Research of nanocomposite structure of boron nitride at proton radiation

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Abstract. Using roentgen diffraction and electron microscopy, the influence of nanosecond irradiation by ion beams of high energy on forming of self-organized nanoblocks in near surface's layers of boron nitride (BN) has been studied. It was shown that low temperature transitions from hexagonal to wrutz boron nitrides is associated with changes of shape and sizes of self-organized particles consisting the nanoblocks. We have calculated the parameters of nanoblocks using the meanings of interplane distances and properties of subreflexes orders. The collective shifting deformations of layers in nanoblocks provides phase transition under the screen and forming the set of nanotubes with escaping of five order axes of symmetry. It has been realized that pentagons and stars arranged in points of entrance of five order axis of symmetry are associated with peculiarity of self-organization of the spiral-cyclic structures.

1. Introduction
Due to the development of nanophysics, the investigations of origin and behavior of the self-organized nanoparticles and nanoblocks of various invariant scales have been carried out. The increasing number of nanoblocks is associated with wave, beam and other impacts of nano- and pica second action providing a low temperature atom shifts and distribution of high electron density band.

The appearing of nanoblocks might be a result of irradiation of the crystal compounds by nanosecond ion beams. Self-organization as a rule is observed in high packed and layered materials. In BN, graphite, SiC this effect could be obtained due to the large number of high packed planes [1-3]. In this work the regimes of creating of nanotubes and filling them by the doped substances was shown. It has been realized the influence of nanosecond irradiation by electron and ion beams on organization of nanotubes. It seems essential to study the impact of nanosecond ion irradiation to shape and linear size of nanoblocks and nanotubes in near-surface region of BN.

2. Experimental methods
The BN plates obtained using pyrolytic methods from chemical clear B and N. It is well-known from the electronic-microscopic dates that in original BN hexagonal phase composes up to 98 percent of the volume, the rest is rhombohedral one. The irradiation was carried out by ion beams of 120–250 KeV and with density 80 A/cm² and time 20–100 ns using the screen made up from foil W of 0.5 mm. thickness restricting the irradiational zone. The roentgen investigations were carried out on diffractometr DRON-3 in Cu-Kα flux. The method of non-focused lau grams was used to
reconstructing the thin subreflex structure. The sample is shifted from the center of goniometer to the side of roentgen source and diffraction pattern was observed using motionless sample. In the roentgen-diffraction investigations by Shtolz the non-focused picture method was used. Microscopic investigations were earned out on electronic microscope EM-125K; the image which allow us to have information about phase composition was obtained in area 0.5–1.0 μm.

3. Numerical results
In original BN and in irradiated by the nanosecond ion beams one the complicated distribution of integrated intensity of diffractiveal stripes can be a result of complicated distribution of electron density in atomic planes (Figure 1). Uneven electron density could be associated with distribution of old nanoblocks and forming the new one. According to the geometry of subreflexes the dependence of interangle distribution can be written as:

\[ \Delta \varphi_0 \tau^0, \Delta \varphi_0 \tau^1, \Delta \varphi_0 \tau^2; \]

\[ \Delta \varphi_0 \tau^0, \Delta \varphi_0 \tau^1, \Delta \varphi_0 (1/2 \tau^2), \Delta \varphi_0 (1/3 \tau^2), \]

where \( \Delta \varphi_0 \) – minimal interangle distance; \( \tau = 1.618 \) - gold number.

![Figure 1. Thin diffraction reflex (002) structure of original (a) and irradiated (b) BN.](image)

The experimental dates of parameters of nanoblocks along the planes [110] and [001] are presented in table 1 taking into account the expressions (1) and (2). Using the experimental dates of interplane distance between the high intensity stripes, the size of nanoparticles- is calculated from the following expression:

\[ A = d_{\text{max}} N^{\frac{1}{2}} \tau^{1/6} K^{1/3} \]

where \( N = H_2 + K^2 + L^2 \) – is the sum of square indexes of high packed plane;

\( K \) - is a shape coefficient of nanoparticles (\( K_{\text{cub}} = 1; K_{\text{oct}} = 0.4714; K_{\text{tet}} = 0.1222179 \)).

