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Energy-band structure of SiC polytypes by interface matching of electronic wave functions

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We interpret SiC polytypes as natural superlattices, consisting of mutually twisted cubic layers. A method is presented to calculate the electron band structure of any polytype, based on an empirical pseudopotential description of cubic SiC. Bloch and evanescent waves belonging to cubic layers are matched at interfaces in order to make up the wave functions of the respective polytypes. Band gaps of hexagonal and rhombohedral modifications are in excellent agreement with experimental data such that the nearly linear relationship between the indirect gap and the hexagonal nature is reproduced. A simple explanation of this relationship is given in terms of a Kronig-Penney-like model.

Silicon carbide (SiC) is the well-known semiconductor compound crystallizing in more than a hundred different modifications, i.e., polytypes.¹ Ground state properties of SiC have been studied extensively for polytypes with relatively small unit cells,²⁻⁶ specifically for the 3C and the 2H modifications. Unfortunately, the *ab initio* density functional schemes employed are not capable of producing reliable electronic band gaps. There is a long standing problem in this connection: in 1964 Choyke, Hamilton, and Patrick⁷ found an intriguing, hitherto theoretically neither reproduced nor explained, linear relation between the electronic gap and the degree of hexagonal nature (h) for polytypes up to $h = 50\%$. In an ultimate theory of this phenomenon it is of course necessary to incorporate dynamical nonlocal correlation effects. However, in view of the enormous primitive cells it is very difficult, if not impossible, to carry through the necessary calculational steps, implying that it is of interest to investigate whether less sophisticated descriptions can be given. An earlier attempt to account for the gap versus h relation within a simple empirical pseudopotential (EP) scheme failed.⁸ The treatment in Ref. 8 was based on the assumption that the atomic pseudopotentials for C and Si are transferable to all polytypic modifications. It led to the necessity of introducing increasing numbers of ill-determined adjustable parameters. In the present paper we propose a treatment in which it is assumed that complete layers are transferable from one polytype to another. It is conjectured that the differences between the model potential and the actual potential thus obtained will have minor influence. Our model is obviously not identical to the earlier model potential proposed in Ref. 8. In Ref. 9 a one-dimensional Kronig-Penney (KP) model was used to model the electron spectra for the various crystal modifications. However, for each polytype the rectangular potential wells and the effective mass of the electrons had to be adjusted in order to achieve best agreement with experimental data.

In this paper we report on a successful method for predicting experimental band gap values of SiC polytypes,

in which the only input parameters are the EP form factors for zinc blende (3C) SiC. Basic in this method is the assumption, *as far as the band gap problem is concerned*, that polytypes may be regarded as natural superlattices consisting of pure 3C SiC segments which differ in size and crystallographic orientation only.⁵ The assumption is comparable to the flat-band approximation in the description of, e.g., GaAs/AlAs superlattices, in which the layers are also assumed to be entirely bulklike.¹⁰⁻¹³ The interesting difference with the present case is that the band offset values are zero by definition, as all layers, though twisted with respect to each other, are in fact identical. All segments can therefore be characterized by the same set of EP parameters pertaining to bulk 3C SiC, for which we take the values employed in Ref. 8. Band structures of polytypes are then subsequently obtained by means of proper interface wave function matching, involving no additional adjustable parameters at all. Only the position of the interface plane between layers has to be chosen. Fortunately, the results turn out to be largely insensitive to this choice. Similar techniques as will be described here have been applied to twinning superlattices of Si and Ge in Ref. 14. As will be shown below, one of the most striking results is that the above mentioned experimentally obtained scaling of the band gap with h is almost perfectly reproduced. Moreover, the method yields complete complex band structures, which have a similar status as commonly obtained EP band structures.

As is well known, the various SiC structures differ in the stacking order of hexagonally close-packed layers of Si and C in the c direction, or for zinc blende in the [111] direction. 3C SiC (zinc blende) and 2H SiC (wurtzite) have stacking sequence *ABCABC...* and *ABAB...*, respectively. Exactly one fcc unit cell fits (for 3C) in the repeating unit *ABC*. One of the most stable¹ polytypes, 6H SiC, contains six SiC pairs per unit cell and has stacking sequence *ABCACB...*. Noting that an *ACB* block is nothing but an *ABC* block rotated by 60° about the stacking axis, the 6H structure can be viewed upon as an alternating sequence of unrotated and rotated *ABC*

blocks. All other polytypes can be built up in a similar way, by stacking multiples of fragments of ABC and ACB blocks.

