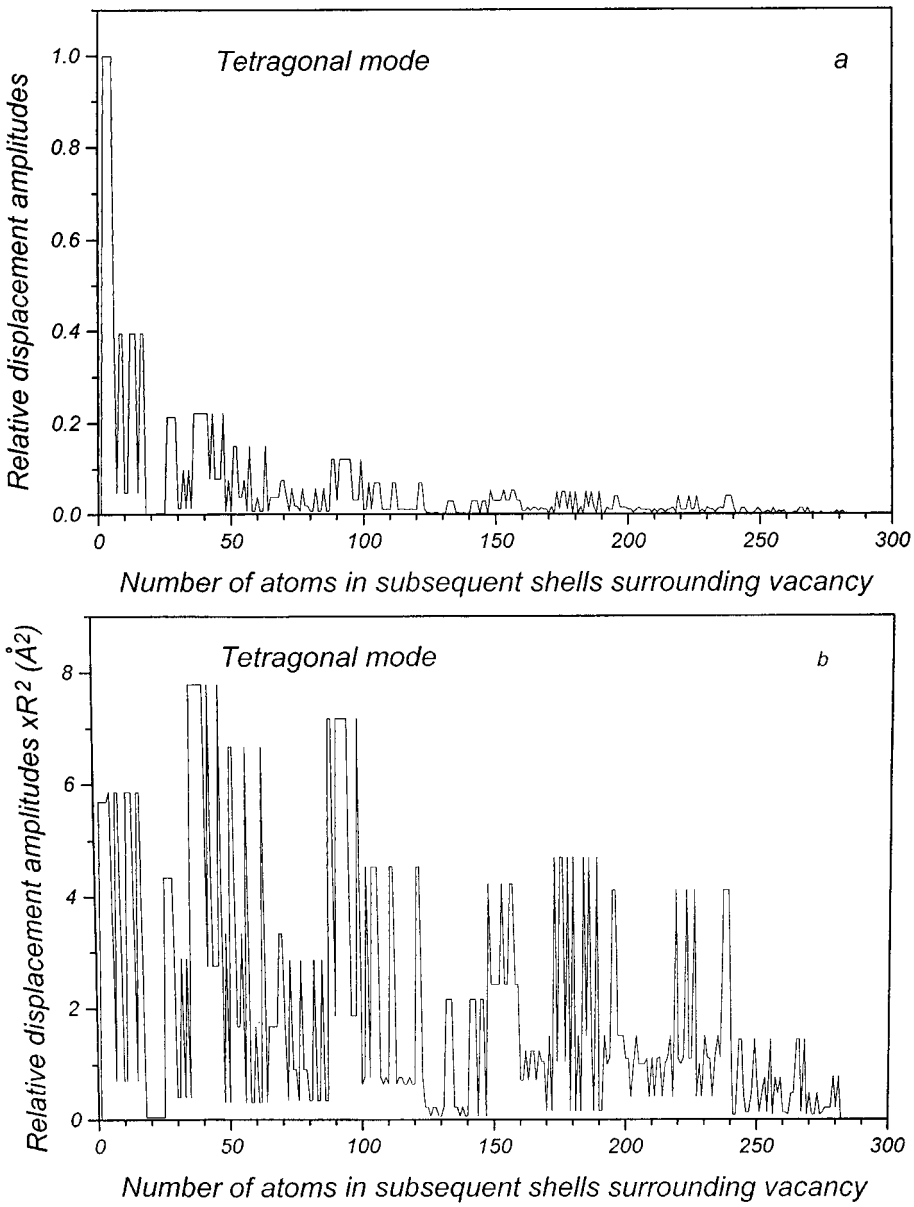

Fig. 3. (a) Relative relaxation amplitudes of tetragonal distortion of amplitude 1 imposed on nearest vacancy neighbors along the z-axis. Note that atoms within a given shell (except that of the four nearest neighbors) have different amplitudes. (b) Relative relaxation amplitudes multiplied by R^2, where R is the distance of the atoms from the vacancy. The amplitudes decrease faster than R^{-2}.

equation can be rewritten as

$$\frac{\Delta d}{d_2}N = \frac{d_{\rm av} - d_2}{d_2}N = N_1\left(\frac{d_1 - 2d_{12} + d_2}{d_2}\frac{N_1}{N} + 2\frac{d_{12} - d_2}{d_2}\right). \quad (6)$$

If in the last equation $\Delta d/d_2$ is determined by X-ray diffraction, then d_{12} can be calculated directly. In such an estimation, it will be sufficient to take into account only the last term in brackets, *i.e.* $2(d_{12} - d_2)/d_2$. The other terms are small due to the factor N_1/N. If $d_{12} = (d_1 + d_2)/2$ is assumed then $d_{\rm av}$ as given by equation (5) depends linearly on the concentration x. This approximation is known as the Vegard rule.

