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Theoretical calculation of the electron-capture cross section due to a dangling bond at the Si(111)-SiO$_2$ interface

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Using an accurate formulation of carrier capture assisted by phonons [D. Goguenheim and M. Lannoo, J. Appl. Phys. **68**, 1059 (1990)], we perform a complete theoretical calculation of the electron-capture cross section σ due to a dangling bond at the Si(111)-SiO$_2$ interface (the so-called P_{b0} center). In order to calculate electron-phonon coupling terms, we describe this defect with a tight-binding cluster model in which, in spite of its simplicity, the interatomic forces found on the trivalent silicon atom for the three charge states of the dangling bond reproduce the results of more developed models. This allows the calculation of the coupling parameters with a good accuracy. Sums over phonon normal modes are evaluated using Green's-function techniques. Finally, we derive numerical values of σ for the P_{b0} center, study its dependence on temperature, and compare our results with experimental values.

I. INTRODUCTION

The dangling bond (called the P_b center) is the major defect present in silicon metal-oxide-semiconductor (MOS) devices, at the interface between bulk Si and SiO$_2$, especially in the case of as-oxidized oxide samples. Even if it can be passivated by a postoxidation thermal anneal, it is believed to be responsible for the two peaks observed in the interface-state density of Si(111) MOS devices by several experimental techniques at $E_v+0.3$ eV and $E_c-0.3$ eV,[1,2] which correspond to the $(+\rightarrow 0)$ and the $(0\rightarrow -)$ transitions of the dangling-bond charge states, respectively. It is also a subject of great interest, which has led to much theoretical work, some of which predict a negative-U center,[3,4] in contradiction to experimental evidence. Moreover, since the P_b center is the basic defect at the Si-SiO$_2$ interface, it plays a major role in radiation-induced or high-field stress-induced interface states,[5] and an accurate knowledge of its electronic properties is needed in order to study P_b-center generation by such ionizing phenomena.[6]

We have recently developed an accurate theoretical formulation of carrier electron capture assisted by phonons, leading to a compact formula for the electron-capture cross section valid over the full temperature range.[7] This approach is quite general and enables applications to specific cases without drastic approximations, especially concerning the strength of the coupling between the defect and the lattice. Thus the aim of our work is, using this formulation, to derive numerical values for the electron-capture cross section due to a dangling bond at the Si(111)-SiO$_2$ interface (P_{b0} center) and to compare them with experimental data. The reason for the choice of the P_{b0} center to illustrate the general calculation of Ref. 2 is the existence of an exact knowledge of the microscopic structure of this defect, which enables us to use a realistic cluster model, despite the fact that it is an interface defect and that it may lead to further complications.

In Sec. II we briefly recall the basis of the calculation, especially the spirit of the static approximation, and detail the general expression induced by the model. In Sec. III we express the coupling between the lattice and the electronic system and we calculate sums over normal-mode frequencies involved in the formulation with the use of a Green's-function technique. In Sec. IV we first describe the tight-binding cluster model used for the trivalent defect at the Si(111)-SiO$_2$ interface. Then we detail the way in which to evaluate the electronic coupling terms in the static approximation and apply the method to the dangling bond. We validate our approach by showing the concordance between the results of the forces on the trivalent silicon atom obtained in our cluster model and more involved calculations. In Sec. V we derive numerical values of the electron-capture cross section for the P_{b0} center, study its dependence on temperature, and compare it to experimental values.

II. GENERAL FORMULATION OF THE ELECTRON-CAPTURE COEFFICIENT

The electron-capture cross section σ is related to the electron-capture coefficient c by

$$\sigma=\frac{c}{v_{\text{th}}}, \tag{1}$$

where v_{th} is the average thermal velocity of a carrier, given in the effective mass (m^*) approximation by

$$v_{\text{th}}=\sqrt{8kT/\pi m^*}. \tag{2}$$

We wish to point out the fact that the actual physically meaningful quantity is the electron-capture coefficient and that the concept of the electron-capture cross section is arbitrarily introduced by Eq. (1). The complete calculation of the electron-capture coefficient c has been developed in Ref. 7. Here we just wish to recall the main results and to clarify the meaning of various terms.

A. Basis of the calculation

We work in the spirit of the Born-Oppenheimer approximation, which separates the electronic motion ψ from the nuclear vibrational motion χ in the total wave function Φ:

$$\Phi=\psi\chi \ . \tag{3}$$

We consider the capture of a conduction-band electron by a deep level associated with a defect in the semiconductor. We start with an initial delocalized state $\Phi_{in}=\psi_i\chi_{in}$ corresponding to the electron in the conduction band (ionized defect) and a final localized state $\Phi_{fn'}=\psi_f\chi_{fn'}$ corresponding to the electron trapped on the defect. In these expressions, the indices n and n' are the quantum numbers of the vibrational motion. These two states are connected by a perturbation Hamiltonian H_p that has to be determined. The complete Hamiltonian H of the system can be written as

$$H=h(x,X)+T_N \ , \tag{4}$$

where T_N is the nuclear kinetic-energy operator and $h(x,X)$ the so-called total Hamiltonian, including the electron-lattice coupling and the lattice potential energy (x represents the set of electronic coordinates, X the set of lattice coordinates). The electronic part of the wave function is the eigenfunction of $h(x,X)$. We now expand $h(x,X)$ to second order in the coordinates of the atomic displacements with respect to some reference configuration (and referring to the configuration coordinate diagram of Fig. 1):

$$h(x,X)=h_0+h_1+h_2 \ . \tag{5}$$

The nonzero first-order term h_1 expresses the linear coupling induced by the defect between the electronic system and the lattice. The electron-phonon coupling terms $\langle\psi_\alpha|h_1|\psi_\beta\rangle$ can be expanded in the $6N$ normal coordinates q_p of the system (N is the number of unit cells of the crystal):

$$\langle\psi_\alpha|h_1|\psi_\alpha\rangle=\sum_p V_{\alpha p}q_p \quad \text{with } \alpha=i,f \ ; \tag{6a}$$

$$\langle\psi_i|h_1|\psi_f\rangle=\sum_p J_p q_p \ , \tag{6b}$$

where each term $V_{\alpha p}$ or J_p has the dimension of a force.

