Diamond & Related Materials 84 (2018) 112–118

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Strain-induced semiconductor-to-metal transitions in C_{36}-based carbon peapods: *Ab initio* study

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ARTICLE INFO

Keywords:
Fullerene
Carbon nanotube
Band structure
Mechanical strain
Density functional theory

ABSTRACT

We present a density functional study of the band structure and some elastic properties of semiconductor carbon nanotube endohedrally doped with the C_{36} fullerenes. We found that the electronic states belonging to C_{36}s lied inside the band gap of the pristine tube. External strain applied along the tube axis results in decreasing of the semiconducting gap from 0.3 to 0 eV. Metallic behavior of the strained system is confirmed via the additional calculations of electronic transmission coefficients. Phonons influence is accounted with the molecular dynamics approach. Strain of about 0.04 corresponds to the linear part of stress-strain curve and is found to be sufficient to observe the semiconductor-to-metal transitions at room temperature.

1. Introduction

Peapods are novel and promising all-carbon compounds [1]. In contrast to the most carbon architectures, they include nanostructures with different dimensionalities (0D and 1D). Every peapod represents a single-walled nanotube with the fullerenes encapsulated inside it [2]. First peapods containing C_{60} cages were prepared by Smith et al. in 1998 via pulsed laser vaporization of graphite [3]. Further peapods based on C_{70} and larger fullerenes [4,5], and metallofullerenes [6,7] were successfully synthesized as well. They are regarded as the prospective materials for hydrogen storage devices [8], tens-of-gigahertz oscillators [9], high-temperature superconductors [10] and field-effects transistors [11,12].

Since C_{60} cage is the most prevalent fullerene, there are many studies focused on C_{60}-based peapods. Their structure and properties were investigated in detail [13–18]. According to *ab initio* calculations the doping effect of C_{60}s depends on their density [19], relative orientation to the nanotube [16] and mutual arrangement [20] in a complex manner. It was found that the process of C_{60}s encapsulation was exothermal for nanotubes with the diameters larger than 11.8 Å [21]. At such values of diameter, the mixing of nanotube and C_{60}s orbitals is pure [21]. It was found that the strength of hybridization between the carbon nanotube and C_{60} cages was sufficiently weak despite the states from C_{60}s lied near the Fermi level [16]. As a result, the behavior of exothermally constructed peapods (metal or semiconductor) is the same as that of the pristine carbon nanotubes [16].

To achieve a wider variability of electronic characteristics of peapods, the other non-C_{60}s fullerenes or metallofullerenes should be considered for the encapsulating inside the nanotube [12,22]. Experiments performed by Sloan and co-workers reveal that the nanotubes prepared via catalytically assisted arc evaporation technique are filled with various fullerenes: from C_{36} to C_{120} [23]. Distribution of the fullerenes size is defined by the nanotube diameter: the narrower tubes contain the smaller fullerenes [23]. Fullerene C_{36} is one of the smallest cage observed inside the nanotubes [23], and in the present study we focus precisely on the C_{36}-based peapods. Although C_{36} is not as prevalent as C_{60}, nevertheless it was successfully synthesized and separated in 1998 [24]. Despite the presence of the conjugated pentagons on its surface, molecular dynamics simulations confirm the high kinetic stability of C_{36} [25]. At the same time, C_{36} possesses some unique features in comparison with the C_{60} that can affect the electronic properties of the C_{36}-based peapods.

Fullerene C_{36} is a highly strained cage, in which the curvature effects are stronger than in C_{60}. The two low-energy isomers of C_{36} are stretched D_{6h}-C_{36} (Fig. 1a) and more spherical D_{2d}-C_{36} (Fig. 1b), possessing D_{6h} and D_{2d} symmetries, respectively. Isomer D_{2d}-C_{36} is more energetically favorable in vacuum, whereas the spatial confinement (for example, the arrangement of these isomers inside the cavity of narrow carbon nanotube) on the contrary makes the D_{6h}-C_{36} more energetically favorable [26]. Note that both these isomers can be transformed to each other via the rotation of one of the C—C bonds by the angle of ~90° around the bond center (so-called Stone-Wales transformation [27]).

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https://doi.org/10.1016/j.diamond.2018.03.023
Received 28 January 2018; Received in revised form 3 March 2018; Accepted 19 March 2018
Available online 20 March 2018
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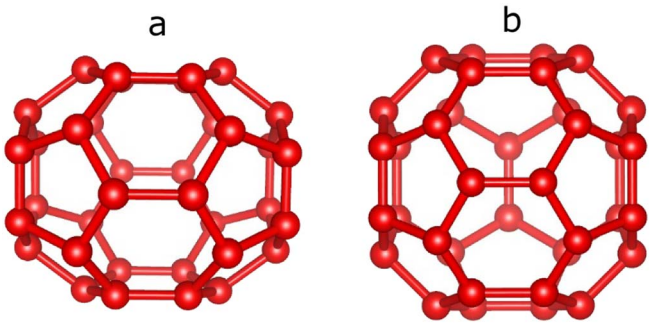

Fig. 1. Atomic structures of the low-energy isomers of the C_{36} fullerene: D_{6h}-C_{36} (*a*) and D_{2d}-C_{36} (*b*).