Using the above equation, Δd can be estimated for the vacancy. We assume that vacancies exist as separate point defects, *i.e.* $d_1 = 0$, $d_{12} = A + d_2$ and $d_2 = d = 2.36$ Å. Taking $N_1 = N_{\rm V} = 10^{15}$ and assuming $A = 0.25$ Å

$$\frac{\Delta d}{d} = \frac{2A}{d}\frac{N_{\rm V}}{N_{\rm Si}} \approx 4 \times 10^{-9} \quad (7)$$

is obtained. The estimation based on equation (7) assumes a homogeneous distribution of displacements (deformation) among atoms around a vacancy. This can be seen in the following direct estimation. The relative

deformation of a single bond length around a vacancy is A/d. In crystal there are $N_{\rm Si}/2$ such single bonds and $N_{\rm Si}/2N_{\rm V}$ of them are related to one vacancy. Therefore the average relative displacement is $(A/d)/(N_{\rm Si}/2N_{\rm V})$, and this is the same result as those of equations (5–7).

Now we estimate the $\Delta d/d$ taking the relaxation into account. We allow for the relaxation effect assuming that in a crystal 1 cm^3 in size the $N_{\rm V}$ vacancies are distributed homogeneously and that every vacancy with surrounding atoms occupies a sphere of the radius $R_{\rm V}$ which can be determined from the condition $4\pi R_{\rm V}^3/3 = N_{\rm V}^{-1}$. The average atomic displacement amplitude $\bar{A}$ within a sphere is given as

$$\bar{A} = \frac{A\int_d^{R_{\rm V}}(d/r)^2{\rm d}V}{(4/3)\pi R_{\rm V}^3} \approx \frac{3Ad^2}{R_{\rm V}^2}\,. \tag{8}$$

The relative interatomic distance change is the ratio of the average amplitude inside the sphere over the radius $R_{\rm V}$. Assuming $A = 0.25$ Å we obtain

$$\frac{\Delta d}{d} = \frac{\bar{A}}{R_{\rm V}} = 4\pi A d^2 N_{\rm V} \approx 2\times 10^{-8}. \tag{9}$$

We see that a model allowing for relaxation gives larger $\Delta d/d$ than a model of homogeneous distribution of the displacement amplitude A but Figures 2 and 3 show that in reality, displacement amplitudes decrease a bit faster than $1/R^2$. Therefore equation (9) gives upper limit of the $\Delta d/d$.

5 Discussion and conclusions

Messmer and Watkins [2] noted that localized t_2 orbitals do not point into the center of the vacancy because the coefficients γ_i^2 by p_x, p_y and p_z are not equal (see Tab. 2). The tilt of t_2 orbitals was explained by the close proximity of the level to the valence-band edge. This question was also briefly mentioned in reference [3]. We shall give a more general explanation of this fact. The pointing of the defect t_2 orbitals into the center of the vacancy assumes expansion of these orbitals in terms of the sp^3 bond orbitals. In tetrahedral coordinated lattices, the sp^3 bond orbitals are directed along lines between atoms. For example, the sp^3 orbital along (111) is $sp^3_{(111)} = (s + p_x + p_y + p_z)/2$, and along $(-1-11)$ it is $sp^3_{(-1-11)} = (s - p_x - p_y + p_z)/2$. The average value of atomic Hamiltonian for any bond orbital is $(\varepsilon_{3s}+3\varepsilon_{3p})/4$. They are orthogonal with respect to themselves. However, there is one basic difference between the s, p_x, p_y, p_z functions and the sp^3 bond orbitals. The latter are not eigenfunctions of the atomic Hamiltonian since the off-diagonal matrix element on a given atom, say between $sp^3_{(111)}$ and $sp^3_{(-1-11)}$ is $(\varepsilon_{3s} - \varepsilon_{3p})/4$. In an ordinary tight-binding scheme (also based on the use of point symmetry of particular atomic site), the atomic functions are the basis for the perturbation calculation where the perturbation are the interatomic integrals. The sp^3 bond orbitals cannot form such a basis because they have nonzero off-diagonal matrix elements (zero-order matrix elements) on a given atomic site. Generally, the tight-binding functions cannot be expressed as a linear combination of sp^3 bond orbitals since the latter are not eigenfunctions of a zero-order atomic Hamiltonian. This explains, discussed in reference [2], the tilt of the defect t_2 orbitals from the vacancy site direction. We note (see Tab. 2) that the a_1 defect function contains equal portions of the p_x, p_y and p_z on the neighboring atoms. This follows from the symmetry requirement and it does not imply that the a_1 function can be expressed in terms of sp^3 orbitals.

