Electronic structures and stability of double-walled armchair (n,n)@(m,m) SiC nanotubes

Tayebeh Movlarooy (web2_tayebeh.movlarooy@shahroodut.ac.ir)
Shahrood University of Technology https://orcid.org/0000-0001-7896-4772
Mehdi Motaharinejad
Shahrood University of Technology
Saeid HessamiPilehrood
Shahrood University of Technology

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Abstract

In this work, we have investigated the stability and electronic properties of armchair double-walled SiC nanotubes (DWSiCNTs) based on density functional theory (DFT) with the SIESTA package. The calculation has been performed on the armchair (4,4)@(n,n) and (5,5)@(n,n) DWSiCNTs with (n = 7 to15). The stability calculation of DWSiCNTs shows that the armchair DWSiCNTs with difference chirality of 4, (n,n)@(n + 4,n + 4) and inter-wall distance of 3.65 Å are the most stable structures. Considering the electronic band structure points that all armchair nanotubes are semiconductors with indirect bandgap. Moreover, it is revealed that the value of the bandgap increases by increasing inter-wall distances, and the process of change at higher inter-wall distances be almost constant. In addition, the bandgap of double-walled SiC nanotubes is smaller than that of their single-walled nanotubes. The consequences of this investigation can certainly be helpful in future experimental studies.

Introduction

Nanotubes are one of the most important nanostructures currently being studied [1–3]. Today, there is a lot of growth in this type of quasi-one-dimensional structure due to its amazing physical properties and its many applications in the electronics industry. Extensive research has been conducted in this field since the discovery of carbon nanotubes in 1991 [4–10]. Meanwhile, silicon carbide (SiC) due to its interesting chemical and physical properties, has high application potential in the optical and electronics industry, because this material has a wide bandgap, high thermal conductivity, and radiation resistance, for use in work environments with conditions hard to fit [11]. Silicon carbide nanotubes (SiCNTs) have been synthesized from the reaction of SiO-derived silicon with multi-walled carbon nanotubes as mold plates at different temperatures and their structure and stability have been investigated using density functional theory [12]. The results indicate that silicon carbide nanotubes with Si-C replacement bonds are more stable than tubes containing C-C or Si-Si bonds [13]. Depending on the diameter and chirality, carbon nanotubes can be metal or semiconductors [5, 7, 9, 10], while all silicon carbide nanotubes are semiconductors and their energy band gaps depend on their diameters and chiralities so SiC nanotubes have superior advantages over carbon nanotubes. Sun and colleagues first synthesized SiC nanotubes in 2002 and studied their structural properties [12]. SiC nanotubes were then successfully synthesized in research of different groups [14–17]. In 2004, the first computational studies on the structural properties of SiC nanotubes were performed by Menon et al. using the molecular dynamics approach. They investigated zigzag (12,0) and armchair (6,6) single-walled silicon carbide nanotubes [13]. Adhikari et al. examined the SiC nanotubes of the double-walled armchair (n, n) @ (5,5) using the density functional theory (DFT) by the GAUSSIAN computational code [18]. They showed that the binding energy of each atom of the studied double-walled structures depends not only on the number of atoms, but also on the conjugation of single-walled nanotubes, and the formation energy will be minimized when the distance between the walls is about 3.5 angstroms. Which corresponds to nanotubes (9,9) @ (5,5). In 2009, Moradian et al. examined the nanotubes of (11,11) @ (n, n) (n = 8 − 5) [19]. The results of their research

showed that the inner tube (6,6) is the most ideal nanotube for the outer nanotube (11,11) with an in-wall spacing of 4.3 angstroms.

Despite the fact that many theoretical and experimental studies have been done on the structural properties of single-walled silicon carbide nanotubes, but on the structural properties and stability of double-walled silicon carbide nanotubes, few studies have been done. Therefore, in this study, the structural, electronic, and stability properties of armchair double-walled silicon carbide nanotubes have been studied in the framework of density functional theory, considering van der Waals forces.

