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Band structure and bulk modulus calculations of germanium carbide

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Band-structure calculations of germanium carbide (GeC) show that it is a new indirect wide band gap semiconducting material, which crystallizes in both cubic and hexagonal phases. Through the density functional and total-energy technique in the generalized gradient approximation, the two polytypes 3C and 2H of GeC were studied. According to our calculations, it is a hard material with a percentage of covalency of about 80–90%. Important energy gaps were determined. The bulk modulus, density of states, and charge density were calculated. For the bulk modulus calculations, Murnaghan's equation of state was used under elastic deformation to measure hardness. Our calculations showed that this semiconducting material crystallizes in zincblend (E_g = 1.76 eV) and wurtzite (E_g = 2.5 eV) structures.

I. INTRODUCTION

Considerable interest has arisen in wide-bandgap materials as possible candidates for applications as blue/ultraviolet (UV) light emitting diodes and laser diodes. Tetrahedrally coordinated wide-bandgap materials that involve the elements of the first row in the periodic table (such as Be, B, C, and N) have extreme properties compared with the other conventional semiconductors also tetrahedrally bonded. The group-III nitrides (BN, AlN, GaN) and group-IV carbide (SiC) have been extensively studied because they show, in addition to wide bandgap, high thermal conductivity and large bulk moduli, making them promising materials. In the last two decades, there have been developments in most areas concerned with these materials.[1]

To discover new materials with extreme properties has always been a desire for modern material scientists. Recent advances in first-principles methods and the availability of increasingly powerful computational resources make this goal increasingly achievable. Due to the excellent properties of SiC,[2,3] which crystallizes into more than 200 polytypes, the authors observed that germanium carbide, GeC, the other group-IV carbide, might also present peculiar properties for optoelectronic applications due to its wide band gap.[4] In spite of this interest, there is still a lack of theoretical development in this important semiconductor.[5–7]

According to experimental development, germanium carbide (Ge_xC_{1-x}) has been prepared as an amorphous material, which has numerous attractive properties, such as high Young's modulus, low stress, and absorption. The refractive index can be varied with composition in the range of 2–4 and graded with thickness as required. The excellent performance in these areas makes Ge_xC_{1-x} films applicable for design and preparation of multilayer anti-reflection and protection coatings of infrared (IR) windows.[8,9] In addition, Ge_xC_{1-x} films may provide the apparent tunability of the band gap over a very wide range. This important characteristic can be used for photovoltaic applications, and this semiconductor has several other applications[10–12] and has prepared by various deposition techniques.[9–11,13–15]

The calculations presented in this paper were motivated by the research of new materials with relevant technological characteristics. We report the calculation of band structure and bulk modulus under elastic deformation of zincblende (β) and wurtzite (α) polytypes of GeC. For total-energy calculations, we used the CASTEP code, which implements the density functional and total-energy pseudopotential techniques in the generalized gradient approximation (GGA).[16–20]

II. COMPUTATIONAL METHOD

We used the density functional and total-energy pseudopotential technique under the generalized gradient approximation, which is the corrected gradient version of

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local-density approximation (LDA). Forces acting on the atoms and stress on the unit cell have been calculated from which the equilibrium structure is obtained. We used the non-local pseudopotential optimization scheme of Lin et al. within the Kleinman–Bylander scheme,[21] in which only one ground state for each component of the angular momentum of the wave function is used.

The electronic wave functions were expanded in 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 cutoff was set at 850.0 eV for 3C–GeC and 670.0 eV for 2H–GeC. The minimization of total energy was 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 calculation scheme,[22] which reduces the set of k points in the Brillouin zone, was used to calculate the electronic energies with geometry optimization. The Fourier transform grid was 24 × 24 × 24 for 3C–GeC and 24 × 24 × 36 for 2H–GeC. Finally, the directional calculational scheme was used for the band-structure calculations by using the high symmetry points in the Brillouin zones of each polytype.

III. RESULTS AND DISCUSSION

We peformed band-structure calculations of the two extreme polytypes: zincblende (pure cubic stacking) and wurzite (pure hexagonal stacking). Lattice constants, cell volume, total energy, and inter-atomic distance between nearest neighbors were calculated after optimization for both polytypes of GeC. Each primitive cell of zincblende-type structure (space group $F43m$ or 216) had two atoms, one cation (Ge) and one anion (C) with lattice parameter a = 4.523 Å with a total of 38 electrons per cell. The primitive cell of wurzite type structure (space group $P6_3mc$ or 186) had four atoms, two cations (Ge), and two anions (C), with lattice parameters a = 3.091 Å and c = 5.059 Å, with a total of 76 electrons per cell.

