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Tight-binding description for the bound electronic states of isolated single and paired native defects in β-SiC

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A theoretical analysis is presented for existing photoluminescence (PL) and deep-level-transient-spectroscopy (DLTS) data, characterizing the optically active impurities and lattice defects in β-SiC films gown by the chemical-vapor-deposition technique. Results are reported for the band structure of β-SiC based on a tight-binding theory and calculations are presented in the Green's-function framework for the electronic energy states of sp^3-bonded native, substitutional (isolated), and pair defects occupying either Si and/or C sites. Local distortions around impurity atoms are estimated in terms of a simple, but *first-principles*, bond-orbital model. To account for the off-diagonal elements in the perturbation matrix, the effects of lattice relaxations are systematically included. For bound electronic states of several isolated and complex defects, the results are discussed and compared with existing theoretical results and experimental (PL and DLTS) data.

I. INTRODUCTION

Silicon carbide (SiC) has been, and still is, regarded as a promising semiconducting material for high-temperature, high-frequency, and high-power device applications.[1-5] The principle driving force for the current resurgence in interest in this material is its fascinating characteristics. These characteristics include high-electron mobility, high-electron saturation velocity, wide band gap, thermal, mechanical, and chemical stability, etc. SiC is exhibited in dozens of polytypes, each of which has a different periodic stacking sequence of identical Si-C layers. The most common polytypes occur in the cubic (zinc-blende) β-SiC (3*C*-SiC) and hexagonal 6*H*-SiC structures. For many years, crystal growth has been the chief obstacle to SiC becoming a useful semiconducting material. Only few mm diameter size crystals were grown in the past by using sublimation or liquid-phase techniques. In recent years, however, substantial progress has been made to grow thin silicon carbide films on Si substrates using chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) techniques. This remarkable success in the growth front has put β-SiC at the center of considerable attention both for basic and applied research. Consequently, several useful electronic devices[1-5] have been fabricated including metal-oxide-semiconductor field-effect transistors, high-speed switching devices, light-emitting diodes, etc.

When epitaxial methods are used to grow compound semiconductors, deviations from stochiometry are likely to occur. These deviations are caused primarily by the differences in the vapor pressures of the two constituent elements and/or in the molecular beam intensities. Several indications have suggested that a CVD-grown SiC is Si rich, and MBE-grown SiC can be made either Si or C rich.[6] Again, a small deviation ($\sim 0.1\%$) in stochiometry may result in native defects (e.g., vacancies, antisites, self-interstitials, etc.) with concentrations as high as 10^{19}. Since vacancies are mobile and migrate in the material, they can be trapped by intentionally doped defects and/or by other native (say, antisite) impurities to form complexes. Such "impurity-vacancy" complexes can produce shallow or deep defect states. In semiconductors, the existence of deep levels has been shown to have a deleterious effect on the lifetime of minority carriers. Therefore, in SiC, the defects which cause deep traps must be identified as they can have important effects on the performance of optoelectronic devices.

There exist several conventional methods[7-22] for identification and characterization of impurities in semiconductors, including infrared (ir) absorption, Raman scattering, photoluminesence (PL), electron spin resonance (ESR), deep-level transient spectroscopy (DLTS), etc. For assessing the crystal quality of CVD-grown SiC films, the PL has proven to be a convenient and nondestructive method.[14,17,18] This technique has also been used to detect optically active impurities and lattice defects. In SiC film, the occurrence of native defects has recently been suggested in several PL measurements.[14,17,18] However, the interpretations of the data differ significantly. The available results of impurity states for native defects from DLTS measurements are equally sparse.[20,21] For example, in CVD-grown SiC films, Nagesh *et al.*[20] did not observe deep localized levels due to native defects. However, the measurements of Zhou *et al.*[21] have suggested the occurrence of two deep impurity states (near ~ 0.34 and ~ 0.68 eV) below the bottom of the conduction band. Quite recently, new DLTS data for deep centers introduced by Al, B, and N complexes in 6*H*-SiC have also appeared in the literature.[13]

One of the purposes of the present paper is to report, in a simple-cubic phase of SiC, the theory of deep impurity levels for ideal vacancies, isolated defects, "impurity-impurity," and "vacancy-impurity" complexes. The calculation described here is carried out in the tight-binding formalism using a Green's-function theory.[23] Since the structural differences between the two phases of SiC occur first at the third-nearest neighbors, many of the conclusions drawn in this paper are likely to apply to the 6*H*-phase too. As the electronegativities and free atomic energies of Si and C atoms in β-SiC show trends identical to those of group-III (Ga) and group-V (As) atoms in III-V (GaAs) compounds,[24] the electronic band structure and defect properties of SiC (c.f., Sec. II) are expected to produce results similar to those obtained in GaAs. For sp^3-bonded impurities, we have considered the perturbation potentials $\underline{P}$ in the modified central-cell atomiclike configuration and have studied the bound electronic states of isolated and pair defects in SiC by using tight-binding Green's-function theory. This study will allow us to discriminate the existing PL, ESR, and DLTS data in CVD-grown SiC films and may be a valuable guide for experimentalists attempting to interpret results on "impurity centers" in β-SiC.