Computational Details

In this work, the electronic and stability properties of DWSiCNTs have been studied by density functional theory (DFT), as performed in the SIESTA 4.1-b4 open source code [20]. For the exchange-correlation functional, we have used the vdw-DF2 functional [21]. In this research, the double-zeta polarization (DZP) basis set has been chosen, and the valence electron wave function is plane-wave basis set with the cutoff energy of 500 Ry for both armchair and zigzag DWSiCNTs. The Monkhorst-Pack mesh has been used with a gamma-centered k-points grid of 1×1×39 for all structures. The geometric structures have been performed by minimizing the forces on atoms with the criterion that all forces on each atom must be smaller than 0.004 eV/Å. The conjugate-gradient minimization scheme is performed for both electronic structure and geometry optimization calculation.

Result And Discussion

I- The stability properties of armchair DWSiCNTs

The electronic structures and stability of armchair DWSiCNTs have been investigated by using density functional theory. To check the stability of armchair DWSiCNTs, we choose (5, 5) and (4, 4) armchair single-walled SiCNTs as the inner nanotubes. Thus the calculation have been performed on the armchair (4,4)@(n,n) and (5,5)@(n,n) DWSiCNTs with (n = 7 to15). Figure 1 shows the top views of optimized geometries of armchair (5,5)@(n,n) and (4,4)@(n,n) DWSiCNTs. As can be seen in these figures in the lower outer tube diameter, in other words at small interlayer spacing, the DWSiCNTs collapse and lose their tubular shape due to the interlayer interaction between the outer and inner tubes as having occurred for (4,4)@(6,6), (4,4)@(7,7), (5,5)@(7,7) and (5,5)@(8,8) DWSiCNTs. The results show the DWSiCNTs with large outer tube diameters are stable by maintaining the cylindrical shape.

To consider the interaction energy among the outer and inner tubes the formation energies of the (n, n)@(m, m) DWSiCNTs (with n = 4 and 5 and m = 7 to 15) are calculated from their total energies relative to the corresponding isolated single-walled SiC nanotubes using the following equation [22–24]:

$$\mathrm{E_{formation}} = \mathrm{E}\left(\mathrm{n1},\mathrm{n2}\right) + \mathrm{E}\left(\mathrm{n3},\mathrm{n4}\right) - \mathrm{E}\left[\left(\mathrm{n1},\mathrm{n2}\right)@\left(\mathrm{n3},\mathrm{n4}\right)\right]$$

1

Where $\mathrm{E}\left(\mathrm{n1},\mathrm{n2}\right),\mathrm{E}\left(\mathrm{n3},\mathrm{n4}\right)\mathrm{and}\mathrm{E}\left[\left(\mathrm{n1},\mathrm{n2}\right)@\left(\mathrm{n3},\mathrm{n4}\right)\right]$ indicates the total energy of inner tube, outer tube and DWSiCNTs, respectively.

The stability of DWNTs is corroborated by calculating the formation energy originating from their inter-wall interactions.

Moreover, we have calculated the binding energies (Eb) per atom for all armchair DWSiCNTs according to the following equation [22–24]:

$$\mathrm{E_b} = \left(\mathrm{aE}\left(\mathrm{Si}\right) + \mathrm{bE}(\mathrm{C}) - \mathrm{E}(\mathrm{SiC})\right)/\left(\mathrm{b} + \mathrm{a}\right)$$