In neutral vacancy defect problem we have competition between two interactions. One is the Coulomb repulsion between two electrons in the degenerate t_2 orbitals, the other is the electron-lattice interaction with breathing and asymmetric modes. The two electrons can be shared among t_2 triplet components in a different way. This leads to many electron terms. The lowest in energy is the term ^3P with the total spin $S = 1$ and the orbital momentum $L = 1$. The repulsion energy between two electrons in this term is $F_0 - 5F_2$, where F_i are the Slater parameters. There are another two terms ^1D and ^1S with a total spin $S = 0$, and their repulsion energy is $F_0 + F_2$ and $F_0 + 10F_2$, respectively. It was found experimentally [1] that neutral vacancy is not active in magnetic resonance, *i.e.* the total spin of the ground state is $S = 0$. Therefore, in such a case, the energy gain due to coupling to the tetragonal mode exceeds the Coulomb repulsion energy. This result can be explained by the remarkable spatial extent of the t_2 wave function, 65% of which is located on the four Si neighbors to the vacancy. The F_2 integral which determines the relative energies between the terms is then strongly reduced. The Coulomb correlation energy in such extended defect like neutral vacancy is quenched by the electron-lattice coupling. This is a reason why one-electron theory gives a reasonable amplitude of the atomic displacements around vacancy as well as the position of the vacancy level in the energy gap. Recently [8], the parameter-free calculations were performed for the negatively charged Si vacancy. They supplied the breathing and the Jahn-Teller distortions around vacant site and also confirmed the validity of one-electron approximation for the extended defect.

There is no confirmed knowledge of the displacement amplitudes around the neutral vacancy. In reference [9] was reported the net displacement 0.12 Å of four neighbors without separation into the symmetric and tetragonal displacements. Our value for the net displacement is 0.093 Å when more distant atoms relaxation is ignored and 0.153 Å when it is accounted for. The tetragonal displacement calculated in reference [3] (0.3 Å) is larger than assumed there symmetric displacement (0.1 Å) and it is larger an order of magnitude than our result (0.031 Å). Such large tetragonal distortion implies that isolated neutral vacancy is a very stable defect. However, on other hand it is believed that neutral vacancies form the vacancy – hydrogen complexes [9,10]. In such a case the hydrogen – Si atom bond is formed and the tetragonal

distortion is remarkably quenched. In fact, the hydrogen atom can induce rebonding where the sp^3 bond is transformed into one p_z pointing to the vacancy position and three sp^2 bonds interacting with sp^3 bonds on the second shell. The calculated minimum energy of such sp^2-sp^3 bond interaction is obtained when vacancy neighbors are displaced from theirs perfect crystal positions by 0.25 Å. One of the hydrogen-related frequencies observed in infrared spectroscopy, 1838.3 cm^{-1} [16], can be explained by the binding of hydrogen to the p_z bond pointing to the vacancy. For this frequency we obtained the value of 1835.1 cm^{-1} at 0 K.

There are two main directions of relaxation of atoms around a neutral Si vacancy. The influence of the trigonal distortion on the t_2 state is similar to the effect of the tetragonal distortion. Both distortions split the t_2 level into the singlet a_1 and the doublet e. We have estimated the electron-lattice coupling coefficient for the trigonal distortion. It is around three times smaller than the corresponding coefficient for the tetragonal distortion. Since the operator for trigonal coupling has no diagonal elements within the eigenstates of tetragonal distortion, the trigonal distortion is quenched in the first order of perturbation theory. The force constants k_A and k_E estimated with regard to free relaxation are around 40% smaller (see Tab. 1). Since bond stretching constant $\alpha = k_h/3$ is greater than bond bending constant β the stretching forces are mainly responsible for the relaxation and, as a result, the distortion diffuses along the zig-zag chains, preserving a symmetry for a particular mode. We find that the displacement amplitudes decrease with the distance R from the vacancy site, approximately, as $1/R^2$. The relaxation around vacancies influence the lattice parameter. The estimation of this influence is given by two independent ways. A similar type of the displacements propagation was found for some substitutional defects [21]. Their influence on the lattice parameter can be roughly estimated using the results for the vacancy provided their concentration is known with respect to the vacancies.

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