Empirical pseudopotential band structure of $3C$, $4H$, and $6H$ SiC using transferable semiempirical Si and C model potentials

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We present an approach to the empirical pseudopotential method (EPM) calculation of the band structure of SiC that overcomes the need for extensive experimental data. The method reduces the roughly 30 EPM fitting parameters needed to just two for $4H$ and one for $6H$ SiC. This allows fitting to the limited amount of experimental data available for these polytypes and the subsequent use of the EPM to calculate their bandstructure. A means of fitting to experimental effective masses through a nonlocal correction is also introduced. The procedure involves the construction of the empirical pseudopotential of diamond phase Si and C from local-model potentials based on the Heine and Abarenkov potential. These potentials successfully reproduce the experimental band energies around the band-gap region using one fitting parameter for each material. Once charge transfer is introduced, the potentials are then transferred to the heteropolar polytypes of SiC and the local potential is fit to the experimental band energies using just one local fitting parameter for each polytype. A nonlocal correction, introducing a second additional fitting parameter, is then included to fit the experimental effective masses of $3C$ and $4H$ SiC. Since reasonable agreement with experimental effective mass measurements was obtained in $6H$ SiC with just the one local parameter, the nonlocal correction was not used.

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1. INTRODUCTION

SiC has attracted a large amount of interest resulting from its potential applications in high-power, high-temperature, and high-frequency electronic devices. It is known to form a large number of similar polytypes that, except for the wurtzite phase, exhibit a roughly linear band-gap variation as a function of increasing hexagonal content. This offers the intriguing possibility that SiC technology could satisfy multiple needs over the band-gap regime of 2.4 eV($3C$) to 3.2 eV($4H$), though presently only $3C$, $4H$, and $6H$ have gained interest.

The harsh environment of the electronics for which SiC is proposed, make knowledge of the band structure, especially near the conduction-band minimum, important in determining electronic device characteristics. When applicable, the empirical pseudopotential method (EPM) is usually the method of choice for such work since it is computationally efficient and easily interpreted when compared to other methods such as density-functional theory (DFT). When calculating semiconductor properties that are influenced weakly by the deep core electronic states, such as the band structure close to the band gap, the method is often highly accurate. The weakness of the EPM is that it often relies heavily on the use of experimental data. Unfortunately, though useful for many diamond and zinc-blende phase semiconductors, the EPM is not as successful for lattice types with larger unit cells since the number of form-factor parameters that must be fit increases while the experimental data available generally decreases. The approach in these cases is to use the transferability of the pseudopotential and approximate the form factors by using those of a similar material. An important example is the success of using the same form factors for many direct band-gap materials that exist in both cubic and wurtzite phases. Due to differences in the density and magnitude of the reciprocal lattice vectors, the three diamond or seven zinc-blende parameters are interpolated to obtain the 10 or 19 parameters needed for homopolar or heteropolar wurtzite, respectively. For progressively larger unit cell phases, as in the polytypes of SiC, the number of form factors increases, such that the zinc-blende form factors alone cannot provide the detail of the Fourier transform of the pseudopotential required.

The EPM has been successfully applied to the $3C$ zinc-blende phase of SiC$^{6-8}$ where there are at least five reliable experimental band energies$^{9,10}$ to fit the seven form factors needed. These studies did not, however, include a fitting to experimental effective masses, which is important in determining transport properties. This is included as a nonlocal correction in this paper. For $4H$ and $6H$ SiC, roughly 30 form factors are needed, while there is only one reliable experimental band energy$^{1}$ for each material. Due to the lack of experimental data, these form factors have, to our knowledge, never been characterized and published until now. We overcome the difficulty in fitting the form factors of $4H$ and $6H$ by using a model potential to represent the empirical pseudopotential. The use of a model potential is highly advantageous when working with large unit cells since the full potential can be calculated and fit to optical data using a limited number of parameters. By extending the nonlocal Abarenkov and Heine model potential$^{11}$ including the nonlocal screening of Animalu, and Heine$^{12,13}$ for use in covalent and partially ionic semiconductors, and refitting one parameter, we found a model empirical pseudopotential that could accurately reproduce the experimental band energies of Si, SiC, and diamond around the band-gap region. The limited number of fitting parameters in SiC , commensurate with the amount of experimental data available for the hexagonal polytypes, is the result of the use of transferable Si and C potentials. A local model potential is used for convenience...
that directly produces fitted form factors that can be used within the EPM. A nonlocal correction with one additional parameter is then added to fine tune the band structure, and is used to fit the effective masses of 3C and 4H. The correction is not used for 6H since the local potential alone gives good results for the effective masses.