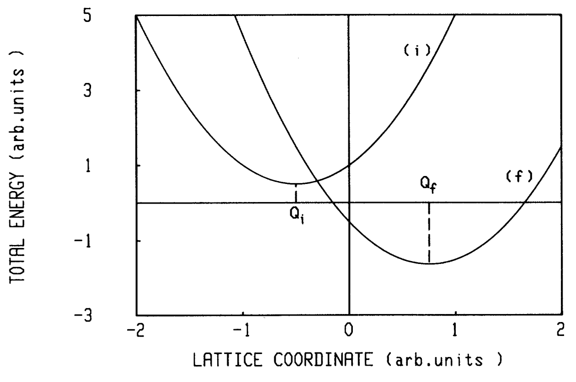

FIG. 1. Configuration coordinate diagram, representing the variation of the total energy versus the atomic displacement for two charge states of the defect [initial (i) and final (f)].

We use the so-called static approximation to perform the calculation. It consists in taking for the electronic motion the states calculated with h_0, i.e., assuming that the lattice coordinates are fixed at some given position. In this case, the perturbation Hamiltonian H_p reduces to the first-order term h_1.

An important quantity, which appears in the calculation, is the elementary Huang-Rhys factor S_p for the pth normal mode defined as

$$\hbar\omega_p S_p=\frac{|V_{fp}-V_{ip}|^2}{2M_p\omega_p^2} \ . \tag{7a}$$

We also define dimensionless factors S_{ip} expressing the adjustment energy of the phonon field in the initial state for the pth normal mode (and normalized by the phonon energy $\hbar\omega_p$):

$$\hbar\omega_p S_{ip}=\frac{|V_{ip}|^2}{2M_p\omega_p^2} \ . \tag{7b}$$

The capture coefficient c is determined from a Fourier-transform analysis of the Fermi golden rule, giving the transition probability per unit time.[8] The calculation performed in Ref. 7 assumes that there are no localized modes and takes the origin of the lattice coordinates at the equilibrium configuration in the initial state (inducing all V_{ip} being equal to zero). Here we prefer to take the origin of the lattice coordinates at the equilibrium position in the perfect crystal (labeled $X=0$). Thus the equilibrium position in the initial (and final) state corresponds to some given lattice coordinate labeled Q_i (and Q_f, respectively), with all $V_{ip}\neq0$. The rest of the calculation remains exactly the same as in Ref. 7 and leads to a similar compact form of the electron-capture coefficient, expressed as a function of an average frequency ω. The expression for the optimum value of ω is given by

$$(\hbar\omega)^2=\frac{\sum_p S_p(\hbar\omega_p)^3}{\sum_p S_p(\hbar\omega_p)} \ . \tag{8}$$

B. Analytic expression of c

We follow the derivation of Ref. 7 in which the electron-capture coefficient may be written as

$$c=c_0R \ . \tag{9}$$

Here c_0 is expressed in cm^3 s^{-1}, while R is dimensionless and comes from the calculation of the vibrational overlap factors:

$$c_0=\frac{2\pi\Omega}{\hbar(\hbar\omega)}\left\{\overline{(A\sqrt{S})}^2\left[1+\alpha-\frac{E_0}{\bar{S}\hbar\omega}\right]^2+\left[\overline{A^2}-\frac{\overline{(A\sqrt{S})}^2}{\bar{S}}\right]\right\}\left[\left[\frac{E_0}{\bar{S}\hbar\omega}\right]^2+\frac{1}{\sinh^2\left[\frac{\hbar\omega}{2kT}\right]}\right]^{1/2}, \tag{10}$$

where

$$A_p=\left[\frac{\hbar}{2M\omega_p}\right]^{1/2}J_p\ ,\quad \alpha=\mp 2\frac{\overline{(A\sqrt{S_i})}}{A\sqrt{S}}\quad (+\text{ if } V_{ip} \text{ and } V_{fp} \text{ are of the same sign})\ ,$$

E_0 is the thermal ionization energy of the defect, M is the average mass of the atom that vibrates, and Ω is the crystal volume. In this expression, $\bar{F}$ denotes an average over the individual mode contribution (the statistic weight of each mode is included in each term F_p):

$$\bar{F}=\sum_p F_p\ . \tag{11}$$

$\bar{S}$ is the usual total Huang-Rhys factor S; the dimensionless factor R is given by[7]

$$R=\frac{1}{\sqrt{2\pi}}\left[\left[\frac{E_0}{\hbar\omega}\right]^2+z^2\right]^{-1/4}\exp\left\{-S\coth\left[\frac{\hbar\omega}{2kT}\right]+\frac{E_0}{2kT}+\left[\left[\frac{E_0}{\hbar\omega}\right]^2+z^2\right]^{1/2}-\frac{E_0}{\hbar\omega}\sinh^{-1}\left[\frac{E_0}{\hbar\omega}\right]\right\}, \tag{12}$$

with

$$z=\frac{S}{\sinh\left[\frac{\hbar\omega}{2kT}\right]}\ . \tag{13}$$

The compact expressions (10) and (12) were established in Ref. 7 on the basis of a single phonon frequency. Moreover, it was proved in the same reference that these expressions remain valid in the case of a substantial dispersion of the vibration frequencies if one considers an average frequency ω given by Eq. (8).

The preceding formulas [(10)–(13)] give the electron-capture coefficient $c(E_0)$ resulting from transitions between the bottom of the conduction band (CB) and a deep level located at E_0 below it. To be more complete, we have to perform the thermal average of c over the density of states $n(\varepsilon)$ in the conduction band:

$$\bar{c}=\frac{\int_{\mathrm{CB}}c(E_0+\varepsilon)n(\varepsilon)e^{-\varepsilon/kT}d\varepsilon}{\int_{\mathrm{CB}}n(\varepsilon)e^{-\varepsilon/kT}d\varepsilon}\ , \tag{14}$$

where $n(\varepsilon)=\text{const}\times\sqrt{\varepsilon}$ in the effective-mass approximation for a three-dimensional system.

The aim of the following sections is to apply this calculation to the case of the dangling bond at the Si(111) surface. The parameters that remain to be determined are E_0, $\hbar\omega$, and all sums over normal modes of the same type of equation as Eq. (11).

