New polymorphic varieties of boron nitride with graphene-like structures

Dmitry S. Ryashentsev, Eugeny A. Belenkov
Chelyabinsk State University, https://www.csu.ru/
Chelyabinsk 454001, Russian Federation
E-mail: ryashentsev_dmitry@mail.ru, belenkov@csu.ru

Abstract: **First-principle calculations of the structure and electronic properties of four new polymorphic varieties of graphene-like boron nitride, the structure of which is similar to the structure of graphene polymorphs, the atoms in which are in the spirit of different structural positions, were performed by the density functional theory method in the generalized gradient approximation. As a result of the studies carried out, the possibility of stable existence of three monoatomic boron nitride layers: $BN-L_{4-6-8a}$, $BN-L_{4-6-8b}$ and $BN-L_{4-10}$ has been established. The $BN-L_{4-12}$ layer is transformed into the $BN-L_{4-6-8}$ layer during geometric optimization. The lengths of interatomic bonds in boron nitride monolayers vary in the range 1.4353 Å ÷ 1.4864 Å, and the bond angles in the range 84.05° ÷ 152.26°. The band gap of the BN layers varies from 3.16 eV to 3.90 eV. Sublimation energies are in the range from 16.67 eV/(BN) to 17.61 eV/(BN).**

CONTENTS

1. INTRODUCTION

The structure of boron nitride crystals can be different and similar to the structure of graphite or diamond [1-3]. In addition, there are boron nitride analogs of carbon nanostructures - nanotubes and graphene layers [4,5]. Crystals of hexagonal boron nitride, like graphite crystals, consist of BN monolayers, the structure of which is similar to the structure of graphene layers [6, 7]. The relevance of studying monatomic layers of graphene and boron nitride is associated with the possibility of their use in electronics for the synthesis of heterostructures with variable properties. The electronic properties of graphene monolayers can change significantly for different structural types [8-10]. It is theoretically predicted that the existence of four main polymorphic varieties of graphene such as L_6, L_{4-8}, L_{3-12} and L_{4-6-12}, in which all atoms are in the same structural positions, are possible [8]. Studies of BN polymorphs with a structure similar to the structure of these graphene polymorphs have shown the possibility of their stable existence, as well as a significant change in their electronic properties [11,12]. In addition to the main polymorphic varieties of graphene, there can

be many other structural types in which carbon atoms are located in two, three, four, or more different structural positions [9,10]. The range of changes in the properties of these polymorphic graphene varieties is much larger than for the four main ones - for example, there may be structural types of graphene, the conductive properties of which are semiconducting rather than metallic. Apparently, the existence of monolayers of boron nitride with a structure similar to the structure of minor graphene polymorphs is possible. Studies of the possibility of the existence of boron nitride analogs of these compounds have not yet been carried out. Therefore, in this work, we performed model studies of structural analogs of boron nitride, similar to graphene layers, consisting of carbon atoms in two different structural positions.

2. MATERIALS AND METHODS

The graphene layers L_{4-6-8a}, L_{4-6-8b}, L_{4-10}, and L_{4-12} described in [10] were taken as the initial structures for modeling BN layers. In these layers, carbon atoms are in two different structural states. The construction of the primary structure of boron nitride layers was carried out by replacing carbon atoms with boron and nitrogen atoms, so that each atom of one type has neighboring atoms with which it forms covalent bonds were of a different type. As a result, the number of different structural positions in boron nitride layers doubles - there are four of them - two unique structural positions for boron and nitrogen atoms. Model calculations were performed using the Quantum ESPRESSO software package [13]. Geometrically optimized structures of BN layers were found by the density functional theory (DFT) method [14]. The structure of three-dimensional crystals was calculated, consisting of graphene layers packed in stacks, so that the distance between the layers was 10 Å. In this case, the distance between the layers and the interaction between them is negligible, and it can be assumed that the layers in such crystals are identical to isolated layers. In the calculations, we used the generalized gradient

