



Ab initio calculation of structural and electronic properties of 3c-Silicon Carbide: Density functional theory calculations

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Abstract: Silicon Carbide has become one of the promising materials that can be used for electronic and optical applications. This is as a result of its superior properties among them structural, thermal, chemical, electronic and mechanical. This work reports both the structural such as bond length, lattice parameter and electronic properties of cubic Silicon Carbide (3C). The theoretical calculations were carried out using an ab initio approach based on Density Functional Theory framework using Ultrasoft pseudopotential as implemented in Quantum ESPRESSO computer code. The lattice parameter was found to be overestimated by +0.66% when compared to the experimental value of 8.24 Bohr while the bulk modulus was underestimated by 11.91%. Cubic Silicon Carbide was found to have an indirect band gap of 1.34 eV between W and K and L and W which is underestimated by the Density Functional Theory calculations.

Keywords: Electronic properties, mechanical properties, Density Functional Theory

1. Introduction

Polytypism is one of the phenomenons evident in some materials. It exists whereby a compound and elements occur in different crystal structures. The main difference between the different polytypes is the stacking sequence along one direction [1]. One of the materials that has attracted a lot of attention due to this phenomenon is Silicon Carbide (SiC) which form such stable polytypes. Another important aspect of SiC is that it is a known group-iv naturally stable compound. This material is among the prominent systems that exhibits several polytypism. It has more than 200 polytypes and among them is 3C polytype which has attracted more attention due to its favorable electronic properties. SiC is used in microelectronic devices such as high-power and high-temperature applications. However, a deep understanding of the physical properties of SiC is necessary due to technological problems that need to be addressed before the material can be used in the production of electronic devices. [2]. One of the most extreme polytype is zincblende [3] which is the main phase considered in this work. It has pure cubic package with double layers of Si-C in the [111] direction.

Silicon carbide referred to as carborundum consist of silicon and carbon atoms and occurs as the extremely rare mineral moissanite in nature. It is a high quality technical grade non-oxide ceramic possessing wide energy band gap, low density and high thermal conductivity with diverse industrial applications. It possesses exclusive properties like high hardness and strength, high elastic constants, oxidation resistance, high erosion resistance as well as chemical and thermal stability. These properties



make SiC a candidate for applications such as high power, high temperature electronic devices, abrasion and cutting applications. It has a variety of polytypes which possess unique structural and electronic properties that attract attention of many researchers. The material has been of immense interest due to its hardness and being a strong ceramic it has other applications in areas requiring high endurance like car brakes, clutches and ceramic plates in bulletproof vests [4,5].

Since the 1980s the interest in the development of wide band gap materials has increased drastically, as their unique physical properties make them very attractive for high-temperature, high-power and high frequency application fields, where the requirements are beyond the limits of Si or GaAs technology. One of the most promising wide band gap semiconductors for such an application is silicon carbide (SiC) with exceptional material properties, like high-electron mobility, high-breakdown field, high saturated electron-drift velocity and high thermal conductivity.

The problem

Having a large bandgap (2.3–6.2 eV), it is much more difficult to thermally excite electrons from the valence band to the conduction band. For example in SiC the probability of thermal excitation of an electron over the band gap is 10^{-26} at room temperature, i.e. there are no thermally excited electrons in the conduction band [15]. In a device this causes the reduction in leakage currents and an increase in thermal stability since intrinsic-type conduction will dominate at higher temperatures (when this happens the devices fail, since there is no longer p-n junction to block the voltages.). The wide band gap is also accompanied by considerably higher breakdown voltage as compared to silicon. This means that for power devices with similar blocking voltage capabilities, the one made of silicon must have about 100 times lower doping level in a 10 times thicker layer, as compared to a SiC device. Thick layers with low doping levels will have high resistance, increasing the power loss and heat generation in the device. Therefore, the use of wide bandgap materials, like SiC, gives the possibility to increase the blocking voltages for high power devices, as well as to make devices smaller and to reduce power losses. It is because of these outstanding properties that much effort has been directed towards understanding and improving the electrical properties of SiC.