III. CALCULATION OF THE SUMS OVER NORMAL MODES

A. Principle of the calculation

Let us call atom 0 an atom of the Si(111) surface supporting a dangling bond in the [111] direction, $|d\rangle$ the displacement vector of the atom 0, $|u_\perp\rangle$ a normalized vector into the [111] direction, and $|u_{1\parallel}\rangle$ and $|u_{2\parallel}\rangle$ two normalized orthogonal vectors in the plane perpendicular to the [111] direction. The outward displacement $Q_\perp$ (along the [111] direction) and the parallel displacements $Q_{1\parallel}$ and $Q_{2\parallel}$ (along the $|u_{1\parallel}\rangle$ and $|u_{2\parallel}\rangle$ directions) of the atom 0 from its tetrahedral position may be written as

$$Q_l=\langle u_l|d\rangle\ , \tag{15}$$

where $l=\perp$, $1\parallel$, or $2\parallel$. The eigenstates $|p\rangle$ of the dynamical matrix D of the crystal (the normal modes) form a complete system of vectors, with

$$D|p\rangle=\omega_p^2|p\rangle \tag{16}$$

and

$$\sum_p |p\rangle\langle p| = 1 \ . \tag{17}$$

Using these notations, the coordinates q_p of the $|d\rangle$ vector in the normal-mode axis system are given by $q_p = \langle p|d\rangle$. The electron-lattice coupling will mainly involve the relative displacement of the trivalent atom. This allows us to write all the coupling parameters J_p and the elementary forces $V_{\alpha p}$ (with $\alpha = i,f$) in terms of a finite number of parameters J^l and V_α^l:

$$\sum_p J_p q_p = \sum_p \sum_{l=1}^{3} J^l \langle u_l|p\rangle q_p = \sum_{l=1}^{3} J^l Q_l \ , \tag{18a}$$

$$\sum_p V_{\alpha p} q_p = \sum_p \sum_{l=1}^{3} V_\alpha^l \langle u_l|p\rangle q_p = \sum_{l=1}^{3} V_\alpha^l Q_l \ , \tag{18b}$$

where the Q_l ($l = \perp$, $1_\parallel$, or $2_\parallel$) are defined by Eq. (15). We are now able to express the sums in (11) in terms of the normal frequencies ω_p and the parameters J^l and V_α^l:

$$\overline{(A^2)} = \frac{\hbar}{2M} \sum_l (J^l)^2 \left[\sum_p \frac{|\langle u_l|p\rangle|^2}{\omega_p} \right] \quad \text{with } l = \perp, 1\|, 2\| \ , \tag{19a}$$

$$\bar{S} = \frac{|V_f^\perp - V_i^\perp|^2}{2M\hbar} \sum_p \frac{|\langle u_\perp|p\rangle|^2}{\omega_p^3} \ , \tag{19b}$$

$$\overline{(A\sqrt{S}\,)} = \frac{J^\perp |V_f^\perp - V_i^\perp|}{2M} \sum_p \frac{|\langle u_\perp|p\rangle|^2}{\omega_p^2} \ , \tag{19c}$$

$$\overline{(A\sqrt{S_i}\,)} = \frac{J^\perp |V_i^\perp|}{2M} \sum_p \frac{|\langle u_\perp|p\rangle|^2}{\omega_p^2} \ . \tag{19d}$$

In these expressions, we have already made some simplifications due to the axial symmetry of the system, implying that the components $V_\alpha^{1\|}$ and $V_\alpha^{2\|}$ of the force in the plane perpendicular to the [111] direction are equal to zero. This means only that the equilibrium position of atom 0 will remain along the [111] axis, keeping the symmetry axial.

B. Green's-function calculation of the sums

We have to calculate sums like

$$I_n^l = \sum_p \frac{|\langle u_l|p\rangle|^2}{\omega_p^{n+1}}$$

over normal frequencies. With such a notation, we can write

$$\bar{S} = \frac{|V_f^\perp - V_i^\perp|^2}{2M\hbar} I_2^\perp \ , \tag{20a}$$

$$\overline{(A^2)} = \frac{\hbar}{2M} [(J^\perp)^2 I_0^\perp + (J^{1\|})^2 I_0^{1\|} + (J^{2\|})^2 I_0^{2\|}] \ , \tag{20b}$$

$$\overline{(A\sqrt{S}\,)} = \frac{J^\perp |V_f^\perp - V_i^\perp|}{2M} I_1^\perp \ , \tag{20c}$$

$$\overline{(A\sqrt{S_i}\,)} = \frac{J^\perp |V_i^\perp|}{2M} I_1^\perp \ , \tag{20d}$$

$$\omega^2 = \frac{1}{I_1^\perp} \ . \tag{20e}$$

From Ref. 18, we get the following expression:

$$\mathrm{Im}(\langle u_l|G|u_l\rangle) = -\pi \sum_p |\langle u_l|p\rangle|^2 \delta(\omega^2 - \omega_p^2) \ . \tag{21}$$

$\mathrm{Im}(\langle u_l|G|u_l\rangle)$ represents the imaginary part of the matrix element, while G is the resolvent operator defined by

$$G = \lim_{\eta \to 0^+} \left[\frac{1}{\omega^2 - D + i\eta} \right] \ .$$

Then, by multiplying both sides by ω^{-n} and by integrating over the frequency spectrum, we obtain

$$I_n^l = -\frac{2}{\pi} \int \frac{1}{\omega^n} \mathrm{Im}(\langle u_l|G|u_l\rangle) d\omega \ . \tag{22}$$

The way to derive numerical values for I_n^l is described in Appendix A. We show that the symmetry of the G matrix implies that $I_n^{1\|} = I_n^{2\|}$. We use a valence-force-field model involving two physical parameters: a radial and an angular force constants k_r and k_θ. We take two sets of values for k_r and k_θ given in Ref. 9 and in Ref. 10. They are recalled in Table I which summarizes our re-

TABLE I. Result of the calculation of the sums over normal modes. The values of the sums I_n are given in mks units.

	k_r (eV/Å^2)	k_θ (eV/Å^2)	$I_2^\perp$ (s^{-3})	$I_1^\perp$ (s^{-2})	$I_0^\perp$ (s^{-1})	$I_0^\|$ (s^{-1})
a	9.805	0.195	$0.014\frac{M^{3/2}}{\pi}$	$0.0252M$	$0.472\frac{\sqrt{M}}{\pi}$	$0.384\frac{\sqrt{M}}{\pi}$
b	7.291	0.399	$0.005\frac{M^{3/2}}{\pi}$	$0.0133M$	$0.354\frac{\sqrt{M}}{\pi}$	$0.318\frac{\sqrt{M}}{\pi}$

[a] Set of parameters given by Baraff, Kane, and Schlüter (Ref. 9).

[b] Set of parameters given by Lannoo and Allan (Ref. 10).

sults. With these values of the radial and angular force constants, one finds an average frequency such that 19.2 meV $< \hbar\omega <$ 26.4 meV.