2

Where E(SiC), E(Si), E(C) represent the total energy of the DWSiCNTs, Silicon, and carbide atoms, and a and b indicate the total number of Si and C atoms in the DWSiCNTs, respectively. The obtained results as the number of atoms, inner and outer tube diameters, inter-wall distances, binding energies per atom, formation energies, and electronic bandgaps for all considered armchair DWSiCNTs, are summarized in Table 1. The DWSiCNTs are stable if their formation energy, which is the inter-wall interaction energy, be a positive value. Thus the DWSiCNTs with the highest positive formation energy are the most stable structure. Therefore, (5, 5)@(9, 9) and (4, 4)@(8, 8) nanotubes have the highest formation energy compared with other armchair-DWNTs. On the other hand, the formation energy of armchair DWSiCNT has a maximum value around the inter-wall distance of about 3.65 Å. Thus, (4,4) and (5,5) are the preferable inner nanotubes for the (8, 8) and (9, 9) outer nanotubes, respectively. The highest value of the formation energy occurs at average values of the inter-wall distance (ΔR) about 3.65 Å for armchair DWSiCNTs. The calculated formation energy and binding energies per-atom for the armchair (4,4)@(n,n) and (5,5)@(n,n) DWSiCNTs predicted the highest value for n = 8 and 9 respectively, which indicates the favorable outer tube wall for the inner (4,4) and (5,5) armchair SiCNTs are (8,8) and (9, 9) tubes respectively. This indicates the armchair DWSiCNTs with difference chirality of 4; (n,n)@(n + 4,n + 4) and average values of inter-wall distance (ΔR) among the outer and inner tubes about 3.65 Å are the most energetically stable structures. Thus, both (4,4)@(8, 8) and (5,5)@(9, 9)DWSiCNTs are energetically favorable DWSiCNTs. The obtained results revealed that the energetic stability of the DWSiCNTs strongly depends on the inter-wall distances among the outer and inner nanotubes. The binding energy in the higher outer tube diameters and interlayer spaces reaches an almost constant value of 5.85 eV. The binding energy of DWSiCNT's at higher inter-wall distances gradually approaches that of the hexagonal SiC nanosheet. While the diameter of the outer tube increases, the interaction between atoms at the edge of the rings is reduced. One can explain that this is the reason that the value of binding energy is almost constant at higher outer tube diameters.

Table 1
The armchair DWSiCNTs, number of atoms (N), inter-wall distance (ΔR), tube diameter (d), the binding energy per atom (Eb), formation energy(E_F), and bandgap (Eg).

Armchair DWSICNTs	N	status	ΔR(Å)	d(Å)	Eb(eV)	E_F(eV)	Eg(eV)
(5,5)@(7,7)	48	collapsed	-	-	-	-	-
(5,5)@(8,8)	52	collapsed	-	-	-	-	-
(5,5)@(9,9)	**56**	**The most stable**	**3.65**	**15.90**	**5.879**	**1.988**	**1.56**
(5,5)@(10,10)	60	stable	4.18	17.18	5.876	1.697	1.84
(5,5)@(11,11)	64	stable	5.08	18.78	5.861	1.507	1.95
(5,5)@(12,12)	68	stable	6.04	20.62	5.857	0.002	2.00
(5,5)@(13,13)	72	unstable	6.89	22.34	5.858	-0.004	2.01
(5,5)@(14,14)	76	unstable	7.76	24.26	5.862	-0.004	2.01
(5,5)@(15,15)	80	unstable	8.61	25.78	5.863	-0.005	2.01
(4,4)@(6,6)	40	collapsed	-		-	-	-
(4,4)@(7,7)	44	collapsed	-		-	-	-
(4,4)@(8,8)	**48**	**The most stable**	3.65	**13.97**	5.863	1.875	1.22
(4,4)@(9,9)	52	stable	4.26	15.75	5.858	1.376	1.55
(4,4)@(10,10)	56	stable	5.07	17.11	5.846	0.538	1.64
(4,4)@(11,11)	60	stable	6.11	18.79	5.843	0.0008	1.68
(4,4)@(12,12)	64	unstable	6.89	20.51	5.848	-0.0013	1.68
(4,4)@(13,13)	68	unstable	7.85	22.21	5.851	-0.0018	1.69
(4,4)@(14,14)	72	unstable	8.71	24.16	5.854	-0.0016	1.69