Electronic wave functions at given energy E and parallel wave vector component $\mathbf{k}_{\parallel}$ in the superlattice are constructed by matching linear combinations of in principle all EP-obtained Bloch and evanescent waves valid for the respective layers. The successive layers are *twisted* with respect to each other, which makes the matching at interfaces between them nontrivial. Particular Bloch or evanescent wave solutions for a given layer j , at given E and $\mathbf{k}_{\parallel}$ can be written as

$$\psi_{E, \mathbf{k}_{\parallel} k_z}^j(\boldsymbol{\rho}, z) = e^{i(\mathbf{k}_{\parallel} \cdot \boldsymbol{\rho} + k_z z)} u_{E, \mathbf{k}_{\parallel} k_z}^j(\boldsymbol{\rho}, z), \quad (1)$$

where k_z is the component of $\mathbf{k}$ along the stacking direction z . The function u has the periodicity of the infinite zinc blende crystal and can be expanded in plane waves $e^{i\mathbf{G} \cdot \mathbf{r}}$ with, say, N reciprocal lattice vectors $\mathbf{G} = \mathbf{G}_{\parallel} + G_z \mathbf{e}_z$ and M different projections $\mathbf{G}_{\parallel}$. Here $\mathbf{r}$ stands for $\boldsymbol{\rho} + z\mathbf{e}_z$ and $\mathbf{e}_z$ is the unit vector in the stacking direction. The well-known Chang-Schulman¹⁵ diagonalization scheme is simply shown to yield $2M$ solutions k_z^s for k_z , such that the real parts of $\mathbf{k}_{\parallel} + k_z^s \mathbf{e}_z$ are in the first Brillouin zone (1BZ). With the help of these we can form linear combinations for each sublayer

$$\psi_{E, \mathbf{k}_{\parallel}}^j(\boldsymbol{\rho}, z) = \sum_{s=1}^{2M} \alpha_s^j \psi_{E, \mathbf{k}_{\parallel}}^{j,s}(\boldsymbol{\rho}, z), \quad (2)$$

in which $z^{j-1} \leq z \leq z^j$, where z^j denotes the interface positions, the choice of which will be commented on below. Note that each solution (1) can also be written

$$\psi_{E, \mathbf{k}_{\parallel} k_z^s}^j(\boldsymbol{\rho}, z) = \sum_{\mathbf{G}_{\parallel}}^M e^{i(\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel}) \cdot \boldsymbol{\rho}} v_{E, \mathbf{k}_{\parallel} \mathbf{G}_{\parallel}}^{j,s}(z), \quad (3)$$

i.e., in terms of M z -dependent two-dimensional Fourier components.

Suppose we are dealing with $6H$ SiC. In order to properly deal with this case we have to connect three segments by means of matching prescriptions at three interfaces, at $z = 0, 3c$, and $6c$, respectively, where c is the length of a SiC bilayer. We have to demand each of the M Fourier coefficients in (3) to be continuous and continuously differentiable at two of the interfaces. This gives $4M$ conditions. Together with the Bloch condition for the superlattice

$$\psi_{E, \mathbf{k}_{\parallel}}(\boldsymbol{\rho}, 6c) = e^{iKL} \psi_{E, \mathbf{k}_{\parallel}}(\boldsymbol{\rho}, 0), \quad (4)$$

we are dealing with precisely $6M$ conditions for $6M$ unknown coefficients α_s^j . Here $\mathbf{k}_{\parallel} + K\mathbf{e}_z$ is a wave vector of which the real part lies in the 1BZ of $6H$ SiC, the length $L = 6c$ representing the period of the $6H$ supercell in the c -direction.

Taking, as a first choice, the interface plane position exactly in between vertical pairs of Si and C atoms, a complete complex band structure for $6H$ SiC is obtained in this way. In Fig. 1 the $6H$ complex band structure, along the M - L symmetry axis, is displayed. By calculat-

ing this band structure along a variety of parallel directions as well, we obtain the $\mathbf{k}$ points at which the valence band has its maximum (Γ) and at which the conduction band has its minimum. The latter $\mathbf{k}$ point happens to be located on the M - L axis, shifted 40% to the L point (camel's back). All other polytypes can be treated similarly, providing us with (indirect) gap values of various width. Table I gives a summary of the thus calculated band gaps for seven polytypes as compared with experimental and earlier obtained theoretical values.