approximation (GGA) [15], a 12×12×12 k-point grid, a temperature of 0.01 K, and a cutoff energy in the plane wave basis of 70 Rydberg. The lengths of the vectors of elementary translations (*a, b*), the lengths of interatomic bonds (Å), and the angles between them (°) were calculated as parameters characterizing the structure of the layers. Interatomic bonds and angles were determined for each of two unique structural states. Since boron and nitrogen atoms were in different structural positions, the number of unique states where measurements were performed was four. As an integral parameter characterizing the deformation of the layer structure in comparison with the ideal structure of the hexagonal graphene layer, we calculated the deformation parameter (Def), which is equal to the sum of the moduli of the differences between the bond angles and the angle of 120°, characteristic of hexagonal graphene. In addition, for the structural states, the values of the Wells ring parameter (Rngi) were determined, which symbolically shows the number of units in the rings from the minimum number of interatomic covalent bonds passing through the atom in the corresponding structural state. Energy characteristics of BN layers (total bond energy E_{total}, sublimation energy E_{sub}) and their electronic properties (band structure, density of electronic states, Fermi energy E_F, band gap) by the DFT-GGA method.

3. RESULTS AND DISCUSSION

As a result of DFT-GGA model calculations, geometric optimization of the structure of the original BN layers was performed. The structure of one of the studied layers, BN-L_{4-12}, turned out to be unstable, and as a result of optimization it was transformed into the structure of the BN-L_{4-6-8} layer. The new layer obtained as a result of geometric optimization consists of atoms in six structural positions, which exceeds the number of structural positions in other layers studied. Compounds with a minimum number of structural positions should have the highest stability. In this work, we considered only boron

nitride layers with four structural positions; therefore, the new BN-L$_{4-6-8}$ layer obtained by transforming the original BN-L$_{4-12}$ layer was not considered further. The remaining three layers: BN-L$_{4-6-8a}$, BN-L$_{4-6-8b}$ and BN-L$_{4-10}$ - have a stable structure, and their images are shown in **Fig. 1**. In this figure, the unit cells of the layers are
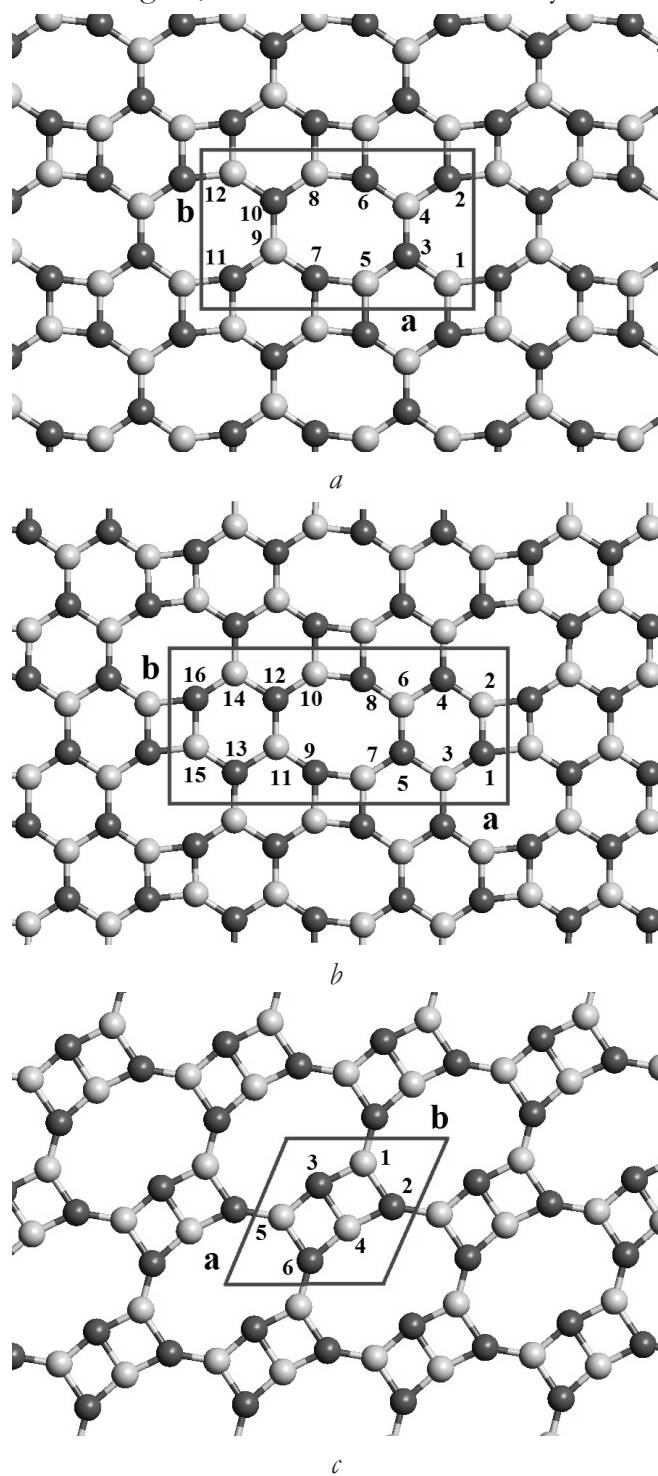