II. METHOD OF CALCULATION

A. Tight-binding Hamiltonian and the Green's function

To introduce the notations for the discussion to follow, we present here a brief outline of the construction of the tight-binding (TB) Hamiltonian reviewed in length elsewhere.[23] For a heteropolar compound of zinc-blende structure, an orthonormal basis of one *s* and three *p* orbitals per site (sp^3) is employed with hopping integrals $(l,l',m)_n$ extending up to and including second-nearest neighbors. These hopping integrals represent the interaction between an electron in the *l*th orbital of one atom with an electron in the *l'*th orbital of the second atom through spherical potentials. In the conventional notation of the molecular-orbital theory, the component of angular momentum around the axis between the two atoms is designated by $m=\sigma$ or π. Again, $n=1$ or 2 signifies the distance of the first- or second-nearest-neighbor atoms. The truncation at the second-nearest neighbors is not essential to the present formalism. However, it provides a useful compromise between ease of parametrization (23) and the quality of the resulting band structure.

Following Koster and Slater,[25] the perfect crystal Hamiltonian $\underline{H}^0$ for zinc-blende-type crystals is constructed as

$$\underline{H}^0=\sum_{i,\mathbf{R}}[|i,a,\mathbf{R}\rangle E^a_{ii}\langle i,a,\mathbf{R}|+|i,c,\mathbf{R}\rangle E^c_{ii}\langle i,c,\mathbf{R}|] + \sum_{i,j\mathbf{R},\mathbf{R}'}[|i,a,\mathbf{R}\rangle E_{ij}(\mathbf{R},\mathbf{R}')\langle j,c,\mathbf{R}'|+\mathrm{H.c.}]\ , \quad (1)$$

where **R** specifies the unit cell containing a cation *c* and an anion *a*. The term *i*, in the minimum basis set, corresponds to s, p_x, p_y, or p_z orbitals and H.c. corresponds to the Hermitian conjugate. The terms E^a_{ii}, E^c_{ii} are the diagonal elements of $\underline{H}^0$ in the basis $|i,a,\mathbf{R}\rangle$ and $|i,c,\mathbf{R}\rangle$, respectively. Again, the transfer matrix elements E_{ij} are considered nonzero only between nearest- and second-nearest-neighbor atoms, i.e., between $|\mathbf{R}-\mathbf{R}'|=\sqrt{3}a_0/4$ and $\sqrt{2}a_0/2$, where a_0 is the cubic lattice constant. The states $|i,a,\mathbf{R}\rangle$ and $|i,c,\mathbf{R}\rangle$ are localized orbitals centered on the anion at **R** and on the cation at $\mathbf{R}+\mathbf{d}$, where $\mathbf{d}=(a_0/4)(1,1,1)$. In this representation, the Hamiltonian $\underline{H}^0$ is an (8×8) matrix with 23 interaction integrals. The advantage of this Hamiltonian is that, besides its good fitting to the band structure of β-SiC, the explicit dependence of the two-center integrals on interatomic separation enables us to construct reasonably accurate perturbation potentials for studying the electronic properties of defects.

In the presence of defects, the Hamiltonian $\underline{H}^0$ is modified to $\underline{H}$, where $\underline{H}=\underline{H}^0+\underline{P}$, and $\underline{P}$ is the perturbation potential. The calculation of the bound electronic states of isolated single and pair impurities in the gap can be achieved by solving the secular equation

$$\det[\underline{I}-(E\underline{I}-\underline{H}^0)^{-1}\underline{P}]=0 \quad (2)$$

or

$$\det\left[\underline{I}-\int_{-\infty}^{\infty}dE'\frac{\delta(E'\underline{I}-\underline{H}^0)}{E-E'}\underline{P}\right]=0\ , \quad (3)$$

