

THE BAND STRUCTURE AND BULK MODULUS OF CUBIC (3C) AND HEXAGONAL (2H) POLYTYPES OF SILICON CARBIDE

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Received 18 February 2002

Revised 4 April 2002

Silicon carbide (SiC) is a high band-gap semiconductor material, which has very important and interesting characteristics for novel semiconductor applications. We have studied the cubic (3C) and hexagonal (2H) polytypes of this important material. For the band structure calculations of these polytypes, the density functional and total-energy technique have been applied in the generalized gradient approximation, which is the most powerful *ab initio* quantum-mechanical method. The important energy gaps have been determined and compared with the previous theoretical and experimental results. The density of state, charge density and bulk modulus have also been calculated.

1. Introduction

From the application point of view, SiC is a rather unique semiconducting material,^{1–5} which has a high thermal conductivity, high melting point, extreme hardness and resistance to chemical attack and mechanical damage.⁶ The energy band-gap of this material is also very large (about 2.2–3.3 eV) and depends upon the structure of the polytype;^{7,8} this property means that the material is good for the fabrication of blue light-emitting diodes^{9,10} and also for the fabrication of the transmitting window layer in photovoltaic cells.^{11,12} It is also a leading candidate for thin film solid-state electronic devices because of its high carrier mobility¹³ and saturated drift velocity.¹⁴ These electronic devices may withstand high temperatures, and are useful for high frequency and power load applications. Moreover, microcrystalline thin films with boron doping provide a wide range of electrical conductivities without a drastic change in the optical wide band gap.

SiC is also known as a material, which crystallizes in various crystal structures or polytypes.^{15,16} Among the many polytypes of SiC, cubic 3C-SiC (pure cubic) and hexagonal 2H-SiC (pure hexagonal) are the most common structures. After the discovery of this very important semiconducting material, work has continued to improve its performance through the optimization of the preparation conditions

for the different preparation methods and by doping of different elements into SiC. From the theoretical point of view, work has also continued to improve its electronic and optical properties. Different theoretical methods have been used for the improvement of this important semiconducting material. The density functional and total-energy pseudopotential, the tight binding, etc. are the most common techniques for the theoretical calculations of different parameters of SiC.

In spite of impressive technological achievements over several years, there are still some problems concerning the basic physical properties of this compound, which have to be solved. Therefore, it is important to re-study the fundamental properties of both polytypes of this important semiconductor.

Several first principle calculations have been performed for group-IV carbides and group-III nitrides. Most of these calculations are based on the Density Functional Theory (DFT) in the local density approximation (LDA). At present, the generalized gradient approximation (GGA) in DFT is receiving much attention since, according to several authors, this approximation considerably improves the results obtained by the LDA. In particular, the description of total, ionization, and cohesive energies, as well as equilibrium distances and structural properties have improved substantially over LDA calculations.^{17,18} On the other hand, Leung *et al.*¹⁹ and Filippi *et al.*,²⁰ have reported that the underestimation of band gaps in band structure calculations by two different GGA functionals have not improved. In this paper, we report the calculation of the band gap, charge density and bulk modulus under elastic deformation of zincblende (β), and wurtzite (α) polytypes of SiC by using the two equations and the results are compared with the reported experimental and theoretical results. For total-energy calculations, we used the CASTEP code, which implements the Density Functional and Total-energy Pseudopotential Techniques in the GGA.^{21–25}

2. Computational Method

We have used the density functional and total-energy pseudopotential technique, under the GGA, which is the corrected gradient version of the LDA, developed by Pedrew and Wang. Forces acting on the atoms and stress on the unit cell have been calculated and from this the equilibrium structure is obtained. We have used a non-local pseudopotential optimization scheme of Lin *et al.* within the Kleiman–Bylander scheme²⁴ in which only one ground state for each component of the angular momentum of the wave-function is used.