IV. CALCULATION OF THE COUPLING PARAMETERS $V_i^{\perp}$, $V_f^{\perp}$, $J^{\perp}$, and $J^{\parallel}$

A. Description of the cluster model for the dangling bond

The dangling bond at the Si(111) surface is oriented along a [111] direction and is also perpendicular to the surface. We will use a very simple cluster model to describe this defect (see Fig. 2): it consists in an isolated atom 0 on the Si(111) surface supporting the dangling bond in the [111] direction and bonded to three background silicon atoms representing the lattice, which are supposed to be fixed at their equilibrium position in the perfect crystal. Only the trivalent atom 0 supporting the dangling bond is allowed to relax.

B. Principle of the calculation

The preceding sums over phonons are also expressed in terms of the coupling parameters. $V_i^{\perp}$ ($V_f^{\perp}$) is the force of axial symmetry applied to the trivalent atom 0 on its initial (final) position before (after) the capture of an electron. $J^{\perp}$, $J^{1\parallel}$, and $J^{2\parallel}$ are the coupling constants along their respective directions. We are going to calculate these terms using the fact that [see Eqs. (18) and (6)]

$$\left| \sum_{l=\perp,1\parallel,2\parallel} J^l Q_l \right|^2 = |\langle \psi_i | h_1 | \psi_f \rangle|^2 . \tag{23}$$

In our case, the final state ψ_f will be the wave function $\xi_{\rm DB}$ of the trapped electron in the dangling bond calculated in our cluster model. On the other hand, in the tight-binding view, the initial state ψ_i is a linear combination of all antibondinglike states $\xi_{\rm AB}$ built from the sp^3 hybrid orbitals of the crystal:

$$\psi_i = \sum_{\rm AB} \Gamma_{\rm AB} \xi_{\rm AB} , \tag{24}$$

where the $\Gamma_{\rm AB}$ are the coefficients of a unitary transformation. In view of the local symmetry, which leads to separate contributions, we can write

$$\left[\sum_l J^l Q_l \right]^2 = \frac{1}{4N} \sum_{\rm AB} |\langle \xi_{\rm AB} | h_1 | \xi_{\rm DB} \rangle|^2 , \tag{25}$$

where the sum over AB is now restricted to the three antibonding states of our cluster model. To obtain this expression, we have replaced $|\Gamma_{\rm AB}|^2$ by an average value $1/4N$, where N is the number of unit cells in a perfect crystal of the same volume Ω. This allows us to avoid a full Green's-function calculation of this quantity, which would be extremely heavy and difficult to perform in view of the lack of translational symmetry.

To calculate (25), we can expand in our cluster model the electronic wave function as a linear combination of hybrid orbitals $|j,Q\rangle$ (here Q represents one of the Q_l):

$$\xi_\alpha(Q) = \sum_j a_j^\alpha(Q) |j,Q\rangle \quad (\alpha = \text{AB,DB}) . \tag{26}$$

The meaning and the orientation of the hybrid orbitals $|j,Q\rangle$ is made clear in Fig. 3. In this expression, both coefficients and wave functions depend on the displacement Q. The spirit of the static approximation would be to take the solutions calculated with $Q=0$ and to evaluate the matrix elements of h_1 in this basis. However, a meaningful tight-binding treatment requires that the atomic basis orbitals remain centered on their atom, i.e., are rigidly translated with the atomic position. In such a situation, the way to stay as close as possible to the static scheme is to keep constant the coefficients a_j^α calculated

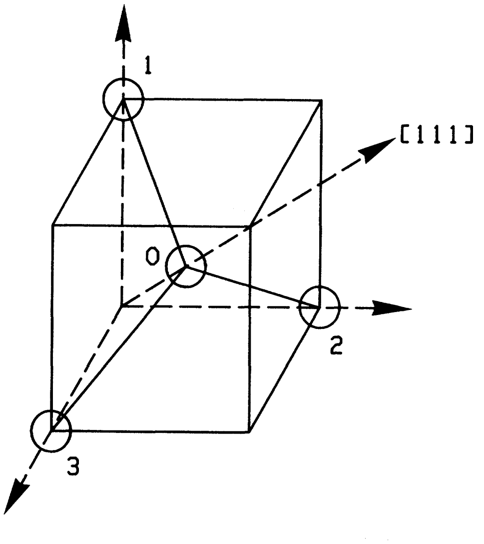

FIG. 2. Cluster model for the dangling bond on the Si(111) surface.

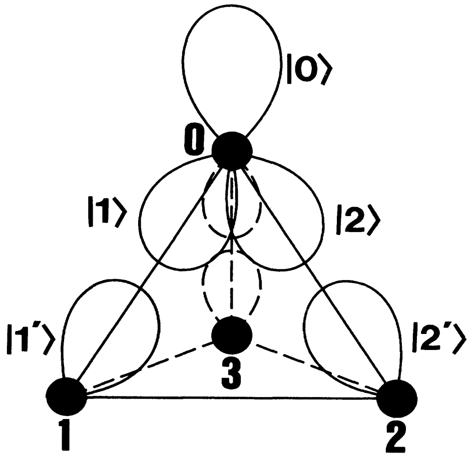

FIG. 3. Description of the hybrid orbitals used in the tight-binding treatment of the cluster model.

at $Q=0$ and to allow the set of hybrid orbitals to follow the relaxation, leading to

$$\xi^s_\alpha = \sum_j a_j^\alpha(0)|j,Q\rangle \ . \tag{27}$$

These coefficients $a_j^\alpha(0)$ will be found through the tight-binding resolution of the molecular model with $Q=0$. We show in Appendix B that we can still consider the perturbation Hamiltonian as being the first-order term h_1 of the total Hamiltonian $h(x,X)$ around $X=0$. The first-order variation of $\langle \xi^s_{\mathrm{AB}}|h|\xi^s_{\mathrm{DB}}\rangle$ can be written as

$$\langle \xi^s_{\mathrm{AB}}|h_1|\xi^s_{\mathrm{DB}}\rangle = \sum_{j,j'} a_j^{\mathrm{AB}}(0)^* a_{j'}^{\mathrm{DB}}(0)\Delta[\langle j|h|j'\rangle] \ , \tag{28}$$

where the variations $\Delta[\langle j|h|j'\rangle]=\langle j,Q|h|j',Q\rangle - \langle j,0|h|j',0\rangle$ are evaluable versus Q, allowing us to get the J^l parameters.