II. HA MODEL POTENTIAL

By adding nonlocal screening to the Heine and Abarenkov potential, Heine and Animalu (HA) developed a model atomic potential that successfully predicted the long-wavelength form factors for many metals.\textsuperscript{12,13} The unscreened core potential was represented as a sum of angular-momentum-dependent square wells extending over a nonlocal core of radius \( R \) within which valence electrons interact with the core electrons. This radius turns out to be quite large, roughly 60–70% of the atomic radius in Si and C. The well depths \( A_l \) were each independently fit to the experimental energy levels of the corresponding free ions. Taking into account their energy dependence, the metallic values were then obtained by extrapolating from the free ion energy to the corresponding equivalent energy relative to the Fermi level of the metal. An approximation to the metal values was thus obtained by fitting to atomic spectroscopic data. For simplicity, the square wells of the metallic core potential were then considered to be energy independent with the same radius \( R \) used for each.

The atomic potential is, in general, a sum over all \( l \)

\[
V_{HA}^{\alpha} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} V_{l|m|} \langle lm | \rangle. \tag{1}
\]

The relevant members of the sum will only involve the \( l \) values of the unexcited valence and core electrons. HA argued that higher harmonics would produce pseudowavefunction nodes within the core. Such structure in the pseudowave function would be incompatible with the concepts of the pseudopotential method. Although others have questioned the theoretical significance of this approximation and have improved the model to eliminate it,\textsuperscript{14} we retain it since it renders the model in a convenient form for fitting to experimental data. For Si and C, we will therefore not need to include members of the sum for \( l > 1 \). Based on the Phillips-Kleinman cancellation theorem,\textsuperscript{15} these unnecessary angular-momentum components of the potential should all be roughly the same size. They can therefore all be removed from the sum by removing the \( l = 2 \) component as an average. The \( l = 2 \) well then forms the local potential. The final form of the Fourier transform of the atomic potential, indicating the wave vector and model parameter dependence of the various terms, is

\[
V_{HA}^{\alpha}(\tilde{q}) = \frac{B(q; A_2, R, Z)}{\epsilon_m(q)} + \sum_{l < 2} \left[ \frac{I(q; A_1 - A_2, R)}{\epsilon_m(q)} + F(\tilde{k}, \tilde{G}; A_1 - A_2, R) \right]. \tag{2}
\]

where the lattice and electron wave vectors are \( \tilde{q} \) and \( \tilde{k} \), respectively. The local, or \( \tilde{k} \) independent, bare potential \( B \) is constructed from a local approximation to the \( l = 2 \) square well, the potential due to the net core charge \( Z \), and correlation and orthogonality hole corrections. \( F \) is the nonlocal bare core potential involving square wells of depth \( \Delta A_2 = A_1 - A_2 \) for each angular momentum considered. Hence, as previously discussed, only wells that differ in depth from \( A_2 \) will enter this term.

HA screened the bare potentials by using the Sham\textsuperscript{16} modification of the Hartree dielectric function appropriate for metals \( \epsilon_m \) and included the screening of the nonlocal potentials through the term \( F \). The “on Fermi sphere approximation” was used to take out the \( \tilde{k} \) dependence in \( F \) when appropriate. This involved setting \( k = k_f \), the Fermi wave vector, and letting

\[
|\tilde{k} + \tilde{q}| = \begin{cases} k_f & q \leq 2k_f \\ q - 2k_f & q > 2k_f. \end{cases}
\]

This also takes care of the angular dependence of \( \tilde{k} \) since it enters \( F \) through the angle between \( \tilde{k} \) and \( \tilde{k} + \tilde{q} \), which becomes

\[
\theta_{\tilde{k}, \tilde{k} + \tilde{q}} = \begin{cases} 0 & q \leq 2k_f \\ \pi & q > 2k_f. \end{cases}
\]

The “on Fermi sphere approximation” is used to construct a local atomic pseudopotential using simple average values for the electron energy and momentum. These average values are used to obtain an average potential that no longer depends on the electron energy and wave vector.

III. SI AND C MODEL POTENTIALS

The Si and C local atomic potentials that will be used in SiC are constructed by fitting the HA model to the band energies of homopolar diamond-phase Si and C. First a number of changes are made to the HA potential in order to convert it into a suitable form to represent the empirical pseudopotential of semiconductors. The metallic dielectric function in Eq. (2) must be replaced by one appropriate for semiconductors. For this we use the result of Penn\textsuperscript{17}

\[
\epsilon(q; E_g) = 1 + \frac{\left( \frac{\hbar \omega_p}{E_g} \right)^2 \left( 1 - \frac{E_F}{4E_g} \right)}{1 + \frac{E_F \left( \frac{q}{E_g} \right)^2 \sqrt{1 - \frac{E_g}{4E_F}}}{4E_F}}. \tag{5}
\]

where \( E_F \) is the Fermi energy, \( \omega_p \) the plasma frequency, and \( E_g \) is a band-gap parameter determined by\textsuperscript{18} the \( q \rightarrow 0 \) limit

\[
E_g = \frac{\hbar \omega_p}{\sqrt{\epsilon(0) - 1}}. \tag{6}
\]