The electronic wave-functions are expanded on a plane-wave basis, set with periodic boundary conditions and the expansion coefficients are varied to minimize the total energy. Initially, an infinite base set of plane waves is required for this expansion. The plane wave energy cut-off was set at 850.0 eV for 3C-SiC and 670.0 eV for 2H-SiC. The minimization of total-energy is made using a “band by band” method in which each wave-function is optimized independently. This method is generally used for small cells with high symmetry. The Monkhorst–Pack calcula-

tion scheme,²⁶ which reduces the set of k -points in the Brillouin zone, is employed to calculate the electronic energies with geometry optimization. The Fourier transform Grid is $24 \times 24 \times 24$ for 3C-SiC and $24 \times 24 \times 36$ for 2H-SiC. Finally, the directional calculational scheme is used for the band structure calculations by using the high symmetry points in the Brillouin zones of each polytype.

3. Polytypism in SiC

SiC is a semiconductor material that has unique thermal and electrical properties. The polytypism inherent in this material^{15,16} results in a variety of different well-known crystal structures which makes SiC fascinating from a fundamental sciences point of view. It is not a single semiconductor but a whole class of semiconductors because of its polytypism which is a one-dimensional variant of polymorphism, i.e. the existence of different stackings of the basic structural elements; in the present case, the $\{111\}$ Si-C bilayers of the cubic (zincblend) structure, or 0001 layers of the hexagonal polytypes. More than 200 polytypes have been reported to date but few of these have practical importance. These include the cubic 3C, hexagonal 2H, 4H, 6H and rhombohedral 25R, 21R forms.

Commonly, the stacking is described by ABC for cubic and AB for wurzite. We can also inspect bonding between successive layers to distinguish cubic from hexagonal stacking. For hexagonal stacking, the bonds are eclipsed and the hexagonal rings joining the layers are boat shaped, while for the cubic stacking, the bonds are staggered and the rings are chair shaped. In fact, by associating a fictitious spin with each layer, one may describe two hexagonally stacked layers by the change in spin direction while cubic stacking corresponds to parallel spins. Cubic is described by \uparrow periodically repeated while wurzite is described by $\uparrow\downarrow$ periodically repeated. A single spin-flip in an otherwise cubic structure corresponds to a twin boundary. Thus, it is sufficient to tell the number of parallel spins or distance between successive twin boundaries to identify a polytype. The relationship between properties and polytype structure can also be made. It is observed that some properties are independent of the polytype while others are very sensitive to it. For example, the bonding and the elastic constants are very similar and show only minor differences.²⁷ On the other hand, it is observed that polytypes are essentially regular arrangements of twin boundaries in either the cubic or hexagonal cases. Electronic band structures and phonon dispersion relations in these systems describe the wave propagation through an assembly of such twin boundaries. The resulting formation of standing wave patterns clearly may lead to intricate dependencies on polytype.²⁸

Another important question arises as to why SiC is so exceptional in showing relatively strong band gap variation among polytypes. Van Haeringen *et al.*²⁹ have given a detail description of the band gap variation among polytypes of SiC in terms of matching wave-functions, and also in terms of a one-dimensional frustration model of propagating waves in building blocks. They have also identified the characteristic features responsible for the rather strong band gap variation among

polytypes of SiC and why other materials like ZnS and *hypothetical* polytypes Si, C, and AlAs, do not show this rather strong variation.

4. Results

In order to understand the mechanism of polytypism in SiC, we have performed band structure calculations of the two extreme polytypes: zincblend (pure cubic stacking) and wurzite (pure hexagonal stacking) after optimization. Each primitive cell of zincblend type structure (space group F43m or 216), has two atoms, one cation (Si) and one anion (C). The primitive cell of wurzite type structure (space group P6₃mc or 186) has four atoms, two cation (Si) and two anions (C). Lattice constants, cell volume, total-energy and inter-atomic distance between nearest neighbors calculated for both polytypes of each material are listed in Table 3 and compared with various previously calculated and experimental values.

