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Structural, elastic and electronic properties of 2H- and 4H-SiC

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ABSTRACT
The structural, five different elastic constants and electronic properties of 2H- and 4H-Silicon carbide (SiC) are investigated by using density functional theory (DFT). The total energies of primitive cells of 2H- and 4H-SiC phases are close to each other and moreover satisfy the condition $E_{2H} > E_{4H}$. Thus, the 4H-SiC structure appears to be more stable than the 2H- one. The analysis of elastic properties also indicates that the 4H-SiC polytype is stiffer than the 2H structures. The electronic energy bands, the total density of states (DOS) are calculated. The fully relaxed and isotropic bulk modulus is also estimated. The implication of the comparison of our results with the existing experimental and theoretical studies is made.
Keywords –Elastic constants, Electronic structures, Structural parameters

I. INTRODUCTION

Silicon carbide (SiC) has a broad prospect of potential applications in the field of high temperature, high power and high frequency devices [1]. The usefulness of SiC in these applications stems largely from its superior mechanical and electronic properties. Considering its electronic properties, SiC is a semiconductor that can be doped, like silicon. It is characterized by a large band gap, and a high value of critical electric field. SiC is therefore used in high power and high temperature devices as mentioned earlier. SiC shows low chemical reaction with a good resistance to corrosion, and therefore has potential applications in harsh environment. Many compound materials exhibit polymorphism, as they exist in different structure called polymorphs. SiC is unique in this regard as more than 250 polymorphs of silicon carbide had been identified by 2006 [2]. The structural, elastic and electronic properties on different phases of silicon carbide have been carried out by several groups by using several different methods [3-10]. Among the SiC polytypes, 2H- and 4H-SiC attracting keen interest for their favorable structural, elastic and electronic behavior. The 2H-SiC structure is equivalent to that of wurtzite and is composed of only elements A and B stacked as ABABAB. The 4H-SiC unit cell is twice longer, and the second half is twisted compare to 2H-SiC, forming ABCB stacking [2]. The purpose of this paper is to present first-principles calculations based on DFT of the structural, elastic and electronic properties of 2H- and 4H-SiC and comparing our data with those of other's works.

II. COMPUTATIONAL TECHNIQUES

The first-principles calculations reported herein were performed using the Cambridge Serial Total Energy Package (CASTEP) code [11], which is based on the density functional theory [12] within the plane-wave pseudopotential approach. The Kohn-sham equations were solved using the Perdew-Burke-Ernzorhof generalized gradient approximation (PBE-GGA) [13] for the exchange-correlation energy. Vanderbilt-type ultra soft pseudopotentials [14] were used to model the electron-ion interactions. Throughout the calculations, a plane-wave cutoff energy of 600 eV was chosen to determine the number of plane waves in expansion. The crystal structures were fully relaxed by the BFGS minimization technique [15]. Special *k*-points sampling integration over the Brillouin zone was employed by using the Monkhorst–Pack method [16] with the 17×17×9 mesh. This set of parameters uses the tolerance in the self-consistent field calculation of 2×10^{-6} eV/atom, the change in total energy of 2×10^{-5} eV/atom, the maximum force of 0.05 eV/Å, the maximum stress of 0.1 GPa, and the maximum atomic displacement of 0.002 Å.

The CASTEP calculates the elastic properties from the first-principles using the finite strain theory [17] which gives the elastic constants as the proportionality coefficients relating the applied strain to the computed stress, $\sigma_i = C_{ij}\,\varepsilon_j$. From C_{ij}, the polycrystalline bulk modulus B and shear modulus G were further evaluated using the Voigt-Reuss-Hill approximation [18-20]. In addition, the Young's modulus Y, Poisson's ratio v, and shear anisotropy factor A were estimated using the equations $Y = (9GB)/(3B + G)$, $v = (3B - 2G)/(6B + 2G)$ and $A = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$, respectively.