The model potential must be adjusted at high \( q \), where the empirical pseudopotential is truncated. For semiconductors,
it has been shown that the potential may be suitably cut off at 
$3k_f$, yet damping should not interfere with the potential for lattice vectors less than $2k_f$.\textsuperscript{19} We therefore damp the potential according to

$$V^a(\mathbf{k}, q) = V_{HA}^a(\mathbf{k}, q) e^{-\alpha \Theta(X)} X,$$

where $X(q) = (q/2k_f - 1)$ and

$$\Theta(X) = \begin{cases} 1 & X \geq 0 \\ 0 & X < 0. \end{cases}$$

The damping factor $\alpha$ is adjusted so that the potential damps to zero for $q > 3k_f$, and the step function ensures that all truncation occurs after $q = 2.2k_f$, and therefore well after $2k_f$. Since the fitting parameter will be used to vary the potential in this region, this simple damping term is chosen so that no new fitting parameters are introduced. It also represents the diminishing importance of EPM form factors for $q > 2k_f$, which is roughly $q^2 > 12$ in reciprocal lattice vector units. For Si and diamond, the only form factor from the damped region occurs at $q^2 = 16$. Since this form factor is found not to improve the fit to experimental data in EPM studies of Si,\textsuperscript{20} we do not include it. For diamond, however, it is needed.\textsuperscript{21}

We also use the “on Fermi sphere” approximation to treat $F$ locally as

$$F(\mathbf{r}) = F(q; A_l - A_2, R).$$

Only the square wells, which differ significantly from the $l = 2$ well, will be considered in order to limit the number of parameters in the model. These are the repulsive $l = 0$ well for Si and the attractive $l = 1$ well for C. This attractive well in C originates from the lack of core $p$ states.

Following EPM theory,\textsuperscript{4} the crystal pseudopotential $V_p$ can be represented as a sum over all reciprocal-lattice vectors $\mathbf{G}$

$$V_p(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}},$$

where

$$V(\mathbf{G}) = \sum_{\alpha} S_a(\mathbf{G}) V^a(\mathbf{G}),$$

with the sum over each atomic species $\alpha$ present. For the diamond phase potential, there is only one species present, but we will keep the potential in a general form applicable to SiC as well. The structure factor is

$$S_a(\mathbf{G}) = \frac{1}{n_a} \sum_{\tau_a} e^{-i\mathbf{G} \cdot \tau_a},$$

where $n_a$ is the total number of atoms of species $\alpha$ in the unit cell and the sum is over the corresponding basis vectors $\tau_a$ of these atoms. The atomic potential in Fourier space, represented in Eq. (7), is evaluated from the real-space atomic pseudopotential according to

$$V^a(\mathbf{G}) = \frac{1}{\Omega_a} \int_{\Omega_a} V^a(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d^3r,$$

where $\Omega_a$ is the atomic volume and $V^a_\alpha$ is the atomic pseudopotential of species $\alpha$. For diamond ($A^3$) or zinc-blende ($A^5B^8$) phases, the Fourier transform of the pseudopotential is represented in terms of symmetric ($V^5$) and antisymmetric ($V^A$) parts

$$V(\mathbf{G}) = V^5(\mathbf{G}) \cos(\mathbf{G} \cdot \mathbf{r}) + iV^A(\mathbf{G}) \sin(\mathbf{G} \cdot \mathbf{r}),$$

where

$$V^5(\mathbf{G}) = \frac{V_A(\mathbf{G}) + V_B(\mathbf{G})}{2},$$

$$V^A(\mathbf{G}) = \frac{V_A(\mathbf{G}) - V_B(\mathbf{G})}{2}.$$

For crystalline Si and C, the diamond-phase potential is then only the symmetric term

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V(\mathbf{G}) \cos(\mathbf{G} \cdot \mathbf{r}) e^{i\mathbf{G} \cdot \mathbf{r}}.$$

With the exception of the C core radius $R_C$, which was chosen $4\%$ less, the HA results were used for the first approximation of the model parameters. One fitting parameter $A_2$ was then increased by $21\%$ for C and decreased by less than $2\%$ in Si, to fit to experiment. This parameter adjusts not only the local well but the nonlocal wells, treated locally here by the “on Fermi sphere approximation,” since $\Delta A_l = A_l - A_2$. The refitting of $A_2$ can be interpreted as accounting for the difficulty in extrapolating the well depths from the free ion values to obtain those for the corresponding metal, in particular, the choice of the free ion equivalent energy in the metal. Also, since $A_2$ should be one of the more energy-dependent parameters, its adjustment may account for the use of energy-independent model parameters and a local approximation to the potential.

To calculate the band structure, we use a plane-wave basis including all plane waves satisfying $(k + \mathbf{G})^2 \approx 21$. This criteria is found to give convergence in diamond and zinc-blende semiconductor structures.\textsuperscript{23} Convergence of the fitted band energies is found within $0.02$ eV for Si and diamond using $125$ plane waves for each material. The model potential and corresponding band structure of Si and diamond, are shown in Figs. 1–4, while the model parameters used are given in Table I. For Si, the model potential agrees closely with EPM form factors and subsequently agrees well with the experimental band energies in Table II. There is less agreement between the model potential and the EPM form factors for diamond, but the band structures\textsuperscript{21} and band energies in Table III are similar. Close to the band gap, the agreement with experiment is good. Several aspects of both the model and EPM diamond band structure,\textsuperscript{21} such as the lowest conduction bands around $\Gamma$ and $L$, and the width of the valence bands, do not agree with experimental data.\textsuperscript{21,24,25} This is most likely due to ignoring the strong
nonlocality of the C potential. Since the motivation here is to obtain a local C potential that can be transferred into the SiC polytypes and is accurate around the band gap, the potential is adequate.

