

An Ab initio Study on the Convergence of Electronic Properties of SiC Nanotubes

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Abstract

Ab initio calculations of the electronic structures of silicon carbide (SiC) nanotubes represented by clusters are presented. The nanotube clusters of chiralities (3,3) and (5,5) are studied using the hybrid density functional B3LYP (Becke's 3-parameter and the Lee-Yang-Parr exchange-correlation) and LANL2DZ (Los Alamos National Laboratory double ζ) and 3-21G basis sets. Evolution of electronic properties of silicon carbide (SiC) nanotubes (3, 3) and (5,5) with their length is discussed. The results suggest that the electronic properties of nanotubes change for short tubes of unit cells with lengths varying from 1 to 5. However, the properties do not seem to change significantly after this. Therefore, an infinite silicon carbide (SiC) nanotube can be approximated by a nanotube cluster of 5 unit cells.*

Keywords: *silicon carbide, nanotube clusters, hybrid density, unit cells.*

Introduction

Discovery of multi-walled carbon nanotubes (CNT) in 1991[1] has led to an explosive growth of research interest in these kinds of quasi-one-dimensional structures. Carbon nanotubes have very interesting physical and electronic properties which make them very useful in electronics industry [2-8]. The properties of carbon nanotubes are strongly dependent on the diameter and chirality. Depending on their chirality, carbon nanotubes are either metallic or semiconductor which makes them useful for a wide range of applications. The strong dependence of electrical properties on chirality limits the application of carbon nanotubes in many nano-electronics applications because the semiconducting and metallic nanotubes are mixed in the sample of nanotubes grown in the lab. This involves an extra work for manufacturing electronic devices of carbon nanotubes because to obtain carbon nanotubes with similar electronic properties one has to do post synthesis separation of metallic and semiconducting nanotubes or control the synthesis of the nanotubes very precisely [9,10]. The strong need of materials which can be used even in harsh conditions has prompted a search for "better" alternatives to CNT. In search for "better" alternatives to CNT, a significant number of experimental and theoretical research works on nanostructures of other

elements have been performed. A typical example is a nanotube formed by group-III nitrides. Group-III nitride nanotubes, such as BN, AlN, and GaN, have been synthesized through different techniques [11-14]. Synthesis of several other nanotubes has been reported, for example, NiCl₂, H₂Ti₃O₃, TiO₂, and Si [15-18]. Dai *et al.* [19] reported the synthesis of nanostructures by converting carbon nanotubes to carbide rods from reaction with volatile oxide and/or halide species. One of the nanorods produced was SiC, among others such as TiC, NbC, Fe₃C, and BC_x. An interesting candidate here is silicon carbide (SiC) which, in bulk form, is one of the hardest materials and is very suitable for electronic devices designed for operations in extreme environments. Bulk silicon carbide has a wide band gap from 2.2eV for 3C-SiC to 3.0eV for 6H-SiC, and to 3.3eV for 4H-SiC [20]. It has high thermal conductivity up to about 500 W/(mK) at room temperature [21] and thermal expansion coefficient smaller than 6 μ /K [22]. It has very high decomposition temperature of about 2545°C [23]. 3C-SiC has very high Young's modulus 360-600 GPa depending upon its orientations [24].

In addition to the properties due to quantum size effects, silicon carbide nanostructures have some of these unique properties of bulk silicon carbide. Studies, in

fact, have shown that silicon carbide nanostructures have additional unique properties compared to the bulk. [25, 26]. Due to its partially ionic nature, SiCNTs have higher reactivity of the exterior surface than that of carbon nanotubes. This might be helpful to facilitate sidewall decoration.