The objectives

The objectives of the research are to determine the:

1. geometrical properties of SiC in the zinc blende phase
2. the electronic properties of SiC in the zinc blende phase

Literature review

SiC has also been studied by several groups using both experimental and theoretical techniques. Chang et al. [6] using ab initio electronic structure approaches showed that the band gap of SiC with cubic phase decreases with increasing pressure while zinc-blende phase transforms to rocksalt structure at 660 Kbar when under hydrostatic pressure. Molecular Dynamics studies have also shown that the zinc-blende phase of SiC is the most stable at ambient condition through pressure-induced structural deformation[7]. Other studies have shown an existence of high mobility in the conduction band being dominant at high temperatures and low mobility impurity conduction band being dominant at temperatures lower than 70K for heavily doped SiC ($n_{RT} \geq 10^{19} \text{ cm}^{-3}$) material [8]. The response of turning and twisting has also not been investigated exhaustively in SiC.

Methodology

The first-principle calculations performed in this work were done in the framework of density functional theory. For the exchange-correlation functional the study employed the generalized gradient approximation (GGA) of Perdew-Berke-Ernzerhof [9]. The geometry optimization was done using the primitive unit cells. Through the Quantum Espresso database, the ultrasoft pseudopotential was taken to optimize the structures. They characterized the interactions occurring between the electrons and



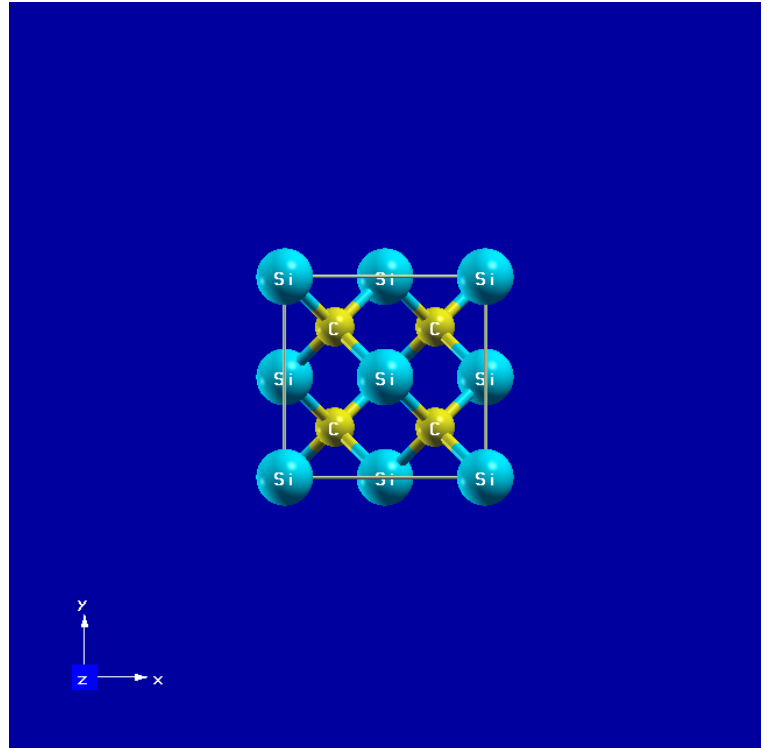
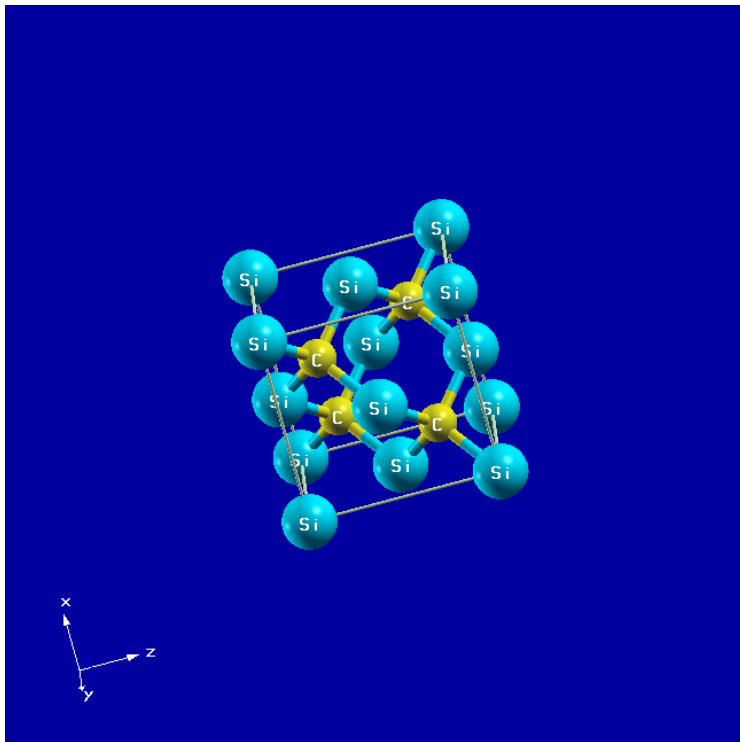
ionic core [10]. The valence electron structures for the nonmetal and metal are $2s^22p^2$ for C and $3s^23p^2$ for Si, respectively. The forces and stress tensors were minimized in order to optimize the atomic positions as well as lattice parameters. The calculations converged when the total energies of successive iterations agreed to within 1×10^{-4} Ry in the iterative solution of the Kohn-Sham equations [11]. The Monkhorst-Pack [12] scheme was applied, and the k-point mesh of the first irreducible Brillouin-zone was used. The scheme ensures that there is an integration of the irreducible region of the zone over a mesh where the special k-points are uniformly spaced though at different sites and coverage.