III. RESULTS

3.1 Structural and elastic properties

The crystal structure of both 2H- and 4H-SiC are hexagonal with space group $P6_3mc$ (186) [21]. Fully relaxed structure is achieved by optimizing the geometry with lattice constants and internal atomic positions. The optimized Si atoms are situated in the 2b Wyckoff site with fractional coordinates (1/3, 2/3, 0), and the C atoms are located in the 2b Wyckoff site with fractional coordinates (1/3, 2/3, 3/8) for 2H-SiC, and Si atoms are situated in the 2a Wyckoff site with fractional coordinates (0, 0, 0), and 2b (1/3, 2/3, 1/4), and the C atoms are located in the 2a Wyckoff site with fractional coordinates (0, 0, 3/16), and 2b (1/3, 2/3, 7/16) for 4H-SiC [22].

The total energy, *E* of both 2H- and 4H-SiC has been calculated at different cell volumes. The energy was minimized as a function of the c/a ratio for selected values of volume. Figure 1(a) and 1(b) show the total energy per atom as a function of unit cell volume, *V*. The total energy per atom of both 2H- and 4H-SiC structures are close to each other. However, the total energy satisfy the condition $E_{2H} > E_{4H}$, which implies that the 4H-SiC structure seems to be more stable than the 2H- one. The calculated fully relaxed equilibrium values of the structural parameters of the two structures of SiC are listed in Table 1 together with other available data on both theoretical [3] and experimental [23-24] results. The comparison shows that the calculated values in our study are in well agreement with available experimental as well as theoretical results.

Table 1: Calculated lattice constants (*a* and *c* in Å), hexagonal ratio *c*/*a* for 4H- and 2H-SiC structures

Structure	*a* (*Å*)	*c*(*Å*)	*c*/*a*	Reference
4H-SiC	3.079	10.07	3.270	Present
	3.090	10.17	3.294	[3]
	3.073	10.051	3.271	[23]
2H-SiC	3.079	5.053	1.641	Present
	3.0885	5.083	1.645	[3]
	3.079	5.052	1.641	[24]
	3.0763	5.048	1.641	[23]

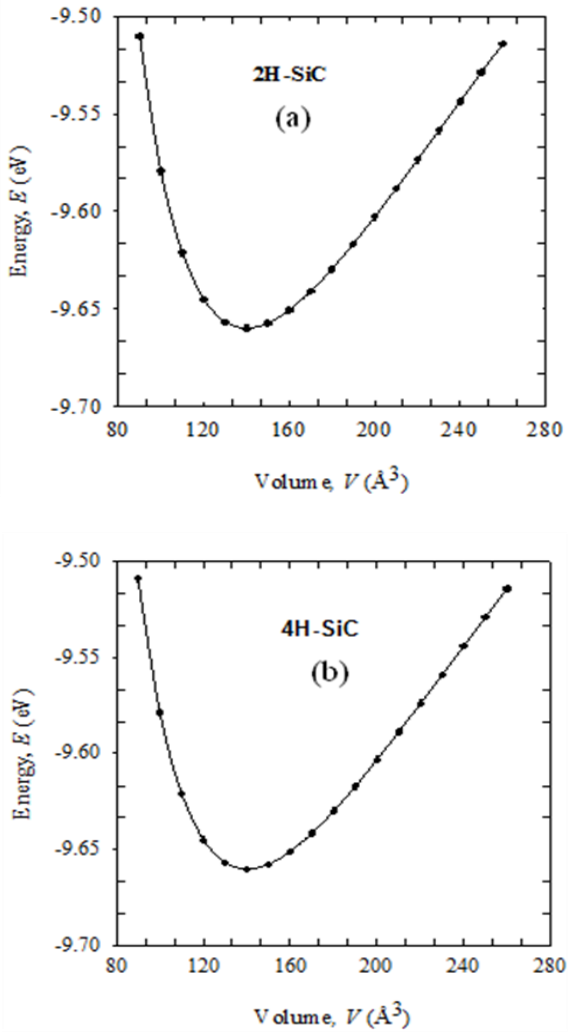

Fig. 1(a) and (b) shows the total energy per atom for 2H- and 4H-SiC as a function of unit cell volume