C. System resolution at $Q=0$

The first step is to solve the problem at $Q=0$ in order to get the coefficients $a_j^\alpha(0)$. Considering the C_{3v} symmetry of our model, we do not expand the electronic wave function in the set of hybrid orbitals, but in a set of symmetrized combinations of them, given in Appendix C. The tight-binding treatment is detailed in the same appendix. The parameters are the intra-atomic and interatomic matrix elements between first neighbors in silicon, as given in Ref. 11. The calculation leads to seven states: three antibondinglike states ξ_{AB}, three bondinglike states ξ_{B}, and a state corresponding to the dangling bond ξ_{DB}.

D. Determination of J

Using (25) and (28), we are able to determine the coupling parameters $J^\perp$ and $J^{1\parallel}$ and $J^{2\parallel}$ separately, letting the atom move along the corresponding direction. The dependence of the interatomic matrix element $\langle j|H|j'\rangle$ with displacement is evaluated by splitting it into elementary $\beta_{\sigma\sigma}$, β_{ss}, $\beta_{s\sigma}$ and $\beta_{\pi\pi}$ terms, whose variations are given by Harrison's formula:

$$\beta_{ij} = \eta_{ij}\frac{\hbar^2}{md^2} \ , \tag{29}$$

where d is the distance between first neighbors (atom 0 and atoms 1, 2, or 3 in our case) and m is the rest mass of an electron. The η_{ij} are given by Harrison in Ref. 12.

The symmetry of the system leads to $J^{1\parallel}=J^{2\parallel}=J^{\parallel}$: a quite simple numerical calculation gives

$$J^\perp\sqrt{4N} = 1.7 \text{ eV/Å} \ ,$$

$$J^\parallel\sqrt{4N} = 0.28 \text{ eV/Å} \ .$$

Of course, we can reproduce exactly the same procedure for the capture of a hole from the valence band, by considering the matrix elements $\langle \xi_B|h_1|\xi_{\mathrm{DB}}\rangle$. We get in this case

$$J^\perp\sqrt{4N} = 1.3 \text{ eV/Å} \ ,$$

$$J^\parallel\sqrt{4N} = 0.53 \text{ eV/Å} \ .$$

E. Determination of $V^\perp$ and S

The calculation of the average Huang-Rhys factor $\bar{S}$ from Eq. (20) requires the knowledge of the axial force $V^\perp$ applied to the atom 0 (which relaxes) when it stays at $Q=0$ (corresponding to the equilibrium position in the perfect crystal). These forces may be deduced from total-energy calculations in our molecular model, including a repulsive potential between first-neighbor atoms. This two-body potential is taken to be

$$V_{\mathrm{rep}} = E_r e^{-qd} \ , \tag{30}$$

where d is the distance between atoms and q is a parameter given by[13,14] $qd_0=4$, where d_0 is the distance between first neighbors in the perfect crystal ($d_0=2.35$ Å). E_r is a repulsive energy fitted to reproduce the correct value of d_0 in the perfect crystal, treated in a similar five-atom cluster model, where the central atom is surrounded by four neighbors. Thus we can write the total energy of the four-atom cluster representing the P_{b0} center as

$$E_{\mathrm{tot}}(Q_\perp) = 4E + 2E_B + \mathcal{N}E_{\mathrm{DB}} + 3E_r e^{-qd} \ , \tag{31}$$

where $d=d_0(1+Q_\perp^2/d_0^2+2Q_\perp/3d_0)^{1/2}$ and $\mathcal{N}$ is the number of electrons in the dangling bond. Of course, E_B, E, and E_{DB} depend on $Q_\perp$ because the interatomic terms do (see Appendix C for the definition of these energies). From the slope of the curve $E_{\mathrm{tot}}(Q_\perp)$ around $Q_\perp=0$, we are able to get the forces $F(\mathcal{N})$ on the atom 0 in its perfect crystalline position and then to predict the relaxation direction. Our results about the forces are compared in Table II to the results of more developed models.

The sign and the strength of the forces agree with previous results. This fact allows us to suppose that the coupling parameters, which are first-order terms just like the forces, are given with a good accuracy by our cluster model. We now get from Eq. (20) the average Huang-Rhys factor for both $(0\rightarrow -)$ and $(0\rightarrow +)$ transitions:

$$9 < \bar{S}_{(0\rightarrow -)} < 25 \ , \tag{32a}$$

$$10 < \bar{S}_{(0\rightarrow +)} < 27 \ . \tag{32b}$$

The dispersion in the results comes from the dispersion in the values for the parameters k_r and k_θ in the calculation of the sums over normal frequencies. The lower bonds correspond to the set of values given in Ref. 10 and the upper bonds to the one given in Ref. 9.

TABLE II. Comparison of our calculation of the force applied to the trivalent silicon atom (at $Q=0$) for the three charge states of the dangling bond with those of more involved calculations.

$\mathcal{N}$	$F(\mathcal{N})$ eV/Å	Ref. 5	Ref. 4	Ref. 19
0	−1.7	−2.22	−1.12	−1.24
1	−0.17	−0.6	0.48	−0.43
2	1.3	1.02	2.08	1.1

V. NUMERICAL APPLICATION FOR THE P_{b0} CENTER

The only parameter that remains to be determined is the thermal ionization energy E_0. It might be theoretically deduced from total-energy calculations leading to a theoretical configuration coordinate diagram. But contrary to the case of the coupling parameters where only first-derivative terms are concerned, we now need an absolute energy scale to insert the energy levels of the cluster model into a realistic band structure, which is uneasy, for instance, because the tight-binding treatment is known to poorly describe conduction states. Moreover, electronic repulsion and the effect of the interface should be precisely quantified.

On the other hand, the ionization energies related to the $(0\to -)$ and the $(0\to +)$ transitions have been experimentally measured with good accuracy by several techniques,[1,2,15] leading to $E_0(0\to -)=0.31$ eV ∓ 0.04 (from the conduction band) and $E_0(0\to +)=0.3$ eV ∓ 0.02 (from the valence band). So, we prefer to use these values in order to get more realistic values of the electron-capture cross section from Eqs. (1), (10), (12), and (14). The results are given in Table III.