The energy barrier dividing the C_{36} isomers is about 6 eV [28,29], and it possesses very slightly dependence on the cage charge [29]. This value is lower than the corresponding energy barrier for C_{60} fullerene that is equal to 7.16 eV [30]. The HOMO-LUMO gaps of the D_{6h}-C_{36} and D_{2d}-C_{36} isomers are equal to 0.48 eV and 0.62 eV, respectively [31]. These values are lower than the C_{60} fullerene HOMO-LUMO gap (~5 eV [32]).

Despite the huge research interest in C_{60}-based peapods, C_{36}-based peapods are insufficiently studied. Electronic structures of zigzag and armchair carbon nanotubes containing C_{36}s were calculated in Refs. [33,34], respectively, by means of density functional approaches within both LDA and B3LYP methods with 3-21G and 6-21G* basis sets. The present study is focused on the investigation of the C_{36}s doping effect of the semiconductor host carbon nanotube, and on analyzing the evolution of the peapod electronic structure under external mechanical strain.

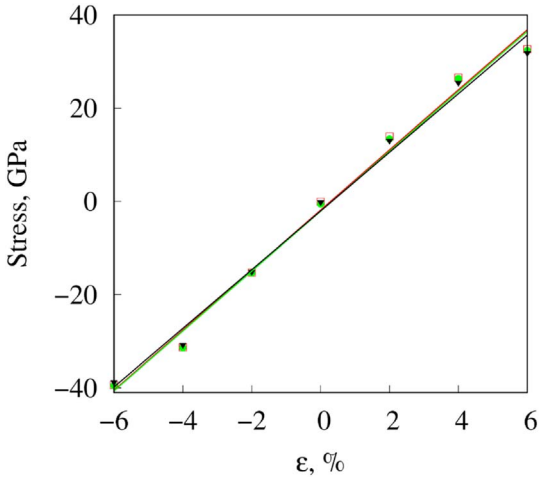

Fig. 3. The stress-strain dependences for the (14,0) carbon nanotube (squares), D_{6h}-C_{36} peapod (circles), and D_{2d}-C_{36} peapod (triangles). Solid lines are the corresponding linear approximations obtained by the least-mean-square method.

2. Computational details

We consider peapods based on the (14,0) semiconductor zigzag carbon nanotube. These chirality indices provide the highest binding energy between the host tube and the guest C_{36} among all zigzag [33] and armchair [34] tubes. Note that the corresponding tube diameter 11.0 Å is sufficiently small that makes the encapsulation of C_{60}s inside the system energetically unfavorable [21].

The infinite peapod is represented by the C_{168} nanotube fragment

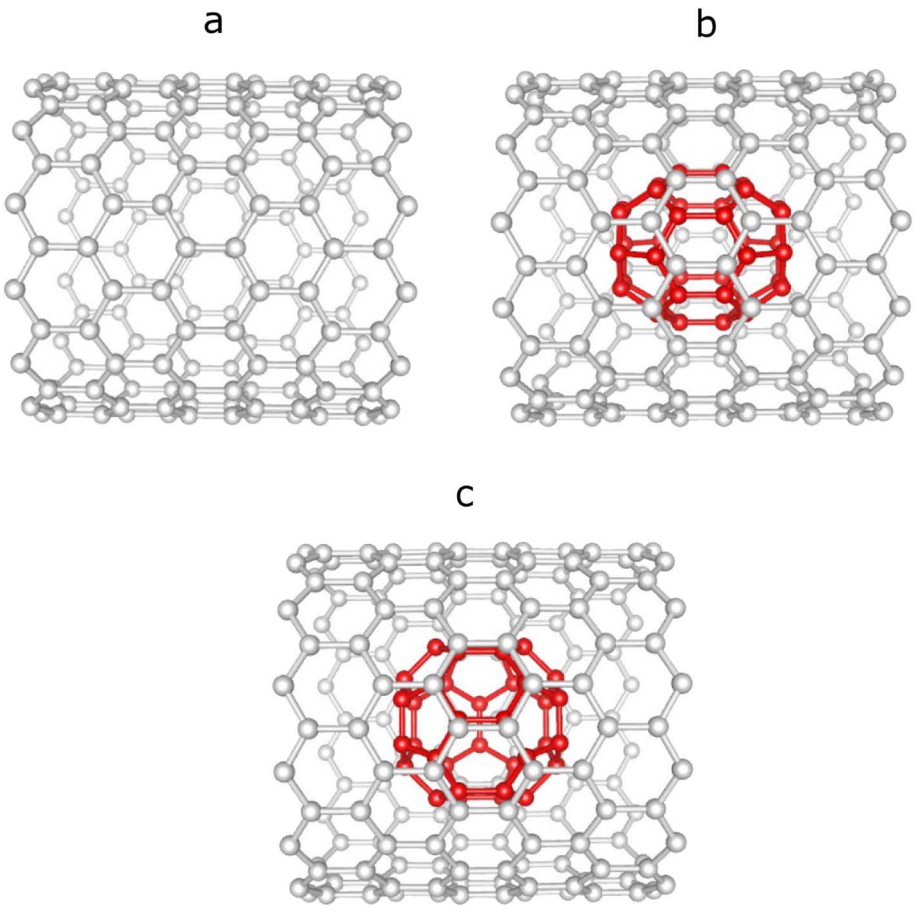

Fig. 2. Atomic structures of the unit cells of three “infinite” one-dimensional systems considered in this study: (14,0) carbon nanotube (*a*), D_{6h}-C_{36} peapod (*b*), and D_{2d}-C_{36} peapod (*c*).