The ground-state properties of both structures of GeC were obtained by minimization of the total energy with respect to the unit-cell volume. A uniform compression and expansion of the lattice, with the relative positions within the unit cell held constant, was used to create isotropical variation of the cell volume. The variation of total energy as a function of the unit cell volume was calculated for both polytypes of GeC. The E(V) curve was fitted by Murnaghan's equation of state to obtain the lattice parameters of the equilibrium structure and to evaluate the bulk modulus.

The band structure and density of states calculated for zincblende 3C–GeC are shown in Figs. 1(a) and 1(b) where Γ, X, K, and L are the high symmetry points. The

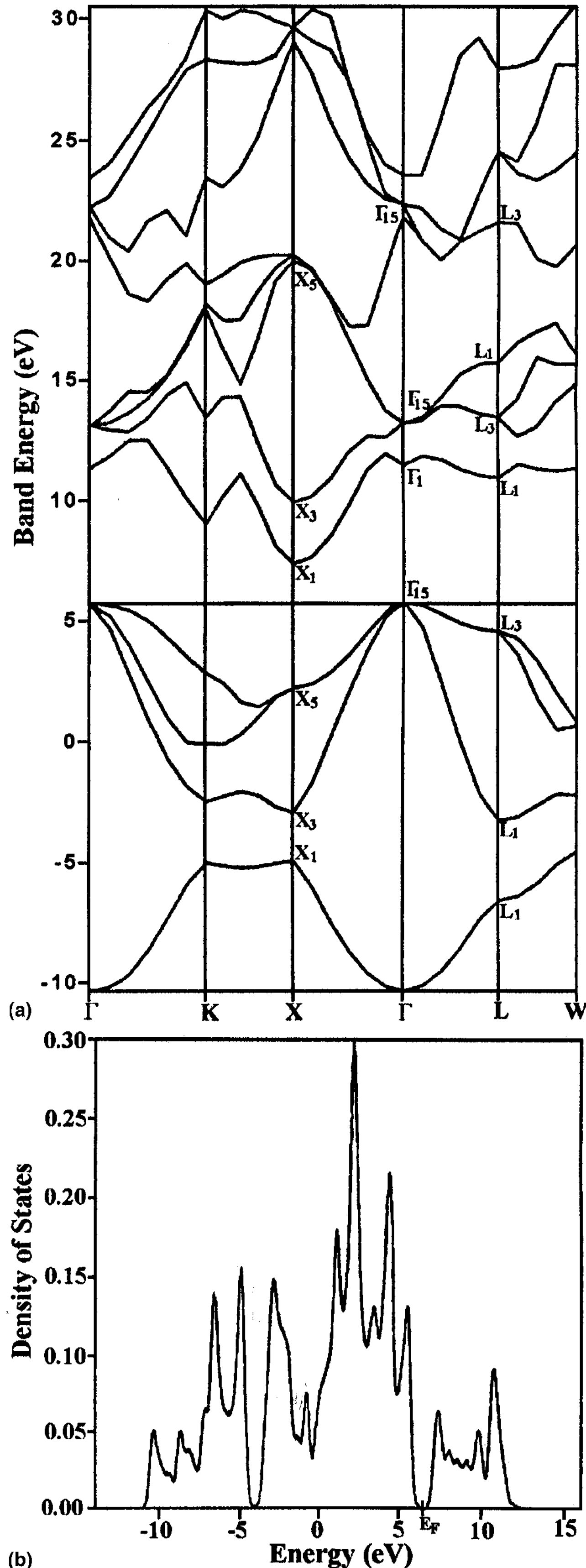

FIG. 1. (a) Band structure and (b) density of states of 3C–GeC.

TABLE I. The theoretically determined values of lattice constant a, fundamental gap E, bulk modulus B and total energy E_0 of both polytypes of GeC in the present study and a comparison with the work of Sankey et al.

