

Onsite matrix elements of the tight-binding Hamiltonian of a strained crystal: Application to silicon, germanium, and their alloys

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We discuss a model for the onsite matrix elements of the $sp^3d^5s^*$ tight-binding Hamiltonian of a strained diamond or zinc-blende crystal or nanostructure. This model features onsite, off-diagonal couplings among the s , p , and d orbitals and is able to reproduce the effects of arbitrary strains on the band energies and effective masses in the full Brillouin zone. It introduces only a few additional parameters and is free from any ambiguities that might arise from the definition of the macroscopic strains as a function of the atomic positions. We apply this model to silicon, germanium, and their alloys as an illustration. In particular, we make a detailed comparison of tight-binding and *ab initio* data on strained Si, Ge, and SiGe.

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I. INTRODUCTION

The oncoming limits of conventional downscaling of field-effect transistors have strengthened the need for innovative device architectures.¹ In this context, the use of mechanical strains has become an attractive solution to improve the electrical performances by enhancing the carrier mobility.^{2,3} As a matter of fact, strain engineering techniques such as the growth of a contact etch stop layer (CESL) (Ref. 4) or Si channels strained by SiGe source and drain extensions are now widely spread in the semiconductor industry. More generally, the electronic properties of strained $Si_{1-x}Ge_x$ layers grown on $Si_{1-y}Ge_y$ buffers are attracting much attention.⁵ These heterostructures, which can be integrated into Si-based electronics and photonics, indeed offer the opportunity to tune the band gap of the active layer.

The modeling of the electrical properties of such devices requires a detailed description of the effects of strains on the band structure. Over the past decades, the *ab initio* methods such as the density functional theory^{6,7} (DFT) have provided comprehensive information about the deformation potentials of semiconductors.^{8–13} However, such *ab initio* methods require heavy computational resources and are not, therefore, suitable for the calculation of the transport properties of large systems. For that reason, the physics and electronic device community is actively developing more efficient semiempirical approaches, such as the $\mathbf{k}\cdot\mathbf{p}$,^{14,15} the empirical pseudopotential,^{16–18} or the tight-binding^{19,20} (TB) methods, which can work out the electronic structure of strained semiconductors devices. Among these semiempirical approaches, the TB method has long been proven to be successful in predicting the electronic properties of semiconductor nanostructures such as nanocrystals or nanowires. The use of an atomic orbitals basis set with interactions limited to a few nearest neighbors indeed allows the calculation of the wave functions of million atom systems.^{21,22} The TB method is

also well suited to quantum transport calculations^{22–26} and to the atomic scale description of, e.g., impurities^{27,28} or electron-phonon coupling.²⁹ In this respect, the first nearest-neighbor $sp^3d^5s^*$ model is one of the most accurate and efficient TB descriptions of semiconductor materials.³⁰

The effects of strains are accounted for in TB models through the bond-length dependence of the nearest-neighbor parameters $V_{\mu\nu}$ (μ and ν being two orbitals on different atoms), which is usually fitted to a power law,^{31,32}

$$V_{\mu\nu}(d) = V_{\mu\nu}(d_0) \left(\frac{d_0}{d} \right)^n_{\mu\nu}, \quad (1)$$

where d is the distance between the two atoms in the strained crystal and d_0 is the equilibrium distance. Although some hydrostatic and uniaxial deformation potentials can be reproduced that way,³³ much better accuracy can be achieved with the introduction of strain-dependent onsite parameters.^{34–38} Indeed, hydrostatic strain shifts the average potential³⁹ in the crystal, while uniaxial and shear strains split the p or d orbitals of a given atom. In their original $sp^3d^5s^*$ parametrization, Jancu *et al.*³⁰ therefore introduced a term that lifts the degeneracy among the d_{yz} , d_{xz} , and d_{xy} orbitals under uniaxial $\langle 001 \rangle$ strain. Jancu and Voisin³⁸ later generalized this approach to uniaxial $\langle 111 \rangle$ strain. These Hamiltonians, however, feature the macroscopic strains $\varepsilon_{\alpha\beta}$, whose expression as a function of the atomic positions (the basic input of the TB method) is not univocal. Boykin *et al.*^{36,37} therefore introduced position-dependent orbital energies in the $sp^3d^5s^*$ Hamiltonian. They could reproduce that way the valence-band deformation potentials a_v and b_v but did not really improve on d_v . This limitation is a consequence of the “diagonal” assumption made in that model. Uniaxial $\langle 111 \rangle$ strain indeed leaves, for example, the p_x , p_y , and p_z orbitals of a given atom equivalent. It however couples these orbitals off the diagonal of the Hamiltonian.

In this paper, we discuss a model for the onsite matrix elements of the $sp^3d^5s^*$ TB model based on an explicit expression for the crystal field, assuming that the total potential is the sum of central, atomic contributions.^{40,41} It features off-diagonal couplings between different orbitals and is able to reproduce the effects of arbitrary strains on the band energies and effective masses at all relevant k points. It only involves a few additional parameters, is fully consistent with the symmetries of the crystal, and is free from any ambiguity that might arise from the introduction of the macroscopic strains $\varepsilon_{\alpha\beta}$ in an atomistic description. We present this model in Sec. II and then discuss its properties in Sec. III. Finally, We apply this model to silicon, germanium, and their alloys, which are the most relevant materials for microelectronics, in Sec. IV. We provide detailed comparisons with *ab initio* data on strained Si, Ge, and SiGe and discuss two important problems: the increase in the longitudinal effective mass under shear strains (missing in previous TB models) and the description of random alloys.

II. MODEL

In this section, we introduce the model for the onsite matrix elements of the $sp^3d^5s^*$ tight-binding Hamiltonian. For the sake of simplicity, we focus on a homogeneously strained diamond or zinc-blende crystal, the application to arbitrary strains, and other crystal structures being straightforward. We assume that the total potential in the crystal is the sum of central, atomic contributions $\nu_1(|\mathbf{r} - \mathbf{R}_i|)$ (sublattice 1) and $\nu_2(|\mathbf{r} - \mathbf{R}_i|)$ (sublattice 2), with \mathbf{R}_i being the atomic positions. In a first nearest-neighbor (NN) approximation, the potential experienced by the orbitals of atom i on sublattice 1 is therefore

$$\nu(\mathbf{r}) = \nu_1(|\mathbf{r} - \mathbf{R}_i|) + \sum_j^{\text{NN}} \nu_2(|\mathbf{r} - \mathbf{R}_j|). \quad (2)$$

This potential shifts the energy of the orbitals and couples them one to each other in the strained crystal. In particular, $\nu(\mathbf{r})$ might lift the degeneracy between the p or between the d orbitals of the atom. Our model is actually based on a first-order expansion of the onsite matrix elements of the potential $\nu(\mathbf{r})$ as a function of the atomic positions. In the following, we calculate the onsite Hamiltonian of the p orbitals of sublattice 1 as an example (paragraph IIA). We then discuss the application to other orbitals and crystal structures in paragraph IIB.

A. Case of p orbitals

Let p_i^x , p_i^y , and p_i^z be the p orbitals of atom i , and

$$V_1 = \langle p_i^x | \nu_1(|\mathbf{r} - \mathbf{R}_i|) | p_i^x \rangle, \quad (3a)$$

$$V_2^\sigma(d_{ij}) = \langle p_i^\sigma | \nu_2(|\mathbf{r} - \mathbf{R}_j|) | p_i^\sigma \rangle, \quad (3b)$$

$$V_2^\pi(d_{ij}) = \langle p_i^\pi | \nu_2(|\mathbf{r} - \mathbf{R}_j|) | p_i^\pi \rangle, \quad (3c)$$

where p_i^σ and p_i^π are the p orbitals aligned (σ) or orthogonal (π) to the bond axis $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$. Slater-Koster relations easily yield^{19,40,41}

$$\begin{aligned} V_x &= \langle p_i^x | \nu | p_i^x \rangle = V_1 + \sum_j^{\text{NN}} V_2^\sigma(d_{ij}) + \sum_j^{\text{NN}} l_{ij}^2 [V_2^\sigma(d_{ij}) - V_2^\pi(d_{ij})] \\ &= V_1 + \frac{1}{3} \sum_j^{\text{NN}} [V_2^\sigma(d_{ij}) + 2V_2^\pi(d_{ij})] \\ &\quad + \sum_j^{\text{NN}} \left[l_{ij}^2 - \frac{1}{3} \right] [V_2^\sigma(d_{ij}) - V_2^\pi(d_{ij})], \end{aligned} \quad (4)$$

where $l_{ij} = \mathbf{x} \cdot \mathbf{R}_{ij} / d_{ij}$ is the cosine director along x . This expression has been arranged so that the last (angular) term of the third line is zero in the unstrained material or under hydrostatic pressure (where $\sum_j^{\text{NN}} l_{ij}^2 = 4/3$ whatever the orientation of the crystal with respect to the principal axes). We next expand $V_2^\sigma(d_{ij})$ and $V_2^\pi(d_{ij})$ in powers of $d_{ij} - d_0$,

$$V_2^\sigma(d_{ij}) = V_2^\sigma(d_0) + \frac{3}{4} \alpha_p^\sigma \frac{d_{ij} - d_0}{d_0} + \dots, \quad (5a)$$

$$V_2^\pi(d_{ij}) = V_2^\pi(d_0) + \frac{3}{4} \alpha_p^\pi \frac{d_{ij} - d_0}{d_0} + \dots. \quad (5b)$$