where $\underline{G}^0(E)=(E\underline{I}-\underline{H}^0)^{-1}$ is the Green's function of the host system. By considering appropriate symmetry of the defect and using group-theoretical arguments, the secular equations (2) or (3) are factorized into smaller size determinants. For example, the presence of an sp^3-bonded defect on a Si or C site with T_d point-group symmetry produces four impurity levels: an orbitally nondegenerate a_1 (or *s*-like) and a triply degenerate t_2 (or *p*-like) state. If a second impurity sits next to an isolated and/or native defect, it forms a nearest-neighbor pair with a reduced point-group symmetry, C_{3v}, at the impurity site. Consequently, the two triply degenerate isolated impurity levels of type t_2 (or *p*) split and produce two sets of doubly degenerate *E* (or π) -like and two nondegenerate A_1 (or σ) -like energy states. The π-like orbitals are derived from the mixing of t_2-like states of the isolated defects. Since these molecular levels have lobes oriented perpendicular to the spine of the "defect molecule," the overlap between them is expected to be small. The energies of doubly degenerate *E*-type states will, therefore, differ little from the t_2 energies of the isolated defects. The term degeneracy used here excludes spin degeneracy. By considering perturbations ($\underline{P}$) in the modified central-cell atomiclike potential[26] and incorporating the band structure of the perfect system obtained from the TB theory, we have solved Eq. (3) in the appropriate irreducible representations of the impurity point groups. A standard (e.g., Lehman-Taut) tetrahedron numerical technique is used in actual computer calculations. The results for the bound electronic states of isolated and complex defects in β-SiC are reported in Sec. III B.

B. Perturbation potential

In any defect calculation of impurity levels, the most important problem has been to give an adequate representation of the perturbation potential $\underline{P}$. The matrix $\underline{P}$ required to define the defect as a *deep trap* demands an accurate description of the short-range central-cell potential, long-range Coulomb potential, lattice relaxation, charge-state splittings, etc. To the best of our knowledge, there does not exist any unified theory where all the above factors are properly included in the perturbation potential.

In the TB method, one can avoid some of these effects and construct the perturbation potential by using the scaling properties and the chemical trends found in the matrix elements of the host-crystal Hamiltonian ($\underline{H}^0$).[26] Since the Coulomb potential produces an infinite number of shallow hydrogenic effective-mass-like levels within 0.1 eV of the relevant band edge, we have neglected such an interaction in our study. This neglect of the Coulomb interaction was motivated partly because it will have little influence on the energy scale of interest, and primarily because of the fact that deep levels are bound by the central-cell atomiclike defect potential. In this scheme, the shallow impurities will have zero binding energy. The effects of Coulomb interactions, if needed, can be incorporated *a posteriori* into the theory.

If the impurity is confined to the central cell alone, the perturbation potential $\underline{P}$ will depend upon the change in the diagonal (on-site energies) as well as upon the nondiagonal elements. Most of the existing calculations using the TB formalism have neglected the change in transfer (nondiagonal) matrix elements.[27] In this approximation, the perturbation matrix is purely diagonal by virtue of the chemical trends built into the Hamiltonian $\underline{H}^0$. Moreover, the diagonal elements P_{ii}^c or (P_{ii}^a) are seen to be proportional to the differences between the defect and the host atomic energies. Here we have included both the diagonal and the nondiagonal elements of the perturbation potential. The nondiagonal terms of $\underline{P}$ require the calculation of the total energy (E_{tot}) of the impurity-host system and the change in bond length (Δd) caused by isolated defects. For several isolated defects in β-SiC, using a first-principles bond-orbital model, we have evaluated the lattice distortions from the minimum of the calculated total energies (cf. Table V). Since Δd is sufficiently small compared to the bond length d, the variations of the transfer matrix elements are obtained to a good approximation by using Harrison's[24] ansatz that the interatomic matrix elements in zinc-blende-type crystals scale as the inverse square power of the bond length.

III. RESULTS

In this section we present the results of our tight-binding calculations for the band structure of β-SiC and for the characteristic energy levels of isolated single and pair defects using Green's-function theory. Although the most studied cases[7-22] in β-SiC are the bound states of isolated and complex defects involving native (vacancy, antisite, etc.) impurities, the interpretation of the data differ considerably. Again, from a theoretical standpoint, only two calculations exist in the literature describing the electronic properties of defects. One such calculation is based on a large-cluster recursion method[28] and the second uses a self-consistent pseudopotential technique.[29] The later study of impurity levels has given us significant physical insight and information for monitoring the success of semiempirical theories. We have therefore compared our results for isolated vacancies and native defects with those reported by Wang, Bernholc, and Davis[29] and by others[7-22,28] and have provided intuitive information for the trends of energy levels predicted in our tight-binding Green's-function study.

