

Electronic properties of boron nitride nanotube fragments (nanorings): simulation by the DFT method

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The energy and electronic structure of fragments (nanorings–BNNTR) and boron nitride nanotubes (BNNT) were studied using the pseudopotential method within the density functional theory. The simulation was performed using the FHI96md package implementing the density functional theory and the pseudopotential method with their variation. The energy dependences of the binding energy $E_b(D)$ per atom for BNNTR nanorings with the armchair and zigzag structures with diameters D from 0.285 to 1.382 nm differed significantly. The changes in $E_b(D)$ for BNNTR had a monotonically decreasing form. The energy gap for BNNTR and BNNT with the zigzag configuration took a minimum value of $E_g = 2.5$ eV. The initial section of the $E_b(D)$ and $E_g(D)$ dependences grew stepwise to $D = 0.414$ nm: for BNNTR nanorings with a zigzag structure by $\Delta E_g = 2$. The $E_g(D)$ dependence in BNNTR and BNNT with an armchair structure showed saturation at $E_g = 4.6$ and 6.4 eV, respectively. The obtained results indicate the possibility of creating BNNTR-based quantum dots with recombination luminescent emission in the visible range.

Keywords: boron nitride nanorings, density functional theory, band gap, visible radiation.

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1. Introduction

Investigations of two-dimensional (2D) materials based on elements of III to IV groups demonstrating a set of unique properties and applications are becoming more important [1]. By now they have rapidly reached the top-rated publication positions. Hexagonal boron nitride, BN, is the leader among them [2]. The interest in BN is to a large extent associated with enhanced polymorphism [3] due to the features of the structure [4], where interatomic bonds between B and N are implemented by both sp^2 and sp^3 -hybridization of electrons. In BN, sp^2 is characterized by rhombic (r -BN) and wurtzite (w -BN) metastable and stable ordering, while sp^3 - is characterized by hexagonal (h -BN) and cubic (c -BN) metastable and stable ordering, respectively. Layer-by-layer structure in h -BN and r -BN is caused by a weak Van der Waals interaction, and in c -BN and w -BN, covalent interactions are predominant at distances of 0.146 nm between B and N and of 0.25 nm between N and N atoms [4]. Besides the above-mentioned structures, nanoribbons, nanotubes, fullerenes and even quantum dots are created from white graphene, BN, after hydroxyl functionalization similar to carbon structures, i.e. actually 0D, 1D, 2D and 3D nanomaterials [5–9]. Such materials are successfully used as model 2D nanostructures for calculations using the density functional theory [8,10–12] and an orbitless approach proposed in [13]. Practical interest in the object under study is caused by the reported stability [14] up to high temperatures, therefore these

materials, together with double tubular boron nitride and carbon structures, are treated as promising materials for hydrogen economy [8]. Stability of the calculated BN nanoclusters in the form of nanotube (nanoring) fragments with different diameters is ensured by the fact that typical uncompensated atomic bonds of either B or N in real conditions appear to be locked with neighboring similar structures. It is this fact, including the natural defects of BN structures, that explains BN nanoparticle adhesion to the surface of primary filaments [11] with diameters of tens of μm , which was implemented in RF Patent № 2822287 as of 03.07.2024 and in RF Patent Application № 2024134073, where effective attachment of specifically nanoparticles formed from hexagonal boron nitride during ultrasonic treatment was validated experimentally. Thus, creation of synthetic fabric material with a unique combination of practically significant properties typical of boron nitride has been confirmed.

We studied and analyzed electronic properties of nanorings consisting of BN nanotube fragments (hereinafter referred to as BNNTR) with variable diameters in the range from 0.285 nm to 1.382 nm. The specified nanoring diameters and heights were assigned by the aspect ratio to 2D-materials [8,10].

2. Research procedure

The calculations were performed using FHI96md package [15] implementing the density functional theory

(DFT) [16,17] and pseudopotential method. Pseudopotentials were constructed using FHI96pp package [18]. Exchange-correlation interaction energy was calculated within the PBE-GGA approximation [19]. Cutoff energy for a plane wave set was 408 eV. Supercell sizes varied depending on the sizes of the simulated system and were limited by the distance between adjacent structures of ≥ 0.7 nm to avoid interaction with virtual twins. Atom coordinates and densities of local states of the structure under study were generated using an original program. Densities of electronic states were constructed by approximation of electron level peaks by the Gaussian distributions. Absolute calculation accuracy of the bond energy E_b and energy gap width E_g in accordance with [15] was 0.1 eV max., thus, making it possible to interpret the provided simulation results. Limited calculation accuracy is caused by the features of the DFT method itself and by the selection of pseudopotentials for the PBE-GGA approximation. For the employed performance, the best results were achieved by comparing the obtained results with calculations and experimental data of other research groups.