The elastic constant tensors of 2H- and 4H-SiC are listed in Table 2 along with available computed [3,25] and experimental [26] elastic constants. Using the second order elastic constants, the bulk modulus *B*, shear modulus *G*, Young modulus *Y* (all in GPa), Poisson's ratio (*v*), and shear anisotropy factor *A* at zero pressure are computed and presented in Table 2. The bulk modulus *B* and shear modulus *G* of both structures are high which is the indication of higher hardness of these materials. The ductility and brittleness of a material can be roughly characterized by the value of the bulk modulus to shear modulus (*B*/*G*) ratios. When *B/G* <1.75, the material is brittle, and *B/G* >1.75 represents material is ductile. As it is evident from Table 2, the calculated (*B/G*) ratios is 1.10 for 4H-SiC is almost same as 1.11 for 2H-SiC, indicates that both materials are brittle in nature. The same can be explained from an additional argument that the ductility/brittleness of material can also be characterized by the values of Poisson's ratio (*v*). However, Poisson's ratio (*v*= 0.15) for both materials

are approximately same and express that both polytypes are brittle since for ductile material v is typically 0.33 [27]. The Young modulus, Y are 441 and 444 GPa for 2H- and 4H-SiC, respectively, indicating that the 4H-SiC is slightly more stiffer than 2H-SiC. It is noted that the Young modulus of another polytype 3C-SiC is 347 GPa [4]. Thus the stiffness of all 3C-, 2H- and 4H- SiC polytypes are between Diamond-C (Y=1046.99 GPa) and Si (Y=137 GPa) [4].

3.2 Electronic properties

The electronic energy bands of 2H-, and 4H-SiC along the high symmetry directions in the first Brillouin zone are shown in Fig. 2 (a) and 2(b) in the energy range -16 eV to + 8 eV. The zero of the energy is set at the top of the valence band. The top of the valence band of both 2H- and 4H-SiC is at the A-point as shown in Fig. 2(a) and 2(b). Our calculated valence bands of the occupied states of 4H-SiC, Fig. 2(b), are very close to the previously reported results of *ab initio* LCAO calculations [28]. The conduction band is minimum at the K-point for 2H-SiC which is similar with theoretical result [7]. For 4H-SiC, the conduction band minimum is at the M-point in our calculation. There is a second minimum of the conduction band at the M-point, which is only about 0.12 eV above the lowest unoccupied state.

Table 2: Calculate elastic constant (C_{ij} in GPa), bulk modulus(B in GPa), shear modulus (G in GPa), Young modulus (Y in GPa), Poisson's ratio (v), and shear anisotropy factor A of 4H- and 2H- SiC.

Structure	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B	G	G/B	B/G	Y	γ	A	Reference
4H-SiC	503	92	48	533	161	213	193	0.89	1.10	444	0. 157	0.682	Present
	501	111	52	553	163								[26]
	498	91	52	535	159								[3]
2H- SiC	506	92	46	542	154	213	191	0.89	1.11	441	0.157	0.647	Present
	499	93	52	533	153								[3]
	541	117	61	586	162								[25]

These results are consistent with the ballistic electron emission microscopy study by Kaczer *et al.* [29] who observed the second minimum of about 0.15 eV, and *ab intio* LCAO calculation which is at 0.18 eV [8]. Thus, we conclude that the highest valence band for the two polytypes 2*H*-, and 4*H*-SiC are very similar whereas, as we have seen above, the lowest conduction band structures differ considerably [7]. The energy band gap calculated in our data is 3.01 eV for 2H-SiC which is good agreement with the experimental data of 3.3 eV [9]. Our calculated value differs from other theoretical result of band gap 2.11 eV [7]. The indirect band-gap from our calculated electronic structure of 4H-SiC is 2.45 eV, which is comparable to the theoretical data of 2.17 eV [7]. The experimental value of the band gap is 3.26 eV [9]. The slight difference in the comparison of our data with available both experimental and theoretical results can be attributed to both computational and experimental limitations. These limitations include uncertainties introduced in the fit procedure in the analysis of the experimental data and computational uncertainties that include rounding errors.

