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MIGRATION PROCESSES ON THE SURFACE OF CARBON NANOTUBES WITH SUBSTITUTE BORON ATOMS

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The paper presents theoretical research into vacancy formation in two types of boron-carbon nanotubes BCn, where n = 3. The research was performed using the MNDO method within the framework of an ionic-embedded covalent-cyclic cluster model, molecular cluster model and DFT method. We found that when a V-defect (vacancy) is introduced in a boron-carbon nanotube, the band gap of the defective tubules increases. This means that physical properties of materials can be purposefully changed by introducing defects. Vacancy migration along the atomic bonds in the tubule was simulated and vacancy transport properties were studied. It was found that the defect migration along different bonds actually represents the process of carbon or boron ions hopping between their stable states on the nanotube surface.

Keywords: Boron-carbon nanotubes, Vacancy, Activation energy, Vacancy migration, Semi-empirical methods of investigation.

1. Introduction

Liquid conductors commonly used in batteries and accumulators possess obvious drawbacks, namely short cycle life, low energy capacity and besides they are prone to leakage and spillage [1]. Structures with ionic conductivity can substantially extend cycle life of batteries since they can function both as electrolytes and electrodes simultaneously.

However, one of the main challenges we face when implementing the ionic conduction mechanism is that the size of an ion is often comparable to a distance between the sites of the crystal lattice, which explains why transport of charged ions similar to that one in metals almost never occurs in crystal structures. Therefore, to design a class of solid-state structures with ionic conductivity we need new materials with conduction properties that can be modified by using different methods. Recent studies have found that carbon nanotubes (CNTs), whose properties and conductive characteristics can be designed by applying different modification methods, can be successfully used as a material for ionic conduction. In [2] the results of research into the mechanism of ionic conductivity in single-walled CNTs with cylindrical symmetry are presented.

However, carbon cannot be regarded as the only element capable of forming nanotubular forms. Papers [3-7] theoretically predict and describe the formation of boron carbide nanotubes. The authors conclude that the calculated 1:3 ratio of boron and carbon in them is a clear sign that BCn type tubular structures, where n = 3 are formed. This finding seems to be promising for research into electron and energy characteristics of boron carbon BC_3 tubules as well as ionic conductivity in them similar to that one displayed by carbon nanotubes. This paper presents the results of computer simulation of ionic conductivity in two types of BC_3 nanotubes (6, 0) by applying the MNDO method [8] within the framework of molecular and ionic-embedded covalent-cyclic cluster models.

2. Electronic structure of BC_3 nanotubes with a vacancy

In our previous work [9] we investigated geometric and electronic characteristics of monolayers in quasi-planar hexagonal boron carbide (BC_3 plane), the structure of which can be of two types that differ by mutual orientation of B and C atoms. We denote them as A and B to have an accurate identification in the text. Boron-carbon BC_3 nanotubes of small diameter (3 – 10 Å) were fabricated by rolling from the relevant segments of quasi-planar exagonal boron carbide. The extended unit cells (supercells) of A and B types BCNT (6, 0) are shown in Fig. 1. The calculations were performed using the semi-empirical MNDO method within the model of the ionic-embedded covalent-cyclic cluster [10] and ab initio DFT [11]. The studies found that these structures are stable with bond lengths between the atoms equal to 1.4 Å. We calculated the strain energy E_{str} values as the difference between specific energy values in quasi-planar boron carbide and those in the corresponding nanotubes. Dependence of strain energy values on the tubule diameter indicates that nanotube formation by rolling BC_3 plane is highly probable for boron carbide BC_3 of both types, since the strain energy values drop when the diameter of a tubule is increased (Fig. 2). For nanotubes of A-type tubule (n, 0) are most likely to form, where n = 6, 8 and 10. The band gap in the BCNT of the selected types allowed us to assign them to a class of narrow-gap semiconductors with conductivity independent of the diameter. This stability of conducting properties makes boron-carbon nanotubes very attractive for nanoelectronics.