Results and discussion

This section reports on the geometrical properties such as bond angles, lattice parameter and bond lengths, bulk moduli as well as electronic properties.

Geometrical properties

In this study, the optimized structure of SiC was obtained using Xcrysden program [13] following rigorous relaxation.



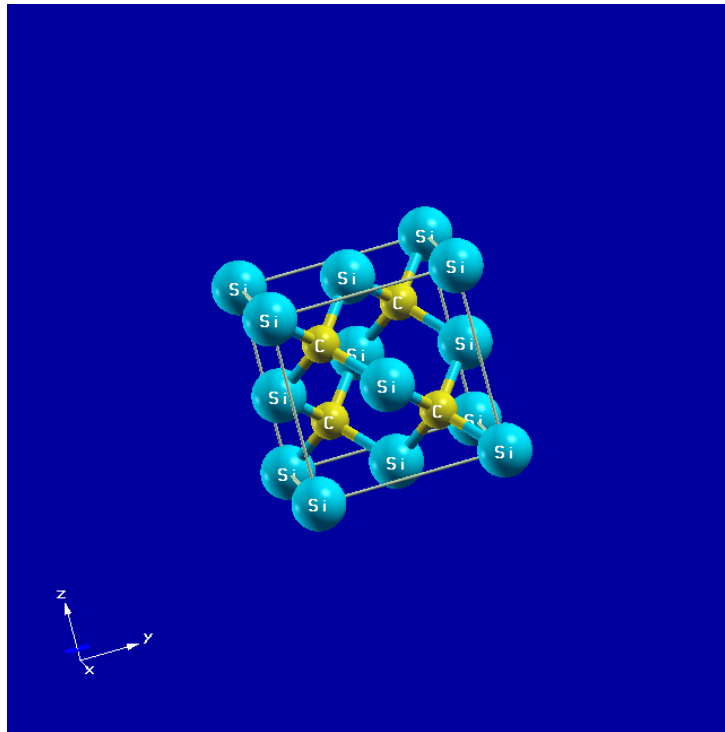


Figure 1: SiC structure in zinc blende phase snapshots. The frame shows xz (L) and yx (R) planes as displayed by Xcrysden. The frame below shows the zy plane

From Fig 1, the bond lengths and the bond angles were determined. The bond angle was 109.471°

Table 1: Calculated DFT-GGA Bond lengths, bond angle and lattice parameter of SiC in zinc blende structure.