Motivated by these extraordinary characteristics of bulk silicon carbide as well as silicon carbide nanowires, there has been numerous attempts, both theoretical and experimental, to study the possible graphitic phases of silicon carbide and possible applications in various fields. Most of the experimental attempts of fabricating SiCNTs showed the formation of β -SiC nanorods. Comparing the total energy of graphitic form with that of β -SiC according to calculation based on density functional theory, Miyamoto and Yu [27] have noted that SiC has a large difference between sp^2 and sp^3 bond structures with a value of 1.25eV per Si-C pair. This energy difference makes the realization of graphitic phase of SiC very difficult. However, in the same study, Miyamoto and Yu have demonstrated the possibility of forming SiC nanotubes. They have reported that the strain energies of SiCNTs are lower than those of carbon nanotubes. They proposed the synthesis pathways by using an electronic technique of an extreme hole injection which would cause the graphitic sheet of SiC exfoliate from SiC (111) surface. Different groups have synthesized the SiCNTs using different techniques [28-36]. Sun *et al.* [38] have reported the synthesis of multi-walled SiC nanotubes through a substitutional reaction with Si atoms replacing half of the C atoms from a multi-walled carbon nanotube. The observed SiC nanotubes were multi-walled but with higher inter-planar spacing than those of multi-walled carbon nanotubes. Also the interlayer separation between the layers of nanotubes was found to be greater than 2.5 Å, which is typical for β -SiC. This indicated that the wall morphology of the observed nanotubes might correspond to graphitic phase rather than the cubic phase of the silicon carbide. Electron-energy-loss-spectroscopy (EELS) of the multi-walled SiCNTs has indicated possible π bonding between Si and C atom. The interlayer separations of the multi-walled nanotubes were observed to be 3.5-4.5 Å. This indicated weak coupling between inner and

outer tubes and the possibility of separating them with ease.

Most of the theoretical studies on SiCNTs are based on the graphene-like structure of silicon carbide. Although SiC graphitic monolayers have not yet been observed experimentally, some theoretical studies have predicted their possibilities. Also, the experimental observation by Sun *et al.* [36] has provided some evidences of graphitic phase of silicon carbide. The major driving force behind all the studies on SiCNTs is mainly their potential applications. Some *ab initio* methods [44] have shown that the most stable SiC nanotube has the ratio of Si to C of 1 to 1. These studies claim that the nanotubes with other ratios will eventually collapse the tube into nanowires or clusters with solid interiors. Some other theoretical studies [38-41] have suggested that the stable silicon carbide nanotubes are of three types- types 1, 2 and 3, depending upon the atomic arrangement in the nanotube. Type 1 consists of alternating Si and C atoms with each Si atoms having three C neighbors and vice versa. In type 2 configuration, each Si atom has two C neighbors and one Si neighbor and vice versa. In type 3, each Si has two C and one Si neighbors but Si and C atoms are arranged alternatively in each layer. In this work, we have considered the armchair SiC nanotubes in type 1 configuration. The evolution of the electronic properties of the SiC nanotubes with increase in length is presented.

Construction of nanotube

Similar to carbon nanotube, a SiCNT can be considered as a roll of silicon carbide graphene-like sheet. This rolling up can be described in terms of the chiral vector \vec{C}_h , which connects two sites of the two-dimensional graphene-like sheet that are crystallographically equivalent. This chiral vector maps an atom from the left hand border onto an atom on the right border line and is an integer multiple of the two basis vectors \vec{a}_1 and \vec{a}_2 , i.e., $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$. So the geometry of any nanotube can be described by the integer pair (n, m) which determines the chiral vector. An armchair nanotube corresponds to the case of $n=m$, and a zigzag nanotube corresponds to the case of $m=0$. All other (n, m) chiral vectors correspond to chiral nanotubes.

A nanotube is constructed by rolling a graphene sheet bounded by chiral vector \vec{C}_h and translation vector \vec{T} as shown in Figure 1. As an example, the figure has a shaded region bounded by chiral vector $\vec{C}_h = 4\vec{a}_1 + 2\vec{a}_2$ and translation vector \vec{T} . When we roll the shaded region we get a nanotube with tube circumference $|\vec{C}_h|$ and tube length $|\vec{T}|$. The chiral indices of the nanotube in this example are therefore (4, 2). If we roll a nanotube along the dotted lines shown in figure, we get the zigzag or armchair nanotubes as indicated in the figure. In this letter we present the study of SiC nanotubes (3, 3) and (5, 5).