IV. SiC MODEL POTENTIAL

For SiC, it is desirable to use modifications of the homopolar diamond-phase Si and C potentials. By using such transferable potentials, a close approximation to the SiC potential may be obtained, which can be further fit to experimental data by slightly adjusting a limited number of parameters. This is useful since band-energy data is limited for the hexagonal polytypes. For heteropolar materials, the model potential must first be amended to incorporate the effects of charge transfer and screening once dissimilar nearest neighbors are introduced.

The partial ionic nature of bonds, resulting from charge transfer, is important in the determination of the band structure of heteropolar materials. This can readily be seen in the ionic gaps in the band structure of polar zinc-blende semiconductors. Charge transfer, fit to experimental band energies of many semiconductors in model calculations, has been shown to approximately agree with the Phillips ionicity of these materials. This involved using a screened charge transfer that was added directly to the core charge of the individual atoms. These good results suggest a means of estimating and including charge transfer in the HA model. However, since the effects resulting from the bonding of C atoms to much larger Si atoms in SiC, are not accounted for in the Phillips ionicity, we cannot use it to estimate the charge exchange. An ionicity scale based on the charge-density asymmetry in the bonds can account for these size effects. Considering the transferred charge in the valence difference, the asymmetry coefficient can be estimated as

\[ g_{\text{SiC}} = 1 - \frac{(Z_C - \Delta Z')}{4} = \frac{\Delta Z'}{4}, \]  

allowing calculation of the charge transfer \( \Delta Z' \). To obtain the screened charge transfer \( \Delta Z \), \( \Delta Z' \) must be adjusted by

\[ \Delta Z = \Delta Z' - \Delta \chi, \]

where \( \Delta \chi \) is the change in charge due to screening.

FIG. 1. Si local-model potential band structure.

FIG. 2. Model potential of Si, with EPM form factors of Ref. 23 (●).

FIG. 3. Diamond local-model potential band structure.

FIG. 4. Model potential of C, with EPM form factors of Ref. 21 (●).
To include these effects in the model, a charge of $2$ is added to the net core charge of C and a charge of $1$ is added to the net core charge of Si. Since the core charge potential is contained in the local bare potential, the transferred charge will alter the potential according to

$$B(q;Z \pm \Delta Z) = B(q;Z) + \frac{8\pi \Delta Z}{\Omega q^2} \cos(qR),$$

where $\Omega$ is the unit-cell volume.

We also alter the homopolar potentials by screening each atom equivalently with the Penn dielectric function of SiC and by adding a nonlocal correction to the C potential. This correction, $F_{C}^{NL}$, enters the potential through $F_{C}$ according to

$$F_{C} = F_{C}^{L}(q;A_{C1} - A_{C2}, R_{C}) + F_{C}^{NL}(k,q;A_{C1}^{NL}, R_{C}).$$

$A_{C1}^{NL}$ is the nonlocal $l=1$ well depth, which is used to fine tune the band structures, fitting the SiC effective masses, once the best fit local potential is obtained.

Once the homopolar potentials are renormalized with respect to the SiC unit-cell volume $\Omega_{SiC}$, we attain the effective atomic potentials transferable into SiC.

**TABLE I.** Model parameters in (a.u.). Fitting parameters are indicated with (*).

<table>
<thead>
<tr>
<th>Material</th>
<th>$A_{Si0}$</th>
<th>$A_{Si2}$</th>
<th>$R_{Si}$</th>
<th>$A_{C1}$</th>
<th>$A_{C1}^{NL}$</th>
<th>$A_{C2}$</th>
<th>$R_{C}$</th>
<th>$\Delta Z$</th>
<th>$E_{g}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.08</td>
<td>2.40</td>
<td>2.00</td>
<td>4.48</td>
<td>0</td>
<td>3.94*</td>
<td>1.44</td>
<td>0</td>
<td>4.8</td>
<td>4.44</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For SiC parameters (-) means Si and C parameter used.

a Reference 22.

b Nonlocal.

c Reference 25.

d Reference 26.

the average value of the inverse dielectric constant

$$\Delta Z \approx \frac{4g_{SiC}}{\varepsilon_{SiC}} \approx 1.$$  (18)

To include these effects in the model, a charge of $-\Delta Z$ is added to the net core charge of C and a charge of $+\Delta Z$ is added to the net core charge of Si. Since the core charge potential is contained in the local bare potential, the transferred charge will alter the potential according to

$$V_{eff} = \frac{B_{C}(q;A_{C2}, Z + \Delta Z) + I_{C}(q;A_{C1} - A_{C2}, Z - \Delta Z)}{\varepsilon_{SiC}(q)}$$

and

$$V_{eff} = \frac{F_{C}(q;A_{C1} - A_{C2}, R_{C})}{\Omega_{SiC}} e^{-a_{C}h(X_{C}X_{C})}.$$  (21)

