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VACANCY TRANSPORT PROPERTIES IN BORON-CARBON BC3 NANOTUBES [1]

Sergey V. Boroznin

Candidate of Sciences (Physics and Mathematics), Associate Professor,
Volgograd State University
boroznin@volsu.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Irina V. Zaporotskova

Doctor of Sciences (Physics and Mathematics), Professor,
Director of Institute of Priority Technologies,
Volgograd State University
sefm@volsu.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Natalya P. Boroznina

Candidate of Sciences (Physics and Mathematics), Associate Professor,
Volgograd State University
boroznina.natalya@volsu.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Pavel A. Zaporotskov

Candidate of Sciences (Physics and Mathematics), Associate Professor,
Volgograd State University
paulzaporotskov@gmail.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Tatyana V. Kislova

Associate Professor,
Volgograd State University
kislovatv@mail.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Vladimir V. Akatiev

Assistant Professor,
Volgograd State University
sefm@volsu.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Vladimir A. Yarmak

Candidate of Sciences (Engineering), Associate Professor,
Volgograd State University
sefm@volsu.ru
Prosp. Universitetsky, 100, 400062 Volgograd, Russian Federation

Abstract. The paper presents results of theoretical research into vacancy formation in B type of boron-carbon nanotubes BC*n*, 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. It 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. The calculated activation energy values revealed dependence of ionic conductivity in boron-carbon tubules on temperature.

Key words: boron-carbon nanotubes, vacancy, *V*-defect, transport properties, ionic conductivity, 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 [4]. 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 [8] the results of research into the mechanism of ionic conductivity in single-walled CNTs with cylindrical symmetry are presented.

However, carbon can not be regarded as the only element capable of forming nanotubular forms. Papers [1; 3; 5–7] theoretically predict and describe 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 BC_n 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 the C type of BC_3 nanotubes (6, 6) by applying the MNDO method [2] within the framework of molecular and ionic-embedded covalent-cyclic cluster models.

2. Electronic structure of BC_3 nanotubes with a vacancy

We studied the electronic structure of C type BC_3 nanotubes (6, 6) (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 1,5 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 *V*-defect was located in the middle of the cluster. Three 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 and their nearest neighbors are carbon atoms, 3) V_c defect, when a carbon atom is removed from the structure but their nearest neighbors are boron atoms.

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 increments of 0,1 Å until its separation. We optimized geometric parameters of 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 (Fig. 2).

The strain energy for all types of nanotubes, except C type is getting higher. So, the ability of their formation is low. Because of this, our further researches have been done only for C type of the nanotubes. The results of calculations of the main electron energy characteristics of the selected boron-carbon nanotubes are presented in Table. The energy values for defect formation was calculated using the formula:

$$E_d = E_{BC3} - (E_{str} + E_x), \quad (1)$$

where E_{BC3} – 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.

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 C-type causes changes in the position of the high occupied and lower unoccupied molecular orbitals (E_{homo} and E_{lumo}). We should point out that the values of the band gap obtained by applying the molecular cluster model turn out to be much bigger 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.

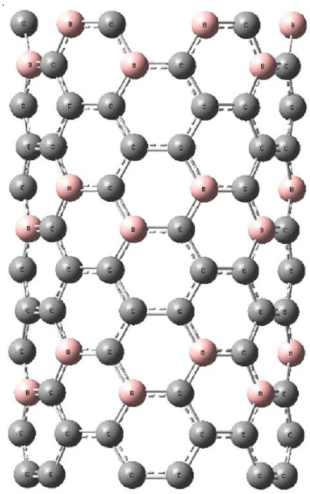

Fig. 1. The extended elementary cell of the BC_3 nanotube (6, 6) C – type of mutual orientation of C and B atoms