A. The band structure of β-SiC

Experimentally, major features of the electronic band structure of β-SiC have been obtained by using soft-x-ray emission, luminescence, optical reflectivity, and absorption techniques;[30-40] however, there remained ambiguities in assigning some of the observed transitions. For example, a structure near 6.0 eV was attributed by several workers to the onset of a direct transition at the Γ point. On the other hand, Nemoshkalenko *et al.*[36] interpreted it as a transition associated with the L point. The optical properties of β-SiC in the energy range (from 2.4 up to 6.0 eV) are believed to be dominated by the effects of indirect electronic transitions. In particular, the observed transition near $\sim$2.4 eV was well established as a (Γ_{15v}-X_{1c}) band gap while the absorption edges near 3.55 and 4.2 eV were assigned as L_{3v}-X_{1c} and Γ_{15v}-L_{1c} transitions, respectively. Although the pseudopotential calculation of Hemstreet and Fong[30] provided support to the interpretation of the feature near 4.2 eV as a Γ_{15v}-L_{1c} transition, the work of Lubinsky, Ellis, and Painter[31] assigned this state to be at a value considerably higher in energy with respect to the conduction-band minimum. Again, Patrick and Choyke[37] reported a narrow absorption band near 3.1 eV and tentatively ascribed it to the X_{1c}-X_{3c} transition. Furthermore, the experimental results for 2H-SiC prototypes had revealed an indirect threshold of 3.3 eV between the zone center and the conduction-band minimum at the K point. It should be mentioned that the K point in the reciprocal lattice of β-SiC lies very close to the K point of the hexagonal Brillouin zone of 2H-SiC.

In calculating the band structure of β-SiC, we have numerically evaluated the involved Slater-Koster parameters (see Table I) by using a nonlinear least-squares fitting procedure. The method has been discussed extensively in Ref. 23. To reduce the arbitrariness associated with a large number of tight-binding parameters, we require that the parametrizations satisfy certain physical criteria in addition to providing a reasonable fit to the crystal bands. This is particularly important in our effort to evaluate both the diagonal and nondiagonal elements of the perturbation matrices in the modified central-cell scheme. Therefore, in calculating the tight-binding parameters, we impose the following specific constraints. (a) The differences in the diagonal (on-site) parameters should closely approximate the differences in the corresponding atomic-energy levels. (b) The nearest-neighbor off-

TABLE I. Tight-binding parameters (in eV) used to fit the available data on the band structure (viz., energy gap, interband optical transition, and optoemission spectra) of β-SiC.

Slater-Koster parameters of β-SiC[a]
$\mathcal{P}_1=E_{ss}((000)_0)=-8.435\,00$
$\mathcal{P}_2=E_{ss}((000)_1)=-3.877\,50$
$\mathcal{P}_3=E_{xx}((000)_0)=2.381\,25$
$\mathcal{P}_4=E_{xx}((000)_1)=3.528\,75$
$\mathcal{P}_5=4E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=-12.034\,10$
$\mathcal{P}_6=4E_{sx}((\frac{1}{2}\frac{1}{2}\frac{1}{2})_{01})=7.633\,90$
$\mathcal{P}_7=4E_{sx}((\frac{1}{2}\frac{1}{2}\frac{1}{2})_{10})=8.256\,60$
$\mathcal{P}_8=4E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=3.034\,00$
$\mathcal{P}_9=4E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})=9.205\,30$
$\mathcal{P}_{10}=4E_{xx}((011)_0)=-2.228\,75$
$\mathcal{P}_{11}=4E_{xx}((011)_1)=-2.401\,25$
$\mathcal{P}_{12}=4E_{xy}((110)_0)=1.175\,00$
$\mathcal{P}_{13}=4E_{xy}((110)_1)=1.205\,00$
$\mathcal{P}_{14}=4E_{xx}((110)_0)=0.801\,25$
$\mathcal{P}_{15}=4E_{xx}((110)_1)=2.058\,75$
$\mathcal{P}_{16}=4E_{sx}((110)_0)=0.020\,00$
$\mathcal{P}_{17}=4E_{sx}((110)_1)=0.030\,00$
$\mathcal{P}_{18}=4E_{ss}((110)_0)=-0.035\,00$
$\mathcal{P}_{19}=4E_{ss}((110)_1)=-0.027\,50$
$\mathcal{P}_{20}=4E_{sx}((011)_0)=2.066\,00$
$\mathcal{P}_{21}=4E_{sx}((011)_1)=-1.255\,00$
$\mathcal{P}_{22}=4E_{xy}((011)_0)=1.662\,20$
$\mathcal{P}_{23}=4E_{xy}((011)_1)=1.771\,50$

[a] In the notations of Talwar and Ting, Ref. 23.

TABLE II. Calculated eigenvalues (in eV) for β-SiC at Γ, X, and L critical points.

