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Stability and electronic structures of double-walled armchair germanium carbide nanotubes

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ABSTRACT

First-principle calculations based on density functional theory have been used to investigate the stability and electronic structures of double-walled $(n_1,n_1)@(n_2,n_2)$ $(4 \leqslant n_1 \leqslant 8, n_1+3 \leqslant n_2 \leqslant n_1+6)$ germanium carbide nanotubes (GeCNTs). For any given (n_1,n_1) inner tube, the corresponding $(n_1,n_1)@(n_1+5,n_1+5)$ GeCNT has the highest formation energy and binding energy per atom, which indicate that the $(n_1,n_1)@(n_1+5,n_1+5)$ nanotube is stable. The (5,5)@(10,10) GeCNT has been found to be a particularly stable geometry. The interlayer interaction between the two layers of the double-walled GeCNT leads to an obvious coupling, which results in a narrowing of the band gap.

1. Introduction

The discovery of carbon nanotubes (CNTs) [1] has led to extensive research interest in one dimensional nanometer materials. Since this initial discovery, a range of other compounds have been identified for the synthesis of nanotubes including zinc oxide [2,3], gallium nitride [4,5], boron nitride [6,7] and silicon carbide [8–11]. A key feature of CNTs is the dependence of electronic properties on their diameters and chiralities, which can't be controlled in the synthesis process of CNTs. Unlike CNTs, theoretical studies indicate that SiCNTs are semiconductors independent of their geometries [12–19]. The stability, mechanical and electronic properties of silicon carbide mean that SiCNTs are ideal materials to develop nanometer electronic devices and sensors for applications in high temperature and high power harsh environments. There is also evidence that SiCNTs can be utilized for toxic gas detection [20–22] and hydrogen storage [23,24].

Germanium is the third member of the Group 14 elements and has similar electronic properties to silicon. Bulk germanium carbide (GeC) can be synthesized in the 3C and 2H polytypes and both forms are semiconductors with wide band gaps. Recent studies of germanium carbide have looked at the properties and modification of 2D monolayer sheets [25,26] of GeC and this has led to increasing interest in exploring the potential of GeC as a material for synthesis of nanotubes. A recent theoretical study indicates that single-walled armchair germanium carbide nanotubes (GeCNTs) are also semiconductors with wide band gaps [27]. Non-equilibrium Green's functions combined with density functional theory (DFT) have been used to investigate the electronic transport properties of zigzag GeCNTs leading to the identification of negative differential resistance (NDR) [28]. The adsorption of small molecules on zigzag GeCNTs has also been investigated using ONIOM type calculations with B3LYP for the higher level and the universal force-field for the lower level [29]. Modulation of the electronic structures of GeCNTs can also be realized with transverse electric fields [30]. A further study has shown that Fe nanowires encapsulated inside GeCNTs can be prevented from oxidation [31]. All these investigations indicate that GeCNTs are appropriate candidates for development of novel electronic devices.

Several different techniques have been successfully applied to synthesize nanotubes including, substitutional reactions, radio-frequency magnetron sputtering, hydrothermal methods and chemical vapor deposition (CVD) [8,10,32,9]. Despite the significant focus on single-walled nanotubes, most synthesized nanotubes actually have multi-walled structures. The interlayer interactions existing in these multi-walled species have been shown to significantly impact the electronic properties relative to single-walled counterparts [33–35]. Theoretical calculation of multi-walled nanotubes is often computationally demanding. However, double-walled nanotubes, formed by two coaxial single-walled nanotubes, generally provide an appropriate approximation of multi-walled

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nanotubes. In this paper, the stability and electronic structures of double-walled $(n_1,n_1)@(n_2,n_2)$ GeCNTs ($n_1 = 4,5,6,7,8$ and $n_2 = n_1 + 3, n_1 + 4, n_1 + 5, n_1 + 6$) are investigated with first-principle calculations based on DFT.

2. Computational methods

Single-walled GeCNTs can be regarded to be formed by rolling up of the graphite-like GeC sheet with their structures described by a chirality vector (n,m). Double-walled GeCNTs can be modeled by assembling two single-walled GeCNTs into a coaxial configuration. In the present study, we focus on forming double-walled nanotubes from pairs of corresponding armchair GeCNTs ($n = m$) [27]. Models for double-walled $(n_1,n_1)@(n_2,n_2)$ GeCNTs are established. Cross-sections of (4,4)@(7,7), (5,5)@(10,10) and (9,9)@(15,15) GeCNTs are shown in Fig. 1. The interlayer distance (Δr) for a double-walled GeCNT is calculated by the equation $\Delta r = 0.912 \times (n_2 - n_1)$ Å. In our calculations, all the double-walled GeCNT models are placed in the center of a hexagonal supercell. The supercell length in the lateral direction is 100 Å to eliminate the interaction between the adjacent images, and the length in the axial direction is the length of the nanotube. With these settings, the properties of the GeCNT of infinite length can be simulated, and the periodicity of the nanotube along its axis can be considered.