The numerical meanings of nanoblocks were obtained according to the model of nanoparticles and their scaling in accordance with Fibonacci sequence. As shown in table 1, use of octahedral nanoparticles of 0.46 nm size can effects on that nanoblocks have the sizes closed to theoretical. The larger nanoblocks in terms of their sizes are formed along the plane (001) and part of these blocks are in self-organized sequences with self-similar transitions. However the experimentally observed nanoblocks of sizes 3.1, 3.9, 4.2 and 11.6 nm prevent the realization of such transitions. Using
topographical observations by Shtolz, the distribution of nanoblocs of size 1–20 nm rightly arranged is observed.

The processing of origin BN by nanosecond ion beams of high energy is accompanied by forming of new wrutz BN phase. A dependence of BN volume has clear minimums of 1.6, 3.2, 4.8 and 7.9 μm depth. The changes in structure are shown also in a distance up to 15 mm under the protective screen from the irradiation zone. Low temperature transition $\text{BN}_G \rightarrow \text{BN}_W$ is concerned with reduction of nanoparticle's linear size on $\Delta a = 0.009$ nm, shifts deformations and formation of nanotubes.

The formation of nanotubes in BN in an enough distance from the irradiation area and modifications in arrangement of spherical packets of nanotubes are proved by the electron-microscopic investigations (Figure 2a). The correlation between the sizes of nanofube's packets and their density in sample and far from irradiation area was shown in table 2. It was noted that the size of the packets of nanotubes becomes smaller and their contribution is decreased and becomes 45 percents on depth of 0.2 μm and 15 mm from the area of irradiation. On a depth of 50 μm the packets of nanotubes in BN of five order symmetry as pentagons of size 32 nm become packets in form of stars of size 62.5 nm in a depth of 500 μm. The mechanism of nanotube's formation in BN is associated with particularities of self-organization of spiral-cyclic structures [4]. The experimental results of block formation in such self-organized structure with axis of five order symmetry can be observed on Figure 2b.

**Figure 2.** The formation of stars in the points of L5 axis escaping on electron-microscopic picture (a) and under the packing of bright blocks in self-organized structure (b); 1,2,3,4,5 – various levels in which the stars appears.
Table 1. The sizes of nanoblocks in BN<sub>w</sub>

| Plane         | (110) | (001) |
|---------------|-------|-------|
| \(a_{\text{exper.}}, \text{nm}\) | 1.37  | 2.614 | 9.596  | 3.66  | 6.40  | 1.156 |
| Step of Fibonacci sequence \(a_{\text{calc.}}, \text{nm}\) | 3     | 4     | 7     | 5     | 6     | 7     |
|               | 1.365 | 2.275 | 9.555 | 3.64  | 5.915 | 9.555 |

Table 2. The arrangement of spherical packets of nanotubes in BN<sub>w</sub>

| Parameters of nanofube's packets | Original | The distance from the irradiation area, mm |
|----------------------------------|----------|---------------------------------------------|
| Size, \(d, \text{nm}\)          | 8.4      | 82                                           | 64.5 | 6.6 |
| \(d_{\text{max}} (d_{\text{min}})\) | 600 (37.5) | 250 (37.5)                                  | 87.5 (50) | 87.5 (50) |
| Volume fraction, \(\Delta V,\%\) | \(-1.0\)  | 35–45                                       | 3–5  | \(\leq 1.0\) |

4. Summary
The irradiation of hexagonal BN by nanosecond ion beams accelerates in near-surface layer the phase transition and formation of nanoblocks characterized to wrutz-like BN. It was shown that a phase transition is reached on the distance far from the irradiation area and accompanied with formation of nanotubes with escaping of five order symmetry axis on the surface. The appearance of nanotubes is associated with collective shift deformations of nanoblocks and it occurs in the self-organization of spiral-cyclic structure.

References
[1] Kiang Ch H, Goddard W A, Beyers R et. al. 1996 J. Phys. Chem. 100 3749–52
[2] Golberg D, Bando Y 1996 Appl. Phys. Lett 69 2043-47
[3] Borodin Y 2011 Proceedings of the 6th International Forum on Strategic Technology, IFOST 2011 1 218–21
[4] Horiuchi S 1995 Jap. J. Appl. Phys. Pt.2 34 Nu 12 A 1612–15