Calculations for „armchair“ or „zigzag“ nanorings with a nanoring height (H) increased to two hexagons were conducted in Abinit software package [20]. Ring-shaped (BNNT) nanotube fragment nanocluster was constructed in Avogadro molecular editor. The largest H equal to 2 hexagons was a fixed height. The number of hexagons varied depending on the nanoring diameter (D). First, the equilibrium nanoring structure was calculated taking into account the intermolecular interaction relaxation forces to determine the bond energy E_b . The following parameters were used for calculations: plane wave cutoff energy — 408 eV; PBE-GGA pseudopotentials [19]; supercell, including from 24 to 84 atoms depending on D of the simulated nanoring similar to the data of [21]. The second calculation stage calculated the energy gap width E_g . The plane wave set ($8 \times 8 \times 8$ k -dots) was generated using the Monkhorst-Pack method.

E_b per atom was calculated as follows

$$E_b = \frac{E_b(BN) - E_b(N) - E_b(B)}{n}, \quad (1)$$

where $E_b(BN)$, $E_b(N)$, $E_b(B)$ are bond energies in the BNNT and BNNT structures of isolated N and B atoms, respectively, n is the number of atoms in the supercell [12].

Nanostructures are characterized by smearing of electron and hole wave functions — size effect, therefore optical recombination was possible even in the case of indirect energy gap. Nanoring luminescence wavelength λ_{\max} was estimated using the following equation

$$\lambda_{\max} = \frac{hc}{E_g}, \quad (2)$$

where E_g is the calculated energy gap width of the BNNT.

3. Results and discussion

Selection of nanoclusters consisting of carbon and boron nitride nanotube fragments in the form of BNNT and

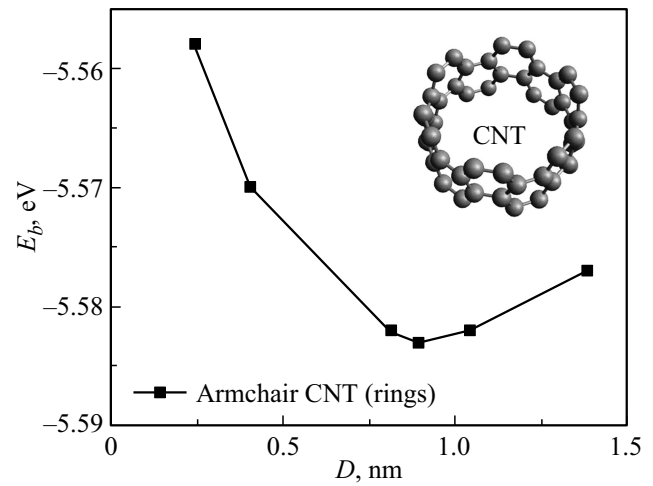


Figure 1. Specific bond energy (per atom) for CNTR.

CNTR is dictated, in particular, by the fact that they were detected and by the findings of previous studies [4]. Figures 1 and 2 shows schematic illustrations of such BNNT and CNTR and the calculated dependences of E_b for them on D — $E_b(D)$. Calculations were performed for nanorings with $H = 0.277$ nm (one hexagon) and $H = 0.64$ nm (two hexagons).

BN-based nanotubes (BNNT) are arranged in the same way as nanotubes (CNT). However, considerable differences both in the values and behavior of E_b were found in the given nanoring diameter range (from 0.285 nm to 1.382 nm) on $E_b(D)$ (Figures 1 and 2). According to the experimental data [21,22] and on the calculated dependence $E_b(D)$ for CNTR, there was a clearly pronounced minimum. E_b per atom reached its minimum at the tube diameter of ~ 1 nm. In the same studied diameter range of both „armchair“ (with chirality indices $m = n$) and „zigzag“ — ($m = 0$) BNNT, the calculated $E_b(D)$ decreased only smoothly (Figure 2), which corresponded to the results of [10,23].

$E_g(D)$ was calculated for BNNT (Figure 3, a) and BNNT (Figure 3, b). The analysis revealed a set distinguishing features in $E_g(D)$ in the given variation range D (from 0.285 nm to 1.382 nm) that agreed with the data of [23].