The 3C SiC wave functions, with which we start our transmission analysis, have been expanded in $N = 113$ plane waves. Consequently the Chang-Schulman matrix dimension is 226×226 . Depending on the value of $\mathbf{k}_{\parallel}$ we select $2M$ wave solutions, with $M = 7, 8$, or 9 , being those with the smallest absolute values of the imaginary part of k_z . It has been checked that incorporation of more of such waves has only minor influence on our results. Convergence of the indirect gap values within 0.02 eV is

FIG. 1. Complex band structure for $6H$ SiC along the M - L axis of the 1 BZ, as obtained by the described transmission method. The solid lines denote Bloch states, while the dashed and dotted lines describe the real and imaginary parts, respectively, of evanescent states. A camel-back-type of minimum is visible (arrow) for the lowest conduction band.

TABLE I. The crystal structure in Ramsdell and *ABC* notation, hexagonality, and energy gaps (eV) of seven SiC polytypes. The gap value 2.40 eV for 3*C* SiC of the present theory has been obtained within a transmission analysis for *untwisted* layers in a 6*H* unit cell, in order to check our procedure. Note that the two gap values of Ref. 8 marked with an asterisk had been adjusted to experiment within that theory.

Polytype (Ramsdell)	Polytype <i>ABC</i>	Percent <i>h</i>	Present theory	Expt.	Theory Ref. 8	Theory Ref. 18
3 <i>C</i>	<i>ABC</i>	0	2.40	2.390	2.40*	
10 <i>H</i>	<i>ABCABC</i> BACB	20	2.66			
8 <i>H</i>	<i>ABCABACB</i>	25	2.76	2.80		
6 <i>H</i>	<i>ABCACB</i>	33.3	3.05	3.023	2.45	2.92
15 <i>R</i>	<i>ABCACBCABA</i> <i>CACBCB</i>	40	3.03	2.986		
4 <i>H</i>	<i>ABCB</i>	50	3.28	3.263	2.8	2.89
2 <i>H</i>	<i>AB</i>	100	4.04	3.330	3.35*	2.76

obtained is this way (0.04 eV for 10*H*). When comparing our results with the experimental gap values presented by Choyke *et al.*^{7,16} it should be remarked that their values suffer from inaccuracies in the order of 0.015 eV. Their reported values refer, moreover, to exciton gaps, which are typically up to 0.03 eV (Ref. 17) lower than electronic band gaps. In view of this the agreement between our results as presented in Table I and Fig. 2 and the optical absorption and luminescence data^{7,16,17} is very satisfactory indeed, except for 2*H* SiC. This implies that we reproduce the observed linear relationship between gap and hexagonality for $h \leq 50\%$. For very small values of h we find deviations from the linear behavior. All polytypes considered, except 2*H*, happen to be indirect between Γ and (almost) *M*. As is observed from Table I and Fig. 2 the earlier interpolation technique in Ref. 8 and the self-consistent linear muffin-tin orbital method of Ref. 18 failed to give satisfactory results. An elegant feature of the present method is of course that large cell calculations are avoided. Note that even the band gap of the rhombohedral modification 15*R*, which has a very large primitive cell, is calculated.

The near linearity of the h -gap relation can be understood within a simplified model in which evanescent waves are jointly responsible for the details of the interface matching but not for the propagation in between the interfaces. In the relevant energy region from 2.4 eV to about 3.3 eV, the complex solutions k_z^s have such large imaginary parts ($|\text{Im}k_z^s| \gtrsim 0.7/c$) that evanescent waves emerging from one interface have negligible amplitudes at the next interface (for not too high values of h). For the propagation from one interface to the next only the two Bloch waves with $\mathbf{k} = \mathbf{k}_M \pm k_z \mathbf{e}_z$, with real k_z , in the lowest conduction band of the 3*C* structure are important. In an envelope function description for the part of the wave function built up by these Bloch waves it is natural to propose the following boundary conditions at the interface $z = z^j$ for the z -dependent envelope functions $\mathcal{F}^j(z)$, defined with respect to $\mathbf{k}_M$:

$$\mathcal{F}^{j+1}(z^j) = \beta \mathcal{F}^j(z^j) + \gamma c \frac{d}{dz} \mathcal{F}^j(z^j), \quad (5)$$

$$\mathcal{F}^j(z^j) = \beta \mathcal{F}^{j+1}(z^j) - \gamma c \frac{d}{dz} \mathcal{F}^{j+1}(z^j).$$

The particular form of these boundary conditions is dic-

tated by symmetry. Furthermore, the envelope functions can be defined with such phases that the parameters β and γ are real and the same for the two different kinds of interfaces. All the effects of the evanescent waves on the matching of the envelope functions are supposed to be incorporated in these parameters. Substituting linear combinations of plane waves $e^{\pm i k_z z}$ for the envelope functions and imposing the Bloch condition, it is straightforward to find the Bloch solutions for, e.g., the *H* structures:

FIG. 2. Indirect gap values as a function of h , according to experiment (filled circles), Ref. 8 (triangles), Ref. 18 (diamonds), and present theory (open circles) for increasing h : 3*C*, 24*H*, 18*H*, 12*H*, 10*H*, 8*H*, 6*H*, 15*R*, 4*H*, and 2*H*. The drawn line is the band gap following from (6) and an effective mass approximation.

$$\cos KL = \beta \cos \frac{k_z L}{2} - \frac{[1 - \beta^2 + (\gamma c k_z)^2] \sin \frac{k_z L}{2}}{2\gamma c k_z}. \quad (6)$$

The corresponding energy can accurately enough be calculated with an effective mass approximation for the lowest conduction band in the 3C structure, with an effective mass $m^* = 0.48m$. The solution (6) is reminiscent of the KP model. In the KP model, however, a periodic array of rectangular potential barriers causes the band formation. In the present model the band formation is caused by a periodic "frustration" of the transmission.

The above model would of course be useless if the parameters β and γ were strongly energy dependent. Fortunately, they are not. One can determine β and γ by requiring that the amplitudes of transmission and reflection of the Bloch waves at one interface calculated with the model are the same as those following from the rigorous calculation. With $\beta = 1.63$ and $\gamma = 0.88$ very good agreement with the rigorous calculations is obtained in the energy interval 2.4–3.3 eV. The resulting band gap calculated from (6) and the effective mass approximation is plotted in Fig. 2 for these values of β and γ . For not too low values of h ($h \gtrsim 15\%$) the resulting relation is indeed linear.

The deviation between our calculated 2H gap and the experimental gap is considerable. This is not unexpected, as 2H SiC is the only case, considered by us, in which the layers are as small as 1/3 of an ABC layer. Indeed, the assumption that such layers exhibit 3C SiC character is rather provocative. Nevertheless, in view of earlier successful attempts to map self-consistently obtained 3C charge densities onto the 2H structure,⁵ we may not *a priori* exclude the possibility that our matching procedure could also work for 2H SiC. Although the result obtained may appear at first sight to be disappointing, we should not forget that we invariably have chosen our interface position precisely in between a Si and a C atom. We therefore investigated the dependence of all our above described results on the position choice of the interface planes. In Fig. 3 we display the dependence of the calculated indirect gap value on the interface position for both the 6H and the 2H case. It is observed that the 6H gap value is largely insensitive to the interface position (this holds for the other polytypes as well, except 2H). Only the 2H value strongly depends on the interface position. There are three remarkable aspects that deserve attention in this connection: (i) The best indirect gap value for 2H is obtained if the interface position is shifted somewhat towards the C planes, the distance ratio to C and Si being roughly 3/7 instead of the earlier 1/1 ratio. (ii) The indirect minimum (see Fig. 3) has then changed from M to K, which is in accordance with experiment.¹⁶ (iii) The gap value result for 6H SiC, though already excellent for the earlier chosen middle position, slightly improves if the new position is chosen.

Indeed, there is no reason at all to choose the interface position precisely in between a Si and a C plane. Proceeding from the inside of a 3C-like layer in either the

FIG. 3. Dependence of the calculated indirect gap value on the interface position. Note the relative insensitivity of the 6H gap result (triangles) in contrast to that of the 2H gap result, as well the change of the 2H minimum, from M (filled squares) into K (open squares) if the interface plane is chosen close to the C atoms.

positive or the negative z direction the first structural changes to be encountered manifest themselves either in twisted Si atoms or in twisted C atoms. There is an inherent asymmetry due to the incomplete covalent binding between Si and C.

In conclusion, a parameter free description has been given from which the indirect gap values of all SiC polytypes with $h \leq 50\%$ can be obtained. The method clearly fails for 2H SiC; however, with a proper choice of the interface position we also find that the 2H gap value can be reproduced. This particular choice hardly influences the gaps obtained for other polytypes. Whether this has a deeper reason or merely is accidental is not clear at this moment. In view of this we might speculate that a good criterion for the choice of the interface position may be obtained by carefully comparing electronic potentials of 2H, 4H, etc. polytypes on the one hand and of 3C SiC on the other, such that optimum zinc-blende-like sublayers can be identified in the various polytypes. To this aim we are presently investigating potentials obtained within the local density approximation for a series of polytypes, on which we will report in due time.

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