The symmetric and antisymmetric potentials are then

$$V_{eff} = \frac{[V_{eff}(\tilde{q} - \tilde{q}) + V_{eff}(\tilde{q})]}{2}.$$ (23)

These can then be used along with the structure factor, with basis vector $\tilde{r}$, to attain the full potential of $3C$-SiC

$$V_{3C}(\tilde{r}, \tilde{k}) = \sum_{G} [V_{3C}(\tilde{k}, G) \cos(G \cdot \tilde{r})$$

$$+ iV_{3C}(\tilde{k}, G) \sin(G \cdot \tilde{r})] e^{iG \cdot \tilde{r}}.$$  (24)

**TABLE II.** Energy levels of Si in (eV).

<table>
<thead>
<tr>
<th>Energy</th>
<th>Model</th>
<th>EPM</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{gap}$</td>
<td>1.10</td>
<td>0.87</td>
<td>1.12</td>
</tr>
<tr>
<td>$\Gamma_{16} - \Gamma_{25'}$</td>
<td>-12.52</td>
<td>-12.60</td>
<td>-12.56</td>
</tr>
<tr>
<td>$\Gamma_{15} - \Gamma_{25'}$</td>
<td>3.56</td>
<td>3.34</td>
<td>3.35</td>
</tr>
<tr>
<td>$\Gamma_{2} - \Gamma_{25'}$</td>
<td>4.04</td>
<td>4.37</td>
<td>4.16</td>
</tr>
<tr>
<td>$L_{1\alpha} - \Gamma_{25'}$</td>
<td>2.09</td>
<td>2.09</td>
<td>2.05</td>
</tr>
<tr>
<td>$L_{1\nu} - \Gamma_{25'}$</td>
<td>4.16</td>
<td>3.88</td>
<td>3.91</td>
</tr>
<tr>
<td>$L_{2\alpha} - \Gamma_{25'}$</td>
<td>-7.24</td>
<td>-7.33</td>
<td>-6.82</td>
</tr>
<tr>
<td>$L_{2\nu} - \Gamma_{25'}$</td>
<td>-1.22</td>
<td>-1.26</td>
<td>-1.22</td>
</tr>
<tr>
<td>$X_{4\alpha} - \Gamma_{25'}$</td>
<td>-10.17</td>
<td>-10.18</td>
<td>-9.34</td>
</tr>
</tbody>
</table>

a Reference 22.

b Reference 23.

c Reference 25.

d Reference 26.

**TABLE III.** Energy gaps of diamond in (eV).

<table>
<thead>
<tr>
<th>Energy</th>
<th>Model</th>
<th>EPM</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{gap}$</td>
<td>5.50</td>
<td>5.46</td>
<td>5.51</td>
</tr>
<tr>
<td>$\Gamma_{16} - \Gamma_{25'}$</td>
<td>-28.47</td>
<td>-29</td>
<td>-21.00</td>
</tr>
<tr>
<td>$\Gamma_{15} - \Gamma_{25'}$</td>
<td>7.12</td>
<td>6.96</td>
<td>6.97</td>
</tr>
<tr>
<td>$\Gamma_{2} - \Gamma_{25'}$</td>
<td>10.66</td>
<td>19</td>
<td>15.35</td>
</tr>
<tr>
<td>$L_{1\alpha} - \Gamma_{25'}$</td>
<td>-15.85</td>
<td>-16</td>
<td>-12.83</td>
</tr>
</tbody>
</table>

a Reference 21.

b Reference 24.

c Reference 25.

d Reference 26.
For other polytypes considered an effective 3C-SiC potential is used and the basis atoms are placed in the perfect tetrahedron.\textsuperscript{30} Deviations from these “ideal” positions have been discovered,\textsuperscript{31} but is ignored here in light of the error involved in treating the potentials locally. Since the lattice spacing and the density of reciprocal-lattice vectors differ from 3C, the model potential is evaluated at wave vectors and reciprocal-lattice vectors represented in units of the corresponding 3C vectors. For a given polytype \( nH \)-SiC, this involves scaling by the ratio of lattice constants \( (a_{2H}/a_{3C}) \).

The form of the potential for the hexagonal polytypes considered is

\[
F_6(\vec{G}) = \frac{1 + 2 \cos(\vec{G} \cdot \vec{\tau}_{6H}) + e^{-(2iG_f/3)}}{6} \left[ \frac{1 + 2 e^{i(G_f/4)} \cos(\vec{G} \cdot \vec{\tau}_{6H} - G_f/12)}{1 + 2 e^{i(G_f/4)}} \right],
\]

with \( \vec{\tau}_{6H} = (1/3)(1/3),(1/n) \) in 3C direct lattice vector units.