We hence get

$$\begin{aligned} V_x &= V_1 + \frac{1}{3} \sum_j^{\text{NN}} [V_2^\sigma(d_0) + 2V_2^\pi(d_0)] + \frac{3}{4} \alpha_p \sum_j^{\text{NN}} \frac{d_{ij} - d_0}{d_0} \\ &\quad + \sum_j^{\text{NN}} \left[\beta_p^{(0)} + \beta_p^{(1)} \frac{d_{ij} - d_0}{d_0} \right] \left[l_{ij}^2 - \frac{1}{3} \right], \end{aligned} \quad (6)$$

where⁴² $\alpha_p = (\alpha_p^\sigma + 2\alpha_p^\pi)/3$, $\beta_p^{(0)} = V_2^\sigma(d_0) - V_2^\pi(d_0)$, and $\beta_p^{(1)} = 3(\alpha_p^\sigma - \alpha_p^\pi)/4$. The first line of Eq. (6) is part of the unstrained p orbital energy E_p^0 . The second line is actually proportional (to first order in the d_{ij} 's) to the hydrostatic strain, i.e., proportional to the relative variation in the volume Ω of the unit cell (also see paragraph III). We thus define for convenience

$$\frac{\Delta\Omega}{\Omega_0} = \frac{\Omega - \Omega_0}{\Omega_0} = \frac{3}{4} \sum_j^{\text{NN}} \frac{d_{ij} - d_0}{d_0} + \mathcal{O}(d_{ij}), \quad (7)$$

where Ω_0 is the unstrained volume of the unit cell. The p_x orbital energy therefore reads with these assumptions as

$$E_x = E_p^0 + \alpha_p \frac{\Delta\Omega}{\Omega_0} + \sum_j^{\text{NN}} \beta_p(d_{ij}) \left[l_{ij}^2 - \frac{1}{3} \right], \quad (8)$$

where $\beta_p(d) = \beta_p^{(0)} + \beta_p^{(1)}(d - d_0)/d_0$.

The equations are similar for E_y and E_z , with l_{ij} replaced by $m_{ij} = \mathbf{y} \cdot \mathbf{R}_{ij} / d_{ij}$ and $n_{ij} = \mathbf{z} \cdot \mathbf{R}_{ij} / d_{ij}$, respectively. Off-diagonal couplings between the p orbitals can be obtained in the same way. Slater-Koster relations¹⁹ yield, for example,

$$\langle p_i^y | \nu | p_i^x \rangle = \sum_j^{\text{NN}} m_{ij} l_{ij} [V_2^\sigma(d_{ij}) - V_2^\pi(d_{ij})] = \sum_j^{\text{NN}} \beta_p(d_{ij}) m_{ij} l_{ij}, \quad (9)$$

which is also zero under hydrostatic pressure.

The onsite p block matrix finally reads in the $\{p_x, p_y, p_z\}$ basis set as

$$\hat{\mathbf{H}}_p = \left(E_p^0 + \alpha_p \frac{\Delta\Omega}{\Omega_0} \right) \hat{\mathbf{I}} + \sum_j^{\text{NN}} \beta_p(d) \begin{bmatrix} l^2 - \frac{1}{3} & lm & ln \\ ml & m^2 - \frac{1}{3} & mn \\ nl & nm & n^2 - \frac{1}{3} \end{bmatrix}, \quad (10)$$

where the explicit dependence of d_{ij} , l_{ij} , m_{ij} , and n_{ij} on the atomic sites i and j has been dropped for simplicity. The p orbitals feature a $\propto \alpha_p$ hydrostatic correction and a $\propto \beta_p$ angular term, whose effects will be discussed in more detail in Sec. III.

B. Case of other orbitals

The onsite Hamiltonians of the s (s^*) and d orbitals, as well as the off-diagonal coupling matrices among the s , p , d , and s^* orbitals are given in the Appendix. Equation (10), (A1), (A2), and (A4)–(A7) of the Appendix are valid for both sublattices 1 and 2, possibly with different parameters in III-V or II-VI materials. They feature hydrostatic ($\propto \alpha$ terms) and/or angular terms ($\propto \beta$ and $\propto \gamma$ matrices). The $\propto \beta$ matrices are all zero in the unstrained crystal and under hydrostatic strain. There are, however, nonzero couplings between the d orbitals [Eq. (A3)], between the s and s^* orbitals [Eq. (A4)], and between the p and $\{d_{yz}, d_{xz}, d_{xy}\}$ orbitals [Eq. (A7)] if the corresponding γ parameters are not zero. In particular, the d orbitals are not degenerate anymore in the unstrained crystal if $\gamma_d^{(0)} \neq 0$ (see paragraph 2 of the Appendix). This is actually consistent with the symmetry of the zinc-blende lattice but is not, usually, accounted for in TB models. As a matter of fact, lifting the degeneracy between the d orbitals does not significantly improve the quality of the TB model in diamond or zinc-blende crystals, while it is essential in lower-symmetry polytypes such as wurtzite materials.

This model has been checked against an *ab initio* (DFT) description of silicon based on atomiclike orbitals (the SIESTA code⁴³). With the single- ζ -polarized basis set used, the self-consistent *ab initio* Hamiltonian is formally equivalent to a nonorthogonal third nearest-neighbor sp^3d^5 TB model. The evolution of the onsite *ab initio* matrix elements under strain compares fairly well with our tight-binding approach (despite the latter being first nearest neighbors only). All $\beta^{(0)}$'s and $\gamma^{(0)}$'s (except $\beta_d^{(0)}$) are found negative within SIESTA, as expected from simple arguments assuming positive exponentially decaying radial parts for the orbitals. The sign of the α 's, $\beta^{(1)}$'s, and $\gamma^{(1)}$'s is, however, expected to be quite sensitive to the choice of orbitals.^{42,44}

The present model can be applied to other crystal structures and inhomogeneous strains. In a wurtzite material for example, the $\propto \beta_p$ and $\propto \beta_d$ or γ_d terms will lift the degeneracy between the p and between the d orbitals in the unstrained crystal, as is usually enforced *a priori* in the TB descriptions of these materials.⁴⁵ We will now discuss some properties of this model and then its application to silicon, germanium, and their alloys.

III. DISCUSSION

Equation (10), (A1), (A2), and (A4)–(A7) directly depend on the atomic coordinates through the interatomic distances d_{ij} and cosine directors l_{ij} , m_{ij} , and n_{ij} . These equations are thus free of any ambiguities that might arise, e.g., from the definition of the strains $\varepsilon_{\alpha\beta}$ as a function of the atomic positions and, in particular, in inhomogeneous environments such as alloys. They also account for internal strains at the atomistic level and should therefore be able to reproduce electron-optical phonon couplings. Moreover, this model for the onsite tight-binding Hamiltonian is consistent with the symmetries of the crystal. In particular, the band structure remains invariant under global rotation of the lattice (since these equations fulfill Slater-Koster's relations¹⁹), a property which is not easily enforced in models depending explicitly on the $\varepsilon_{\alpha\beta}$'s or in the model of Refs. 36 and 37. In practice, the input atomic positions can be calculated using, for example, Keating's⁴⁶ or Stillinger-Weber force fields.⁴⁷

We next discuss the effects of biaxial stress on the p orbitals as an illustration of the versatility of this model. In a homogeneously strained crystal, the strained atomic positions \mathbf{R}_i read as a function of the unstrained coordinates \mathbf{R}_i^0 ,

$$\mathbf{R}_i = (\hat{\mathbf{I}} + \hat{\varepsilon}) \mathbf{R}_i^0 \pm \frac{\zeta a}{4} (\varepsilon_{yz}, \varepsilon_{xz}, \varepsilon_{xy}), \quad (11)$$

where the + (respectively, –) sign holds for sublattice 1 (respectively, sublattice 2), ζ is Kleinman's internal strain parameter, a is the lattice parameter, $\hat{\mathbf{I}}$ is the identity matrix, and $\hat{\varepsilon}$ is the matrix of the strains $\varepsilon_{\alpha\beta}$. The internal strain parameter ζ describes the motion of one sublattice with respect to the other under shear strain.⁴⁸ We successively consider the cases of biaxial $\langle 001 \rangle$ and $\langle 111 \rangle$ strains.

