Influence of nanosecond laser irradiation on the structure and conductivity of \( \text{BC}_x \) films

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Abstract. Thin-film precursors of \( \text{BC}_x \) were formed by pulsed laser codeposition of boron and carbon. Targets made of pressed boron and carbon powders with an equal element content (\( \text{B/C} = 1/1 \)) and an increased carbon content (\( \text{B/C} = 1/3 \)) were used. The films were deposited on sapphire substrates at elevated temperature (700\(^\circ\)C) which determined the initial properties of the precursor \( \text{BC}_x \) films. Irradiation of the films was carried out by laser pulses of nanosecond duration with varying intensity. The films obtained by laser annealing of \( \text{Q-BC}_x \) were studied by scanning electron microscopy and micro-Raman spectroscopy. Irradiation under optimal conditions made allowed to realize pulsed melting of the films and partial preservation of their continuity on the substrate. The local structure of \( \text{Q-BC}_x \) films and the nature of the changes in their electrophysical properties depended on the composition of the precursor films and the laser irradiation regimes.

1. Introduction
Thin films of \( \text{BC}_x \) attract the interest of researchers from various fields of science and technology, since they can have a whole complex of interesting and useful properties \([1,2]\). Particularly, the interest in this thin-film material increased after the discovery of superconductivity which is established for the metastable modification of \( \text{Q-BC}_x \) \([3,4]\). This modification is formed by pulsed laser melting of the films that initially consisted of alternating layers of boron and diamond-like carbon. The mixing of the film components proceeded in highly non-equilibrium conditions of the superheated liquid phase, and the superconducting phase was formed as a result of quenching of a highly supercooled liquid phase/alloy.

Due to the appearance of new important information on the superconducting properties of \( \text{Q-BC}_x \) films, there is an increasing interest to find more controlled and reproducible methods for obtaining continuous and smooth films of \( \text{BC}_x \) with superconducting properties. The aim of the work was to study the influence of the nature of the thin-film precursor \( \text{BC}_x \) on the character of structural and
electrophysical changes under the action of laser pulses of nanosecond duration. For this research, BC$_x$ films of various structure and composition were created by pulsed laser deposition (PLD) at elevated temperature.

2. Experimental methods

Pulsed laser deposition of BC$_x$ films was carried out from targets containing microparticles of diamond and boron, up to 5 $\mu$m in size. The atomic ratio of the elements in one B-C target was B/C = 1/1 (the target with a high concentration of B) and another B-C target was enriched with carbon (B/C=1/3). Targets were ablated by laser pulses with a wavelength of 266 nm in a vacuum chamber at a pressure of $\sim 10^{-3}$ Pa. The radiation energy of laser pulses of nanosecond duration (~ 10 ns) was 40 mJ. After focusing the radiation on the targets, the fluence reached 7 J/cm$^2$. The films were deposited on sapphire substrates, the temperature of which was $\sim 700^\circ$C. The thickness of the prepared films was approximately 100 nm.

The obtained BC$_x$ films were irradiated by the pulses of the same laser in air at room temperature of the substrate. The intensity of irradiation was reduced, and it was varied in the range 0.1–1 J/cm$^2$. The structure and composition of the films before and after irradiation was studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), and micro-Raman spectroscopy (MRS). The wavelength of the analyzing laser radiation was 532 nm. The registration time varied from 2 to 10 min. To obtain additional information on the structure of the precursor BC$_x$ films obtained by the PLD, very thin films were studied by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Very thin films were deposited on NaCl crystals and transferred to metal grids for TEM analysis.

The electrical properties of the films were measured by a four-contact method in the van der Pauw geometry. Contacts to the sample with a circular mesa were formed from the InSn alloy, the linearity of the volt-ampere characteristics of all contacts was monitored. The assembled samples were placed on the insert in the cryostat, the resistance of the sample was measured by successive heating in the temperature range 4–300 K. The temperature was measured by a calibrated Lakeshore sensor. During the measurements, the direction of the current was switched to eliminate the effects of thermoelectric power. The resistivity was calculated by averaging the values from all pairs of contacts.

3. Results and discussion

Figure 1 (a) shows results of the SEM study of the morphology of BC$_x$ film obtained from the target B/C=1/3. For this target, relatively smooth films with a small number of particles of submicron sizes were formed. Laser irradiation of the deposited films caused the surface to melt (figure 1 (b)) that manifested itself in a change in the topography of the sample surface. For an area of reduced fluence

![Figure 1](image_url)  

**Figure 1.** SEM images of BC$_x$ film prepared from the target B/C=1/3: (a) – after preparation by PLD; (b) – after pulsed laser irradiation. Zones A and B are discussed in the text.
irradiation, the film remained continuous (Zone A), and for an area of increased fluence of irradiation, film breaks (Zone B) were detected. EDXS studies showed no change in the B/C ratio after laser irradiation. Figure 2 (a) shows the results of the SEM studies for the film obtained by ablation of the target B/C = 1/1. When using a target with a higher concentration of B, the deposited films contained many particles of submicron and micron sizes. Laser irradiation caused melting and mixing of submicron-sized particles with the main material of the film (figure 2 (b)). However, micron-sized particles retained a rounded shape after laser irradiation and were partially incorporated into the film matrix. According to the EDXS studies (scanning was carried out over a sufficiently large area), the chemical composition of the films was preserved after laser irradiation.