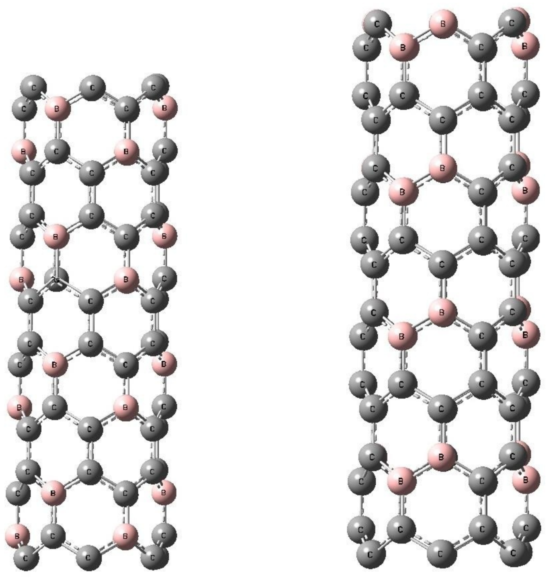
We studied the electronic structure of A and B type BC_3 nanotubes (6, 0) (Fig. 1) with a vacancy (V-defect) using the MNDO method within the framework of the molecular cluster model. For the calculations we selected clusters in the form of a supercell consisting of four layers. The circumference of the system was geometrically closed. The distance between the nearest atoms was equal to 1.4 Å. The choice of the molecular cluster model was determined by the fact that the process under consideration is local. To eliminate the influence of boundary effects, the V-defect was located in the middle of the cluster. Two types of defects were considered: 1) V_B defect, when a boron atom is removed from the structure, 2) V_C defect, when a carbon atom is removed from the structure.

Our purpose was to study the process of vacancy formation on the BC_3 nanotubes surface and its influence on their geometric and electronic structure. To model this process, a boron or carbon atom was removed from the surface of the nanotube in 0.1 Å increments until its separation. We optimized geometric parameters for the atoms in the vicinity of the defect. The atoms in the vicinity of the vacancy had three degrees of freedom, which allowed them to move from their equilibrium positions in the process of simulation. Analysis of the tubule structure in the vicinity of defect showed that atoms on the surface do not change their positions and do not display any movement in the direction of vacancy location.

The results of calculations for the main electron energy characteristics of the selected boron-carbon nanotubes are presented in Table 1. The energy values for defect formation was calculated using the formula:

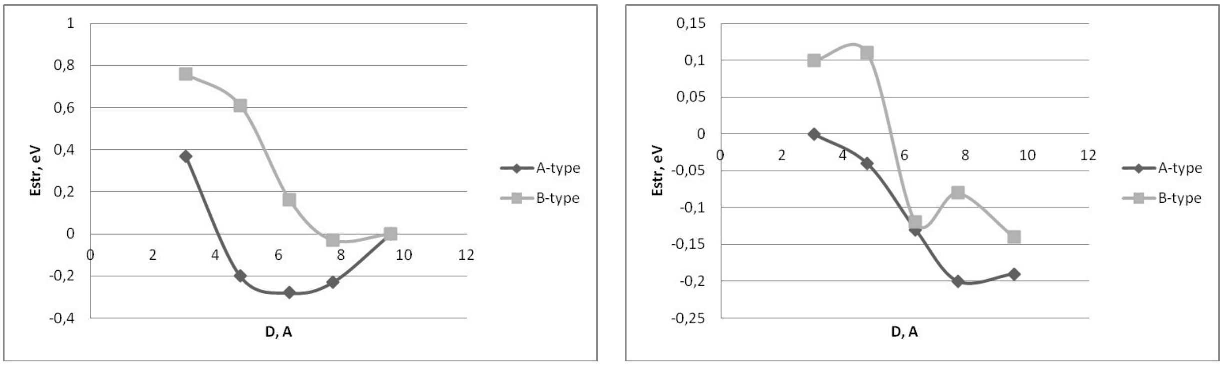
$$E_d = E_{BC_3} - (E_{str} + E_x)\,, \tag{1}$$