The total and partial density of states of 2H-, and 4H-SiC are shown in Fig. 3(a) and (b). The values of the total DOS at the Fermi level is very small in both structures. The shape of the DOS located between -20 to -10 eV are similar for both polytypes considered here while those near the conduction band edge changes appreciably [Fig. 3].

The slope of DOS at the conduction band edge become steeper for 4H- SiC structure which look similar to the self-consistent *ab initio* pseudopotential calculations [30]. The value of the total DOS at the Fermi level is 0.47 states per eV for SiC-4H phase and that for SiC-2H phase is 0.17. Thus the value of the total DOS at the Fermi level is slightly higher for 4H-SiC than that of 2H-SiC. Contribution to the total DOS at the Fermi level for 4H-SiC comes from both Si-3*p* and C-2*p* states. On the other hand for 2H-SiC the DOS at the Fermi level comes mainly from 2*p* states of carbon. Only the conduction band contributes to the total DOS at the Fermi level for both phases.

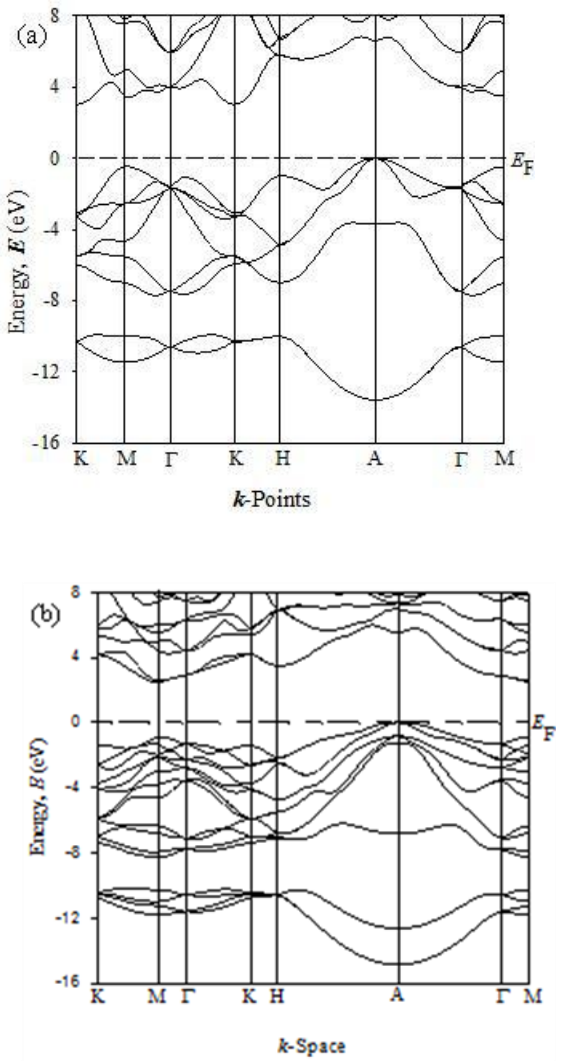

Fig. 2 (a) and (b) shows the electronic band structure of 2H- (top) and 4H- SiC (bottom), respectively.