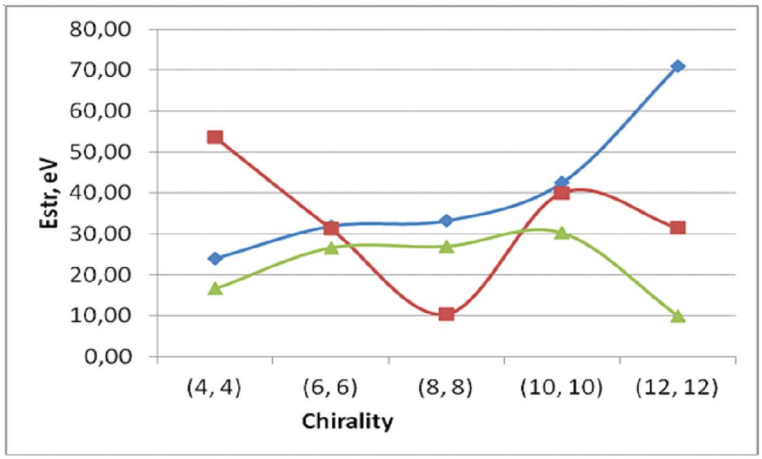

Fig. 2. Dependence of strain energy E_{str} on the diameter (d) of BC_3 tubule (n, n):
blue – A type, red – B type, yellow – C type

Energetic characteristics of nanotubes with a vacancy

Migration way	Type C with V_b defect	Type C with V_c defect (way I)	Type C with V_c defect (way II)
Activation energy,eV	3,05	5,46	2,06

3. Vacansy transport properties

Further, we investigated energy characteristics of defect migration on the surface of boron-carbon nanotubes. We considered two types of movement for three chemically inequivalent valence bonds between neighbouring atoms that we denoted as I, II and V_b: I – when the vacancy lies between two boron atoms, II – the vacancy lies between two carbon atoms and V_b – when the vacancy lies on the place of carbon atom and boron atom moves to them. They are not equivalent because of the tubule structural features that are discussed in details in [8]. 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 (E_a) of the process. The curves (Fig. 3) 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 5.46 eV, 2.06 eV and 3.05 on migration paths I, II and V_b, respectively. We identify the barrier with activation energy of the defect. Analysis of the geometry of the migration process showed that a topological defect in the surface, the pentagon, is observed. While one carbon or boron ion moves toward the vacancy position, the other two surface atoms can form a chemical bond. Structural rearrangement of the surface leads to a change in the interatomic interactions. Pentagons deform the surface, and the surface of the tube has became buckled. Thus, the process of defect transfer leads to the formation of pentagons and actually represents hopping of carbon and boron ions between stable states on the surface of the tube.

Conclusion

We investigated the vacancy formation mechanism in boron-carbon BC_3 nanotubes (6, 6) of C type that is the most stable. 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. It means that