a

b

c

Fig. 1. *Layer structure and unit cells of polymorphic species of boron nitride geometrically optimized as a result of DFT-GGA calculations: (a) BN-L$_{4-6-8a}$; (b) BN-L$_{4-6-8b}$; (c) BN-L$_{4-10}$.*

Table 1
Properties and structural parameters of polymorphic varieties of boron nitride

Layer	BN-L$_{4-6-8a}$	BN-L$_{4-6-8b}$	BN-L$_{4-10}$
a, Å	7.6686	10.1945	4.6395
b, Å	4.5600	4.4891	10.000
c, Å	10.000	10.000	4.6375
β, °			115.12
Rng$_I$	416181	416181	41102
Rng$_{II}$	6182	6281	42101
N, atom	12	16	6
ρ, g/cm^2	0.7071	0.7204	0.6339
E_{total},eV(e.n.)	-21.1647	-2823.23	-1055.88
E_{total},eV(*BN*)	-352.75	-352.90	-351.96
E_{subl},eV(*BN*)	17.45	17.61	16.67
Δ, eV	3.156	3.896	3.166
E_F, eV	-3.9967	-3.9399	-4.0960

highlighted. The BN-L$_{4-6-8a}$ and BN-L$_{4-6-8b}$ layers have rectangular unit cells containing 12 and 16 atoms, respectively (**Table 1**). The lengths of the vectors of elementary translations are *a* = 7.67 Å, *b* = 4.56 Å and *a* = 10.19 Å, *b* = 4.49 Å for the boron nitride layers BN-L$_{4-6-8a}$ and BN-L$_{4-6-8b}$, respectively. The word density of new polymorphic varieties varies from a minimum value of 0.6339 g/cm^2 for the BN-L$_{4-10}$ layer to a maximum value of 0.7204 g/cm^2 for the BN-L$_{4-6-8b}$ layer (Table 1).

The crystal lattice of the BN-L$_{4-10}$ layer belongs to the oblique Bravais lattices. The elementary translation vectors of the unit cell of this layer are 4.64 Å, the angle between the vectors is 115.12°, and the number of atoms in the unit cell is 6. Atomic positions in the BN layers are characterized by Wells ring parameters (Rng). The BN-L$_{4-6-8a}$ layer is characterized by two different values of the parameter Rng 416181 and 6182, in the BN-L$_{4-6-8b}$ layer Rng of the first atomic position 416181 and the second - 6281, and in the BN-L$_{4-10}$ layer the values of the ring parameter 41102 and 42101 for each of two different atomic positions. The ratio of the number of atomic positions of the first and second types in boron nitride monolayers is 2:1, 1:1, and 2:1 for the BN-L$_{4-6-8a}$, BN-L$_{4-6-8b}$, and BN-L$_{4-10}$ layers, respectively. Polygons 4, 6, 8, 10,