Critical point	Our calc.	
Γ	-18.50	(Γ_{1v})
	0.00	(Γ_{15v})
	6.00	(Γ_{1c})
	7.00	(Γ_{15c})
X	-13.79	(X_{1v})
	-10.99	(X_{3v})
	-3.96	(X_{5v})
	2.40	(X_{1c})
	5.69	(X_{3c})
	14.50	(X_{5c})
L	-15.94	(L_{1v})
	-10.35	(L_{3v})
	-2.00	(L_{3v})
	3.86	(L_{1c})
	10.29	(L_{3c})
	11.26	(L_{1c})

diagonal elements (or the transfer integrals) should scale inversely as the square of the bond length. (c) All the second-nearest-neighbor parameters, in the hybrid basis, should be smaller compared to the nearest-neighbor hopping integrals. The parametrizations reported in Table I appear to be fairly unique although no attempt has been made at optimization.

With the parameter values of Table I, we have calculated the band structure (eigenvalues and eigenfunctions) of β-SiC, and the results of the energy bands at Γ, X, and L critical points are reported in Table II. Comparison with published results[30–41] has revealed that (cf. Table III) our tight-binding calculations are consistent with the available experimental and pseudopotential data. In Figs. 1 and 2 we display the complete energy-band dispersions and electronic density of states for β-SiC. Using the energy-band structure, the result for effective electron mass associated with the conduction-band minimum $m_c^*=0.69m_e$ is seen to be in very good agreement with the existing cyclotron resonance[42] $[m_c^*=(0.667\pm0.015)m_e]$ and the Zeeman $[m_c^*=(0.667\pm0.02)m_e]$ luminescence[43] data.

B. Bound electron states of defects in β-SiC

To study the bound electron states of isolated (or pair) defects, the spectral density functions are calculated in the a_1 (s-type) and t_2 (p-type) [or A_1 (σ-type) and E (π-type)] representations by incorporating the band structure (eigenvalues and eigenfunctions) of the host system. Appropriate spectral densities and the perturbation potentials are used in Eq. (3) for estimating the electronic states of impurities occupying either Si and/or C sites in β-SiC. We report here the results of our calculations for the bound states of isolated point defects and/or ideal vacancies preserving T_d symmetry and for the nearest-neighbor pair defects of C_{3v} symmetry.

TABLE III. Comparison of the important optical gaps (in eV) in β-SiC.

		Theoretical					
Transition	Expt.[a]	Our	Ref. 31	Ref. 30	Ref. 33	Ref. 35	Ref. 34
Γ_{15v}-Γ_{1c}	6.00	6.00	6.50	5.92	5.90	6.80	5.14
Γ_{15v}-X_{1c}	2.417	2.40	2.40	2.35	2.30	2.70	2.40
Γ_{15v}-K_{1c}	3.00	3.03					
Γ_{15v}-Γ_{15c}		7.00	7.20	6.49	7.80	8.60	10.83
X_{1c}-X_{3c}	3.05	3.29	3.70	3.08	2.60	3.20	3.24
L_{3v}-X_{1c}	4.20	4.40	3.10	3.90	3.10	6.00	3.26

[a] References 36–40.

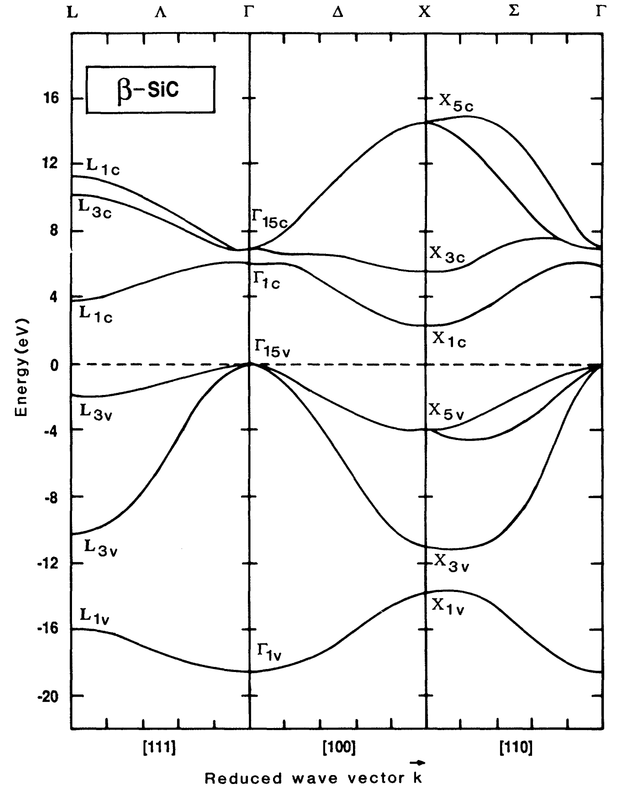

FIG. 1. Calculated electronic energy bands of β-SiC based on a second-neighbor tight-binding scheme (see Table I for model parameters).