Figures 1(a) and (b) are the band structure and density of state calculations of the 3C polytype of SiC. Important energy gaps have been calculated and compared with the previous theoretical results of Herman *et al.*³⁰ (first principal Orthogonalized Plane Wave technique, OPW), Hemstreet *et al.*³¹ (Empirical Pseudopotential method, EP), Junginer *et al.*³² (EP method), Bassani *et al.*³³ (OPW method), and the experimental results extrapolated from the absorption and reflectivity data^{34–37}

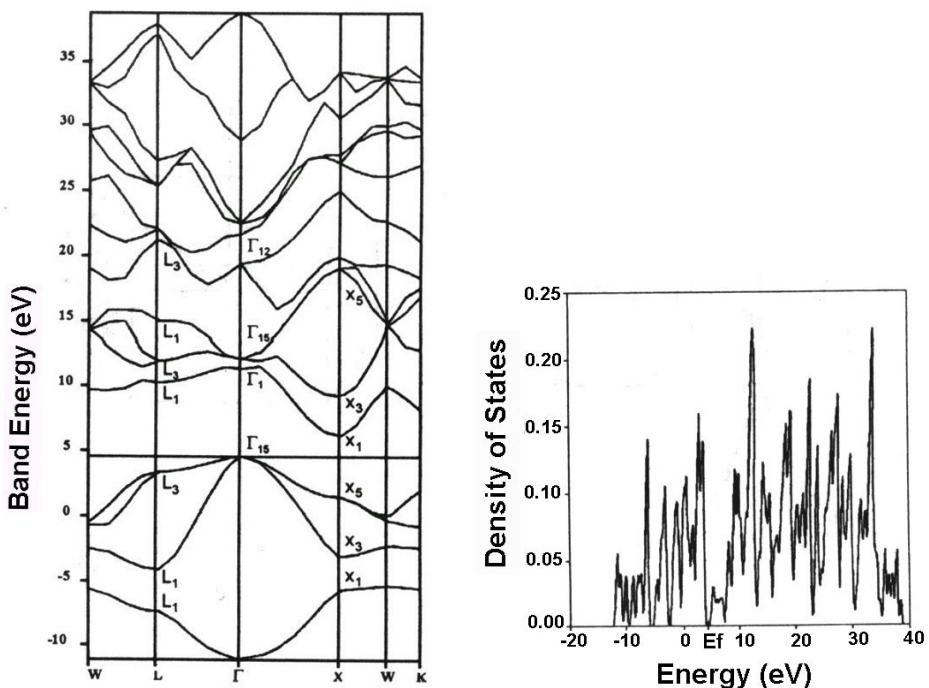


Fig. 1. The band structure and density of states of 3C-SiC.

Table 1. Important energy gaps for 3C-SiC.

| Energy gaps (eV) | Present calculations | Herman <i>et al.</i> | Hemstreet <i>et al.</i> | Junginer <i>et al.</i> | Bassani <i>et al.</i> | Exp. |
|-----------------------------|----------------------|----------------------|-------------------------|------------------------|-----------------------|------|
| $\Gamma_{15V}-\Gamma_{1c}$ | 6.92 | 5.90 | 5.92 | 5.14 | 6.80 | 6.00 |
| $\Gamma_{15V}-\Gamma_{15C}$ | 7.70 | 7.80 | 6.49 | 10.83 | 8.60 | — |
| $X_{5V}-X_{1C}$ | 4.50 | 5.30 | 6.36 | 5.27 | 5.80 | — |
| $X_{1C}-X_{3C}$ | 3.00 | 2.60 | 3.08 | 3.24 | 3.20 | 3.10 |
| $L_{3V}-L_{1C}$ | 6.92 | 6.40 | 6.02 | 6.75 | 9.90 | — |
| $\Gamma_{15V}-L_{1C}$ | 5.77 | 5.50 | 4.38 | 5.93 | 6.80 | 4.20 |
| $\Gamma_{15V}-X_{1C}$ | 1.80 | 2.30 | 2.35 | 2.40 | 2.70 | 2.39 |
| $L_{3V}-X_{1C}$ | 2.70 | 3.10 | 3.90 | 3.26 | 6.00 | 3.55 |