Table2
Coordinates of atoms in unit cells of layered polymorphic varieties of boron nitride

Num-ber	Atom	X,Å	Y,Å	Num-ber	Atom	X,Å	Y,Å
BN-$L_{4\text{-}6\text{-}8a}$								
1	B	0.7309	0.6651	7	N	4.5591	0.8222
2	N	0.7258	3.7388	8	B	4.5654	3.8959
3	N	1.9373	1.4759	9	B	5.7508	1.6222
4	B	1.9176	2.9384	10	N	5.7511	3.0847
5	B	3.1029	0.6647	11	N	6.9425	0.8218
6	N	3.1093	3.7384	12	B	6.9375	3.8955
BN-$L_{4\text{-}6\text{-}8b}$								
1	N	0.6209	1.2308	9	N	5.7185	0.6244
2	B	0.6363	2.7063	10	B	5.7334	3.6384
3	B	1.8071	0.4549	11	B	6.9045	1.4010
4	N	1.8279	3.4794	12	N	6.9253	2.8660
5	N	3.0645	1.2345	13	N	8.1619	0.6210
6	B	3.0853	2.6995	14	B	8.1827	3.6455
7	B	4.2565	0.4621	15	B	9.3535	1.3941
8	N	4.2713	3.4762	16	N	9.3689	2.8696
BN-$L_{4\text{-}10}$								
1	B	-0.2439	2.3033	4	B	1.6886	2.6589
2	N	0.5760	3.5972	5	B	2.1897	0.7599
3	N	8.7808	1.3819	6	N	3.0119	2.0523

Table 3
Lengths of interatomic bonds and the angles between them in boron nitride layers

Atom	Layer	BN-$L_{4\text{-}6\text{-}8a}$	BN-$L_{4\text{-}6\text{-}8b}$	BN-$L_{4\text{-}10}$
N	L_1(I), Å	1.4863	1.4752	1.5125
	L_2(I), Å	1.4353	1.4711	1.4519
	L_3(I), Å	1.4647	1.4176	1.4516
	L_1(II), Å	1.4626	1.4652	1.5318
	L_2(II), Å	1.4370	1.4203	1.4059
	L_3(II), Å	1.4366	1.4795	1.4554
B	L_1(I), Å	1.4864	1.4752	1.5125
	L_2(I), Å	1.4370	1.4203	1.4554
	L_3(I), Å	1.4653	1.4711	1.4557
	L_1(II), Å	1.4626	1.4652	1.5318
	L_2(II), Å	1.4353	1.4176	1.4063
	L_3(II), Å	1.4356	1.4796	1.4519
N	φ_1(I), °	84.05	122.64	83.012
	φ_2(I), °	123.69	84.24	82.97
	φ_3(I), °	152.26	153.11	168.98
	Def_N(I), °	71.89	71.51	120.00
	φ_1(II), °	124.36	122.61	132.73
	φ_2(II), °	124.37	122.13	82.22
	φ_3(II), °	111.27	115.26	145.04
	Def_N(II), °	17.46	9.48	75.56
B	φ_1(I), °	95/93	123.57	97.74
	φ_2(I), °	124.62	95.77	97.78
	φ_3(I), °	139.45	140.66	164.48
	Def_B(I), °	48.14	48.45	88.96
	φ_1(II), °	123.88	120.98	132.65
	φ_1(II), °	123.87	124.01	97.03
	φ_1(II), °	112.24	115.01	130.33
	Def_B(II), °	15.52	9.98	45.94
	Def, °	38.25	34.86	82.62

of which the layers are formally not ideal and significantly deformed (Fig. 1). This is due to the nonequivalence of the atomic positions in which the boron and nitrogen atoms are located. The coordinates of atoms in the unit cells of boron nitride polymorphs are shown in **Table 2**.