1. *Isolated vacancies and defects*

If one of the two lattice sites in β-SiC is converted to an ideal vacancy, one should take the appropriate matrix elements of $\underline{P}$ to be infinite in magnitude. This allows for the vacancy atom to be decoupled from the host lattice. The assumption that no electron is allowed to reside at the vacancy site simulates the effect of a missing atom.[27] This procedure is equivalent to the so-called bond-cutting technique of creating an ideal vacancy. Thus, for an isolated cation (anion) vacancy we consider, in Eq. (3), the diagonal elements of the perturbation potential to be infinite [i.e., P_{ii}^{c} $(P_{ii}^{a}) \rightarrow \pm\infty$] and set a zero value for the off-diagonal matrix elements.

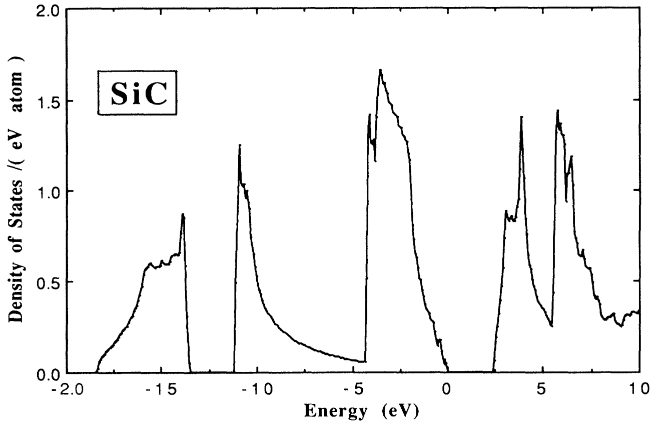

FIG. 2. Calculated electronic density of states of β-SiC.

Since the perturbation for an isolated vacancy is repulsive, it can push the levels from the valence band into the fundamental band gap. Again, since large differences exist in the electronegativity between Si (1.8) and C (2.5),[44] the electronic structure of isolated vacancies in SiC is likely to produce results similar to those of a III-V compound (viz., GaAs) with Si and C atoms acting in part as "cations" and "anions," respectively. Moreover, the creation of a cation vacancy is expected to produce weaker perturbation than the creation of an anion vacancy. Consequently, the energy state of silicon dangling bonds of a C *vacancy* is expected to be at a higher value relative to the carbon dangling bonds of a Si *vacancy*. Our Green's function calculations (see Table IV) suggest that the energies of the bound states (t_2 symmetry) of silicon and carbon vacancies are near $E_v+0.54$ eV and $E_v+1.66$ eV, respectively. In other words, the C and Si vacancies (V_C and V_{Si}) in β-SiC will behave as donors and acceptors. Although, the calculated trends of energy values for bound states of V_C and V_{Si} are different from the recursion method calculations of Li and Lin-Chung,[28] these are found, however, to be in good agreement with the pseudopotential results of Wang, Bernholc, and Davis.[29]

For substitutional defects (including antisites) in the unrelaxed host, one may reasonably consider the change in the off-diagonal matrix elements of $\underline{P}$ (which will be negligibly small) to be zero. Here, the perturbation $\underline{P}$ will be diagonal, which reduces the determinantal Eq. (3) to a product of two scalar equations, one for each basis state *i* [a_1 (*s*-like) or t_2 (*p*-like)]. In this approximation, our calculations for isolated acceptor (B or Al) and donor (N) defects in β-SiC show resonance states in the valence and conduction bands, respectively. No real bound states are found in the forbidden gap. For an isolated nitrogen donor, on the other hand, we find an a_1-type resonance state in the conduction band. The lattice distortion caused by a nitrogen donor in silicon carbide, if it is large, will lower the electronic energy state into the band gap and, consequently, this resonance state of a_1-type

TABLE IV. Comparison of the calculated bound electronic states of native defects in β-SiC with the existing PL and DLTS data, Refs. 7–22. All energies are measured from the top of the valence band.

Impurity center	Energy level E_v +eV	Character
V_{Si}	0.54	t_2 (T_d)
V_C	1.66	t_2 (T_d)
V_{Si}-V_C	0.48	E (C_{3v})
	1.62	E (C_{3v})
V_{Si}-Si_C	0.44	E (C_{3v})
V_C-C_{Si}	1.69	E (C_{3v})

TABLE V. Predicted variation of impurity-host distortion ($\Delta d/d$) (see Ref. 26 for details) and bond length for several impurities in β-SiC.