Let us compare our results to the experimental determination of $\sigma_{(0\to -)}$ and $\sigma_{(0\to +)}$ made by Johnson using energy-resolved deep level transient spectroscopy. At $T=170$ K, he gives[16,17]

$$1.4\times 10^{-15}<\sigma_{(0\to -)}<10^{-14}\ \text{cm}^2\ ,$$

$$4\times 10^{-15}<\sigma_{(0\to +)}<2\times 10^{-14}\ \text{cm}^2\ .$$

Our calculation does give at this temperature the values reported in Table III. In both cases, our upper results are a factor of 3 or 8 smaller than the reported experimental values. This could be explained by a dipole or electric-field effect, which would enhance the transition probability at the Si-SiO$_2$ interface. Indeed, Massoud[20] reports the polar nature of this interface due to the difference of electronegativity between bulk Si and amorphous SiO$_2$, which induces charge transfers at the interface. The other possible explanation of this discrepancy might be that phonon-assisted capture is not the dominant electron-capture mechanism of the P_b center, but the fact that all the effects of the interface have not been taken into account in the calculation prevents us from making such a definitive conclusion.

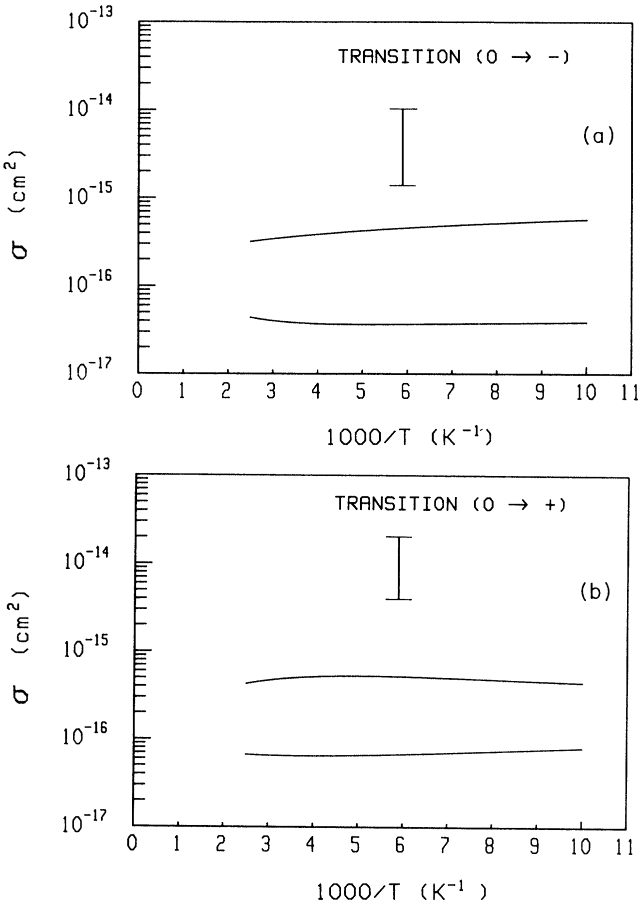

FIG. 4. Temperature dependence of $\sigma_{(0\to -)}$ (a) and $\sigma_{(0\to +)}$ (b) deduced from our model. The straight lines give the experimental values of Johnson (Refs. 16 and 17) at 170 K.

We show in Fig. 4 the thermal behavior of the electron-capture cross section in our model. It appears to be weakly thermally activated which is coherent with the thermal independence found by Johnson.[16,17] This may be explained by the fact that the Franck-Condon shift

TABLE III. Values of the electron-capture cross section deduced at $T=170$ K from our calculation for both transitions $(0\to -)$ and $(0\to +)$ of the dangling-bond charge state.

Transition $(0\to -)$	Transition $(0\to +)$
$E_0=0.31\text{eV}\mp 0.04$	$E_0=0.3\text{eV}\mp 0.02$
$m_n^*=0.33m$	$m_p^*=0.55m$
$9<S<25$	$10<S<27$
$19.2<\hbar\omega<26.4$ meV	$19.2<\hbar\omega<26.4$ meV
$J^{\perp}\sqrt{4N}=1.7$ eV/Å	$J^{\perp}\sqrt{4N}=1.3$ eV/Å
$J^{\parallel}\sqrt{4N}=0.28$ eV/Å	$J^{\parallel}\sqrt{4N}=0.53$ eV/Å
$\Omega/4N=10$ Å^3	$\Omega/4N=10$ Å^3
$4\times 10^{-17}<\sigma_{(0\to -)}<5\times 10^{-16}$ cm^2	$7\times 10^{-17}<\sigma_{(0\to +)}<5\times 10^{-16}$ cm^2

$S\hbar\omega$ we find is close to the thermal ionization energy E_0 in both cases, considering that the thermal activation of σ is mainly determined by the difference $(E_0 - S\hbar\omega)$ and increases with it.[7]

VI. CONCLUSION

We have shown that the model of carrier electron capture assisted by phonons may be applied to specific cases in order to determine electron-capture cross sections. This fact is illustrated in the case of the dangling bond at the Si(111) surface. We give a method to derive values of the electronic coupling parameters $J^{\perp}$ and $J^{\parallel}$ in the static approximation. The results concerning the electron-capture cross section related to the $(0 \rightarrow -)$ and to the $(0 \rightarrow +)$ transitions of the P_{b0} center are just a bit lower than experimental values around 10^{-15} cm^2. We think that the difference is due to a dipole or electric-field effect at the interface. Our model predicts a weak thermal activation for σ, in agreement with experiment. We think that the method can be applied to other defects, especially known bulk defects, and we hope that the fitting to experimental values may yield further comprehension of the mechanisms involved in carrier trapping.

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APPENDIX A: CALCULATION OF THE INTEGRALS OVER THE FREQUENCY SPECTRUM

