CONDENSED MATTER PHYSICS

Theoretical study of the band structure of 2H-SiC and 4H-SiC of silicon carbide polytypes

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We have studied the electronic band properties of 2H-SiC and 4H-SiC silicon carbide polytypes. The structures of the electronic bands and density of state (DOS) using ab initio Density Functional Theory (DFT) were calculated for the first Brillouin zone both in the generalized gradient approximation and taking into account quasiparticle effects according to the GW scheme. The calculated bandgaps obtained using the GW approximation $E_{g\,2H-SiC} = 3.17$ eV and $E_{g\,4H-SiC} = 3.26$ eV agree well with experimental values. The shape and values of total DOS are within agreement with calculations performed by other authors. The calculated total energy values for 2H-SiC and 4H-SiC were close, but they satisfy the condition $E_{2H} > E_{4H}$, which implies that the 4H-SiC structure is more stable than 2H-SiC. Our calculations of the band structure and DOS of 2H-SiC and 4H-SiC by the DFT method showed that the application of the GW approximation is an optimum approach to the study of the electronic structure of 2H-SiC and 4H-SiC polytypes.

Key words: silicon carbide, 2H-SiC and 4H-SiC polytypes, density functional theory, electronic structures

1. Introduction

Silicon carbide (SiC) is one of the most promising materials for high-temperature, radiation-resistant, power and high-speed electronics, as it has unique physical and electronic properties. These properties include: a wide band gap (approximately three times larger than that of silicon), a high critical avalanche breakdown field (approximately 10 times greater than that of silicon), and a high electron drift saturation rate (2.5 times greater than in silicon and gallium arsenide), high thermal stability, chemical inertness, excellent mechanical properties, etc. [1–4]. Silicon carbide exists in many polytype modifications (more than 250 have been established [5]), which are derivatives of hexagonal and rhombohedral close-packed crystal lattices [6]. All silicon carbide polytypes crystallize according to the laws of close ball packing and are binary structures built of identical layers, differing both in the order of arrangement of the cubic or hexagonal layer, and in the number of these layers in the unit cell. Despite the fact that studies of the structural and electronic properties of SiC polytypes have been carried out for more than 100 years, there is still no unified approach to describing the dependence of polytype properties on their degree of hexagonality [6], and there is a scatter of theoretical and experimental data on the main values of the electronic parameters of polytypes [7–14]. The most widespread and, accordingly, the most studied are 4H-SiC, 6H-SiC, 3C-SiC, 15R-SiC polytypes. This is due to the technological capabilities of obtaining single crystals of these polytypes. Obtaining other SiC polytypes, for example, such as 2H-SiC, is difficult, due to the difficulty of providing stable conditions that prevent the growth of energetically more favorable polytypes (for example, 3C-SiC, 4H-SiC, 6H-SiC). In this regard, in the literature there are very little data from experimental studies of this SiC polytype. In addition, there are quite large differences in the results of theoretical studies. At the same time, the properties of 2H-SiC are of great interest, due to its largest band gap among SiC polytypes [3]. It is advisable to carry out the theoretical analysis of the electronic properties of 2H-SiC in comparison with other polytypes with established experimental data. The most convenient is a tandem with the well experimentally measured 4H-SiC polytype, the unit cell of which is two times longer than in 2H-SiC [5].

In this work, we presented the results of first-principles calculations based on the DFT band electronic properties of 2H-SiC and 4H-SiC in comparison with the results of the studies obtained by other authors.