A. Case of biaxial $\langle 001 \rangle$ strain

Let us apply a biaxial stress perpendicular to $z=[001]$ and let $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{\parallel}$ and $\varepsilon_{zz}=\varepsilon_{\perp}$ be the strains in the crystal. Equations (10) and (11) then yield, to first order in strains,

$$\hat{\mathbf{H}}_p = \left(E_p^0 + \alpha_p \frac{\Delta\Omega}{\Omega_0} \right) \hat{\mathbf{I}} + \frac{8}{9} \beta_p^{(0)} (\varepsilon_{\perp} - \varepsilon_{\parallel}) \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}. \quad (12)$$

The first line features the hydrostatic strain $\Delta\Omega/\Omega_0 = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = 2\varepsilon_{\parallel} + \varepsilon_{\perp}$. It accounts for the variation of the average potential in the crystal and shifts the three p orbitals equally. As expected, the stress also lifts (second line) the degeneracy between the $\{p_x, p_y\}$ and the p_z orbitals. The splitting between $\{p_x, p_y\}$ and p_z , $\delta E_p = 8\beta_p^{(0)}(\varepsilon_{\perp} - \varepsilon_{\parallel})/3$, is actually proportional to the uniaxial component of the strain tensor but does not depend on $\beta_p^{(1)}$. The degeneracy between $\{d_{yz}, d_{xz}\}$ and d_{xy} is likewise lifted for the d orbitals. This model thus reproduces the effects of the $\propto \delta_{001}$ term in the parametrizations of Jancu *et al.*^{30,38} or of the diagonal energy shifts in the parametrization of Boykin *et al.*^{36,37}

TABLE I. Tight-binding parameters of relaxed, bulk Si, and Ge (first nearest-neighbor, two-center orthogonal $sp^3d^5s^*$ model). The notations are those of Slater and Koster (Ref. 19). The valence bands of Si and Ge have been aligned at $E=0$ eV; the onsite energies E_s , E_p , E_d , and E_{s^*} of Ge must, therefore, be shifted by $\Delta_{\text{VBO}}=0.68$ eV to account for the valence-band offset between the two materials. λ_{so} is the spin-orbit coupling parameter of the p orbitals.

	Si (eV)	Ge (eV)
E_s	-2.55247	-4.08253
E_p	4.48593	4.63470
E_d	14.01053	12.19526
E_{s^*}	23.44607	23.20167
λ_{so}	0.01851	0.12742
$V_{ss\sigma}$	-1.86600	-1.49093
$V_{ss^*\sigma}$	-1.39107	-1.59479
$V_{sp\sigma}$	2.91067	2.91277
$V_{sd\sigma}$	-2.23992	-2.10114
$V_{s^*s^*\sigma}$	-4.51331	-4.86118
$V_{s^*p\sigma}$	3.06822	2.92036
$V_{s^*d\sigma}$	-0.77711	-0.23561
$V_{pp\sigma}$	4.08481	4.36624
$V_{pp\pi}$	-1.49207	-1.58305
$V_{pd\sigma}$	-1.66657	-1.60110
$V_{pd\pi}$	2.39936	2.36977
$V_{dd\sigma}$	-1.82945	-1.15483
$V_{dd\pi}$	3.08177	2.30042
$V_{dd\delta}$	-1.56676	-1.19386

B. Case of biaxial $\langle 111 \rangle$ strain

Let us now apply a biaxial stress perpendicular to $z'=[111]$. The strains in the $\{x'=[1\bar{1}0], y'=[11\bar{2}], z'=[111]\}$ axis set are thus $\varepsilon_{x'x'}=\varepsilon_{y'y'}=\varepsilon_{\parallel}$ and $\varepsilon_{z'z'}=\varepsilon_{\perp}$. Equations (10) and (11) then yield, to first order in strains,

$$\hat{\mathbf{H}}_p = \left(E_p^0 + \alpha_p \frac{\delta\Omega}{\Omega_0} \right) \hat{\mathbf{I}} + \frac{8}{27} \beta_p^{\text{eff}} (\varepsilon_{\perp} - \varepsilon_{\parallel}) \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}, \quad (13)$$

where $\beta_p^{\text{eff}} = \beta_p^{(0)}(1+2\zeta) + \beta_p^{(1)}(1-\zeta)$. As expected, biaxial $[111]$ strain leaves the p_x , p_y , and p_z (diagonal) energies equivalent. It however couples these orbitals off the diagonal of the Hamiltonian. The eigenvectors of $\hat{\mathbf{H}}_p$ are indeed: (i) the p orbital aligned with $[111]$ ($p_{z'}$), with energy $E_p^0 + \alpha_p \delta\Omega / \Omega_0 + 16\beta_p^{\text{eff}}(\varepsilon_{\perp} - \varepsilon_{\parallel})/27$, and (ii) the two degenerate p orbitals perpendicular to $[111]$ ($\{p_{x'}, p_{y'}\}$), with energies $E_p^0 + \alpha_p \delta\Omega / \Omega_0 - 8\beta_p^{\text{eff}}(\varepsilon_{\perp} - \varepsilon_{\parallel})/27$. The splitting between these orbitals is again proportional to the uniaxial component of the strain tensor. It also depends on the internal strain parameter ζ (through β_p^{eff}). The value of ζ used as a reference to compute the deformation potentials must therefore be provided with the TB parameters.

TABLE II. Harrison and onsite strain parameters of Si and Ge.

	Si	Ge
d_0 (Å)	2.35169	2.44999
$n_{ss\sigma}$	3.56701	3.57536
$n_{ss^*\sigma}$	1.51967	1.03634
$n_{sp\sigma}$	2.03530	2.88203
$n_{sd\sigma}$	2.14811	1.89283
$n_{s^*s^*\sigma}$	0.64401	1.07935
$n_{s^*p\sigma}$	1.46652	2.64809
$n_{s^*d\sigma}$	1.79667	2.33424
$n_{pp\sigma}$	2.01907	2.40576
$n_{pp\pi}$	2.87276	2.95026
$n_{pd\sigma}$	1.00446	0.51325
$n_{pd\pi}$	1.78029	1.62421
$n_{dd\sigma}$	1.73865	1.68410
$n_{dd\pi}$	1.80442	2.64952
$n_{dd\delta}$	2.54691	3.83221
α_s (eV)	-0.13357	-0.33252
α_p (eV)	-0.18953	-0.43824
α_d (eV)	-0.89046	-0.90486
α_{s^*} (eV)	-0.24373	-0.52062
$\beta_p^{(0)}$ (eV)	1.13646	1.01233
$\beta_p^{(1)}$ (eV)	-2.76257	-2.53951
$\beta_{pd}^{(0)}$ (eV)	-0.13011	-0.22597
$\beta_{pd}^{(1)}$ (eV)	-3.28537	-3.77180
$\beta_d^{(0)}$ (eV)	3.59603	1.99217
$\beta_{sp}^{(0)}$ (eV)	1.97665	1.27627
$\beta_{s^*p}^{(0)}$ (eV)	-2.18403	-2.02374
$\beta_{sd}^{(0)}$ (eV)	3.06840	2.38822
$\beta_{s^*d}^{(0)}$ (eV)	-4.95860	-4.73191

Such off-diagonal couplings between the p (or d) orbitals do not exist in the parametrization of Ref. 36. As a consequence the degeneracy between the p and between the d orbitals is not lifted by biaxial $\langle 111 \rangle$ strain, and the value of d_v is the same whether the diagonal energy corrections are included or not. $\beta_p^{(1)}$ and $\beta_d^{(1)}$ also reproduce the effects of the $\propto \delta_{111}$ and $\propto \pi_{111}$ terms in the parametrization of Ref. 38. However, the effective $\beta_d^{(0)}$ is assumed to be zero for the $[111]$ strain (but not for the $[001]$ strain), which makes the model of Ref. 38 hardly consistent with an explicit description of the crystal field, even beyond first nearest neighbors.

IV. APPLICATION TO SI, GE, AND THEIR ALLOYS

In this section, we discuss the application of the above model for the onsite matrix elements of the TB Hamiltonian to silicon, germanium, and their alloys. We therefore attempted to reproduce the band structure of Si, Ge, and of the ordered $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy with a first nearest-neighbor, two-

TABLE III. First nearest-neighbor two-center tight-binding parameters of SiGe. The onsite energies and onsite strain parameters of the Si and Ge atoms are those of bulk Si and Ge, respectively. The Harrison parameters are the same for Si/Ge and Ge/Si interactions. The relaxed SiGe bond length is $d_0=2.39792$ Å.

