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Boron Monolayer χ_3-type. Formation of the Vacancy Defect and Pinhole

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This research is focused on a local vacancy defect formation and pinholes formation in a two-dimensional boron structure – boron monolayer χ_3 - type. The main characteristics of defects formation have been carried out by using the semi-empirical quantum-chemical scheme MNDO. The variants of atomic configurations which give pinholes defect have been found.

Keywords: Boron monolayer, Pinhole, Vacancy formation, Theoretical research.

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1. INTRODUCTION

Among known elements in nature, just a few can exhibit multiple forms of low-dimensional allotropic structures, such as 0D cage molecules, 1D nanotubes, or 2D sheets. Carbon is an exception as all three low-dimensional allotropes of carbon, including 0D fullerenes, 1D carbon nanotubes, and 2D graphene monolayer sheet, and all of them have been isolated in the laboratory. In fact, graphene, a monolayer of carbon with a honeycomb lattice structure, is the first planar (i.e., unbuckled) sheet revealed in nature. However, recently, an element has joined it is near neighbor carbon – boron. In 2004 the first pure single-walled boron nanotubes have been synthesized, and in 2015 scientists from the Stony Brook University have had success with two-dimensional boron synthesizing [1, 2]. So, the second two-dimensional material which consists from one type of element has been discovered. That is why now the interest in boron nanostructures has increased. Nowadays, many research teams and laboratories are engaged in the research connected with boron nanostructures.

The uniqueness of this element (B) is the ability to form both ionic and covalent bonds. The boron atoms can form chained frames, lattices etc. Boron nanostructures are able to create a large variety of structures, because of polymorphism [3-6].

In this paper the object of our research is two-dimensional boron. We have chosen one of the low-energy structures of boron monolayer sheets – the boron monolayer χ_3-type [7] (figure 1).

The aim of this study is to investigate the process of vacancy defect formation, and the ability to form pinholes on the surface of the boron monolayer χ_3-type.

It is known that even the point defects affect the physical-chemical properties of materials, this ability can be used in many fields of nanotechnology, producing materials with predetermined parameters. But more than that, the pinholes materials with regular lattice structures can use as a template or matrix for the growth of periodic bumps nanostructures – nanotubes [8].

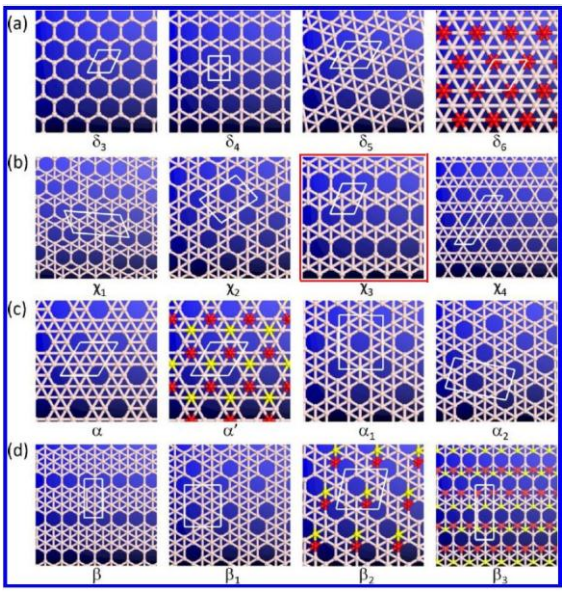

Fig. 1 - Families of low-energy boron monolayers: (a) δ-, (b) χ-, (c) α-and (d) β-types, respectively. Red and yellow balls denote boron atoms moving outward or inward from the plane, resulting in buckled boron sheets [7].

2. VACANCY DEFECT FORMATION ON THE SURFACE OF BORON MONOLAYER χ_3 - TYPE

The calculations are carried out within the model of the molecular cluster with the use of quantum chemical MNDO scheme [9]. Molecular cluster model works correctly with local objectives, which include the formation of a single vacancy. The cluster of boron monolayer consists of 103 boron atoms. Uncompensated chemical bonds on the ends of the cluster have been completed by hydrogen atoms. The length of B-B bonds is equal to 1,67 Å. This data was obtained after total parameters optimization of structures and they are in good agreement with previously obtained value of bond lengths of similarly boron structures [10]. The fragment of boron monolayer χ_3-type with marked defect localization is shown on Fig. 2.

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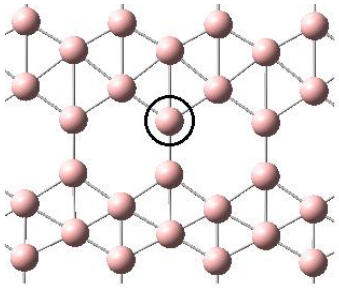

Fig. 2 – The fragment of boron monolayer χ_3-type. Circle indicates the location of future vacancy

To model the process of vacancy formation, a central B-atom has been moved from the surface of boron monolayer along the perpendicular to it with a step of 0,1 Å until the moment of separation.The geometry of boron structure has been optimized at each iteration.