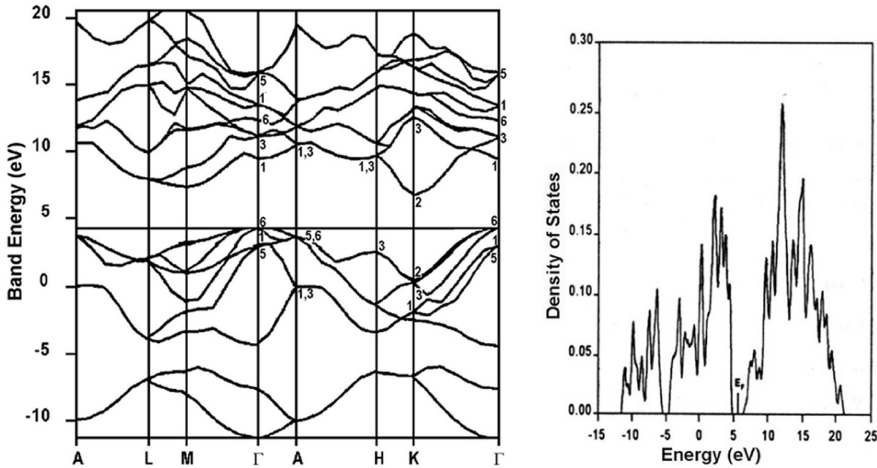


Fig. 2. The band structure and density of states of 2H-SiC.

as shown in Table 1. The minimum occurs at the X_1^c state, which is a mixture of s - and p -like components while the top of the valence band is at the Γ_{15}^c state, which is purely p -like in the zincblend structure.

Band structure and density of state calculations of 2H polytypes are shown in Figs. 2(a) and (b), respectively. The important energy gaps have been compared with the theoretical results of Hemstreet *et al.*,³¹ Herman *et al.*³⁰ and Junginer *et al.*³² in Table 2. The high symmetry points in the wurzite case are A, L, M, H, K and Γ . The minimum of the conduction band is at the K_c^2 state, which is purely p -like while the top of the valence band is at Γ_6^v , which is purely s -like in the wurzite case.

Since the early work on the band structure of SiC,³⁷ it is clear that due to the similarity in the Brillouin zones of the two structures, the band structure of the two polytypes can be compared along various symmetry directions. If the two zones are

Table 2. Important energy gaps for 2H-SiC.

| Energy gaps (eV) | Present Calculations | Hemstreet <i>et al.</i> | Herman <i>et al.</i> | Junginger <i>et al.</i> |
|---------------------------|----------------------|-------------------------|----------------------|-------------------------|
| $\Gamma_{6V}-K_{2C}$ | 2.80 | 3.30 | 3.30 | 4.02 |
| $\Gamma_{1V}-K_{2C}$ | 2.85 | 3.77 | 3.35 | 3.70 |
| $\Gamma_{6V}-M_{1C}$ | 3.00 | 3.40 | 4.42 | 4.00 |
| $\Gamma_{1V}-M_{1C}$ | 3.05 | 3.87 | 3.75 | 4.40 |
| $\Gamma_{6V}-L_{1C}$ | 3.50 | 3.81 | 4.49 | 3.30 |
| $\Gamma_{1V}-L_{1C}$ | 3.55 | 4.28 | 3.82 | 3.70 |
| $\Gamma_{6V}-\Gamma_{1C}$ | 5.55 | 4.39 | 5.09 | 6.00 |
| $\Gamma_{1V}-\Gamma_{1C}$ | 5.60 | 4.86 | 4.46 | 6.40 |