Si(1)Ge(2)					
$V_{s_1 s_2 \sigma}$ (eV)	-1.67650		$n_{ss\sigma}$	3.90172	
$V_{s_1^* s_2^* \sigma}$ (eV)	-4.63349		$n_{s^* s^* \sigma}$	0.85993	
$V_{p_1 p_2 \sigma}$ (eV)	4.21933		$n_{pp\sigma}$	2.34995	
$V_{p_1 p_2 \pi}$ (eV)	-1.54668		$n_{pp\pi}$	3.08150	
$V_{d_1 d_2 \sigma}$ (eV)	-1.41949		$n_{dd\sigma}$	1.66975	
$V_{d_1 d_2 \pi}$ (eV)	2.62540		$n_{dd\pi}$	2.24973	
$V_{d_1 d_2 \delta}$ (eV)	-1.39382		$n_{dd\delta}$	3.06305	
$V_{s_1 s_2^* \sigma}$ (eV)	-1.50940	$V_{s_2 s_1^* \sigma}$ (eV)	-1.50314	$n_{ss^* \sigma}$	1.03801
$V_{s_1 p_2 \sigma}$ (eV)	2.82890	$V_{s_2 p_1 \sigma}$ (eV)	3.01033	$n_{sp\sigma}$	2.37280
$V_{s_1 d_2 \sigma}$ (eV)	-2.13989	$V_{s_2 d_1 \sigma}$ (eV)	-2.04737	$n_{sd\sigma}$	1.99537
$V_{s_1^* p_2 \sigma}$ (eV)	3.06299	$V_{s_1^* p_2 \sigma}$ (eV)	2.79296	$n_{s^* p\sigma}$	1.94143
$V_{s_1^* d_2 \sigma}$ (eV)	-0.46386	$V_{s_2^* d_1 \sigma}$ (eV)	-0.51235	$n_{s^* d\sigma}$	2.01051
$V_{p_1 d_2 \sigma}$ (eV)	-1.43412	$V_{p_2 d_1 \sigma}$ (eV)	-1.61322	$n_{pd\sigma}$	0.75549
$V_{p_1 d_2 \pi}$ (eV)	2.57110	$V_{p_2 d_1 \pi}$ (eV)	2.43552	$n_{pd\pi}$	1.67031

center orthogonal $sp^3d^5s^*$ TB model. We used experimental data when available and *ab initio* calculations otherwise as a reference for the optimization of the TB parameters. We first review the *ab initio* calculations and the optimization process in paragraph IVA, then discuss the TB model of Si, Ge, and $\text{Si}_{0.5}\text{Ge}_{0.5}$ in paragraph IVB, and finally the case of arbitrary SiGe alloys in paragraph IVC.

A. First-principles calculations and optimization procedure

A series of first-principles calculations was performed with the ABINIT (Refs. 49–51) code on Si, Ge, and the ordered $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy to set up a reference for the optimization of the TB parameters. These calculations are based on the local density approximation (LDA) to DFT,^{6,7} using relativistic Hartwigsen-Goedecker-Hutter pseudopotentials.⁵² The LDA band structure was further corrected with Hedin's *GW* approximation to the self-energy used as a post-DFT scheme.^{53,54} In general, the *GW* band energies were found in good agreement with the available experimental data.⁵⁵ The properties of a large set of strained crystals have been computed, including hydrostatic as well as biaxial deformations perpendicular to [100], [110], and [111].⁵⁶ The biaxial strains were chosen to be large enough (up to $\epsilon_{\parallel}=\pm 5\%$) to span the whole range of lattice mismatches encountered in epitaxial $\text{Si}_{1-x}\text{Ge}_x$ layers grown on relaxed $\text{Si}_{1-y}\text{Ge}_y$ buffers. The atomic positions within the cell were carefully optimized as they strongly affect the band structure.¹⁵

The TB parameters were fitted to the *ab initio* (or experimental, when available) band structures, effective masses, and deformation potentials using global optimization methods⁵⁷ refined with local optimizers.⁵⁸ The least-squares convergence of the band structures was monitored on a dense set of k points in the first Brillouin zone.

The $sp^3d^5s^*$ model of Si and Ge features 4 onsite energies and α parameters, 14 nearest-neighbor and Harrison ($n_{\mu\nu}$)

parameters, and up to 20 β and γ parameters. However, only nine of them appeared to have significant impact on the electronic structure of strained Si and Ge around the band gap (see Table II for a list). In particular, all γ parameters and most $\beta^{(1)}$'s were set to zero. This left 45 parameters in the model, which were optimized in following way:

(1) the 4 onsite energies and 14 nearest-neighbor parameters were fitted on the band structures of relaxed Si and Ge;

(2) the 4 α 's and 14 Harrison parameters were fitted on one positive and one negative hydrostatic strain;⁵⁹

(3) the 7 $\beta^{(0)}$'s were fitted on one [100] and one [111] biaxial strain that do not change the first nearest-neighbor bond lengths ($\epsilon_{\perp}=-2\epsilon_{\parallel}$ and $\zeta=1$); and

(4) the 14 Harrison, 7 $\beta^{(0)}$'s, and 2 $\beta^{(1)}$'s were further refined on one [100] and two [111] biaxial strains [one with $\zeta=0.557$ (Si) or $\zeta=0.536$ (Ge) and one with $\zeta=0$].

Steps 2 and 3 ensure a reasonable starting point for step 4. The resulting parametrization was also checked against [110] biaxial strains, and its transferability was tested on strained Si/Ge films and wires.

The TB model of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy only involves seven additional first nearest-neighbor parameters (since the Si/Ge and Ge/Si interactions are different). The onsite energies and onsite strain parameters of the Si and Ge atoms were chosen equal to those of bulk Si and Ge, respectively.

The TB parameters of Si, Ge, and $\text{Si}_{0.5}\text{Ge}_{0.5}$ are listed in Tables I–III. The onsite strain parameters have the sign expected from simple considerations about the shape of the orbitals, except $\beta_p^{(0)}$, $\beta_{sp}^{(0)}$, and $\beta_{sd}^{(0)}$. We point out that the sign of these three parameters is extremely robust; including the missing $\gamma^{(0)}$'s in the onsite corrections will not, in particular, change the picture.⁶⁰ The positive sign of $\beta_p^{(0)}$ seems characteristic of first nearest-neighbor orthogonal models: the model of Ref. 37 indeed splits the p orbitals the same way as ours; while this is hidden in Ref. 38 by the choice of an effective $\beta_p^{(0)}=0$ but different effective $\beta_d^{(0)}$'s for biaxial [001] and [111] strains (see discussion in paragraph IIIB).

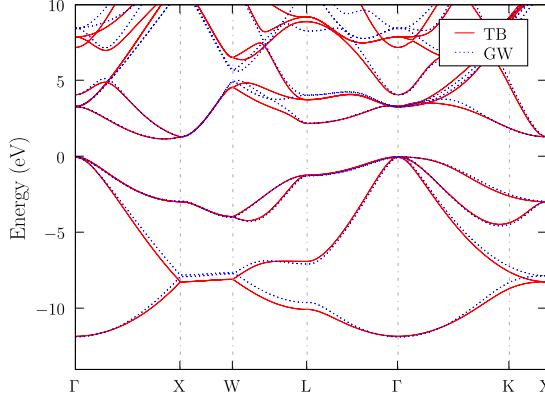


FIG. 1. (Color online) Band structure of bulk, unstrained silicon in the $sp^3d^5s^*$ TB and GW approximations.

The reasons are twofold: first, the orbitals hidden behind orthogonal TB models are much more complex than usually assumed when discussing the sign of the interactions. The radial parts must indeed have at least one zero to fulfill (near) orthogonality relations with the neighboring atoms. Second, some deformation potentials, such as b_v and Ξ_u^Δ , are independent of the first (but not on the second) nearest-neighbor Harisson parameters (b_v , for example, depends on $\beta_p^{(0)}$ and $\beta_d^{(0)}$ only). The onsite parameters will therefore likely renormalize the missing long-range interactions beyond their “bare” definition given in Sec. II and the Appendix. The renormalization of long-range interactions into first nearest-neighbor and onsite terms is underlying every short-range TB model and is a key to their success. We have carefully checked our parametrization in bulk (including properties that were not included in the optimization, such as the nonlinearities of the band edges and the behavior of the masses under shear strains discussed in the next paragraph) and tested its transferability to random SiGe alloys (paragraph IVC) and to a variety of test nanostructures such as strained Si/Ge films and wires. This model (as the previous ones) actually shows excellent transferability of the bulk physics to the nanostructures.