	Lattice parameters (Å)		Fundamental gap E		Bulk modulus B (GPa)			E_0 (eV)	
Polytype	Present	Sankey et al.[5]	Present	Sankey et al.[5]	Present (Murnaghan's equation)	Present (Cohen's equation)	Sankey et al.[5]	Present	Sankey et al.[5]
β-GeC	a = 4.523	4.49	1.76	1.42	176.94	182.94	218	−132.651	−131.54
α–GeC	a = 3.091	…	2.5	…	179.21	211.57	…	−132.452	…
	c = 5.059								
β-SiC	a = 4.292	a = 4.28	1.80	1.22	222.47	222.07	245	−132.425	−131.65
α–SiC	a = 3.052	…	2.80	…	237.53	216.54	…	−132.388	…
	c = 4.988								

minimum of the conduction band occurs at X_{1c} state, which is a mixture of s- and p-like components, while top of the valence band is at Γ_{15v} state, which is purely p-like in zincblende structure. Our calculations show that 3C–GeC is an indirect bandgap semiconductor with fundamental gap, Γ_{15v}–X_{1c} = 1.76 eV, which is consistent with the previous work of Sankey et. al.,[5] who applied the LDA in DFT and observed an indirect band gap in this material. For comparison, we also performed band-structure calculations of zincblende and wurzite polytypes of SiC. Table I presents the calculated values of the lattice parameter, fundamental gap, bulk modulus, and total energy of both polytypes of GeC and SiC and a comparison with the calculations of Sankey et al., while Table II presents the important energy gaps like Γ_{1c}–Γ_{15c}, Γ_{15v}–Γ_{15c}, X_{5v}–X_{1c}, etc. The total density of states calculations show that the valence band was separated into two regions by a 1.33 eV band gap; the upper bandwidth was 9.07 eV while the lower bandwidth was 5.75 eV.

Figures 2(a) and 2(b) show the band structure and density of states for 2H–GeC. The high symmetry points in the wurtzite case are A, L, M, H, K, and Γ. The minimum of the conduction band is at K_{2c} state, which is purely p-like, while the top of the valence band is at Γ_{6v} state, which is purely s-like in the wurtzite case. It was observed that 2H–GeC is also an indirect bandgap semiconductor, and the fundamental gap occurs at Γ_{6v}–K_{2c} = 2.5 eV. Other important energy gaps were also calculated, as shown in Table III. The valence band was separated in two regions by a 1.09 eV band gap; the upper bandwidth was 9.2 eV while the lower bandwidth was 5.78 eV.

Figure 3 shows the total charge density of zincblend structure of GeC, a IV-IV compound, in the (100) plane containing all the Ge and C atoms in the primitive cell, which presents a clear asymmetry between Ge and C. It shows that C atoms have more charge concentration than the Ge atoms have. The charge density of GeC shows that bonding has a significant ionic nature because of the large energy difference between the Ge (4s, 4p) and C (2s, 2p) valence levels. The 2s and 2p have about equal

TABLE II. Important energy gaps for 3C–GeC.

Transition	Calculated energy gaps (eV)
Γ_{15v}–X_{1c}	1.76
Γ_{1c}–Γ_{15c}	1.75
Γ_{15v}–Γ_{15c}	7.65
Γ_{15v}–L_{1c}	5.0
X_{5v}–X_{1c}	5.09
L_{3v}–L_{1c}	6.42
X_{1c}–X_{3c}	2.57

spatial extent as opposed to latter rows where the p-like valence orbitals tend to be more diffuse than the s-like orbitals. Since C do not have p-like core states below the 2p valence level, it has rather deep valence lavel. This is the reason that GeC has small lattice constant, high cohesive energy, and large elastic constant for both polytypes.

The band structure of the two polytypes can be compared along various symmetry directions. If the two zones are 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 wurtzite; 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 onto hexagonal point Γ. This mapping is indeed reflected in the two band structures.

The 2HGeC direct gap of 4.5 eV, identified with the Γ_6^v–Γ_1^c transition, compares very nicely to the value of 5.0 eV for the corresponding cubic Γ_{15}^v–L_1^c transition. The crystal-field splitting near the valence band edge (Γ_6^v–Γ_1^v) is about 0.3 eV. The differences between the wurtzite energy levels at Γ and those of the corresponding zincblendestates 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 zincblende and wurtzite. For example the cubic point K is mapped on two regions at the