SiC	Bond angle (Si-C-Si, C-Si-C)	Bond length, Å (Si-C)	Lattice parameter, Å	Lattice parameter, bohrs
This work	109.471°	1.9006	4.38	8.2344
Experimental work			4.36 ^a	8.1968
Other works	109.00 ^d	1.89 ^c	4.34 ^b	8.1592
%deviation			0.66	

^aReference [18] ^bReference [14] ^cReference [15] ^dReference [16]

The lattice parameter of SiC in zinc blende structure is calculated as the value corresponding to minimum total energy of the entire system at ground state and using the Murnaghan equation to extract the value.

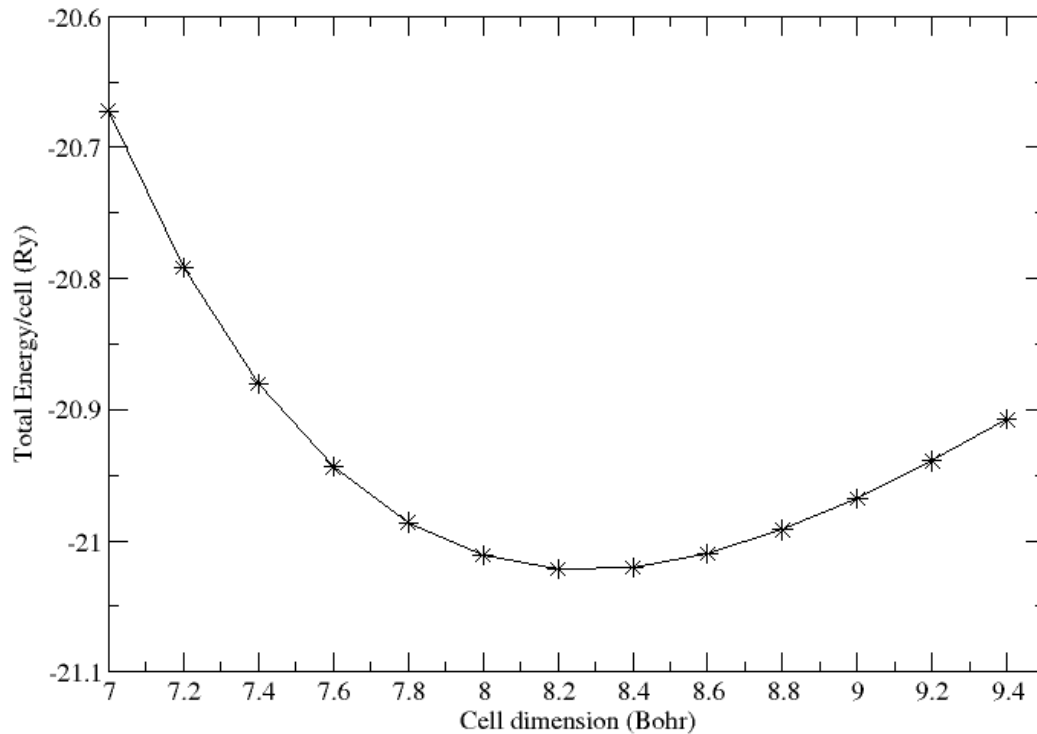


Fig 2: Total energy/cell vs cell dimension

The fitting to this equation of state extract not only the equilibrium lattice parameter but also the bulk modulus and its derivative. By use of GGA for exchange and correlation functional, the lattice parameter was overestimated by 0.66% which reveals a good agreement between the theoretical and experimental value. The bulk modulus for this system was determined to be 198.2 Gpa which is compared to an experimental value of 225 Gpa [17].