Computational method and discussions of results

In this work, hybrid density functional theory incorporating Hartree-Fock (HF) exchange [42, 43, 44] with density functional theory (DFT) exchange-correlation [45] has been used to study the electronic and geometric structure properties of the SiC SWNTs. In particular, we have used the B3LYP hybrid functional [46-49] and two basis sets namely - the all electron 3-21G* basis set [44], and the Los Alamos National Laboratory double ζ (LANL2DZ) basis set [50] as implemented in the GAUSSIAN 09 suite of programs [51] for *full* geometry optimizations without any symmetry constraints of the nanotube structures. Hybrid functionals are in general found to be efficient in reproducing the band gaps of semiconductors and insulators [52, 53] by treating the exchange part of the interactions better. We note here that, though different DFT functionals *may* produce slightly different quantitatively but not qualitatively different results, studies on semi-conducting materials have shown that, hybrid functionals, in particular B3LYP, is one of the most efficient and computationally inexpensive among all the DFT functionals available for calculation of electronic and structural properties of the semiconducting materials. All computations reported here have been performed at the supercomputing facilities of the University of Texas at Arlington.

Nanotubes are constructed as described in the previous section. The dangling bonds at the end of nanotubes are saturated with hydrogen atom. Length of nanotubes (3,3) and (5,5) is gradually increased by increasing the

number of unit cells of the nanotubes. The purpose of this work is to study the convergence of electronic properties of SiC nanotubes with length. Figure 2 shows side and top views of the SiC nanotubes (3, 3) and (5, 5) with length equal to five unit cells.

To check the stability of the nanotubes, the cohesive energy or the binding energy per atom of each nanotube is calculated from:

$$E_b = [aE(\text{Si}) + bE(\text{C}) + cE(\text{H}) - E(\text{Si}_a\text{C}_b\text{H}_c)] / (a + b + c) \quad (1)$$

where a, b and c are the numbers of Si, C, and H atoms respectively and $E(\text{Si}_a\text{C}_b\text{H}_c)$ is the total energy of the clusters representing the nanotubes.

Tables 1 and 2 and figure 3 show the variation binding energy per atom of nanotubes (3,3) and (5,5) with the number of unit cells. It is evident that, as we increase the length of nanotubes binding energy increases. However, the rate of increment in binding energy with length is not very significant after a few number of unit cells. For example, the binding energy of nanotube (3,3) increases by more than 10% from unit cell 1 to unit cell 2 whereas the increment is merely 1 % from unit cell 5 to unit cell 6. This indicates that the stability of a silicon carbide nanotube reaches saturation at about five unit cells. Given the same number of unit cells, the binding energy of nanotube (3,3) is consistently smaller than that of (5,5). Diameter of nanotube (3,3) is 5.20 Å, and that of (5,5) is 8.63 Å. The result therefore suggests that the nanotubes with greater diameter are more stable than those with the smaller diameter, given the same tube length. This has been confirmed by all the *ab initio* studies of such binary nanotubes [54].

The energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) give a measure of the “band gap” for the infinite nanotubes. This is approximate because the tubes studied here are “finite” in length, apart from the fact that hybrid density functional B3LYP tends to slightly over estimate energy gap [38]. Also, the purpose of this study is to determine the optimum length of a silicon carbide nanotube which can reasonably represent infinite nanotube. This