2. Computational methods

The calculation of the energy band structure of electrons from the first principles in this work was carried out in the framework of the density functional theory (DFT) using the software package *exciting* [15]. As the electron wave functions, this package utilizes the approximation of linearized augmented plane waves (LAPW) and localized orbitals (LO) as basis functions. The exchange-correlation component of the potential was chosen in the form of asymptotically corrected generalized gradient approximation (acGGA) using the Burke functional [16]. The acGGA functional is chosen for its accurateness in minimizing atomic and energy errors for large-Z atoms and it is pure first-principle (not relying on empirical data). The first circumstance is key in the procedure used for optimization of atomic positions. Since within the framework of LDA (local density approximation) and GGA-DFT, it is not possible to obtain accurate values of the band gap for semiconductor and dielectric materials [17]. We calculated the band structure taking account of quasiparticle (QP) effects using the GW approximation of the electron self-energy that takes quasiparticle effects into account [18]. We used the single-shot GW (also known as G_0W_0) approximation. To obtain the starting position for GW calculations, the band structure was first calculated according to the GGA-DFT scheme. The self-consistent calculations GGA-DFT were performed until the convergence condition was reached: the absolute change in the total energy and effective potential is less than 10^{-6} eV per cell. The lattice was relaxed using the method of Broyden-Fletcher-Goldfarb-Shanno [19], while the unit cell dimensions remained constant, and only atomic positions varied.

3. Results and discussion

The results of the band structure calculations of 2H-SiC and 4H-SiC crystal structures using the GGA-DFT functional and subsequently using the correction based on GW approximation of self-energy are presented in figure 1. The corresponding energies of the band structure at the points of high symmetry near the band gap are given in table 1.

The electron energy bands for 2H-SiC and 4H-SiC in the energy range from -15 to $+8$ eV along the directions of high symmetry in the first Brillouin zone are shown in figure 1 (a) and (b), respectively. The energy in the diagrams is relative to the Fermi energy level. The occupied states of the 4H-SiC valence band calculated by us, figure 1 (b) are close to the previously published results of ab initio LAPW-LDA [11], LCAO (linear combination of atomic orbitals)-LDA [12] and PW (plane wave)-GGA [24] calculations. The minimum of the conduction band is at point K of Brillouin zone for 2H-SiC, which is similar to the theoretical result [7, 24]. For 4H-SiC in our calculations, the minimum of the conduction band is at the point M. At point M the second minimum of the conduction band is observed, which is only 0.13 eV and 0.16 eV higher than the lowest unoccupied state in the GGA and GW approximations, respectively. These results are consistent with the ballistic electron emission microscopy study [14], in which the second minimum was observed at about 0.15 eV, as well as with other ab initio calculations, in which it is at 0.12 eV [11] and 0.18 eV [12]. In our quasiparticle band structure calculations, the split-off band and the bands of light and heavy holes overlap at the point Γ. There is no overlap on the GGA band structures. This overlap maximizes at the point Γ and reaches 0.17 eV and 0.36 eV for 2H-SiC and 4H-SiC, respectively. The calculated indirect band gap with QP correction using GW scheme according to our data is 3.17 eV for 2H-SiC (see table 1), which is in good agreement with the experimental data of 3.3 eV [3]. This value differs from the theoretical results of the 2H-SiC calculations performed by other authors: 3.68 eV (QP-GW calculation) [20], 3.75 eV (self-consistent QP-GW) [23], 3.01 eV [24] and is very close in other QP-GW calculations 3.15 eV [22], 3.12 eV [23]. Indirect band gap in our calculated electron band structure of 4H-SiC is 3.26 eV, which is comparable with the theoretical data of 3.56 eV (QP-GW calculations) [20], close to 3.35 eV (QP-GW calculations) [22] and differs from the DFT-GGA calculations in [24], which reported 2.45 eV. The experimental value of the band gap in 4H-SiC is
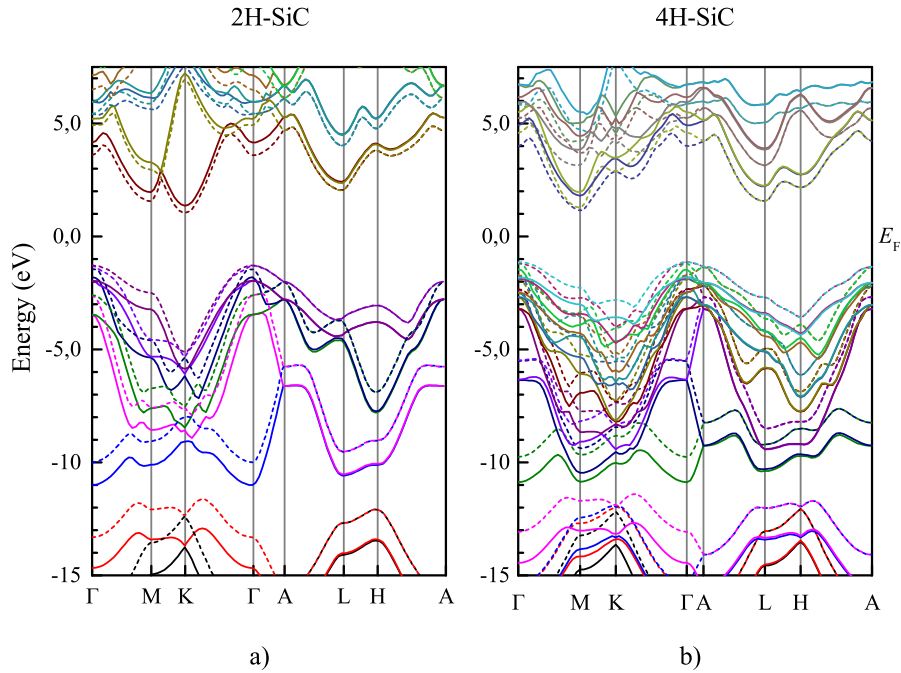
Figure 1. (Colour online) Band structure diagrams for 2H-SiC (a) and 4H-SiC (b) obtained using GGA-DFT (dashed lines) and taking into account the quasiparticle effects of GW-DFT (solid lines).