Electronic structures of double-walled GeCNTs are calculated by means of all-electron linear combination of atomic orbital density functional theory implemented in the DMol^3 package [36]. The exchange–correlation potential is realized with the generalized gradient approximation (GGA) provided by Perdew, Burke and Ernzerhof (PBE) [37]. Double numerical plus d-function is used as atomic orbital basis set throughout the calculations. The Brillouin zone sampling is performed using special k points generated by the Monkhorst–Pack grid with a value of $1 \times 1 \times 8$, which is suitable for one-dimensional materials [38]. To release stress in these models, geometry optimizations were performed on the double-walled GeCNTs. The convergence criteria for total energy, stress and displacement of each atom, were set as less than 1×10^{-4} Ha, 0.02 Ha/Å and 5×10^{-3} Å, respectively.

3. Results and discussions

3.1. Stability of double-walled armchair GeCNTs

Rathi's studies indicate that single-walled armchair GeCNTs have stable structures and wide band gaps nearly independent of their diameters [27]. Our studies complement this work by identifying stable geometries and the electronic structures of double-walled armchair GeCNTs. The cohesive energy or binding energy per atom in a double-walled GeCNT is defined as

$$E_b = \frac{aE(\mathrm{Ge}) + bE(\mathrm{C}) - E(\mathrm{Ge}_a\mathrm{C}_b)}{a+b} \quad (1)$$

where a and b are the numbers of Ge and C atoms in the GeCNT, respectively, and $E(\mathrm{Ge}_a\mathrm{C}_b)$ is the total energy of the nanotube.

The formation energy for a double-walled GeCNT is calculated from

$$\Delta E = E(n_1,n_1) + E(n_2,n_2) - E[(n_1,n_2)@(n_2,n_2)] \quad (2)$$

where $E(n_1,n_1)$ and $E(n_2,n_2)$ are the optimized ground state total energies of single-walled (n_1,n_1) and (n_2,n_2) GeCNTs, respectively, and $E[(n_1,n_1)@(n_2,n_2)]$ is the optimized ground state total energy of the double-walled $(n_1,n_1)@(n_2,n_2)$ GeCNT.

The interlayer separation between the inner and outer tubes of $(n_1,n_1)@(n_1+3,n_1+3)$ GeCNTs is quite small. This leads to a strong chemical interaction between the atoms of the two tubes with formation of covalent bonds between the two layers, which collapses the structures of these double-walled GeCNTs. Fig. 2 shows the cross-sections of collapsed (4,4)@(7,7) and (8,8)@(11,11) GeCNTs, which clearly demonstrates that these $(n_1,n_1)@(n_1+3,n_1+3)$ GeCNTs are no longer double-walled nanotubes. Therefore this type of GeCNTs is not considered further in this study.

Formation energies (ΔE) and binding energies per atom (E_b) for double-walled $(n_1,n_1)@(n_2,n_2)$ GeCNTs are presented in Table 1. The first point to note is that the stabilities of the double-walled GeCNTs vary systematically as a function of interlayer separation. For any given inner tube (n_1,n_1), the corresponding $(n_1,n_1)@(n_1+5,n_1+5)$ nanotube has the highest (ΔE) and (E_b). For example, the formation energy of (5,5)@(10,10) GeCNT is 0.5695 eV, which is about 0.35 and 0.49 eV higher than (5,5)@(9,9) and (5,5)@(11,11) GeCNTs. In addition, the binding energy per atom of the (5,5)@(10,10) GeCNT is about 0.043 eV higher than that of the (5,5) GeCNT.

From the above results, we can establish that the most stable double-walled GeCNTs have an interlayer separation of ~4.560 Å. Table 1 also reveals that for any given interlayer separation the binding energy per atom increases with the increase in diameter of the inner tube. In comparison, the formation energies exhibit a much less systematic variation with size of the inner tube, and we find that the (5,5)@(10,10) GeCNT has the largest formation energy. Ge–C bond lengths in the inner tube of (5,5)@(10,10) GeCNT vary from 1.890 Å to 1.906 Å with an average value of 1.898 Å, which is longer than that of the isolated (5,5) GeCNT. Bond

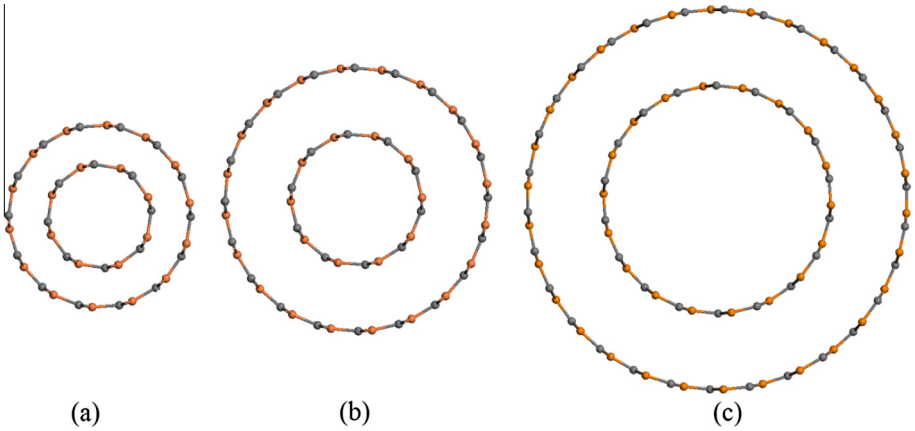

Fig. 1. Models for (4,4)@(7,7) (a), (5,5)@(10,10) (b) and (9,9)@(15,15) (c) GeCNTs. Yellow and gray balls indicate Ge and C atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)