aligned with the cubic Λ -axis parallel to the hexagonal Δ -axis, each vector k along the Γ - Λ - L direction in zincblend corresponds to an identical k vector along the Γ - A - Γ direction in wurzite, i.e. the cubic Λ -axis is mapped onto the hexagonal Δ -axis from Γ to A and back to Γ , while the cubic point L is folded back on to hexagonal point Γ . This mapping is indeed reflected in the two band structures. The 2H-SiC direct gap of 5.0 eV, identified with the $\Gamma_6^v-\Gamma_1^c$ transition, compares very nicely to the value of 5.3 eV for the corresponding cubic $\Gamma_{15}^v-L_1^c$ transition. The crystal field splitting near the valence band edge ($\Gamma_6^v-\Gamma_1^v$) is about 0.2 eV. The differences between the wurzite energy levels at Γ and those of the corresponding zincblend states along Γ and L are near this value for all states up to and including the second Γ_1 state in the conduction band. It is also possible to make some comparisons between k vectors and states along directions perpendicular to the ‘polar’ direction discussed above. However, there is no longer unique one-to-one correspondence between zincblend and wurzite. For example the cubic point K is mapped on two regions at the wurzite zone — a region around M , extending along the Σ direction to Γ , and a region between the wurzite points M and K and extending upward along Z . Such mappings manifest themselves in the optical constants of the two solids and are generally indicated by the mappings of the cubic zone points onto the hexagonal zone as shown in Fig. 3, taken from the work of Bergstresser *et al.*³⁸

We have also calculated the charge density of SiC, a IV-IV compound, which shows that bonding has a significant ionic nature because of the large energy difference between the Si ($3s$, $3p$) and C ($2s$, $2p$) valence levels. A plot of charge density presents the clear asymmetry between Si and C as shown in Fig. 4.

5. Calculation of Bulk Moduli of SiC

For the calculation of bulk moduli of zincblend and wurzite polytypes of SiC, total-energy calculations were done under hydrostatic pressure to obtain energy against volume curves for both polytypes of SiC separately. The lattice parameters, cell volume v_0 , total energy and enthalpy were calculated at pressures 5.0, 2.0, 0 and

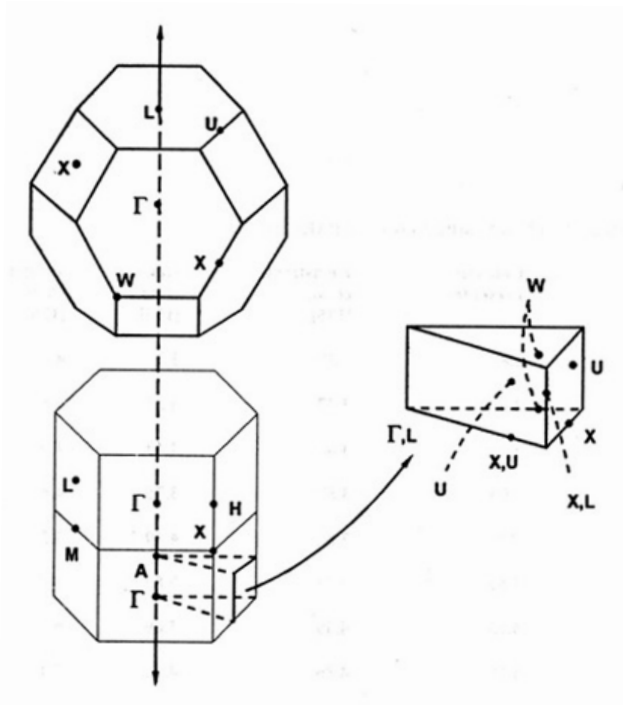


Fig. 3. Comparison of zincblend and wurzite polytypes of SiC.

Table 3. Lattice parameters of the equilibrium structure, minimum energy and bulk modulus.

| | 2H-SiC | 3C-SiC |
|-------------------------------------------------------------|----------------------------|-------------|
| Lattice parameters (\AA) (after optimization) | $a = 3.052$ $c = 4.988$ | $a = 4.292$ |
| Cell volume (\AA^3) | 39.636 | 19.727 |
| Minimum energy (eV) | -265.4485 | -265.797 |
| Bulk moduli B calculated from Ref. 39 | 237.53 | 222.47 |
| Interatomic distance d (\AA) | 1.88 | 1.866 |
| Bulk moduli B calculated from Ref. 40 | 216.54 | 222.07 |

-5.0 GPa. A linear fit was performed to the generated values of $1/[1 - (\Delta V/V_0)]^2$ versus pressure, by using Murnaghan's equation of state.³⁹

From this fit, the values of the lattice parameters of the equilibrium structure, the minimum energy, and the bulk modulus are obtained. These results are presented in Table 3. The bulk modulus of 3C-SiC is 222.47 GPa while that of 2H-SiC is 237.53 GPa, which is lower than the reported value of SiC which is 226 ± 9 GPa.