Energy gap for BNNT and BNNT with the „zigzag“ configuration took the same minimum value $E_g = 2.5$ eV at $D = 0.414$ nm. The minimum level of E_g for the „armchair“ structures in BNNT equal to 3.6 eV and in BNNT equal to 4.4 eV was reached at the smallest studied diameter $D = 0.285$ nm. As the diameters on $E_g(D)$ in BNNT increased, as in [10,14], a spike in ΔE_g was observed and reached $\Delta E_g = 2$ eV for the „zigzag“ structure and $\Delta E_g = 1$ eV for the „armchair“ structures. For BNNT with the same structures, this spike was the same $\Delta E_g = 1.6$ eV. With further growth of D , values of E_g on $E_g(D)$ in BNNT and BNNT for the „armchair“ structures remained almost unchanged and were equal to 4.6 eV and 6.4 eV, respectively. In the same variation range of D in BNNT

and BNNT with the „zigzag“ structures, a smooth increase in E_g to 4.8 eV was observed.

Calculated $E_b(D)$ and $E_g(D)$ for the BNNTR nanorings with the largest $H = 0.64$ nm (two hexagons) in the diameter range from 0.27 nm to 1 nm are shown in Figure 4, *a, b*. Comparison with the corresponding dependences $E_b(D)$ and $E_g(D)$ in Figure 3, *a* indicated that they coincided by the above-mentioned typical features and agreed adequately with the experimental data [10,14]. Actually, $E_b(D)$ in such system decreased smoothly as D increased. Estimate by the variation level of E_b could be indicative of the presence of a combined ion-covalent bond. According to Figure 4, *b*, the minimum value of E_g on $E_g(D)$ was 3.8 eV. At the same D and H , the calculated $E_g(D)$ for the „zigzag“ BNNTR nanoring had the same form and was lower. It is significant that the calculated variations $\Delta E_g(D)$ of „zigzag“ and „armchair“ BNNTR were ~ 0.3 eV in the largest calculated region $D = 1$ nm, however, at $D = 0.4$ nm there was a spike $\Delta E_g(D) \sim 2$ eV that coincided with that in Figure 3, *a*. Appearance of typical features in the calculated dependences $E_b(D)$ and $E_g(D)$ common for the

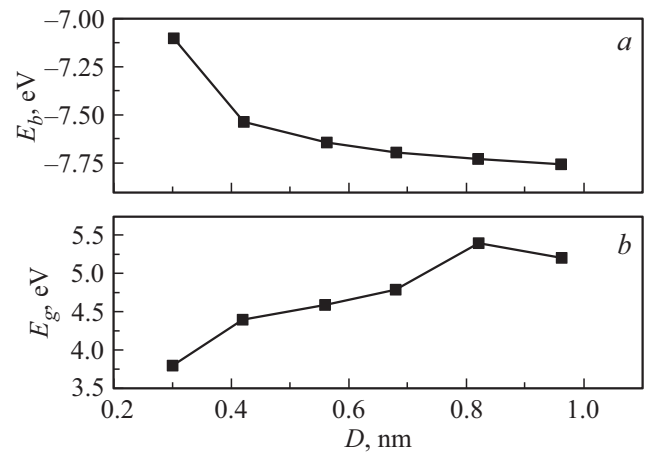


Figure 4. Electronic properties of the „armchair“ BNNTR with a height of 0.64 nm (two hexagons): bond energy per atom (*a*) and energy gap width (*b*).

„armchair“ and „zigzag“ BNNTR both in the dependence on D and on H that agree with the results of [10,14] indicates additionally that the calculations were conducted adequately.

Electronic properties of double „armchair“ BNNTR systems were analyzed. Double nanorings were formed by embedding nanorings with substantially different diameters into each other. Double systems with the internal nanoring with $D_{in} = 0.285$ nm and 0.414 nm were studied. Diameter of the external nanoring was the same and was equal to $D_{out} = 0.831$ nm. The studies were performed by constructing the density of electronic states (DOS) and local density of electronic states (LDOS) of the constituent fragments similar to work [8]. The measurements of E_g are given in the table. The shown data indicated a significant decrease in E_g in the double nanoring compared with separate constituent fragments with both D_{in} and D_{out} . The observed narrowing of the energy gap is supposed to be caused by the interaction between the constituent fragments leading to the appearance of new energy levels in the band gap and by the change of DOS in the radial direction. A set of these rearrangements of the electronic structure typical of the fragments included in the double system reduces E_g .