For each of the SiC polytypes, the local model potential is used to produce form factors for \( G^2 < 16 \) in 3C reciprocal-lattice vector units. This is accomplished by retaining all of the Si and C parameters in the model potentials as a first approximation and then varying \( A_2 \) of C slightly to fit to the band energies. In this way, the large number of EPM form factors needed are obtained by the adjustment of one model parameter only. To fit the effective masses the addition of the nonlocal correction to the C \( A_1 \) well is needed in 3C and 4H, such a correction was not needed for 6H. As for Si and diamond, a plane-wave basis is used that includes the contribution of all plane waves satisfying \( (k + \vec{G})^2 \leq 21 \) for 3C, and by analogy \( (k + \vec{G})^2 (a_{3C}/a_{2H})^2 \leq 21 \) for the hexagonal polytypes. These criteria are met with 125, 270, and 390 plane waves for 3C, 4H, and 6H respectively. Convergence is found to within 0.02 eV for the fitted band energies and effective masses.

Both the local and nonlocal fitting parameters adjust the core potential of the C atoms in SiC. This choice is made since the simplifications used in the model potential are expected to be less reliable for C. As previously discussed, this is evident from the diamond model band structure and is a consequence of the lack of \( l = 1 \) core states that produce a strong attractive well in the C core, allowing the valence electrons to occupy the core with greater ease. Except for the nonlocal correction, the dependence of the core potential on electron wave-vector and energy is ignored in the model. The more the valence electrons test out the core, the less valid these approximations should be. Hence, it is the core potential of C that is adjusted in accordance with experimental data.

### V. RESULTS FOR SiC

By varying \( A_{C2} \) by less than 3% from the fitted value for carbon and adding a charge transfer of \( \Delta Z = 1 \), we obtained good fits to experimental band energies of 3C, 4H, and 6H.

<table>
<thead>
<tr>
<th>Band</th>
<th>Model(local)</th>
<th>Model(nonlocal)</th>
<th>EPM</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_{1e} )-( \Gamma_{150} )</td>
<td>2.30</td>
<td>2.30</td>
<td>2.35,\textsuperscript{1}2.42,\textsuperscript{4}2.39\textsuperscript{e}</td>
<td>2.39\textsuperscript{a}</td>
</tr>
<tr>
<td>( X_{3e} )-( X_{1c} )</td>
<td>2.90</td>
<td>2.74</td>
<td>3.03,\textsuperscript{1}2.5\textsuperscript{d}</td>
<td>3.10\textsuperscript{b}</td>
</tr>
<tr>
<td>( \Gamma_{1e} )-( \Gamma_{150} )</td>
<td>5.73</td>
<td>5.73</td>
<td>5.92,\textsuperscript{1}6.0\textsuperscript{d},\textsuperscript{4}6.0\textsuperscript{e}</td>
<td>6.0\textsuperscript{e}</td>
</tr>
<tr>
<td>( L_{1e} )-( \Gamma_{150} )</td>
<td>4.26</td>
<td>3.95</td>
<td>4.38,\textsuperscript{1}4.26,\textsuperscript{4}4.20\textsuperscript{d}</td>
<td>4.20\textsuperscript{b}</td>
</tr>
<tr>
<td>( X_{1e} )-( L_{3v} )</td>
<td>4.00</td>
<td>4.33</td>
<td>3.99,\textsuperscript{4}4.18\textsuperscript{d}</td>
<td>3.55\textsuperscript{a}</td>
</tr>
<tr>
<td>( m_f^t )</td>
<td>0.22±0.02(XW)</td>
<td>0.24±0.02</td>
<td>0.24±0.02</td>
<td>0.24\textsuperscript{e}</td>
</tr>
<tr>
<td>( m_f^t )</td>
<td>0.22±0.02(XW)</td>
<td>0.24±0.02</td>
<td>0.24±0.02</td>
<td>0.24\textsuperscript{e}</td>
</tr>
<tr>
<td>( m_f^t )</td>
<td>1.2±0.02(XG)</td>
<td>0.7±0.1</td>
<td>0.7±0.1</td>
<td>0.66\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference 9.  
\textsuperscript{b}Reference 10.  
\textsuperscript{c}Reference 6.  
\textsuperscript{d}Reference 11.  
\textsuperscript{e}Reference 12.  
\textsuperscript{f}Reference 13.
SiC using the local model potential. Nonlocal corrections were needed in 3C and 4H to fit the effective masses, along with a slight adjustment of the local parameter in 4H to retain the fitted band gap. The parameters used are shown in Table I and comparisons of the band energies and effective masses with other methods and with experiment is given in Table IV for 3C and in Table V for the hexagonal polytypes.

For 3C-SiC, the local band structure in Figs. 5–7 and the calculated band energies agree well with EPM results and experimental data. A band gap of 2.3 eV at the X point is found. The effect of charge transfer is clearly shown in Fig. 8. The asymmetric potential agrees well with the EPM form factors once charge transfer is added. An exact fit of the tail of the potential is not expected since we have used \(V_{12}^{1/2}\). The addition of charge transfer also changes the symmetrical potential, decreasing the \(q^2\) point where the potential passes through zero and raising the maximum.