We have to calculate

$$I_n^l = -(2/\pi)\int \omega^{-n}\,\mathrm{Im}(\langle u_l|G|u_l\rangle)d\omega \;,$$

which requires the knowledge of the matrix element $\langle u_l|G|u_l\rangle$. The whole Green's-function matrix G has already been evaluated on an atom connected to a Bethe lattice, which has the same coordination as the diamond lattice, but with no closed loops of atoms.[10] The situation of this atom is actually similar to the one of our trivalent atom 0 supporting the dangling bond in the microscopic model we use. And for the quantity to be calculated later, the replacement of the true lattice by a Bethe lattice is not a serious approximation. From the general form of the lattice, we deduce that $\langle u_{1\parallel}|G|u_{1\parallel}\rangle = \langle u_{2\parallel}|G|u_{2\parallel}\rangle$. So, we just reproduce here the imaginary part of the matrix elements $\langle u_{\perp}|G|u_{\perp}\rangle$ and $\langle u_{\parallel}|G|u_{\parallel}\rangle$. They come immediately from Eqs. (23) and (24) in Ref. 11, with a shift of $28k_\theta/3M$ of ω^2 in G_{xx} $(\langle u_{\perp}|G|u_{\perp}\rangle)$ and a shift of $16k_\theta/3M$ of ω^2 in G_{yy} and G_{zz} $(\langle u_{\parallel}|G|u_{\parallel}\rangle)$ (see Ref. 11 for the meaning of G_{xx}, G_{yy}, and G_{zz}). These shifts come from a contribution of the angular term of the lattice potential energy to the diagonal elements of the dynamical matrix, as explained in the same reference. Finally we get

$$\mathrm{Im}\langle u_{\perp}|G|u_{\perp}\rangle = \mathcal{J}_1^{\perp} + \mathcal{J}_2^{\perp} \;, \tag{A1a}$$

$$\mathrm{Im}\langle u_{\parallel}|G|u_{\parallel}\rangle = \mathcal{J}_1^{\parallel} + \mathcal{J}_2^{\parallel} + \mathcal{J}_3^{\parallel} \;, \tag{A1b}$$

where

$$\mathcal{J}_1^{\perp} = -\frac{2\pi}{3}\delta\left[\omega^2 - \frac{28}{3}\frac{k_\theta}{M}\right] , \tag{A2a}$$

$$\mathcal{J}_2^{\perp} = -\frac{1}{2}\frac{1}{\omega^2 - \frac{28}{3}\frac{k_\theta}{M}} \times\left[\frac{4}{3} - \left[\frac{\omega^2}{k_r/M} - \frac{28}{3}\frac{k_\theta}{k_r} - \frac{4}{3}\right]^2\right]^{1/2} , \tag{A2b}$$

valid for $\alpha_{\perp}^2 < \omega^2 < \nu_{\perp}^2$, with

$$\alpha_{\perp}^2 = \left[\frac{4}{3} - \frac{2}{\sqrt{3}}\right]\frac{k_r}{M} + \frac{28}{3}\frac{k_\theta}{M} , \tag{A3a}$$

$$\nu_{\perp}^2 = \left[\frac{4}{3} + \frac{2}{\sqrt{3}}\right]\frac{k_r}{M} + \frac{28}{3}\frac{k_\theta}{M} , \tag{A3b}$$

and

$$\mathcal{J}_1^{\parallel} = -\frac{\pi}{3}\delta\left[\omega^2 - \frac{16k_\theta}{3M}\right] , \tag{A4a}$$

$$\mathcal{J}_2^{\parallel} = -\frac{\pi}{3}\delta\left[\omega^2 - \frac{16k_\theta}{3M} - \frac{8k_r}{3M}\right] , \tag{A4b}$$

$$\mathcal{J}_3^{\parallel} = -\frac{2}{3}\frac{1}{\frac{\omega^2}{k_r/M} - \frac{16k_\theta}{3k_r}}\,\frac{\left[\frac{4}{3} - \left[\frac{\omega^2}{k_r/M} - \frac{16k_\theta}{3k_r} - \frac{4}{3}\right]^2\right]^{1/2}}{\left[\frac{1}{2}\left[\frac{\omega^2}{k_r/M} - \frac{16k_\theta}{3k_r}\right] - \frac{5}{3}\right]^2 + \frac{1}{4}\left[\frac{4}{3} - \left[\frac{\omega^2}{k_r/M} - \frac{16k_\theta}{3k_r} - \frac{4}{3}\right]^2\right]} , \tag{A4c}$$

valid for $\alpha_{\parallel}^2 < \omega^2 < \nu_{\parallel}^2$, with

$$\alpha_{\parallel}^2 = \left[\frac{4}{3} - \frac{2}{\sqrt{3}} \right] \frac{k_r}{M} + \frac{16}{3} \frac{k_\theta}{M} , \tag{A5a}$$

$$\nu_{\parallel}^2 = \left[\frac{4}{3} + \frac{2}{\sqrt{3}} \right] \frac{k_r}{M} + \frac{16}{3} \frac{k_\theta}{M} . \tag{A5b}$$

k_r and k_θ are the radial and the angular force constants intervening in the writing of the harmonic potential energy of the crystal (their values are given in the text), and M is the mass of the atom that vibrates.

The integration of the δ functions is immediate. In fact, the most important contribution comes from the integration of $\mathcal{J}_1^{\perp}$ and $\mathcal{J}_1^{\parallel}$ as soon as $n \geq 1$ because of the ω^{-n} term in the integral. The integrals over $\mathcal{J}_2^{\perp}$ and $\mathcal{J}_3^{\parallel}$ are performed numerically using classical methods. The results are given in the text for $\mathcal{J}_0^{\perp}$, $\mathcal{J}_0^{\parallel}$, $\mathcal{J}_1^{\perp}$, and $\mathcal{J}_2^{\perp}$.

APPENDIX B: PERTURBATION HAMILTONIAN IN THE STATIC SCHEME

The exact static approximation requires us to consider the solutions of the total Hamiltonian $h(x,X)$ calculated for some fixed lattice coordinates taken as the origin for the lattice displacements (in our case, $X=0$). In this case, the perturbation Hamiltonian exactly reduces to the first-order term h_1 of $h(x,X)$ around $X=0$.

Using our cluster model for the dangling bond, we consider the wave functions issued from the tight-binding treatment, and in the development of the wave function we keep the coefficients calculated with $X=0$, in order to stay as close as possible to the static scheme:

$$\xi_\alpha(Q) = \sum_j a_j^\alpha(0) |j,Q\rangle \quad (\alpha = i,f) . \tag{B1}$$

Q is generalized lattice coordinate along a given direction. These wave functions are not exact static solutions, so that the perturbation Hamiltonian does not *strictly* reduce to the first-order term h_1. Let us evaluate the matrix element intervening in the transition probability:

$$\begin{aligned} |\langle \xi_i | H | \xi_f \rangle|^2 &= |\langle \xi_i | T_N + h | \xi_f \rangle|^2 \\ &= \left| \sum_{j,j'} a_j^i(0)^* a_{j'}^f(0) \langle j,Q | T_N | j',Q \rangle \right. \\ &\quad \left. + \sum_{j,j'} a_j^i(0)^* a_{j'}^f(0) \langle j,Q | h | j',Q \rangle \right|^2 . \end{aligned} \tag{B2}$$

We can neglect the terms $\langle j,Q | T_N | j',Q \rangle$ compared to the others (which are of order $1/m_e$, m_e being the rest mass of an electron) because they are of order $1/M_N$ (where M_N is the atomic mass). This is just the classic approximation of the Born-Oppenheimer scheme (the ratio $m_e/M_N \rightarrow 0$).