B. Results in bulk Si, Ge, and SiGe

The TB and GW band structures of bulk, unstrained Si, Ge, and $Si_{0.5}Ge_{0.5}$ are compared in Figs. 1–3. They are in very good agreement one with each other, with the difference between the TB and GW principal band gaps being <0.01 eV. The lifting of the degeneracies at, e.g., the X point in SiGe are also well reproduced. The TB conduction-band effective masses and valence-band Luttinger parameters of Si and Ge are given in Table IV. They are compared with the GW and experimental data, and with two other $sp^3d^5s^*$ parametrizations.^{30,68}

The TB deformation potentials of the conduction- and valence-band extrema of Si and Ge are listed in Table V and are compared with the experimental and LDA data. The TB model performs well on all relevant deformation potentials. Also shown are the results obtained with the $sp^3d^5s^*$ model and parametrization of Refs. 37 and 68. The present model

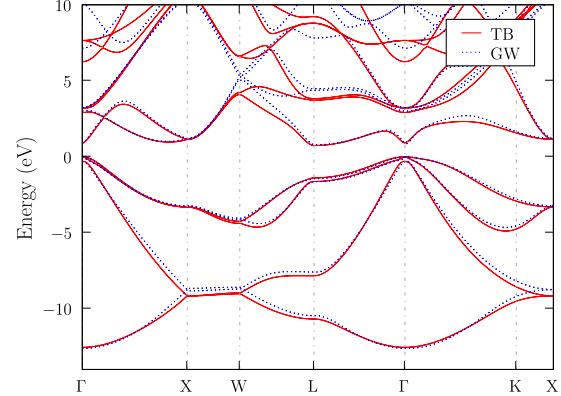


FIG. 2. (Color online) Band structure of bulk, unstrained germanium in the $sp^3d^5s^*$ TB and GW approximations.

reproduces the uniaxial $\langle 111 \rangle$ deformation potentials d_v and Ξ_u^L significantly better as it is able to account for the onsite couplings between the orbitals under shear strains. The hydrostatic valence-band deformation potential a_v , which controls the position of the band structure on an *absolute* energy scale, has been fitted to Ref. 13 ($a_v=2.38$ eV for Si and $a_v=2.23$ eV for Ge). Accordingly, the *unstrained* valence-band offset between Si and Ge has been set to $\Delta_{VBO}=0.68$ eV to reproduce the experimental valence-band discontinuity between $Si_{1-x}Ge_x$ alloys and Si as best as possible (see Table I and paragraph IVC). We achieve that way *strained* valence-band offsets $\Delta_{VBO}=0.79$ eV on Si [001] and $\Delta_{VBO}=0.28$ eV on Ge [001], within the experimental error bars⁶⁹ and in between the theoretical LDA values of Refs. 8 and 70. The unstrained valence-band offset and hydrostatic deformation potential, which are still somewhat controversial,^{8–13} can be tuned by shifting all onsite energies and a 's.

The typical behavior of the valence and conduction bands of Si and Ge under biaxial [001], [110], and [111] strains is plotted as a function of the in-plane deformation ε_\parallel in Figs. 4 and 5.⁷¹ As a reference, the lattice mismatch of Si grown on Ge is $\varepsilon_\parallel=4.18\%$, while the lattice mismatch of Ge grown on Si is $\varepsilon_\parallel=-4.01\%$. Under biaxial [001] strain, the six conduction-band minima of silicon split in two groups:¹⁰ the $\Delta_{x,y}$ valleys oriented along [100] and [010], and the Δ_z valleys oriented along [001]. The conduction-band edges are

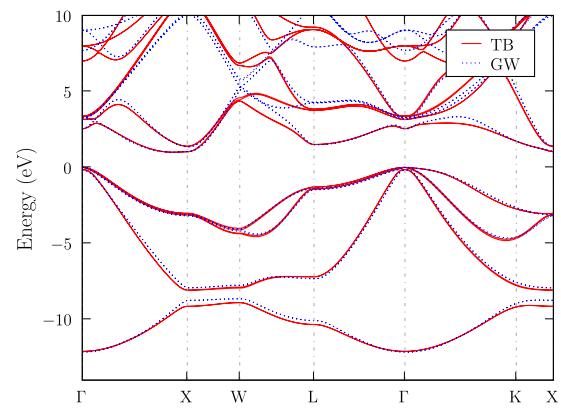


FIG. 3. (Color online) Band structure of bulk, unstrained $Si_{0.5}Ge_{0.5}$ in the $sp^3d^5s^*$ TB and GW approximations.

TABLE IV. Effective masses and Luttinger parameters of Si and Ge.

Si	Exp.	<i>GW</i>	<i>sp</i> ³ <i>d</i> ⁵ <i>s</i> * TB	Present model
m_l^Δ	0.9163 ^a	0.925	0.702 ^h ;0.891 ⁱ	0.900
m_l^Δ	0.1905 ^a	0.189	0.227 ^h ;0.201 ⁱ	0.197
m_l^L		1.808	1.378 ^h ;3.433 ⁱ	2.125
m_l^L		0.124	0.161 ^h ;0.174 ⁱ	0.151
γ_1	4.26 ^a ;4.285 ^a 4.22 ^b ;4.340 ^c	4.54	4.51 ^h ;4.15 ⁱ	4.22
γ_2	0.38 ^a ;0.339 ^a 0.39 ^b ;0.31 ^c	0.33	0.15 ^h ;0.26 ⁱ	0.37
γ_3	1.56 ^a ;1.446 ^a 1.44 ^b ;1.46 ^c	1.54	1.55 ^h ;1.39 ⁱ	1.43
Ge	Exp.	<i>GW</i>	<i>sp</i> ³ <i>d</i> ⁵ <i>s</i> * TB	Present model
m_l^L	1.588 ^d ;1.74 ^e	1.626	1.363 ^h ;1.584 ⁱ	1.594
m_l^L	0.08152 ^d ;0.079 ^e	0.074	0.083 ^h ;0.081 ⁱ	0.082
m_l^Δ		0.881	0.655 ^h ;0.701 ⁱ	0.837
m_l^Δ		0.176	0.223 ^h ;0.201 ⁱ	0.178
m_Γ			0.038 ^h ;0.039 ⁱ	0.038
γ_1	13.0 ^f ;12.8 ^g 13.25 ^a	13.54	13.13 ^h ;13.14 ⁱ	12.96
γ_2	4.4 ^f ;4.0 ^g 4.20 ^a	4.32	4.01 ^h ;3.68 ⁱ	4.11
γ_3	5.3 ^f ;5.5 ^g 5.56 ^a	5.77	5.75 ^h ;5.63 ⁱ	5.59

^aReference 61.^bBalslev and Lawaetz, as presented in Ref. 62.^cReference 63.^dReference 64.^eReference 65.^fReference 66.^gReference 67.^hReference 30.ⁱReference 68.

almost linear with strain, with $\Delta_{x,y}$ being the lowest energy valleys when $\varepsilon_{\parallel} < 0$ and Δ_z when $\varepsilon_{\parallel} > 0$. Biaxial [110] strain also splits the conduction-band minima in the same way; the Δ_z minima are, however, markedly nonlinear, being the lowest energy valleys for both $\varepsilon_{\parallel} < 0$ and $\varepsilon_{\parallel} \gtrapprox 2\%$. This behavior, which is not accounted for by the simplest deformation potential theories, results from the shear strain component $\varepsilon_{xy} = (\varepsilon_{\perp} - \varepsilon_{\parallel})/2$ (see discussion below). As a matter of fact, biaxial [111] strain (which does not split the conduction-band minima¹⁰) also exhibits the same nonlinear trends [$\varepsilon_{yz} = \varepsilon_{xz} = \varepsilon_{xy} = (\varepsilon_{\perp} - \varepsilon_{\parallel})/3$]. It is worthwhile to note that these nonlinearities have not been specifically targeted in the optimization of the TB parameters.

In germanium, a biaxial [001] strain likewise splits the Δ valleys (but not the L ones). The $\Delta_{x,y}$ valleys are the lowest energy bands for compressive strain $\varepsilon_{\parallel} \lesssim 2\%$, while the Γ valley falls below the L valleys for tensile strain $\varepsilon_{\parallel} \gtrapprox 2\%$. Germanium then becomes a small direct band-gap semicon-

TABLE V. Deformation potentials of Si and Ge (eV).