The transverse effective mass (X-W) calculated from the local 3C band structure, agrees well with experiment, but the longitudinal effective mass (X-G) is somewhat higher. This is brought into agreement by adjusting the nonlocal correction and attaining a nonlocal band structure that is very similar to the local results. The valence bands are noticeably altered by the nonlocal term, especially along the K-X symmetry line, while except at the L point, the conduction bands appear relatively unaltered. The slight adjustment of the conduction bands by the nonlocal term is enough to fit to the experimental effective masses. The improvement in the fit is given in Table IV. Agreement with experiment is slightly worse at the conduction-band L point once the nonlocal term is included, but this is overshadowed by the benefits of improving the effective masses.

In 4H, the local potential was fit to the experimental band

<table>
<thead>
<tr>
<th></th>
<th>Model (local)</th>
<th>Model (nonlocal)</th>
<th>DFT</th>
<th>Expt.</th>
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<tr>
<td>4H-SiC</td>
<td>3.21</td>
<td>3.20</td>
<td>3.2b</td>
<td>3.26a</td>
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<tr>
<td>(m_1)</td>
<td>1.50±0.05(M(\Gamma))</td>
<td>0.60±0.05</td>
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<td>(m_2)</td>
<td>0.19±0.02(MK)</td>
<td>0.20±0.02</td>
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<td>0.29</td>
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<tr>
<td>(m_3)</td>
<td>0.39±0.02(ML)</td>
<td>0.36±0.02</td>
<td>0.31</td>
<td>0.33</td>
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<tr>
<td>(m_4)</td>
<td>0.53±0.03</td>
<td>0.35±0.02</td>
<td>0.42</td>
<td>0.42d</td>
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<tr>
<td>(m_5)</td>
<td>0.19±0.04</td>
<td>0.31±0.05</td>
<td>0.29</td>
<td>0.29</td>
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</table>

6H-SiC

<table>
<thead>
<tr>
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<th>Model (local)</th>
<th>Model (nonlocal)</th>
<th>DFT</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.99(L)</td>
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<td></td>
<td>3.0b</td>
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<td>3.02a</td>
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</tr>
<tr>
<td>(m_1)</td>
<td>0.90±0.03(LA)</td>
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<td>0.77</td>
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<tr>
<td>(m_2)</td>
<td>0.22±0.02(LH)</td>
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<td>0.24</td>
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</tr>
<tr>
<td>(m_3)</td>
<td>1.43±0.02(LM)</td>
<td>1.42</td>
<td></td>
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</tr>
<tr>
<td>(m_4)</td>
<td>0.44±0.02</td>
<td>0.42</td>
<td>0.42d</td>
<td></td>
</tr>
<tr>
<td>(m_5)</td>
<td>1.14±0.14</td>
<td>1.1-2.0</td>
<td>2.0</td>
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</tr>
</tbody>
</table>

\(\text{Table V. Band energies (eV) and effective masses (units of electron mass) of 4H and 6H SiC.}\)

\(a\)Reference 1.
\(b\)Reference 33.
\(c\)Reference 3.
\(d\)Reference 34.

FIG. 5. 3C-SiC Local(-) and nonlocal(- -) model band structure.

FIG. 6. 4H-SiC nonlocal model band structure.

FIG. 7. 6H-SiC local-model potential band structure.
gap with an $A_{C2}$ closer to the C value. A conduction-band minimum or 3.20 eV was found at the $M$ point agreeing with experiment. As obtained by other methods, the splitting between the first two conduction bands at $M$ was found to be about 0.1 eV. Greater anisotropy is found in the effective masses than for $3C$, with a large mass found along $M-L$, while smaller, yet clearly distinct masses are found in the transverse directions. As seen in Table V, it is expected from experiment that the bands should be flatter along $M-K$ and much steeper along $M-L$. The other transverse mass in the $M-L$ direction agrees reasonably with experiment.

The experimental values of $m_{\perp}$ and $m_{\parallel}$ in Table V were obtained by experiments in which variations in the effective mass, as determined for magnetic fields in the plane perpendicular to the $c$ direction, where not resolved. These "in-plane invariant" effective masses were approximated from the model band structure for comparison. As with the longitudinal and transverse masses relative to $M-\Gamma$, it is desirable to bring these masses in closer agreement with experiment using the nonlocal correction. As in $3C$, this altered the conduction bands in Fig. 6 only slightly, but the curvature of the bands is altered quite significantly along the $M-\Gamma$ line in Fig. 9. Also, the degeneracy of the first two conduction bands at $L$ is lifted. The nonlocal results were able to attain good agreement with the $M-\Gamma$ and $M-L$ results, but did not improve the $M-K$ effective mass much. Better agreement for $m_{\perp}$ and $m_{\parallel}$ are also attained. To retain the correct band gap, the local parameter $A_{C2}$ was readjusted slightly in the nonlocal potential.