Electronic properties

The calculated electronic band structure and the PDOS in the selected high symmetry points for the first Brillouin zone are presented in Fig 3. They were obtained using the determined equilibrium lattice constant of SiC in this study. The band structure indicate that SiC is a semiconductor.

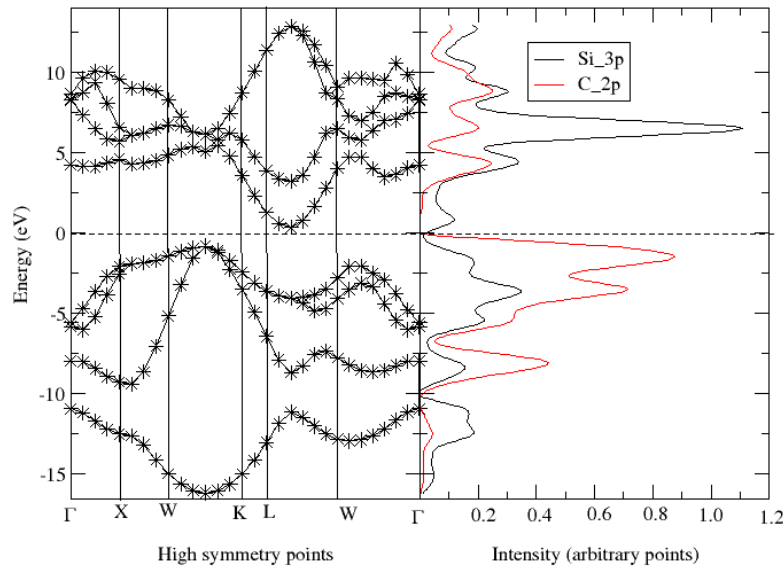


Fig 3: Superimposed graph of band structure and PDOS of SiC in the zinc blende structure.

From Fig 3, the band structure of 3C-SiC shows that it is a semiconductor as the valence band is clearly separated from the conduction band. The system has an indirect band gap of 1.34 eV around W and L whereby VBM is between W and K, while CBM is between L and W high symmetry directions which can be compared to the experimental value of 2.36 eV. This is an underestimation of the band gap which is associated with DFT calculations. The width of CB is found to be 12.32 eV while that of VB is 15.33 eV. From this figure the levels at all symmetry points between gamma and gamma are connected by smooth curve. The Si 3p states are the most dominant states in the conduction band between 0 eV and 12 eV while in the valence band the C 2p are the most predominant between 0 eV and -10 eV. The strong hybridization of the C-2p and Si-3p orbitals contributes to the mechanical properties of the system such as high value of bulk modulus which give rise to the numerous applications of SiC. The small bandgap suggest that SiC is a semiconductor.

Recommendation

Since DFT underestimates the value of the bandgap, I recommend the use of hybrid functionals which provide more accurate values or DFT+U which is considerably cheaper compared to hybrid functional calculations. Hybrid functionals are a class of approximations to the exchange–correlation energy functional in density functional theory (DFT) that incorporate a portion of exact exchange from Hartree–Fock theory with exchange and correlation from other sources (ab initio or empirical). The exact exchange energy functional is expressed in terms of the Kohn–Sham orbitals rather than the density, so is termed an implicit density functional. One of the most commonly used is the B3LYP, which stands for Becke, 3-parameter, Lee–Yang–Parr, PBE0, Meta hybrid GGA. Surface calculations



would provide more information since a large number of applications for SiC are related to surface properties.

Conclusion

The thrust of this work was to investigate the geometrical and electronic properties of SiC in the zinc blende crystal phase using DFT. The obtained lattice parameter was found to be overestimated by 0.66% while the band gap was underestimated. In the crystal form it is an indirect bandgap semiconductor which allows it to be used in technological and industrial applications.

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