Si	Exp. ^a	LDA ^b	<i>sp</i> ³ <i>d</i> ⁵ <i>s</i> * ^c	Present model
b_v	-2.10 ± 0.10	-2.27	-1.85	-2.12
d_v	-4.85 ± 0.15	-4.36	-5.46	-4.91
$\Xi_d^\Delta + \frac{1}{3}\Xi_u^\Delta - a_v$	1.50 ± 0.30	1.67	0.97	1.43
Ξ_u^Δ	8.60 ± 0.40	8.79	6.88	8.70
$\Xi_d^L + \frac{1}{3}\Xi_u^L - a_v$		-3.14	-2.61	-3.20
Ξ_u^L		13.85	3.69	16.19
Ge	Exp. ^a	LDA ^b	<i>sp</i> ³ <i>d</i> ⁵ <i>s</i> * ^c	Present model
b_v	-2.86 ± 0.15	-2.90	-2.48	-2.74
d_v	-5.28 ± 0.50	-6	-3.74	-5.09
$a_g(\Gamma)$			-9.54	-9.01
$\Xi_d^L + \frac{1}{3}\Xi_u^L - a_v$	-2.00 ± 0.50	-2.86	-2.85	-3.19
Ξ_u^L	16.20 ± 0.40	17	8.09	15.39
$\Xi_d^\Delta + \frac{1}{3}\Xi_u^\Delta - a_v$		1.43	3.50	1.10
Ξ_u^Δ		10	6.50	9.02

^aCited by Ref. 8.^bPresent work.^cReferences 37 and 68.

ductor and even a semimetal (zero gap) when $\varepsilon_{\parallel} \gtrapprox 4\%$. Biaxial [111] strain splits the L valleys into two groups:¹⁰ the three $L\langle 11\bar{1} \rangle$ valleys (lowest energy for compressive strains) and the $L[111]$ valley (lowest energy for tensile strains). The band gap again closes when $\varepsilon_{\parallel} \gtrapprox 3.5\%$. The behavior of germanium under biaxial [110] strain is much more complex, Δ_z , the two $L\langle 11\bar{1} \rangle$ valleys, the two $L\langle 111 \rangle$ valleys, and Γ being successively the lowest energy band(s) when going from compressive to tensile strains, with a zero band gap for $\varepsilon_{\parallel} \lesssim -5\%$ and $\varepsilon_{\parallel} \gtrapprox 4\%$.

These results are in good agreement with the *ab initio* data (black diamonds⁷² in Figs. 4 and 5). Though the *sp*³*d*⁵*s* parametrization of Refs. 37 and 68 also shows reasonable agreement with *ab initio* data for [001] biaxial strain, it notably misses the strong nonlinearity of the conduction-band energy in Si [110] or [111]. As stated previously, this nonlinearity results from the peculiar behavior of the Δ valleys under shear strains, as further evidenced in Fig. 6. Indeed, the conduction-band minima move toward the X points with increasing compressive or tensile [111] strain and finally hang to the latter when $\varepsilon_{\parallel} > 4\%$ or $\varepsilon_{\parallel} < -3.3\%$.¹⁵ The position of the conduction-band minima along the ΓX axis as well as the longitudinal effective mass are plotted in Fig. 7. The longitudinal effective mass dramatically increases with $|\varepsilon_{\parallel}|$ and eventually diverges (quartic conduction-band dispersion) before decreasing again when the conduction-band minima reach the edge of the first Brillouin zone. Likewise, the Δ_z valleys shift to the X point under biaxial [110] strain, with a divergence of the longitudinal effective mass at $\varepsilon_{\parallel} \simeq 2.1\%$ and $\varepsilon_{\parallel} \simeq -2.4\%$.^{15,73,74} The splitting of the transverse masses under uniaxial $\langle 110 \rangle$ strain is also well reproduced.¹⁵ These effects, which were not accounted for by previous TB parametrizations, are fundamental for the understanding of

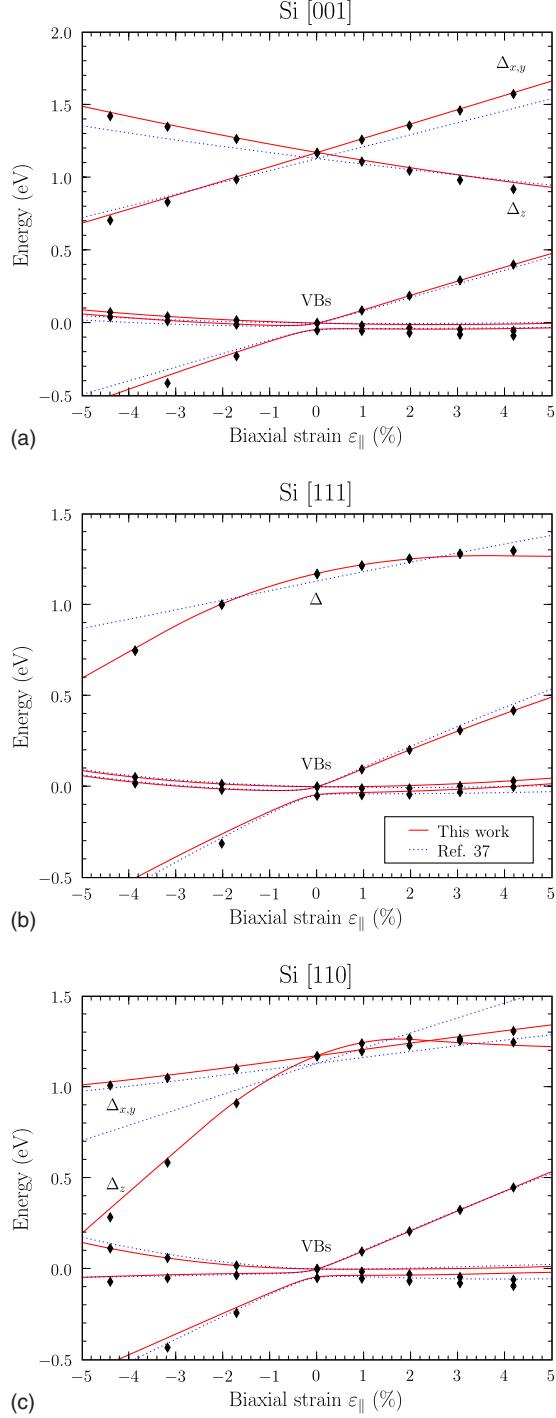


FIG. 4. (Color online) (a) [001], (b) [111], and (c) [110] biaxial strain behaviors of bulk silicon (Ref. 71). The black diamonds are the *ab initio* data (Ref. 72).

the transport properties of strained metal-oxide-semiconductor field-effect transistors (MOSFETs) or SiGe nanowire heterostructures.^{2,3,73}

C. Results in disordered $\text{Si}_{1-x}\text{Ge}_x$ alloys

The TB method offers the opportunity to describe semiconductor alloys as random distributions of atoms instead of

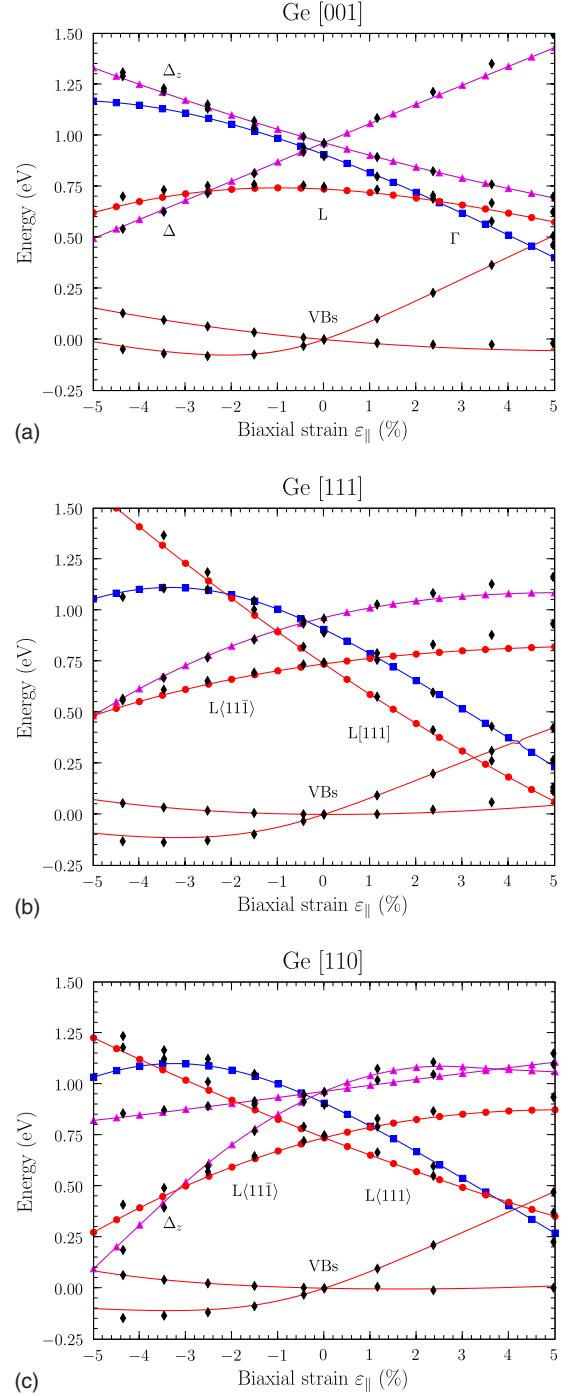


FIG. 5. (Color online) (a) [001], (b) [111], and (c) [110] biaxial strain behaviors of bulk germanium (Ref. 71). The (red) dots, (blue) squares, and (magenta) triangles are the L , Γ , and Δ valleys, respectively. The black diamonds are the *ab initio* data (Ref. 72).