For $6H$, the band gap was fit without varying $A_{C2}$ appreciably from the C value. The conduction-band minimum, found at the $L$ point, was fit to the experimental value of 3.0 eV. In DFT band structures and other studies, the minimum is usually found closer to the $M$ point along $M-L$, but as found in this paper, the lowest conduction band is extremely flat along $M-L$ as seen in Fig. 10, varying by less

FIG. 8. Asymmetric ($V^{A}$) and symmetric ($V^{S}$) model potentials, with EPM form factors of Ref. 6(). The form factor for $V^{A}_{11}$ of both Refs. 7 and 8 (*) varies significantly and is also shown. The model potentials without charge transfer (--), with charge transfer (- -), and fitted to $3C$-SiC band energies (——) are shown.

FIG. 9. Model potential conduction-band edge of $4H$-SiC with (- -) and without(——) the nonlocal correction. The $M-\Gamma$ and $M-K$ distances shown are equal to the $M-L$ distance.

FIG. 10. Model potential conduction-band edge of $6H$-SiC. The L-H and L-H distances shown are equal to half the total L-M distance.
than 0.1 eV. The minimum has been found to be along $M-L$ in experiment, but since its exact position is still uncertain, our results are consistent. As in the DFT studies, we find the minimum to be essentially doubly degenerate with the splitting of the first and second conduction bands to be less than 0.01 eV, while the third conduction band at $L$ is found to be approximately 1.5 eV higher than the minimum. The effective masses at the conduction-band minimum parallel and transverse to the $L-A$ direction are consistent with the DFT work. When compared to experiment though, $m_\parallel$ is fitted well, whereas $m_\perp$ is found to be much lower than experiment. This may result from band filling complications in the experiments due to the flat band structure along $M-L$. The longitudinal and transverse components of the effective mass have still not been determined experimentally for 6$H$, but since the results of the local model potential are consistent with DFT results and what is known experimentally, we see no need for including a nonlocal correction for 6$H$ at this time.

Since band structures accurate close to the band gap are desired, it is useful to examine the density of states in this region. As found experimentally and theoretically, the major differences between the density of states of the individual SiC polytypes calculated with the model band structure is in the conduction bands. The results are compared with results from density-functional theory (DFT) in Fig. 11, with the band gaps of the latter adjusted to match experimental results. Both results show not only an increasing band gap, but an increase in the steepness of the rise in the density of states at the conduction-band edge with increasing hexagonality. This is also found experimentally, as shown in

![TABLE VI. EPM form factors of 4$H$, and 6$H$-SiC in Rydbergs, obtained from the model potential. Form factors which exist for $G^2$, in units of 3$C$-SiC reciprocal vectors, but whose structure factor vanishes are not shown.](image)

![FIG. 11. Conduction-band density of states for the model potential(−) and that calculated from density-functional theory of Ref. 39 (−−). For 4$H$, the nonlocal(−) and local(−) results are shown.](image)

![FIG. 12. Experimental results of Ref. 38 and local model density of states at conduction edge for 3$C$(−−), 4$H$(−−), and 6$H$(−−). For comparison, the conduction-band minimum is set to zero for each method. Nonlocal results for 3$C$ and 4$H$ do not vary noticeably.](image)
Fig. 12, where we have combined the Si $L_{\alpha\beta}$ and $C$ $K$ soft x-ray absorption density of states. As in other work$^{23}$ and experiment,$^{38}$ the valence-band density of states was found to be very similar for the different polytypes. In Table VI, the EPM form factors corresponding to the model potential for 4$H$ and 6$H$ are given. To our knowledge, these represent published form factors for these materials. They can be used within the EPM to reproduce the local model band structure of these polytypes. If it is desired to include the nonlocal correction for 4$H$, the set of appropriate form factors for the local potential are to be used.

VI. CONCLUSION

We found that by including the appropriate screening and charge transfer, and then refitting, the HA potential could be effectively modified for use as a semiempirical pseudopotential for semiconductors. A SiC local model potential was developed using Si and C potentials that were each successfully fitted to the homopolar experimental band energies around the band-gap region. This potential could then be fitted with one local and one nonlocal parameter to obtain the band structure for 3$C$ and 4$H$ SiC. The nonlocal parameter is included as a means to fit the effective masses. For 6$H$, only the local parameter was needed since the local potential was found to be consistent with experiment. Agreement with experimental band energies and most effective masses is found to be good. The large number of EPM form factors needed for 4$H$ and 6$H$ are obtained from the local potential and can be used to reproduce the local band structures, while the nonlocal term can be included to obtain the fitted effective masses. This represents an enormous reduction in the empirical fitting parameters needed since roughly 30 EPM form factors are needed for 4$H$ and 6$H$-SiC.

It is likely that the local approach could be applied to SiC polytypes with even larger unit cells than 6$H$ using the variation in band gap with hexagonality$^{1,2}$ in cases where experimental band gaps are undetermined. When effective mass data is available, then the nonlocal correction may be included. It is also expected that a similar approach could be applied to other materials for which the HA model potential represents a reasonable approximation to the atomic core potentials in the solid. Another possible application is the use for defects that retain the bulk bonding characteristics such as low-energy stacking faults.

ACKNOWLEDGMENTS

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