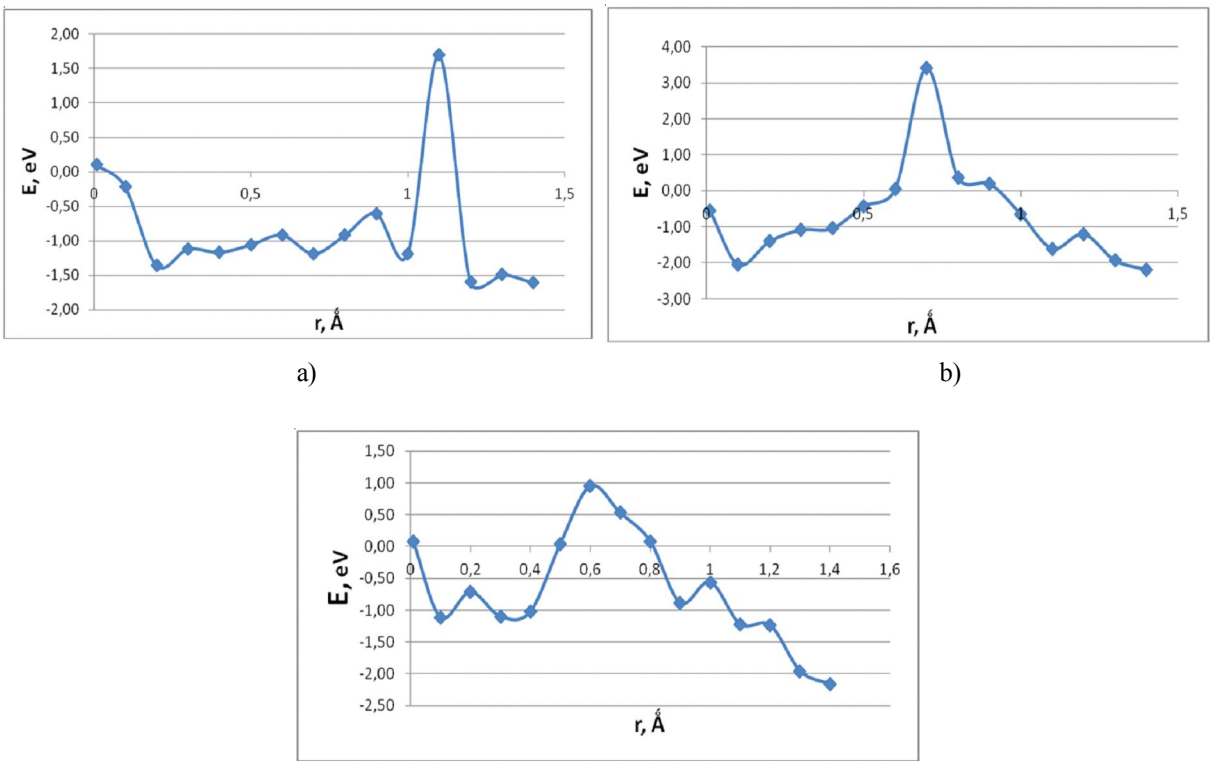

Fig. 3. The energy curves for defect transfer (vacancy transfer) in BC_3 nanotubes (6, 6) type C:
a) path V_b of defect transfer; b) path I of defect transfer; c) path II of defect transfer

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 surface.

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ТРАНСПОРТНЫЕ СВОЙСТВА ВАКАНСИЙ В БОР-УГЛЕРОДНЫХ BC_3 НАНОТРУБКАХ

Сергей Владимирович Борознин

Кандидат физико-математических наук, доцент,
Волгоградский государственный университет
boroznin@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Ирина Владимировна Запороцкова

Доктор физико-математических наук, профессор,
директор института приоритетных технологий,
Волгоградский государственный университет
sefm@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Наталья Павловна Борознина

Кандидат физико-математических наук, доцент,
Волгоградский государственный университет
boroznina.natalya@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Павел Александрович Запороцков

Кандидат физико-математических наук, доцент,
Волгоградский государственный университет
paulzaporotskov@gmail.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Татьяна Викторовна Кислова

Доцент,
Волгоградский государственный университет
kislovatv@mail.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Владимир Витальевич Акатьев

Доцент,
Волгоградский государственный университет
sefm@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Владимир Алексеевич Ярмак

Кандидат технических наук, доцент,
Волгоградский государственный университет
sefm@volsu.ru
просп. Университетский, 100, 400062 г. Волгоград, Российская Федерация

Аннотация. В статье представлены результаты теоретических исследований формирования вакансий в бор-углеродных нанотрубках типа BC_n, где $n = 3$. Моделировалась миграция вакансий вдоль атомных связей в трубке и изучались свойства переноса вакансий. Установлено, что миграция дефектов по различным связям фактически представляет собой процесс перехода ионов углерода или бора между их стабильными состояниями на поверхности нанотрубки.

Ключевые слова: бор-углеродные нанотрубки, вакансия, *V*-дефект, транспортные свойства, ионная проводимость, энергия активации, миграция вакансий, полуэмпирические методы исследования.