virtual crystals, thus allowing, e.g., the investigation of alloy disorder scattering. The present TB model is particularly well suited to such random alloys as it does not depend on macroscopic strains that would be ill defined in a disordered environment. We have therefore computed the band-gap energy of bulk $\text{Si}_{1-x}\text{Ge}_x$ alloys modeled as random distributions of Si and Ge atoms in large $\sim 65\,000$ atom supercells (in order to reduce the statistical noise). The lattice parameters

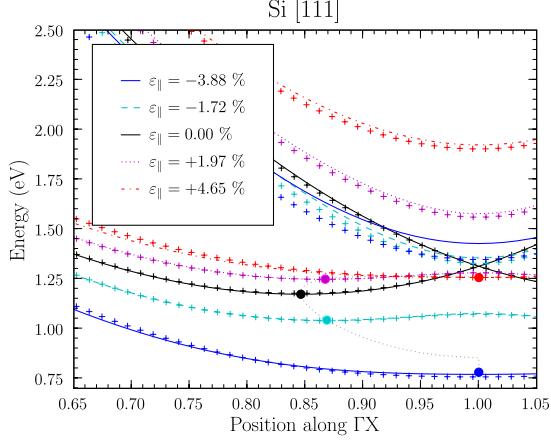


FIG. 6. (Color online) Lowest two conduction bands (plotted along the ΓX axis) of bulk silicon under the [111] biaxial strain. The conduction-band minimum is marked with a dot. Its motion with strain is plotted as a dotted gray line. The crosses are the *ab initio* data (also see Fig. 7).

of these supercells and the internal coordinates of the atoms were optimized with Keating's valence force field model.⁴⁶ The bond-bending and bond-stretching constants of the SiGe alloy are given in Table VI.

The calculated band-gap energy of the alloy is plotted as a function of the Ge mole fraction x in Fig. 8 and compared with luminescence data.⁷⁵ The lattice parameter of the alloy (computed from the valence force field) is also plotted in the inset and matches Dismukes's law⁷⁶ $a(x)=5.431+0.2x+0.027x^2$ Å (solid line). The present model predicts a crossing between the Δ - and L -valley conduction-band minima around $x=0.84$, in agreement with the experimental data. The bowing of the band-gap energy for $x < 0.84$ is, in particular, very well reproduced by the tight-binding calculation. We find that the band-gap energy of the disordered $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy is only ≈ 5 meV lower than the band-gap energy of the ordered alloy.

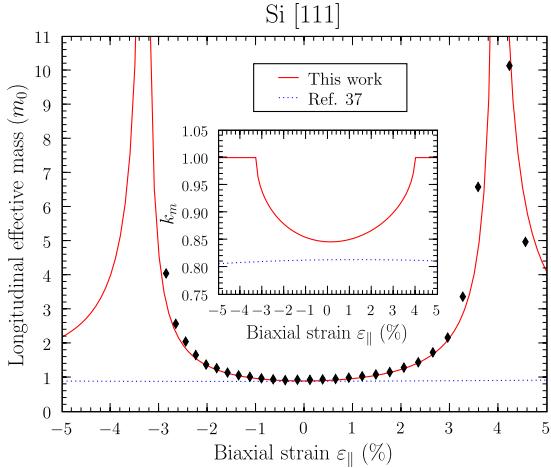


FIG. 7. (Color online) Conduction-band, longitudinal effective mass of bulk silicon under the [111] biaxial strain. Inset: position of the conduction-band minimum along the ΓX axis. The black diamonds are the *ab initio* data.

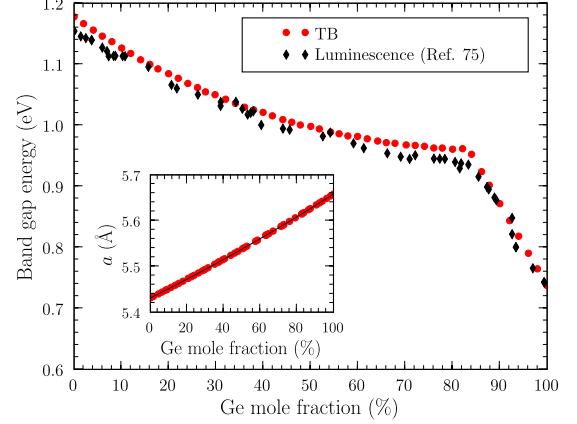


FIG. 8. (Color online) Band-gap energy of random bulk $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of the Ge mole fraction x . Inset: lattice parameter of the alloy. The solid line is Dismukes's law (Ref. 76) $a(x)=5.431+0.2x+0.027x^2$ Å.

As another illustration, the band-gap energy of random SiGe alloys biaxially strained on Si [001] (Refs. 77–79) or [110] (Ref. 80) is plotted in Fig. 9. Also shown in the inset of Fig. 9(a) is the valence-band discontinuity in $\text{Si}_{1-x}\text{Ge}_x$ alloys on Si [001]. The band gap decreases much faster with the Ge mole fraction than in bulk alloys due to the strains. This decrease is again very well reproduced by the TB model, showing its ability to describe random alloys under arbitrary strains. The conduction- and valence-band offsets of disordered $\text{Si}_{1-x}\text{Ge}_x$ alloys on $\text{Si}_{1-y}\text{Ge}_y$ [001] buffers are likewise in agreement with the 30 band $\mathbf{k} \cdot \mathbf{p}$ model of Ref. 15 in the virtual crystal approximation.

V. CONCLUSION

We have presented a model for the onsite matrix elements of the $sp^3d^5s^*$ TB Hamiltonian of a strained diamond or zinc-blende crystal. This model improves over previous parametrizations by including the onsite couplings among the s , p , and d orbitals of the atoms under uniaxial and shear strains. It is able to reproduce the deformation potentials and the dependence of the effective masses on strains at all relevant k points of the first Brillouin zone and is fully consistent with the symmetries of the crystal. We have successfully applied this description to Si, Ge, and their alloys. This tight-binding model should allow predictive modeling of the electronic properties of strained Si/Ge heterostructures and is numerically efficient enough to be included, e.g., in full-band Monte Carlo⁸² or Kubo-Greenwood⁸³ calculations of the transport properties of semiconductor devices.

ACKNOWLEDGMENTS

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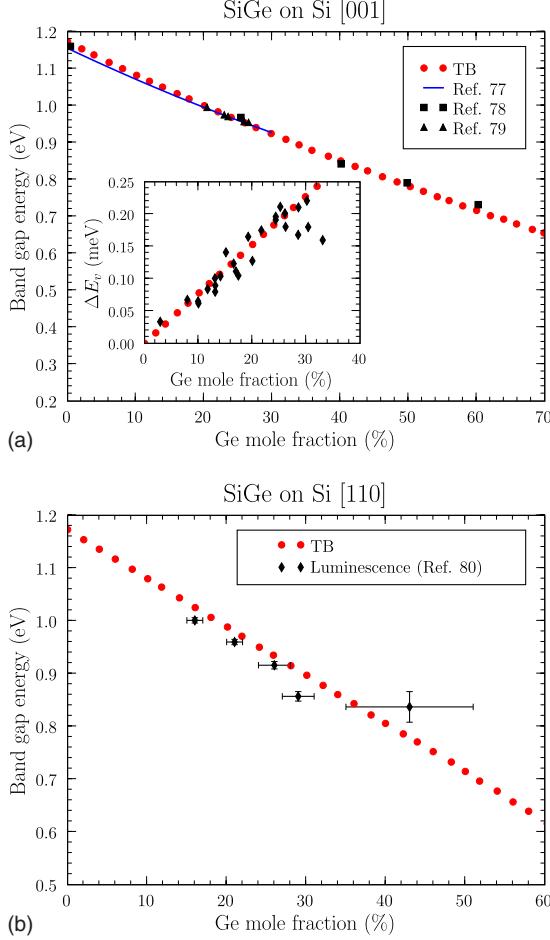


FIG. 9. (Color online) (a) Band-gap energy of random Si_{1-x}Ge_x alloys biaxially strained on Si [001] as a function of the Ge mole fraction x . The inset is the TB valence-band discontinuity ΔE_v (dots) compared to various experimental sources (diamonds) compiled in Ref. 81. (b) Band-gap energy of random Si_{1-x}Ge_x alloys biaxially strained on Si [110].