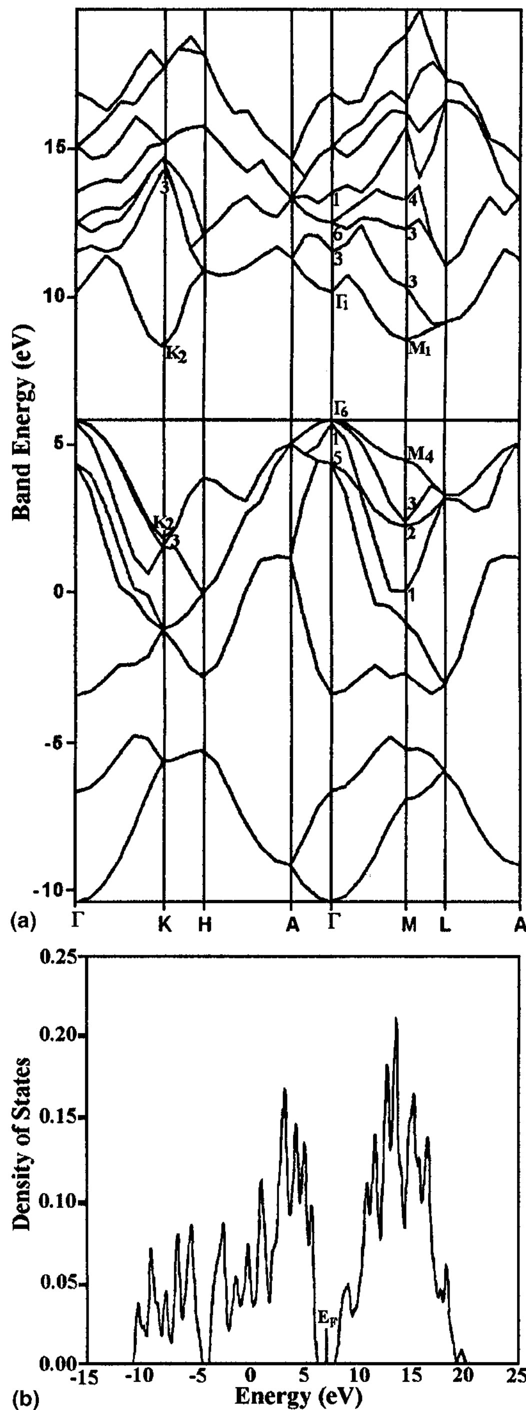

FIG. 2. (a) Band structure and (b) density of states of 3H–GeC.

TABLE III. Important energy gaps of 2H–GeC.

Transition	Calculated energy gaps (eV)
Γ_{6v}–K_{2c}	2.5
Γ_{1v}–K_{2c}	2.59
Γ_{6v}–M_{1c}	2.65
Γ_{1v}–M_{1c}	2.75
Γ_{6v}–L_{1c}	3.25
Γ_{1v}–L_{1c}	3.34
Γ_{6v}–Γ_{1c}	4.5
Γ_{1v}–L_{1c}	4.7

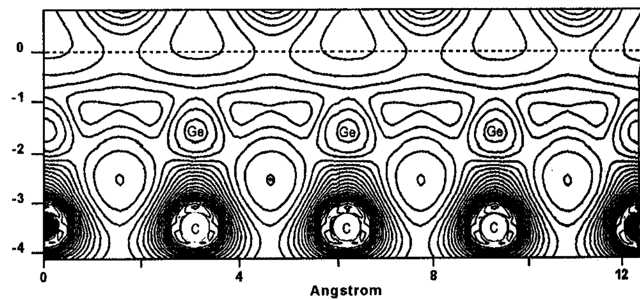

FIG. 3. Charge density of zincblend structure of GeC in (100) plane.

wurtzite zone-a region around M, extending along the Σ direction to Γ, and a region between the wurtzite points M and K and extending upward along Z. Such mapping 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. 4, taken from the work of Bergstresser et al.[23]

For the calculation of bulk modulus of zincblende and wurtzite polytypes of GeC, total-energy calculations have been performed under hydrostatic pressure to obtain energy against volume curves for both polytypes of GeC separately. The lattice parameters, cell volume υ_0 and total energy were calculated at each pressure, 5.0, 2.0, 0.0, −2.0, and −5.0 GPa. From Murnaghan's equation of state,[24] the values of the lattice parameters of the equilibrium structure, the minimum energy, and the bulk modulus were obtained. The bulk modulus of 3C–GeC is 176.94 GPa while that of 2H–GeC is 179.21GPa.

It was observed that the density-functional theory under GGA approximation underestimates the fundamental gap, especially in which the cation is a heavy element because DFT is based on one-electron approximation.[4] It is, therefore, expected that the fundamental gap and the lattice parameters of GeC are underestimated by applying GGA, which is consistent with the work of Leung et al.[25] and Filippi et al.[26] However, the bulk modulus calculated by applying Murnaghan's equation of state is in good agreement with the work of Pandey et al.[6] and Benzair et al.[7] for 3C–GeC, which is also consistent with the observation of Leung et al.[25] and Filippi et al.[26] about the generalized gradient approximation. It is observed that GeC can also be crystallized in the wurtzite structure, which is also an indirect wide bandgap semiconductor with high bulk modulus and small interatomic distance.