where E_{BC_3} — the energy value of an ideal BCNT, E_{str} — the energy value of the structure with a vacancy E_x — the energy value of carbon or boron, respectively. It was found that in A-type of BC_3 nanotubes, the formation of a V-defect by breaking off a boron or carbon atom is possible, which may be proved by negative activation energy values on the curve. Positive activation energy values obtained from the calculations for B-type of BC_3 nanotubes show that the process of defect formation is unlikely to take place on this type of tubule surface. This fact can be explained by lower stability of BC_3 nanotubes of B-type compared



(a) (b)

FIG. 1. The extended elementary cell of the BC_3 nanotube (6, 0):) A - type of mutual orientation of C and B atoms; b) B - type of mutual orientation of C and B atoms



(a) (b)

FIG. 2. Dependence of strain energy E_{str} on the diameter (d) of BC_3 tubule (n, 0) of A and B types calculated by the methods a) MNDO, b) DFT

with those of the A-type. Therefore, we shall further consider the A-type boron-carbon nanotube.

TABLE 1. Energetic characteristics of nanotubes with a vacancy

Type of a tubule	Type A with V_c defect	Type A withV_B defect	Type B with V_c defect	Type B with V_B defect	Flawless nanotube, type A	Flawless nanotube, type B
E_{homo},eV	-7.21	-6.15	-8.03	-6.23	-7.37	-6.09
E_{lumo},eV	-4.67	-3.84	-4.73	-4.52	-6.16	-6.02
E_d, eV	-0.83	-3.43	5.97	10.72	–	–
ΔE_g, eV	2.54	2.31	3.30	1.71	1.21	0.07

Analysis of the electron and energy structure of tubules with vacancies and flawless tubules allowed us to come to the following conclusions. Introduction of V_B and V_C defects into a nanotube of A-type causes changes in the position of the highest occupied and lowest unoccupied molecular orbitals (E_{homo} and E_{lumo}). In both cases, a significant increase in the band gap in comparison with the value of ΔE_g 1.21 eV for flawless boron-carbon nanotubes (6, 0) is observed. We should point out that the values of the band gap obtained by applying the molecular cluster model turn out to be much larger than the ones obtained from calculations when using other more precise methods. However, we think that this model is convenient and efficient for the study of local processes, to which the formation of a single defect can be attributed. Single electron energy spectra (Fig. 3) show differences between nanotubes with V_B and V_C defects and a flawless nanotube.