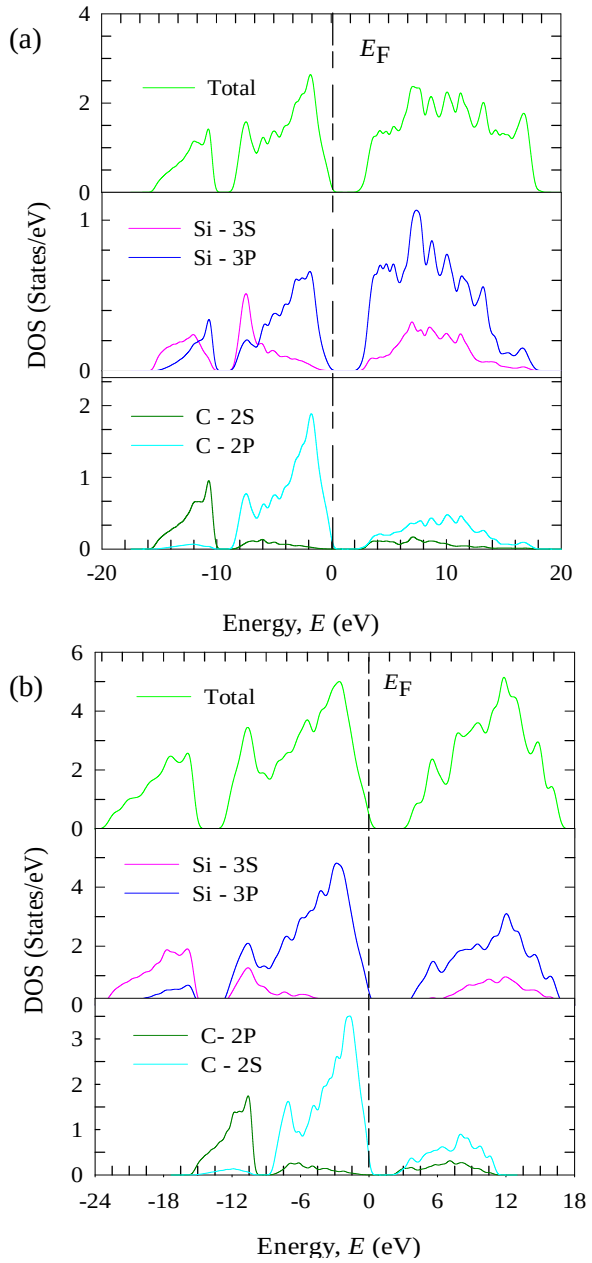

Fig. 3(a) and (b) shows the total and partial density of states of 2H- (top) and 4H- SiC (bottom), respectively.

Density of states also reveals the types of bonding of a solid, especially it detect the covalent bonding. The steeper peak near the Fermi level at the total DOS for 4H-SiC is due to the hybridization between Si-3*p* and C-2*p* states. Thus a strong Si-C covalent bond is observed for 4H-SiC. Same phenomena also observed for 2H-SiC phase. But the Si-C covalent bond of 4H-SiC is stronger than the Si-C covalent bond of 2H-SiC.

IV. CONCLUSION

We studied the structural, elastic and electronic properties of two polytypes 2H- and 4H-SiC. The calculated lattice parameters and elastic properties agree well with the available reported theoretical and experimental data. The total energy calculations minimized at different cell volumes by changing c/a ratios for both 2H- and 4H- led us to satisfy the condition $E_{2H}>E_{4H}$, which infer that the 4H-SiC structure is more stable than 2H- one. The structural stability maximized in 4H-SiC may be because of the maximum attractive interaction between the stacking layers. The analysis of the elastic properties indicates that the 4H- structure is relatively stiffer than 2H-structure. The electronic band structures and DOS of 2H- and 4H-SiC using the *ab initio* DFT are calculated in the first Brillouin zone. The highest

valence band for the two polytypes 2H-, and 4H-SiC are very similar whereas, the lowest conduction band structures differ considerably as mentioned earlier. Our calculated band gaps for both polytypes of SiC agrees considerably well with reported theoretical and experimental values. Our DOS calculations shows that the slope of DOS become steeper for 4H-SiC structure than the 2H- one at the conduction band edge which can be attributed to the strong Si-C covalent coupling of 4H- structure than those of 2H-SiC.

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