APPENDIX: COMPLETE ONSITE COUPLINGS BETWEEN THE s (s^*), p , AND d ORBITALS

1. Onsite energy of the s (s^*) orbitals

The onsite energy of the s orbitals reads as

$$H_s = E_s^0 + \alpha_s \frac{\Delta\Omega}{\Omega_0}, \quad (\text{A1})$$

where E_s^0 is the unstrained s orbital energy and α_s characterizes the dependence of H_s on the hydrostatic strain. The same

TABLE VI. The valence force field bond-stretching constant α , bond-bending constant β , elastic constants c_{ij} and internal strain parameter of Si, Ge and Si_{0.5}Ge_{0.5}. In the disordered SiGe alloys, we choose $\beta=13.31$ N/m for Si-Si-Ge and $\beta=12.30$ N/m for Ge-Ge-Si pairs of bonds.

Material	α (N/m)	β (N/m)	c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)	ζ
Si	48.54	13.83	165.8	63.9	79.3	0.557
Ge	39.14	11.81	131.8	48.3	64.1	0.536
Si _{0.5} Ge _{0.5}	43.80	12.81	148.5	55.9	71.6	0.547

model applies to the s^* orbitals (possibly with a different α_s^* coefficient).

2. Onsite couplings between the d orbitals

The onsite d block matrix $\hat{\mathbf{H}}_d$ reads in the $\{d_{yz}, d_{xz}, d_{xy}, d_{x^2-y^2}, d_{3z^2-r^2}\}$ basis set as:

$$\begin{aligned} \hat{\mathbf{H}}_d = & \left(E_d^0 + \alpha_d \frac{\Delta\Omega}{\Omega_0} \right) \hat{\mathbf{I}} + \sum_j^{\text{NN}} \beta_d(d) \\ & \times \begin{bmatrix} l^2 - \frac{1}{3} & -lm & -ln & mn & -\frac{1}{\sqrt{3}}mn \\ -lm & m^2 - \frac{1}{3} & -mn & -ln & -\frac{1}{\sqrt{3}}ln \\ -ln & -mn & n^2 - \frac{1}{3} & 0 & \frac{2}{\sqrt{3}}lm \\ mn & -ln & 0 & n^2 - \frac{1}{3} & \frac{2}{\sqrt{3}}u \\ -\frac{1}{\sqrt{3}}mn & -\frac{1}{\sqrt{3}}ln & \frac{2}{\sqrt{3}}lm & \frac{2}{\sqrt{3}}u & -n^2 + \frac{1}{3} \end{bmatrix} \\ & + \sum_j^{\text{NN}} \gamma_d(d) \begin{bmatrix} m^2n^2 & lmn^2 & lm^2n & mnu & mnv \\ lmn^2 & l^2n^2 & l^2mn & lnu & lnv \\ lm^2n & l^2mn & l^2m^2 & lmu & lm v \\ mnu & lnu & lmu & u^2 & uv \\ mn v & lnu & lm v & uv & v^2 \end{bmatrix}, \end{aligned} \quad (\text{A2})$$

where E_d^0 is the “bare” d orbital energy (see discussion below), $u=(l^2-m^2)/2$, and $v=(3n^2-1)/(2\sqrt{3})$. Like $\beta_p(d)$, $\beta_d(d)$, and $\gamma_d(d)$ can be written as

$$\beta_d(d) = \langle d_i^\delta | \nu_2 | d_i^\delta \rangle - \langle d_i^\pi | \nu_2 | d_i^\pi \rangle = \beta_d^{(0)} + \beta_d^{(1)} \frac{d-d_0}{d_0}, \quad (\text{A3a})$$

$$\begin{aligned} \gamma_d(d) = & 3 \langle d_i^\sigma | \nu_2 | d_i^\sigma \rangle + \langle d_i^\delta | \nu_2 | d_i^\delta \rangle - 4 \langle d_i^\pi | \nu_2 | d_i^\pi \rangle \\ = & \gamma_d^{(0)} + \gamma_d^{(1)} \frac{d-d_0}{d_0}, \end{aligned} \quad (\text{A3b})$$

where $\beta_d^{(0)}$, $\beta_d^{(1)}$, $\gamma_d^{(0)}$, and $\gamma_d^{(1)}$ are additional TB parameters.

$\hat{\mathbf{H}}_d$ is the sum of the bare d orbital energies of a $\propto \alpha_d$ hydrostatic correction and of two $\propto \beta_d$, γ_d angular matrices. Like $\hat{\mathbf{H}}_p$, the diagonal of the $\propto \beta_d$ matrix has been shifted [by $-1/3\sum_{\text{NN}}\beta_d(d)$] so as to be zero in the unstrained diamond or zinc-blende crystal. The five d orbitals are not, however, de-

generate anymore as soon as $\gamma_d^{(0)} \neq 0$. They indeed split in two groups: (i) the $\{d_{yz}, d_{xz}, d_{xy}\}$ orbitals with energy $E_d^0 + 4\gamma_d^{(0)}/9$ and (ii) the $\{d_{x^2-y^2}, d_{3z^2-r^2}\}$ orbitals with energies E_d^0 (since, e.g., $\sum_j^{NN} m^2 n^2 = 4/9$).⁸⁴ This is consistent with the symmetry of the zinc-blende or diamond lattice, though it is usually not accounted for in TB models.

3. Couplings between the s and s^* orbitals

The onsite matrix element coupling the s and s^* orbitals reads as

$$H_{ss^*} = \sum_j^{NN} \gamma_{ss^*}(d), \quad (A4)$$

where $\gamma_{ss^*}(d) = \langle s_i | \nu_2 | s_i^* \rangle = \gamma_{ss^*}^{(0)} + \gamma_{ss^*}^{(1)} \frac{d-d_0}{d_0}$. It is nonzero in the unstrained diamond or zinc-blende crystal if $\gamma_{ss^*}^{(0)} \neq 0$.

4. Couplings between the s (s^*) and p or d orbitals

The onsite matrices coupling the s and p/d orbitals read as

$$\hat{H}_{sp} = \sum_j^{NN} \beta_{sp}(d) [l \ m \ n] \quad (A5)$$

$$\hat{H}_{sd} = \sum_j^{NN} \beta_{sd}(d) [mn \ ln \ lm \ u \ v], \quad (A6)$$

where $\beta_{sp}(d) = \langle s_i | \nu_2 | p_i^\sigma \rangle = \beta_{sp}^{(0)} + \beta_{sp}^{(1)} \frac{d-d_0}{d_0}$ and $\beta_{sd}(d) = \sqrt{3} \langle s_i | \nu_2 | d_i^\sigma \rangle = \beta_{sd}^{(0)} + \beta_{sd}^{(1)} \frac{d-d_0}{d_0}$. Both matrices are zero in the unstrained diamond or zinc-blende crystal.

5. Couplings between the p and d orbitals

The onsite matrix coupling the p and d orbitals reads as

$$\begin{aligned} \hat{H}_{pd} = & \sum_j^{NN} \beta_{pd}(d) \begin{bmatrix} 0 & n & m & l & -\frac{1}{\sqrt{3}}l \\ n & 0 & l & -m & -\frac{1}{\sqrt{3}}m \\ m & l & 0 & 0 & \frac{2}{\sqrt{3}}n \end{bmatrix} + \sum_j^{NN} \gamma_{pd}(d) \\ & \times \begin{bmatrix} lmn & l^2n & l^2m & lu & lv \\ m^2n & lmn & lm^2 & mu & mv \\ mn^2 & ln^2 & lmn & nu & nv \end{bmatrix}, \end{aligned} \quad (A7)$$

where $\beta_{pd}(d) = \langle p_i^\pi | \nu_2 | d_i^\pi \rangle = \beta_{pd}^{(0)} + \beta_{pd}^{(1)} \frac{d-d_0}{d_0}$ and $\gamma_{pd}(d) = \sqrt{3} \langle p_i^\pi | \nu_2 | d_i^\sigma \rangle - 2 \langle p_i^\pi | \nu_2 | d_i^\sigma \rangle = \gamma_{pd}^{(0)} + \gamma_{pd}^{(1)} \frac{d-d_0}{d_0}$. This matrix is nonzero in the unstrained diamond or zinc-blende crystal if $\gamma_{pd}^{(0)} \neq 0$.

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