As a result, we obtained a potential energy profile of the vacancy formation process shown in Fig. 3. It is the functional relationship between the potential energy of boron monolayer and the distance "boron monolayer - break-out atom B" (Fig. 3).

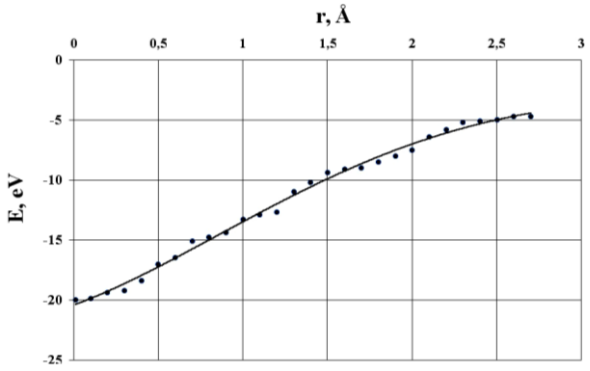

Fig. 3 – Energy curve for vacancy formation process for boron monolayer χ_3-type

Energy of defect formation has been calculated by the formula (1):

$$E_d = E_m - (E_v + E_B), \quad (1)$$

E_d – energy of defect formation,
E_m – energy of ideal boron monolayer χ_3 – type,
E_v – energy of boron monolayer χ_3 – type with vacancy,
E_B – energy of single boron atom.

The energy of vacancy defect formation is equal to about 14, 9 eV.

The analysis of parameters optimization during the vacancy formation process has been carried out. It showed that B-B bonds have been broken when the atom B located on the 0,7Å above the monolayer. After this, the adjacent atoms which surround the vacancy, started to displace the vacancy direction. Intermolecular interaction between boron monolayer surface and boron atom have completely disappeared at a distance of about 2,6 Å from the surface of boron monolayer to boron atom. So, the structure with vacancy has stayed planar but with restructured B-B bonds near defect localization. We can see instead of removed atom B two irregular pentagons which are shown on Fig. 4.

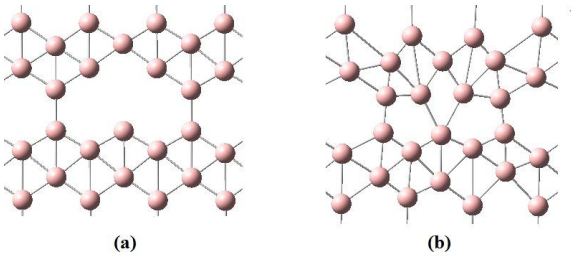

Fig. 4 – Fragment of boron monolayer χ_3 – type with vacancy defect: a) without parameters optimization, b) after parameters optimization

3. PINHOLE FORMATION ON THE SURFACE OF BORON MONOLAYER χ_3 – TYPE

Next step of our research was to study pinholes formation on the boron monolayer surface. To understand what case to give us surface defect which we could call a pinhole we considered four variant of boron atom configurations which have been removed from the boron surface:

1. two boron atoms have been removed from the boron surface. The number of B-B bonds connecting the atoms is six;
2. two boron atoms have been removed from the boron surface. The number of B-B bonds connecting the atoms is seven;
3. three boron atoms have been removed from the boron surface;
4. four boron atoms have been removed from the boron surface.

All considered variants are shown in figure 5.

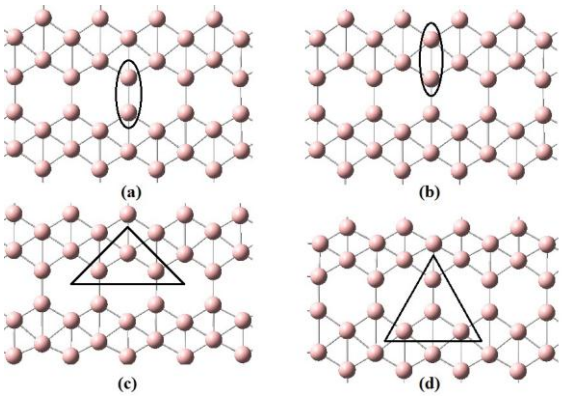

Fig. 5 – Configurations of boron atoms which have been removed from the boron surface: a) variant 1; b) variant 2; c) variant 3; d) variant 4

The model of the process of pinhole formation was analogical to vacancy formation. Configuration of boron atoms have been moved from the surface of boron monolayer along the perpendicular to it with a step of 0,1 Å until the moment of separation. So, when the first atoms configuration variant has been moved to a distance where the interaction forces between surface and boron atoms are inessential and after full parameters optimization; we can see an irregular circle which has minimum and maximum diameters 5,40 Å and 6,17 Å respectively (Fig. 6b). This hole can be called a "pinhole" or "pore" because the parameters of it are almost two times bigger than the diameter of monolay-

er structure boron hexagon (d = 3,34 Å).