II- The electronic properties

In this section, the electronic properties of armchair SWSiCNTs and DWSiCNTs have been investigated. We have studied the effect of the nanotubes' diameter on the value of the bandgap. Figure 2. show the electronic band structure of a sample of armchair DWSiCNTs and the band structure of their inner and outer SWSiCNTs. The calculations indicate that all studied SiC nanotubes are semiconductors having indirect band gap. The obtained calculations for electronic properties are in agreement with previous studies [22, 24]. In addition, the bandgap of double-walled SiC nanotubes is smaller than that of their single-walled constituent nanotubes. For example, the bandgap of (4, 4) and (8, 8) SWSiCNTs are 1.66 and 2.16 eV, respectively. While the bandgap of (4, 4) @ (8, 8) DWSiCNT is 1.22 eV. It can be said that the electronic properties of SiC nanotubes can be modified by double-walled. Figure 3 shows the variation of

bandgap as a function of nanotube diameter and inter-wall spacing. It was found that armchair (5, 5) @ (n, n) DWSiCNTs have higher bandgap than (4, 4) @ (n, n) at the same diameters and interlayer distances. In addition, the bandgap of double-walled SiC nanotubes is smaller than that of their single-walled nanotubes Moreover, it is revealed that the value of the bandgap increases by increasing tube diameters and inter-wall distances, and the process of change at higher inter-wall distances would be almost constant. This can be attributed to weaker interaction between the inner and outer tubes at higher interlayer spaces.

Conclusions

In this study, we have investigated the stability and electronic properties of double-walled SiC nanotubes based on density functional theory. The calculation have been performed on the armchair(4,4)@(n,n) and (5,5)@(n,n) DWSiCNTs with (n = 7 to15). By calculating the formation energy of nanotubes, the result revealed that armchair (5,5)@(9, 9) and (4,4)@(8, 8) DWSiCNTs have the highest formation energy. Thus they are the most stable nanotubes among other DWSiCNTs with an inter-wall distance of about 3.65 Å.The investigation of the electronic characteristics of nanotubes indicates all armchair nanotubes are semiconductors having indirect bandgap. Their bandgap increases with increasing tube diameter, also the trend of change at higher diameters is slow. The bandgap of double-wall SiCNTs is less than its constituent single-walled nanotubes. Modulating the bandgap is essential in optoelectronic systems, for instance, diodes and lasers. The consequences of this investigation offer these nanotubes provide a wide range of applications.