Let us study the pure electronic terms developed to the first order into the generalized lattice coordinate Q:

$$\begin{aligned} \langle j,Q | h(x,Q) | j',Q \rangle &= \langle j,0 | h(x,0) | j',0 \rangle \\ &\quad + \left[\frac{\partial}{\partial Q} \langle j,Q | h(x,Q) | j',Q \rangle \right]_{Q=0} Q . \end{aligned} \tag{B3}$$

The sum over terms $\langle j,0 | h(x,0) | j',0 \rangle$ is equal to zero because the functions $\sum_j a_j^\alpha(0) |j,0\rangle$ are the eigenfunctions of the electronic Hamiltonian $h(x,0) = h_0$. We can finally write the complete matrix element to first order and in the limit where $m_e/M_N \rightarrow 0$ as follows:

$$|\langle \xi_i | H | \xi_f \rangle|^2 = \left| \sum_{j,j'} a_j^i(0)^* a_{j'}^f(0) \Delta(\langle j | h | j' \rangle) \right|^2 \tag{B4}$$

with

$$\Delta(\langle j | h | j' \rangle) = \langle j,Q | h(x,Q) | j',Q \rangle - \langle j,0 | h(x,0) | j',0 \rangle .$$

APPENDIX C: SYSTEM RESOLUTION AT $Q=0$

We use a tight-binding treatment to solve the problem at $Q=0$, only including nearest-neighbor interactions. We expand the wave function in the following symmetrized set of combinations of hybrid orbitals:

$$\begin{aligned} \varphi_0 &= |0\rangle , \\ \varphi &= \frac{|1\rangle + |2\rangle + |3\rangle}{\sqrt{3}} , \\ \varphi' &= \frac{|1'\rangle + |2'\rangle + |3'\rangle}{\sqrt{3}} , \\ \varphi_1 &= \frac{|1\rangle - |2\rangle}{\sqrt{2}} , \\ \varphi_1' &= \frac{|1'\rangle - |2'\rangle}{\sqrt{2}} , \\ \varphi_2 &= \frac{|1\rangle + |2\rangle - 2|3\rangle}{\sqrt{6}} , \\ \varphi_2' &= \frac{|1'\rangle + |2\rangle - 2|3'\rangle}{\sqrt{6}} . \end{aligned} \tag{C1}$$

In this basis, the Hamiltonian matrix can be written as a block-diagonal matrix

$$\begin{array}{c|ccccccc|} & \varphi_0 & \varphi & \varphi' & \varphi_1 & \varphi_1' & \varphi_2 & \varphi_2' \\ \hline \varphi_0 & & & & & & & \\ \varphi & & (H_{\mathrm{I}}) & & & & & \\ \varphi' & & & & & & & \\ \varphi_1 & & & & & & & \\ \varphi_1' & & & & (H_{\mathrm{II}}) & & & \\ \varphi_2 & & & & & & & \\ \varphi_2' & & & & & & (H_{\mathrm{III}}) & \end{array} \tag{C2}$$

1. Resolution of H_{I}

Developing H_{I} into inter- and intra-atomic terms, we get

$$\begin{array}{c|ccc|} & \varphi_0 & \varphi & \varphi' \\ \varphi_0 & E_h & \sqrt{3}\Delta_m & \sqrt{3}\beta' \\ \varphi & \sqrt{3}\Delta_m & E_h+2\Delta_m & \beta+2\beta' \\ \varphi' & \sqrt{3}\beta' & \beta+2\beta' & E_h \end{array} , \qquad \text{(C3)}$$

where β and β' are, for $Q=0$ in silicon, given by $\beta=-4.45$ eV and $\beta'=-0.25$ eV. $\Delta_m=(E_s-E_p)/4$ is the promotion energy ($\Delta_m=-1$ eV in silicon) and E_h is the sp^3 hybrid energy in silicon. The resolution leads to three states: an antibonding state ξ^3_{AB}, a state representing the dangling bond ξ_{DB}, and a bonding state ξ^3_B.

2. Resolution of H_{II} and H_{III}

Those two parts are structurally identical to the same following Hamiltonian submatrix:

$$\begin{bmatrix} E_h-\Delta_m & \beta-\beta' \\ \beta-\beta' & E_h-\Delta_m \end{bmatrix} . \qquad \text{(C4)}$$

Its resolution leads to two degenerated energy levels:

$$E'=E_h-\Delta_m-\beta+\beta'\times\begin{cases}\xi^1_{\mathrm{AB}}\\ \xi^2_{\mathrm{AB}}\end{cases} ,$$

$$E=E_h-\Delta_m+\beta-\beta'\times\begin{cases}\xi^1_{B}\\ \xi^2_{B}\end{cases} . \qquad \text{(C5)}$$

3. Numerical results

We summarize here our numerical results, giving especially the coefficients $a^{\alpha}_{j}(0)$:

$$E'=5.2 \text{ eV} , \quad \xi^1_{\mathrm{AB}}=\frac{\varphi_1-\varphi'_1}{\sqrt{2}} , \quad \xi^2_{\mathrm{AB}}=\frac{\varphi_2-\varphi'_2}{\sqrt{2}} ;$$

$$E_{\mathrm{AB}}=4.204 \text{ eV} , \quad \xi^3_{\mathrm{AB}}=0.187\varphi_0-0.645\varphi+0.740\varphi' ;$$

$$E_{\mathrm{DB}}=0.264 \text{ eV} , \quad \xi_{\mathrm{DB}}=0.951\varphi_0-0.069\varphi-0.301\varphi' ; \qquad \text{(C6)}$$

$$E=-3.200 \text{ eV} , \quad \xi^1_{B}=\frac{\varphi_1+\varphi'_1}{\sqrt{2}} , \quad \xi^2_{B}=\frac{\varphi_2+\varphi'_2}{\sqrt{2}} ;$$

$$E_B=-6.469 \text{ eV} , \quad \xi^3_B=0.244\varphi_0+0.761\varphi+0.600\varphi' .$$

The origin of energies is taken to be E_h, the sp^3 hybrid energy in silicon.

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