Analysis of minimum calculated band gaps for the „zigzag“ BNNTR (Figure 3, *a*) — $E_g = 2.5$ eV, „armchair“ BNNTR (Figure 4, *b*) — $E_g = 3.8$ eV and according to the table data for double systems — $E_g = 2.7$ eV is

Energy gap width E_g of the „armchair“ BNNTR: total for the double system, internal and external nanorings according to the DOS and LDOS data

E_g measured from DOS, eV			E_g measured from LDOS, eV	
Total	For internal ring	For external ring	For internal ring	For external ring
2.7	3.2	4.7	2.7	2.7

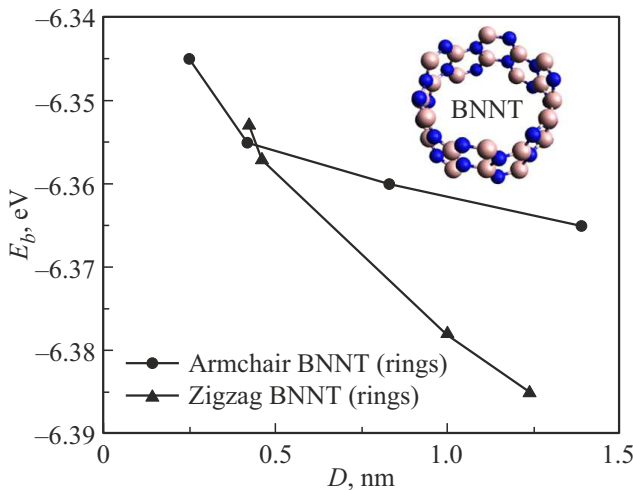


Figure 2. Specific bond energy (per atom) for BNNTR.

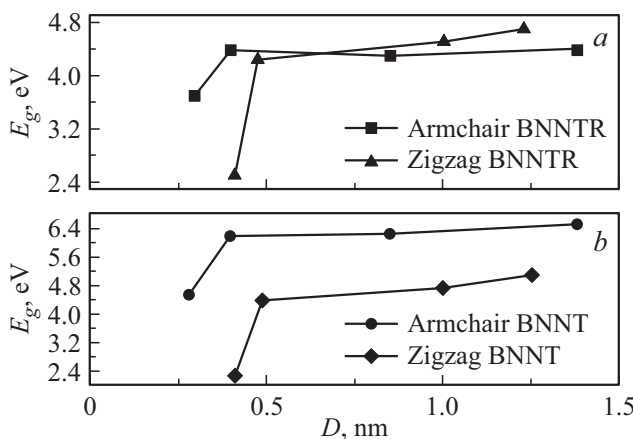


Figure 3. Energy gap width for the BNNTR nanorings (*a*); BNNT nanotubes (*b*).

of practical interest. Due to optical recombination at trap levels, the specified values of E_g estimated using equation (1) may cause luminescence excitations in these structures with λ_{\max} in the range from 450 nm to 630 nm, i.e. in the optical range as reported in [9]. Actually, for a „zigzag“ nanoring with the minimum $D = 0.285$ nm and $H = 0.277$ nm, the calculated optical response corresponds to $\lambda_{\max} = 500$ nm, for an „armchair“ nanoring with $D = 0.285$ nm and $H = 0.64$ nm — to $\lambda_{\max} = 630$ nm, for a nanoring in the form of a double „armchair“ nanoring system with $D_{\text{out}} = 0.831$ nm and $D_{\text{in}} = 0.414$ nm — to $\lambda_{\max} = 450$ nm.

4. Conclusion

Electronic and energy properties of BN nanoclusters in the form of nanotube (ring) fragments assigned to 2D structures by the aspect ratio are much different from CNT compared with tubular BNNT. BNNTRs with different types of chirality, „zigzag“ and „armchair“ have an enhanced size dependence $E_b(D)$ and $E_g(D)$.

It was found that, as the diameter decreased and approached the nanoring height (two hexagons), the bond energy and band gap decreased in absolute magnitude.

For the nanocluster model with the embedded „armchair“ BNNTR nanorings, the band gap appeared to be the smallest.

Due to optical recombination from BNNTR with different types of chirality, „zigzag“ and „armchair“, and for the double system consisting of embedded „armchair“ nanorings, the estimated luminescence wavelengths λ_{\max} are in the long-wavelength optical range.

Conflict of interest

The authors declare that they have no conflict of interest.

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