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Figures

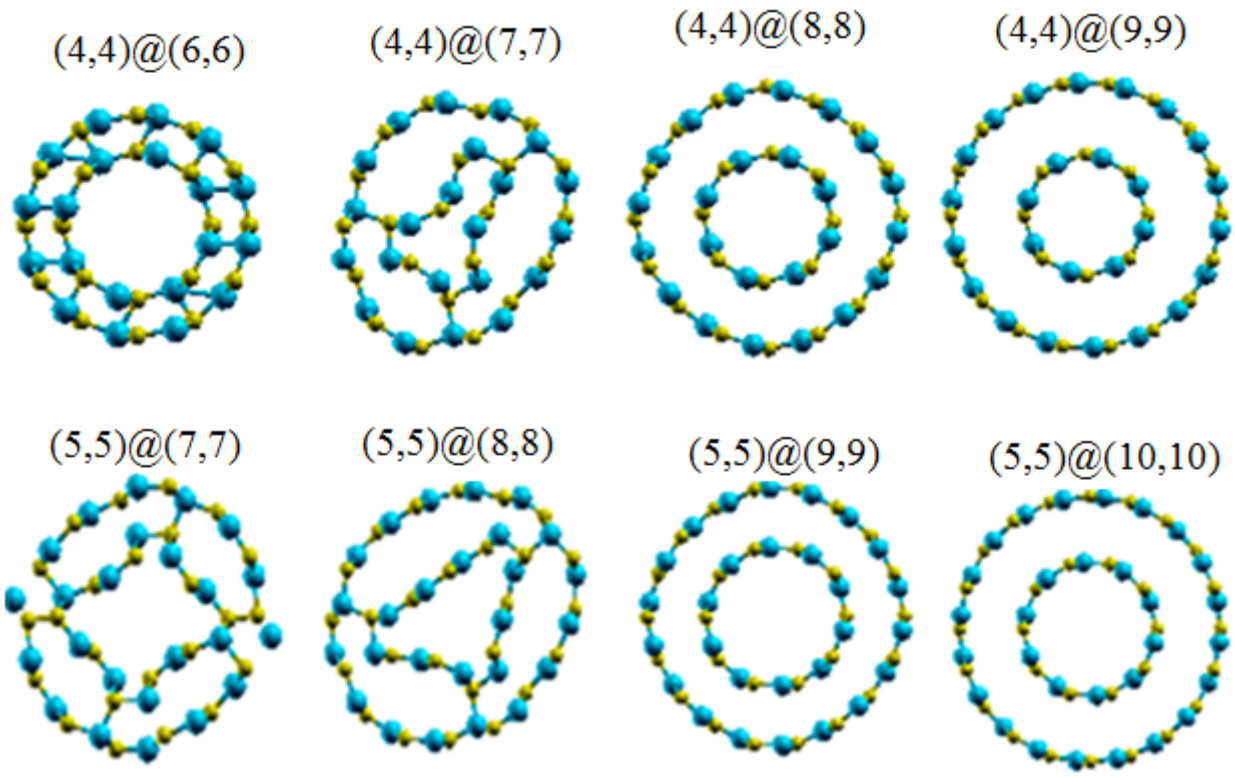

Figure 1

The top view of optimized (4,4)@(n,n) and (5,5)@(n,n) armchair DWSiCNTs. Blue and yellow circles denote the Si and C atoms, respectively.