3.29 eV [3]. A significant difference between our values of the band gap from the values obtained in the LDA and GGA approximations is due to the known limitations of this approach. Obviously, the use of quasiparticle correction of the self-energy of the electron allows us to obtain the values of the band gap that are in good agreement with the values measured experimentally.
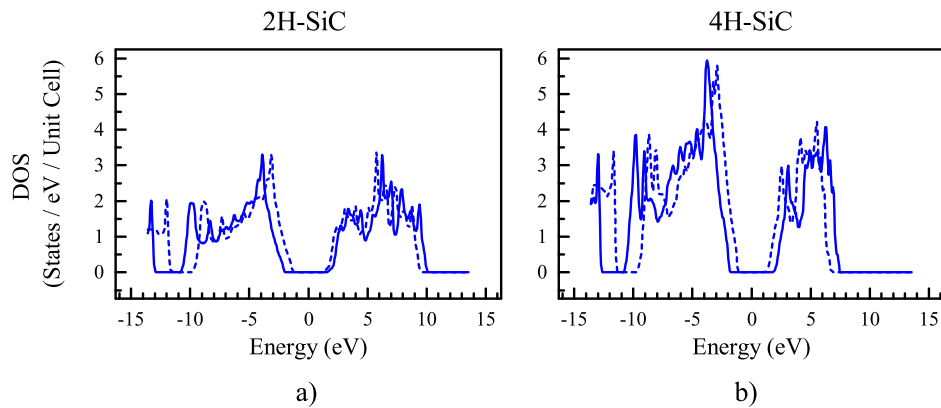

Figure 2. (Colour online) The total density of states for 2H-SiC (a) and 4H-SiC (b) obtained using GGA-DFT (dashed lines) and taking into account the quasiparticle effects using GW-DFT (solid lines).

The calculated total density of states of 2H-SiC and 4H-SiC is shown in figure 2 (a) and (b), respectively. The shape of the DOS located below -10 eV has similar form for both of the considered polytypes, while those states that are near the edge of the conduction band are significantly different (figure 2). The slope of the DOS at the edge of the conduction band becomes steeper for the 4H-SiC structure. The difference between the DOS form according to the results of GGA and GW calculations is insignificant: only a relative shift of the bands along the energy axis is observed. The value of DOS in the entire energy range for 4H-SiC is on average higher than that in 2H-SiC, which agrees with the recent DFT-GGA calculations [24].

Table 1. The energy values of the band structure (eV) at the points of high symmetry of the Brillouin zone, as well as the band gap values in the GGA-DFT approximation and in the GW approximation. The band gap values obtained from the results of theoretical and experimental studies of other authors are also presented.