TEM studies of a very thin BC\textsubscript{x} films showed (results not presented) that they had a homogeneous amorphous structure. According to EELS analysis, the concentration of diamond-like sp\textsuperscript{3}-bonds reached 80%. The boron atoms were embedded in an amorphous matrix of the film, forming a solid solution of B-C.

![Figure 2](image)

Figure 2. SEM images of the BC\textsubscript{x} films prepared from the target B/C=1/1: (a) – after deposition by PLD; (b) – after pulsed laser irradiation.

Figure 3 shows the MRS spectra measured before and after laser irradiation of the BC\textsubscript{x} films obtained from the two B-C targets. Spectra, which corresponded to areas irradiated with low (LF) and high (HF) fluence, differ only a little. The spectra of the as-deposited and laser irradiated films strongly depended on their composition. The appearance of relatively narrow lines on the spectrum of the film enriched in carbon (figure 3 (a)) indicated that after irradiation the structural state of the film became more equilibrium than immediately after the PLD. For the BC\textsubscript{x} film possessing approximate equal concentrations of B and C, laser irradiation did not cause strong changes in the MRS spectra (figure 3 (b)).

![Figure 3](image)

Figure 3. MRS spectra for as-deposited and laser irradiated BC\textsubscript{x} films. The films were prepared by PLD from B/C=1/3 (a) and B/C=1/1 (b) targets.
Figure 4 shows the results of a rigorous mathematical processing of some of the MRS spectra, based on published data on the analysis of B-C materials by the MRS method (for example, [5-7]). The model spectrum of as-deposited film enriched in carbon (the target B/C=1/3) contained several lines, which could be due to the following factors (figure 4 (a)). The lines at 270, 645, 810, and 1040 cm$^{-1}$ were determined by singularities in the phonon density of states. The lines at 1325 and 1560 cm$^{-1}$ corresponded to the D and G states and were shifted from the characteristic positions due to disordering and introduction of boron. The line at 1470 cm$^{-1}$ was due to hydrocarbons. After irradiation with high fluence, the spectrum contained two lines at 1337 and 1570 cm$^{-1}$, which corresponded to D and G lines displaced due to the structural features of the film. The lines at 1470 and 1135 cm$^{-1}$ were caused by hydrocarbons.

Figure 4. (a, b) – deconvolution of the MRS spectra for the BC$_x$ film enriched with carbon before (a) and after (b) pulsed laser irradiation; (c) – deconvolution of MRS spectrum for a boron enriched BC$_x$ film, illustrating the states which arise after the pulsed laser irradiation of the film.

Figure 4 (c) shows the result of processing the MRS spectra for an enriched in boron BC$_x$ film (the target B/C=1/1). For the difference spectrum obtained by subtracting the spectrum of the as-deposited film from the spectrum of the irradiated (HF) film, three lines were revealed. There were G (1552 cm$^{-1}$) and D lines (1331 cm$^{-1}$), as well as a line at 1054 cm$^{-1}$ which characterized the changes in the phonon density of states.

The characteristic results of measuring the resistance of BC$_x$ films before and after laser irradiation are shown in figure 5. As-deposited BC$_x$ films possessed semiconductor–type conductivity. The resistance of the films increased with decreasing temperature. After laser irradiation of a carbon-enriched film, the temperature dependence of the resistance was generally preserved, however, at very low temperatures, the effect of decreasing resistance was observed. After laser irradiation of the film enriched with boron, a metallic type of temperature-resistance dependence appeared in the range of 50–300 K. At temperatures below 50 K, a sharp increase in the resistance of the film was observed.

Figure 5. (a) – dependence of the resistivity of the carbon enriched BC$_x$ film (target B/C=1/3) on the temperature; (b, c) – the temperature dependence of the surface resistance after laser irradiation of the films BC$_x$ obtained from the targets B/C=1/3 and B/C =1/1, respectively.
4. Conclusions
Pulsed laser irradiation of amorphous BC\textsubscript{x} films caused a decrease in the degree of nonequilibrium of the state which was formed by pulsed laser deposition on a sapphire substrate heated to 700°C. This is manifested in an increase in the contribution of graphite-like carbon bonds in both the enriched in carbon BC\textsubscript{x} and containing high concentration of boron BC\textsubscript{x}. For the BC\textsubscript{x} films enriched in carbon, the semiconductor type of conductivity is retained after pulsed laser irradiation. However, for them, a drop of resistance is possible at very low temperatures. The BC\textsubscript{x} films enriched with boron showed a metallic type of conductivity after pulsed laser melting. Such behaviour was broken at 50 K and manifested itself in a sharp increase in film resistance.

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