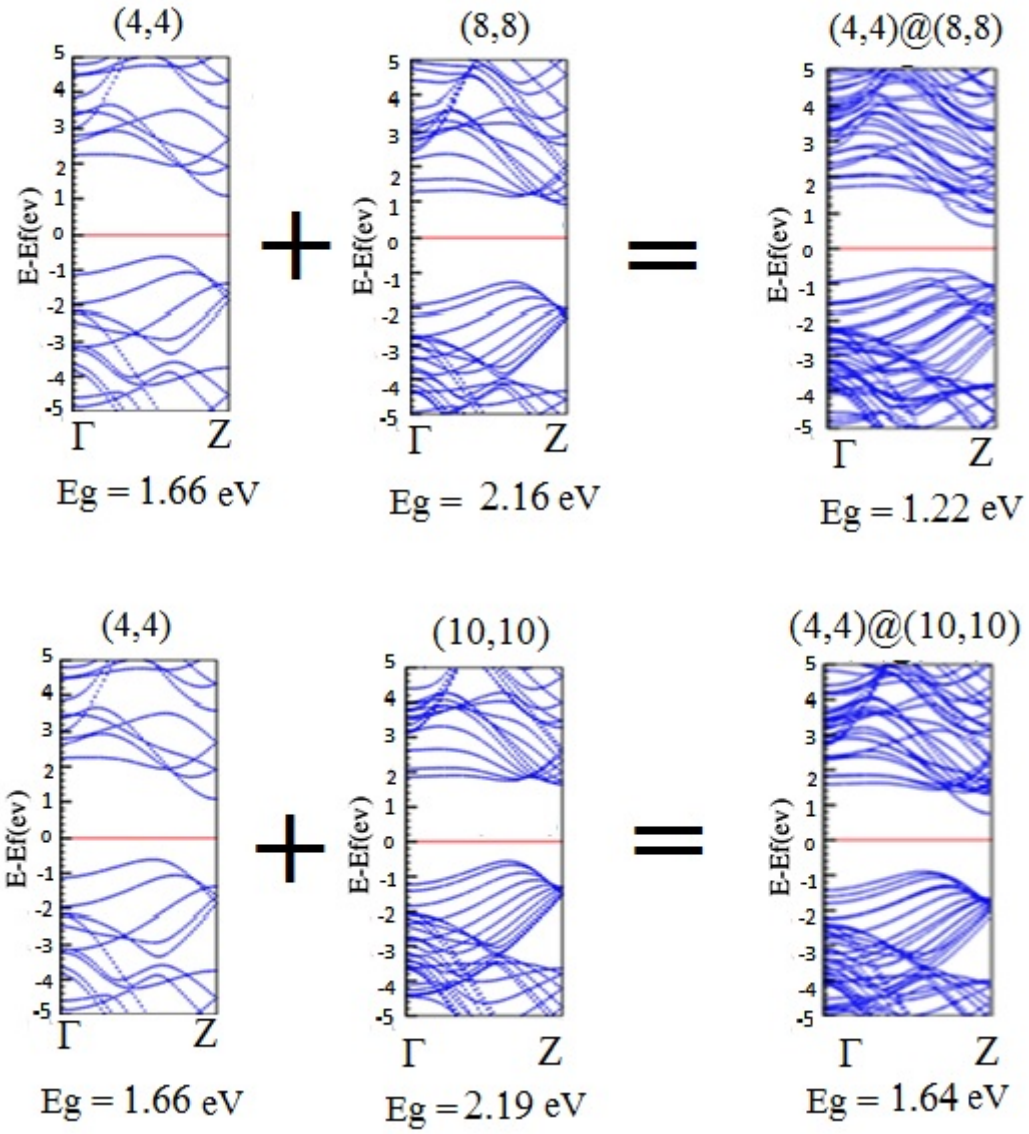

Figure 2

Electronic band structure of armchair– inner, outer, and DWSiCNTs.

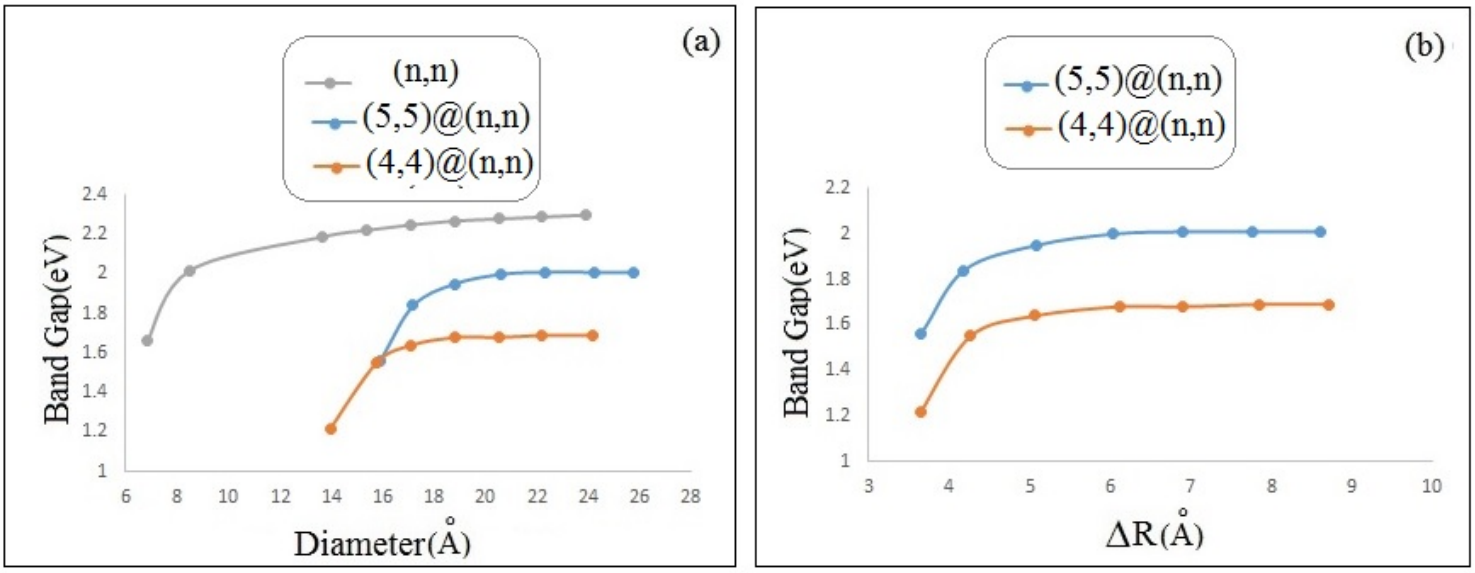

Figure 3

(a) Bandgap of SWSiCNTs and DWSiCNTs in term of outer tube diameter and (b) bandgap of DWSiCNTs in term of inter-wall distance.