Band state	2H-SiC		4H-SiC	
	GGA	GW	GGA	GW
Γ_{6v}	0	−0.17	0	−0.36
Γ_{1v}	−0.15	0	−0.06	0
Γ_{1c}	4.89	5.96	5.36	6.59
M_{4v}	−1.19	−1.42	−1.10	−1.54
M_{1c}	2.87	3.76	2.30	3.26
K_{2v}	−3.81	−4.04	−1.66	−2.11
K_{2c}	2.33	3.17	4.03	4.91
H_{3v}	−1.77	−1.98	−2.44	−2.84
H_{3c}	5.08	5.86	3.32	4.19
$A_{5,6v}$	−0.70	−0.96	−0.19	−0.59
$A_{1,3c}$	5.98	7.08	5.36	6.59
$L_{1,2,3,4v}$	−2.39	−2.68	−1.54	−1.92
E_g (direct)	4.06 (M)	5.18 (M)	3.40 (M)	4.80 (M)
E_g (indirect)	2.33 (Γ-K)	3.17 (Γ-K)	2.30 (Γ-M)	3.26 (Γ-M)
E_g (GW [20])	3.68		3.56	
E_g (PBE-GGA [21])	3.01		2.45	
E_g (GW [22])	3.15		3.35	
E_g (GW [23])	3.12			
E_g (QPscGW [23])	3.75			
E_g (exp. [3])	3.3		3.29	

4. Conclusion

The total energy of the 2H-SiC and 4H-SiC polytypes per atom was calculated for relaxed crystal lattices optimized during the self-consistent calculations (table 2). The calculated values of the total energy of both structures are very close to each other. However, the total energy ratio satisfies the condition $E_{2H} > E_{4H}$, which means that the 4H-SiC structure is more stable than 2H-SiC, which is consistent with the known theoretical and experimental data [1–3]. For comparison, the table shows the total energy for the 2H-SiC and 4H-SiC structures from [21, 24].

Table 2. The calculated total energy values per atom (eV) of 2H-SiC and 4H-SiC structures as well as results from other studies.

	2H-SiC	4H-SiC
E_{tot} (present)	−7.388	−7.392
E_{tot} [21]	−9.659	−9.660
E_{tot} [24]	−7.396	

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fects according to the GW scheme. The calculated bandgaps obtained using the GW approximation, $E_{g\,2H-SiC} = 3.17$ eV, $E_{g\,4H-SiC} = 3.26$ eV agree well with the known theoretical and experimental values. The shape and values of total DOS are within agreement with calculations performed by other authors. The calculated total energy values for 2H-SiC and 4H-SiC are close, but they satisfy the condition $E_{2H} > E_{4H}$, which implies that the 4H-SiC structure is more stable than 2H-SiC. Our calculations of the band structure and DOS of 2H-SiC and 4H-SiC by the DFT method showed that the application of the GW approximation is an optimum approach for studying the electronic structure of 2H-SiC and 4H-SiC polytypes.

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Теоретичне дослідження зонної структури 2H-SiC та 4H-SiC політипів карбіду кремнія

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Ми провели дослідження властивостей електроних зон 2H-SiC and 4H-SiC політипів карбіду кремнія. Були проведені ab initio розрахунки зонної структури та щільності станів для першої зони Брилюена з використанням теорії функціоналу щільності, як у рамках апроксимації узагальненого градієнту, так із врахуванням квазічастинкових ефектів по схемі GW. Розраховані ширини забороненої зони з використанням GW апроксимації $E_{g2H-SiC} = 3.17$ eB та $E_{g4H-SiC} = 3.26$ eB добре узгоджуються з експериментальними значеннями. Форма та значення повної щільності станів узгоджуються з обчисленнями інших авторів. Розраховані значення повної енергії 2H-SiC та 4H-SiC є близькими, але вони задовільняють умові $E_{2H} > E_{4H}$, що означає, що структура 4H-SiC більш стабільна ніж 2H-SiC. Наші обчислення зонної структури та щільності станів 2H-SiC та 4H-SiC методом теорії функціоналу щільності показало що застосування апроксимації GW є оптимальним для вивчення електронної структури політипів 2H-SiC та 4H-SiC.

Ключові слова: *карбід кремнія, політипи 2H-SiC та 4H-SiC, теорія функціоналу щільності, електронна структура*