System	$\Delta d/d$	$d+\Delta d$ (Å)
Si*C*:Si	0.1219	2.117
Si*C*:Ge	0.1325	2.137
Si*C*:Sn	0.1643	2.197
Si*C*:B	0.053	1.987
Si*C*:Al	0.159	2.187
*Si*C:C	−0.1484	1.607
*Si*C:Ge	0.0159	1.917
*Si*C:Sn	0.0530	1.987
*Si*C:B	−0.0954	1.707
*Si*C:Al	0.0371	1.957
*Si*C:N	−0.2014	1.507

will become a real bound state.[13] If the inward relaxation for N_{Si} in SiC (see Table V) estimated from the bond-orbital model is included appropriately in the nondiagonal elements of the perturbation matrix $\underline{P}$, we do see a shift in the a_1-type resonance state towards the conduction-band edge. On the other hand, for impurities causing outward relaxation, the resonance levels are seen to be shifted away from the conduction-band edge. In β-SiC, although insufficient data exist to allow comparison for the effects of lattice distortions on deep trap energies, the calculated trends are found to be consistent with the observed deep levels for chalcogen (S, Se, Te) defects in silicon. Unlike the predictions of bound states for antisite defects in III-V compounds,[23] no such levels are seen to exist in β-SiC for Si_C or C_{Si} in the forbidden band gap. On the other hand, our results for the lattice distortions in Si*C*:Si obtained at the minimum of total energy (E_{tot}) (see Fig. 3) are seen to be in excellent agreement with the pseudopotential calculations of Wang, Bernholc, and Davis.[29]

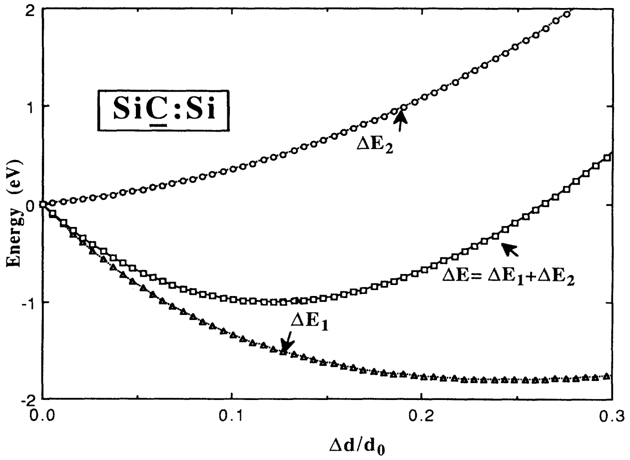

FIG. 3. Calculated lattice distortion in Si*C*:Si based on our bond-orbital model (see Ref. 26 for more details). The impurity-host (ΔE_1), host-host (ΔE_2), and total ($\Delta E = \Delta E_1 + \Delta E_2$) bond-energy variation against $\Delta d/d$ for a single antisite defect. The minimum of the total energy predicts the impurity-host relaxation.

2. *Pair defects*

In a nearest-neighbor pair defect of C_{3v} symmetry, the two triply degenerate t_2-type isolated-impurity levels will split and produce two sets of doubly degenerate E (or π) -type and two nondegenerate A_1 (or σ) -type levels. Since σ-type levels are derived from the mixing of s- and p-like orbitals of the two isolated defects, the A_1 states of the pair defects will be at energies significantly different form the two isolated defect states. In other words, the a_1-type resonance state of an isolated defect (if it exists in the conduction or in the valence band) can be pulled into the band gap by pairing it with an appropriate impurity. Similar to isolated antisite defects in β-SiC, no impurity-induced bound states in the forbidden gap are found for "C_{Si}-Si_C" antisite pairs. On the other hand, for nearest-neighbor divacancy "V_{Si}-V_C" and "antisite-vacancy" (viz., C_{Si}-V_C, Si_C-V_{Si}) pair defects of C_{3v} symmetries our calculations suggest the possibility of localized impurity states to be detected in the gap (cf. Table IV).