The second variant of atomic configuration has given us another kind of structural changes. After removing atoms and after full parameter optimization we can see two elliptical cells, which are perpendicular to each other. But their diameters are comparable with the diameter of a boron hexagon of a boron monolayer structure. That is why we can not call these kind of defects a "pinhole" or "pore".

When the three boron atoms have been removed from the surface (variant 3) this leads to reform B-B bonds of the structure, nearest the boron atoms that have moved from their positions and have made three irregular hexagons, the pinhole formation did not form (Fig. 8b). Removal of four boron atoms from the surface of monolayer leads to the formation of a circle of twelve boron atoms, the diameters of it are d_1 = 5,4 Å and d_2 = 5,6 Å, respectively (Fig. 9b).

Thus, we can conclude, that removal of boron atom groups (2-4 atoms) from the boron monolayer surface χ_3-type leads to the formation of topological defects, and in some cases to the pinhole formations (d ~ 0,5 nm). The planarity of the considered structure is not disturbed.

A potential energy profile of the defects formation process is shown in figure 10. If we compare the two variants of pinhole formation (1 and 4) we can see that the different of potential energy of this two variants is equal 13,8 eV. This result is predictable. It is easier to remove two boron atoms which are connected to the monolayer by six B-B bonds than four atoms which are connected to the monolayer by 12 B-B bonds. All energy curves are similar. The basic characteristics of the defect formation process are shown in the Table 1.

Table 1 – The basic characteristics of the defect formation process on the boron monolayer surface. E_d – energy of defect formation, E_c – cohesive energy, d – diameter of pinhole (defect)

	Configurations of the removal boron atoms			
	variant 1	variant 2	variant 3	variant 4
d_1 (d_1´), Å	5.40	3.01 (5.20)	4.80	5.40
d_2 (d_2´), Å	6.17	4.36 (3.74)	3.40	5.60
E_d, eV	19.90	25.30	24.40	33.70
E_c, eV	3.32	3.45	3.27	3.13

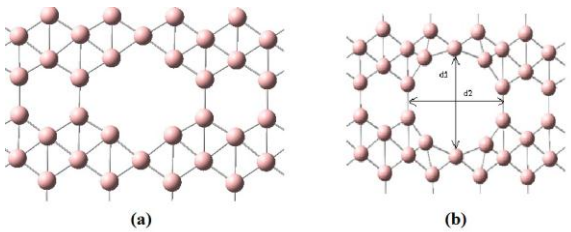

Fig. 6 – Boron monolayer with pinhole (variant 1): a) without parameters optimization, b) after parameters optimization

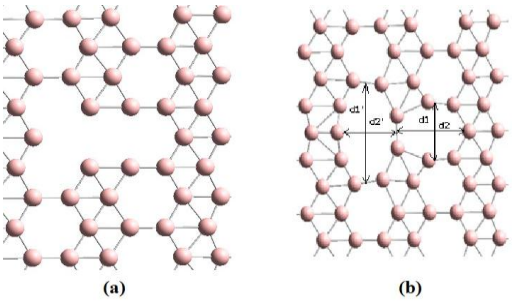

Fig. 7 – Boron monolayer with vacancies (variant 2): a) without parameters optimization, b) after parameters optimization

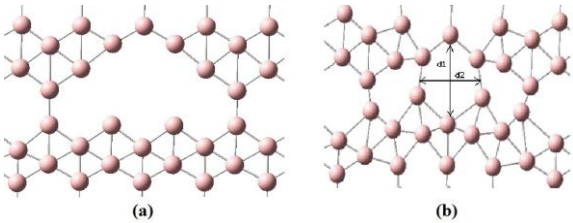

Fig. 8 – Boron monolayer with vacancies (variant 3): a) without parameters optimization, b) after parameters optimization

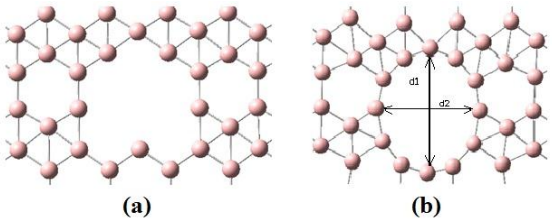

Fig. 9 – Boron monolayer with pinhole (variant 4): a) without parameters optimization, b) after parameters optimization

4. CONCLUSION

In this paper we studied the local vacancy defect formation and the pinhole formation on the surface of a two-dimensional boron structure - boron monolayer χ_3-type. Our calculations have shown that in some cases the removal of boron atoms could lead to pinhole formations (d ~ 0,5 nm) and structures with defect will stay planar and stable. The first variant of pinhole formation (two boron atoms have been removed from the boron surface. The number of B-B bonds connecting the atoms is six) is more possible. Pinholes in our structure are circles composed of 10 B or 12 atoms. We guess that one of the possible applications of this pinholes boron structure could be synthesis of nanotubes. Pinholes surface can be used as a matrix or template for future nanotubular structures such as boron, carbon or boron-carbon nanotubes.

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