measure is at least qualitatively correct to compare within a given type of nanotubes with different diameters, and this is sufficient for our present discussions. Tables 1, 2 and figure 4 show the variation of HOMO-LUMO gap with length of the nanotubes. It is clear from the figure that the gap changes with length of the nanotube and stabilizes after about 5. The gap does not change significantly after 5 unit cells. The density of state (DOS) plot of SiC nanotubes (3, 3) and (5, 5) with length equal to 5 and 10 unit cells is shown in figure 5. Figure 6 shows the HOMO-LUMO plot of the nanotubes (3,3) and (5,5) with 5 and 10 unit cells. Both these figures suggest that there is no significant difference in electronic characteristics of the nanotubes along the direction of tube axis (increasing number of unit cells). However, along the circumferential direction (changing the chirality) the electronic properties change. Mulliken population analysis of the nanotubes shows that the silicon atoms lose charge and carbon atoms gain charge. The charge transfer between the atoms is $0.90e$ in SiC nanotube (3, 3) irrespective of its length. The charge transfer is $0.96e$ in SiC nanotube (5,5), irrespective of its length. The increased ionicity of the bond in (5,5) is the reason why it has more HOMO-LUMO gap than (3,3). The curvature of the nanotube suppresses the ionicity of the bond in (3,3). A detailed analysis of the effect of curvature on the ionicity and hence the band gap of the nanotube is presented in our previous work [54].

Conclusion

We have presented a study on evolution of electronic properties and stability of silicon carbide nanotubes along the nanotube axis. The results suggest that although the properties of a nanotube changes with its length for very short nanotubes of 1-5 unit cells, they do not change significantly after 5 unit cells. Hence an infinite SiC nanotube can be approximated by a nanotube of length 5 unit cells. Also, this result confirms that the properties of a nanotube are continuous along the axial direction while they are quantized along the circumferential direction.

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Table 1: Binding energy per atom (eV) and HOMO-LUMO gap (eV) of SiC nanotube clusters (3,3) calculated using basis sets LANL2DZ and 3-21G*.

No. of unit cells	Stoichiometry	B.E./atom(eV)		HOMO-LUMO gap(eV)	
		3-21G*	LANL2DZ	3-21G*	LANL2DZ
1	Si ₆ C ₆ H ₁₂	3.822	3.621	4.346	4.244
2	Si ₁₂ C ₁₂ H ₁₂	4.342	4.003	3.681	2.977
3	Si ₁₈ C ₁₈ H ₁₂	4.606	4.202	3.435	2.872
4	Si ₂₄ C ₂₄ H ₁₂	4.764	4.320	3.408	2.868
5	Si ₃₀ C ₃₀ H ₁₂	4.869	4.399	3.335	2.769
6	Si ₃₆ C ₃₆ H ₁₂	4.945	4.455	3.352	2.750
7	Si ₄₂ C ₄₂ H ₁₂	5.001	4.497	3.289	2.677
8	Si ₄₈ C ₄₈ H ₁₂	5.045	4.530	3.293	2.678
9	Si ₅₄ C ₅₄ H ₁₂	5.080	4.557	3.262	2.621
10	Si ₆₀ C ₆₀ H ₁₂	5.109	4.578	3.254	2.614

Table 2: Binding energy per atom (eV) and HOMO-LUMO gap (eV) of SiC nanotube clusters (5,5) calculated using basis sets LANL2DZ and 3-21G*.

No. of unit cells	Stoichiometry	B.E./atom(eV)		HOMO-LUMO gap(eV)	
		3-21G*	LANL2DZ	3-21G*	LANL2DZ
1	Si ₁₀ C ₁₀ H ₂₀	3.859	3.656	3.138	2.620
2	Si ₂₀ C ₂₀ H ₂₀	4.424	4.102	3.805	3.229
3	Si ₃₀ C ₃₀ H ₂₀	4.710	4.327	3.437	2.965
4	Si ₄₀ C ₄₀ H ₂₀	4.880	4.462	3.434	2.978
5	Si ₅₀ C ₅₀ H ₂₀	4.994	4.551	3.541	3.094
6	Si ₆₀ C ₆₀ H ₂₀	5.075	4.615	3.469	2.998
7	Si ₇₀ C ₇₀ H ₂₀	5.135	4.663	3.486	3.031
8	Si ₈₀ C ₈₀ H ₂₀	5.183	4.701	3.476	3.055
9	Si ₉₀ C ₉₀ H ₂₀	5.220	4.730	3.470	3.027
10	Si ₁₀₀ C ₁₀₀ H ₂₀	5.252	4.755	3.472	3.055