For the case of 2H–GeC, no work has been reported to our knowledge; however, it can be compared with SiC, which is of the same family of the periodic table, i.e.,

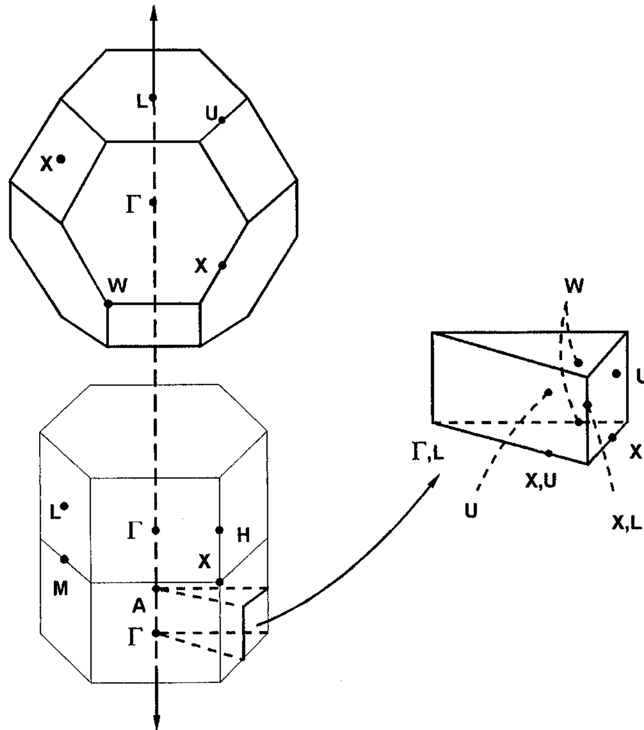

FIG. 4. Comparison of zincblende and wurtzite polytypes of GeC.

group IV-IV compound. SiC and GeC have several common properties. Both are indirect bandgap semiconductors, and the minimum of the conduction band and maximum of the valence band occur at the same symmetry points. It was observed that the fundamental gaps in both polytypes of GeC are smaller than those of SiC. It is also expected that GeC can crystallize into various structures or polytypes like SiC, which can be used for several electronic and optoelectronic applications; therefore it can be said that GeC is a new material in the semiconductor technology with has properties very similar to SiC.

The bulk modulus, which measures hardness, was calculated for both polytypes of GeC from Murnaghan's equation of state under elastic deformation. It was also observed that like SiC, GeC is also on the list of hard semiconducting materials due to its small lattice constant and large elastic constant; however, the bulk modulus of GeC is less than that of SiC. This is because the covalent character of the bond of SiC is a little bit higher than that of GeC as proposed by Cohen,[27] who developed a semi-empirical model for the bulk modulus of covalent solids for characterizing the covalent and ionic nature of tetrahedral solids by means of the spectral properties. According to this model, the bulk modulus can be related to the ionicity and bond length of a solid:

$$B = \frac{19.71 - 2.20\lambda}{d^{3.5}} \quad ,$$

B is the bulk modulus, d is the interatomic distance, and λ is a measure of ionicity of a compound, which is 0 for group-IV compounds. By using this model, the bulk modulus for 3C–GeC is 182.94 GPa while for 2H–GeC, it is 211.57 GPa.

It has been proposed that the shear modulus (the resistance to reversible deformation upon shear) measures the hardness more correctly for the actual deformation process, but our results show that the bulk modulus is also a good prediction of hardness.

IV. CONCLUSION

It was observed that GeC is an indirect wide band gap semiconductor in both polytypes, but the fundamental gap is lower than that of SiC. Another important parameter, bulk modulius B, which measures hardness, was calculated for both polytypes of GeC by fitting Murnaghan's equation of state and using the nearest neighbor distance d. Both results were compared with each other and with SiC. GeC has properties very similar to SiC, and it can be an important candidate in electronic and optoelectronic applications. It has a wide bandgap, high bulk modulus, and small lattice parameter, and its percentage of covalency is comparable to SiC.

A plot of charge density showed the clear asymmetry between Ge and C, which shows that GeC is significantly ionic in nature due to the reason that its orbital are rather compact. It was also observed that the covalent component of the bonding in GeC is stronger, which leads to the conclusion that it has a large elastic constant.

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