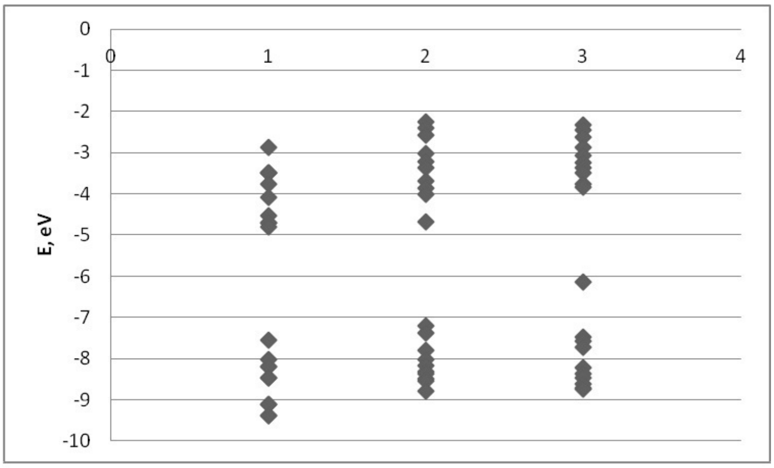


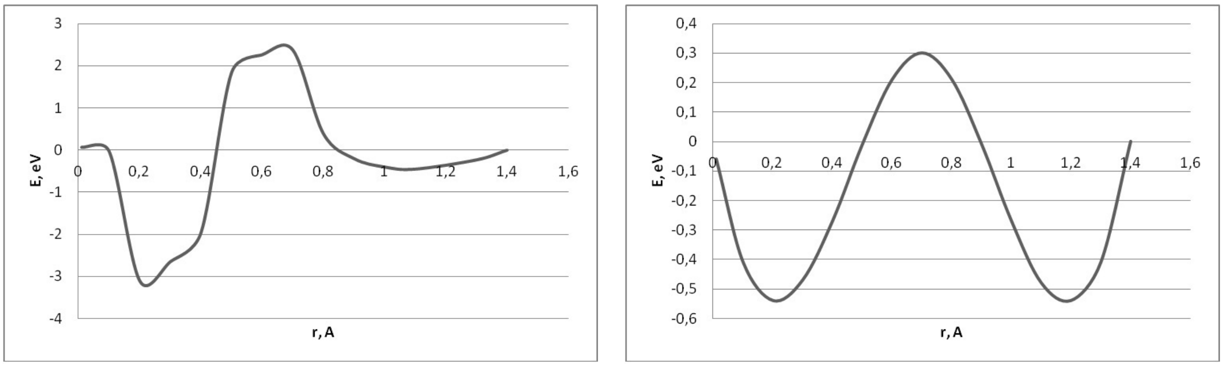
FIG. 3. Single electron energy spectra of BC_3 nanotube (6, 0) type A: 1 – flawless structure; 2 – structure with V_C defect; 3 – structure with V_B defect

3. Vacancy transport properties

Further, we investigated energy characteristics of defect migration on the surface of boron-carbon nanotubes. We considered two types of movement for two chemically inequivalent valence bonds between neighboring atoms that we denoted as I and II: I - when one bond lies on the fracture face of the nanotube, and the other two (II) lie symmetrically on either side of the fracture. They are not equivalent because of the tubule structural features that are discussed in detail in [2]. Vacancy transfer along the above described chemical bonds was modeled by using incremental approach of a neighboring carbon (or boron) atom along the virtual C-V or B-V bond to the site of vacancy location. Thus, the surface atom of the nanotube had two degrees of freedom, which allowed it to move within the surface and freely deviate from it. The geometrical parameters of the other two B and C atoms nearest to the vacancy were fully optimized during the calculation. Therefore, it seemed that the vacancy moved in a direction reverse to the atom migration.

Incremental method allowed us to build energy curves for vacancy transfer process and calculate activation energies (Ea) of the process. The curves (Fig. 4) are qualitatively similar: they have two energy minima corresponding to a stationary position of the vacancy on the tubule surface. The energy barrier between the minima have heights of 2.38 eV and 3.44 eV on migration paths I and II, respectively. We identify the barrier with activation energy of the defect. By comparing the activation energies for boron-carbon and carbon nanotubes

(6, 0) we found that the activation energy of the defect in BCNT of BC_3 type is 1 eV lower than that one in CNTs [2] for both migration paths. This means that the mechanism of ionic conductivity in the BC_3 nanotubes is energetically more favorable compared with that one in carbon nanotubes, so BCNTs with predicted conductivity might find application in nanoelectronics.



(a) (b)

FIG. 4. The energy curves for defect transfer (vacancy transfer) in BC_3 nanotubes (6, 0) type A: a) path I of defect transfer; b) path II of defect transfer

We investigated the vacancy formation mechanism in boron-carbon BC_3 nanotubes (6,0) of A and B types that differ by mutual orientation of boron and carbon atoms. The obtained activation energies showed that the formation of defects on the B-type BCNT surface was energetically unfavorable and, probably, can lead to the destruction of a tubular structure. We found that introduction of V-defects (vacancy) in the boron-carbon nanotube causes an increase in the band gap of the defective nanotubular structures. This means that physical properties of materials can be purposefully changed by introducing defects. Defect migration follows the paths along different bonds and actually represents the process of carbon or boron ions hopping between their stable states on the nanotube's surface.

Acknowledgment

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