IV. DISCUSSION AND CONCLUSIONS

A second-neighbor tight-binding scheme developed in this work provides an accurate set of model parameters within the limitations imposed by the tight-binding theory and predicts reasonably well the band structure of β-SiC. Although, the exciton gap of β-SiC was established earlier,[38] the data for the exciton binding energy (13.5 meV) had resulted to a lower value of E_g (=2.4018 eV).[39] Using a high-resolution wavelength modulated absorption spectroscopy, Humphreys, Bimberg, and Choyke[40] have recently reported a new value for the exciton binding energy (27 meV). This has provided an improved data for the fundamental band gap of cubic SiC (2.417 eV). A perusal of Table III reveals that our theoretical results for the energy bands at critical points are in reasonably good agreement with the published data.[30–41]

By incorporating the eigenvalues and eigenfunctions obtained in the tight-binding scheme, we have numerically evaluated the Green's functions and, consequently, the bound states of several impurity centers involving native defects. Since the existing data for impurity levels are sparse, our discussion is limited here to those defect centers which are believed to be highly probable in cubic silicon carbide. Choyke and Patrick[7] first observed the so-called D_I center in He-ion-implantated and/or in fast-electron-bombarded cubic silicon carbide samples. The authors (of Ref. 7) speculated the origin of the D_I center to be related either to an "impurity-vacancy complex" or to some form of a divacancy.[8] For this radiation-related defect center, a model involving silicon vacancy (V_{Si}) and a nitrogen atom on a carbon site (N_C) was also proposed.[9] The polarization behavior of the D_I luminescence spectrum was studied by Suleimanov, Grekhov, and Grekhov.[10] The authors of Ref. 10 suggested this center to be an "impurity-vacancy complex" of local C_{3v} symmetry.

If the values of E_g ($=2.417$ eV) (Ref. 39) and $E(D_I)$ ($=1.972$ eV) (Ref. 14) are to be accepted, one finds a difference of 0.445 eV for the transition between the conduction-band X minimum and the D_I center. This value of 0.445 eV for the so-called D_I center compares reasonably well with our theoretical result for the V_{Si}-Si_{C} (0.44 eV) center and is not far from the V_{Si}-Si_{C} divacancy (0.48 eV). Our study also confirms the point-group symmetry of the D_I center to be C_{3v}. This center involves either a nearest-neighbor "divacancy" or a "vacancy-antisite complex," most likely a V_{Si}-Si_{C} complex. In several PL measurements on CVD-grown β-SiC/Si films, a sharp feature is observed near 1.972 eV which possesses a linewidth of about ~ 5 meV.[14] We believe that the width of the structure near 1.972 eV is a combination of transitions involving vacancy-antisite V_{Si}-Si_{C} divacancy centers with former center providing the major contribution.

Quite recently Choyke, Feng, and Powell[14] studied the G-series PL bands in cubic silicon carbide with the zero-phonon G band around 1.91 eV. This value is seen to be relatively lower than the existing data for the D_I band in CVD-grown samples. Earlier, in ion-implanted and annealed bulk samples of β-SiC, Choyke and Patrick[7] reported the 1.84–1.98-eV PL spectrum. They suggested that the observed 66.5-meV sideband is a resonant mode shifted to lower energy from the LA phonon replica. Although the low-frequency mode is located at ~ 1.91 eV, roughly the same position as the G band observed in recent PL measurements of CVD β-SiC films,[14] the intensity, shape, and lower-energy sidebands extending to 1.50 eV are distinctly different from the phonon sideband spectrum of the D_I center. A recent study[18] of the dependence of PL spectra on excitation power and temperature in a variety of SiC films has suggested the possible involvement of a deep acceptor (binding energy $E_A=470$ meV) in the G-band transitions. This acceptor level is found in every film (doped or undoped), independent of the growth reactor. In undoped samples, the results of native pair defects (cf. Table IV) suggest the possibility of a V_{Si}-Si_{C} level, while in doped materials the background acceptor impurity whose incorporation can be influenced by the film stochiometry might be responsible for the G-series luminescence transitions. In neutron-irradiated β-SiC samples, Makarov[11] observed similar luminescence transitions and suggested nonstochiometeric related defect centers for the observed energy levels between 0.44 and 0.48 eV. Earlier, in neutron-irradiated CVD-grown β-SiC samples and using DLTS, Nagesh *et al.*[20] have also revealed an electron trap with activation energy of 0.49 eV. All these experimental results lend support to our model calculations for the V_{Si}-V_{C} center of 0.48 eV and for the V_{Si}-Si_{C} center of 0.44 eV.

Using realistic lattice dynamical models for both the perfect and imperfect β-SiC we are studying the vibronic sidebands in the D_I spectrum. Our preliminary calculations have suggested that the main strength of the D_I vibrational spectrum lies in the acoustical phonon branch with a general shift towards lower energies from the normal lattice modes. This, together with the work reported in the present paper, supports the notion[8] that the complexes related to native defects are responsible for the D_I center. The results of detailed lattice dynamical calculations in cubic silicon carbide for the vibrational properties of several isolated native defects and defects in more complex configurations will be reported in the near future.

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