The bulk modulus can also be calculated by evaluating the average distance

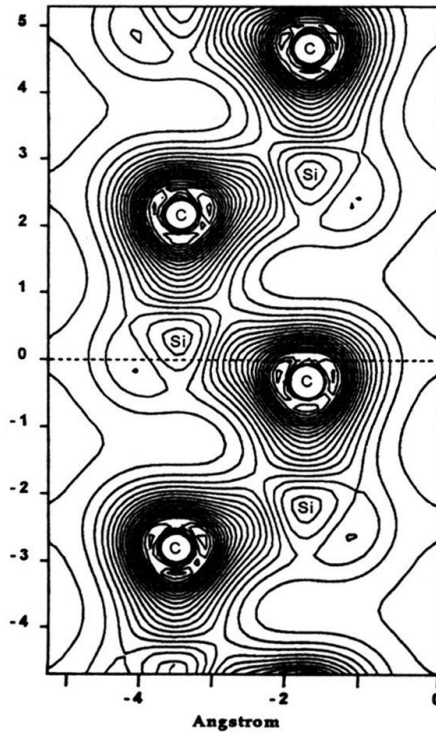


Fig. 4. The charge density of SiC.

between nearest neighbors, which is a semi-empirical method used by Cohen *et al.*⁴⁰:

$$B = \frac{19.71 - 220\lambda}{d^{3.5}},$$

where d (Å) is the bond length and λ is the ionicity parameter which is 0 for group-IV carbides. According to this equation, $B = 222.07$ GPa for 3C-SiC and 216.54 GPa for 2H-SiC.

6. Discussion

Due to important characteristics and polytypism, SiC is an important candidate in semiconducting technology. In spite of impressive technological achievements over several years, there are still some problems concerning basic physical properties of this compound, which have to be solved. Moreover, theoretical capabilities including computational programming is to be improved increasingly. The electronic structure of SiC has been calculated by using various theoretical techniques including first principal Orthogonalized Plane Wave,³⁰ Empirical Pseudopotential,³¹ DFT in local density approximation,²⁷ etc. but we apply the density functional theory under the generalized gradient approximation (GGA). The important band gaps and

electronic transitions are compared with the previously reported results calculated by the other methods. It is observed that DFT under GGA does not improve the lattice parameters and the fundamental gap^{19,20} but the elastic properties are in good agreement with the reported values⁴¹ in both polytypes of SiC. However, several important energy gaps are comparable to the work of Herman *et al.* for both polytypes.

The bulk modulus, which measures hardness, has calculated for both polytypes of SiC by using Murnaghan's equation of state under elastic deformation and also Cohen's equation (a semi-empirical method) by using nearest neighbor distance, d . The bulk modulus calculated by the two methods is compared with each other and with the reported one.⁴¹ SiC is extremely hard due to its small lattice constant and large elastic constant. It is proposed that the shear modulus (the resistance to reversible deformation upon shear) measures the hardness more correctly in view of the actual deformation process, but our results show that the bulk modulus is also a good prediction of hardness.

7. Conclusion

The main objective of this work is the calculation of the band structure, density of states, charge density and bulk modulus of the 3C (cubic) and 2H (Wurzite) cases of SiC by using the density functional and total-energy pseudopotential technique in the generalized gradient approximation, and comparing with the previous theoretical results calculated by different computational methods. The two polytypes are also compared by using the symmetry between the two Brillouin zones. It is clear that our results are in good agreement with the previous theoretical and experimental calculations. By comparing with previous results, it is also observed that the bulk modulus is a good prediction of hardness.

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