As parameters characterizing the structure of the layers, the lengths of interatomic distances in the boron nitride layers and the angles between the bonds were also determined, the values of which are given in **Table 3.** The structure of boron nitride BN-L$_{4\text{-}10}$ is characterized by the lengths of three types of bonds for each atomic position and varies in range from 1.4059 Å to 1.5318 Å, and the angles between bonds vary in the range from 82.22° to 165.98°. The maximum and minimum bond lengths are observed for the BN-L$_{4\text{-}10}$ monolayer, which indicates strong deformations of the structure of this layer. To assess the degree of deformation of the layer structure, the values of the deformation parameters were calculated, which were found as the sum of the moduli of the differences in the angles between bonds and the equilibrium value of the angle of 120° in an ideal hexagonal structure. The range of variation of the deformation parameters (Def(I) and Def(II)) of various atomic positions is from 45.94° to 120.00°. The maximum average value of the deformation parameters (Def) equal to 82.62° is observed for the BN-L$_{4\text{-}10}$ layer, for the remaining layers the deformation is more than two times less (Table 3). This indicates that layers BN-L$_{4\text{-}6\text{-}8a}$ and BN-L$_{4\text{-}6\text{-}8b}$ have a less deformed structure and should be more stable compared to layer BN-L$_{4\text{-}10}$. This is confirmed by the fact that the calculated value of the sublimation energy E_{sub} for the BN-L$_{4\text{-}10}$ layer is minimal and amounts
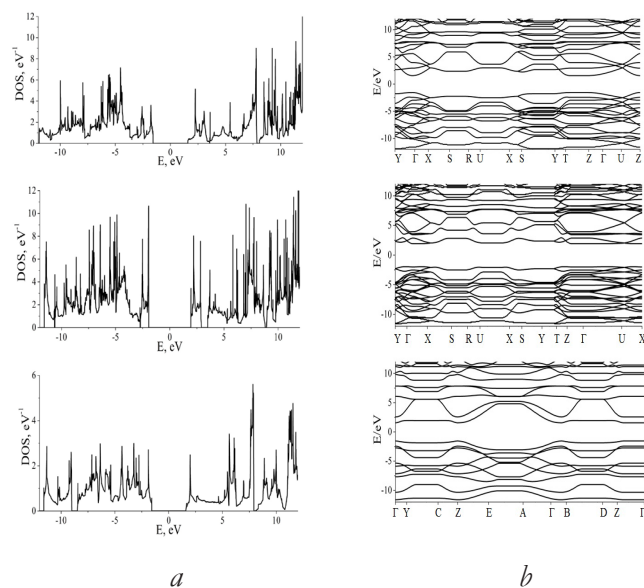
a *b*

Fig. 2. *Density of electronic states (a) and band structure (b) of new layered BN polymorphs.*

to 16.67 eV/(BN), i.e. about 5 percent less than the sublimation energy of other layers (Table 1).

The results of DFT-GGA calculations of the electronic structure of new polymorphic varieties of boron nitride are shown in **Fig. 2**. A band gap is observed in the images of the band structure of BN layers and graphs of changes in the density of electronic states at the Fermi energy (E_F) level, whose width varies from 3.156 eV for the BN-L$_{4-6-8a}$ layer, to 3.896 eV for the BN-L$_{4-6-8b}$ layer. This indicates that the conducting properties of boron nitride layers must be semiconducting and the band gap in them can vary depending on the features of the structure.

4. CONCLUSION

As a result of theoretical studies of the structure and properties of new polymorphic varieties of boron nitride monolayers, the possibility of stable existence of three layers - BN-L$_{4-6-8a}$, BN-L$_{4-6-8b}$ and BN-L$_{4-10}$ - was established. The structure of the BN-L4$_{-12}$ layer turned out to be unstable during geometric optimization. Of the three layers with a stable structure, the maximum sublimation energy (17.61 eV) and the minimum value of the deformation parameter (34.86°) are observed for the BN-L$_{4-6-8b}$ layer, which, apparently, should have the highest

stability, and it is precisely this layer that should be attempted to be synthesized experimentally. Firstly new polymorphs of boron nitride with a layered structure can find practical application in nanoelectronics [16].

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