Magnetron sputtering and electron beam evaporation systems for pure boron thin film coatings

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Abstract. Deposition of boron-containing coatings is determined by their promising use for surface modification goals. In this work, we consider the equipment for the implementation of two plasma methods for the deposition of thin films of pure boron on the surface. These are a magnetron sputtering with a crystalline boron target heated in the discharge, and a system of an evaporation of pure boron target by an electron beam generated using forevacuum plasma source. The features of functioning, and operating parameters of these devices are presented. The deposition rate of boron coatings on the samples was about 20 nm/min for magnetron sputtering. The boron film deposition rate was significantly higher and reached 1 µm/min.

1. Introduction

Interest in obtaining boron-containing coatings is determined by the prospects of their use for goals of modifying the surface properties of a wide range of parts and equipment. First of all, boron-based coatings are resistant to mechanical wear [1, 2], corrosion [3], have significant thermal stability [4] and a low friction coefficient [5]. Boron-containing coatings have high hardness [6]. For example, the hardness of wurtzite boron nitride is comparable to the hardness of natural diamond [7]. In addition, the stable isotopes of boron ¹⁰B and ¹¹B have specific nuclear properties. For example, the cross section for the reaction of thermal neutron capture by the ¹⁰B boron isotope nucleus is anomalously large and amounts to 4 kb [8]. Therefore, coatings based on this boron isotope are promising for the creation of neutron detectors [9], a burn-out absorber of the core of a nuclear reactor [10]. Pure boron thin films are attractive for application as protective layers in thermonuclear fusion devices [11], elements in electronic devices [12, 13] and extreme ultra-violet optics [14]. Thus, the development of boron-based coating methods is an important task for science and applications.

Currently, several plasma methods are used to deposit boron films and boron-containing coatings. First of all, this is a deposition of coatings from the plasma of boron-containing gaseous compounds, the ionization of which is carried out in direct current (DC) [15] or high-frequency discharges [16]. The main disadvantages of this approach are that such compounds, as a rule, are toxic and chemically aggressive, as well as the fact that the composition of the boron coating is contaminated with foreign impurities formed during the decomposition of volatile boron compounds. For plasma deposition of boron-containing coatings, it is possible to use the vacuum arc method [17]. However, since the resistivity of solid boron is about 10 MOhm·cm, which is not enough for the functioning of the...
vacuum arc. But the resistivity of conductive boron compounds, such as, for example, lanthanum hexaboride, is 10 µOhm×cm, and such boron compounds are usually used for stable functioning of the arc [17]. The disadvantages of this approach are the presence of impurities in the coatings and the need to use special filters to purify the plasma from the macroparticle fraction generated of the vacuum arc [18]. To deposit boron coatings, a radio-frequency magnetron sputter with pure crystalline boron target can be used, but deposition rate for such devices is relatively low and amounts to a few nanometers per minute [19]. The implementation of the processes of evaporation and ionization of boron by electron beams is hampered by low electrical conductivity of the target material made of pure boron, which, in turn, makes it difficult to focus the beam on it, due to the electrical charging of its surface by the beam.

This article discusses the equipment for the implementation of two plasma methods developed by us for depositing thin films of pure boron to the surface. The first is the use of a magnetron with a heated target made of pure crystalline boron, in which its specific resistance decreases to a value at which the magnetron discharge can function normally [20]. The second is the use of a fore-vacuum source of electrons for heating a pure boron target and its evaporation. When the source is operating, the surface charge of the target, induced by the beam, will be neutralized by the dense plasma formed by the electron beam [21].

2. Magnetron sputtering device for pure boron coating

For stable operation of a pulsed planar magnetron with a target of crystalline boron, first of all, it was necessary to provide its sufficient electrical conductivity. This was realized by heating the target using a special design and a circuit for supplying the discharges of the magnetron sputter (Fig. 1). The heat-insulated crystalline boron target used in the magnetron sputter had a diameter of 50 mm and a thickness of 3 mm. Thermal insulation of the boron target from the water-cooled holder which contains permanent magnets inside was carried out using a spacer made of expanded graphite 0.6 mm thick and 5 mm wide, placed on the edge of the boron target. Since the expanded graphite is an elastic springy electrically conductive material, the spacer provided good electrical contact between the target and the holder at cathodic potential.

To heat the boron target, before turning on the main pulsed discharge, a low-current direct current discharge with a current of up to 50 mA was switched on when a constant voltage of 2 kV was applied between the target and the magnetron anode. When the working gas (argon, krypton) was supplied to the discharge gap of the magnetron sputter at a flow rate of more than 20 sccm and the pressure in the gap increased to 50 mPa, a low-current DC auxiliary magnetron discharge was ignited in the gap. Initially, the magnetron discharge current was limited by the electrical conductivity of the boron target and amounted to about 1 mA. At the same time, this discharge began to heat up the target, while the target resistance decreased, and the auxiliary discharge current increased. Approximately 2–3 minutes later, the auxiliary discharge current reached a value of 20-50 mA, and the target temperature increased to 870 K, at which its resistivity decreased to a level of about 1 Ohm×cm [22]. Ensuring sufficient conductivity of the heated boron target made possible the ignition and stable operation of a pulsed high-current magnetron discharge.
After heating the target with an auxiliary DC discharge, an adjustable pulse-periodic voltage of up to 2 kV was applied to the magnetron gap with an adjustable pulse repetition rate from 1 to 25 p.p.s. and adjustable pulse duration from 50 to 400 µsec. This ensured stable combustion of a pulsed high-current magnetron discharge with a current pulse amplitude of 10–40 A. It should be noted that during a pulsed magnetron discharge exists at a pulse repetition rate of 10 p.p.s. and higher, with a current amplitude of more than 20 A and a pulse duration of more than 200 µsec, the target temperature could be maintained only by a pulsed discharge, and there was no need for continuous operation of a continuous auxiliary discharge. The deposition rate of boron coatings on the samples was about 20 nm/min.

3. Electron beam boron deposition system
A forevacuum plasma source of electrons was used to deposition pure boron coatings on the surface by electron-beam evaporation. [21]. The main feature of such an electron source was the possibility of its operation in pressure of about 10 Pa. At this pressure, the negative charge introduced by the electron beam onto the surface of the nonconducting target made of crystalline boron was neutralized by the flow of positive gas ions from the beam plasma. This, in turn, provided the possibility of focusing the electron beam on the target surface, its local heating and evaporation for deposition of boron film on a surface of the samples.

When a voltage of up to 2 kV was applied between the hollow cathode and a stainless steel anode and the working gas (argon, nitrogen, or helium) was supplied to the vacuum chamber, a glow discharge with a current of up to 1 A was initiated between these electrodes. The hollow cathode and anode were cooled by running water. The electron beam was formed by applying an accelerating voltage of 20 kV between the emission and accelerating electrodes. The beam current was up to 300 mA. He focused on a crystalline boron target using an electromagnetic lens. The diameter of the focused electron beam on the target surface, which was placed at a distance of 30 cm from the source, did not exceed 8 mm. In this case, the power density at the focus reached values of 10 kW/cm². This power density was sufficient to start the process of heating and evaporation of the pure boron target.
Figure 2. Scheme of the method of applying coatings from pure boron by electron-beam evaporation using a forevacuum plasma electron source.

The evaporated by electron beam from the target surface boron atoms partially ionized by the beam, and deposited on the surface of the experimental samples, which were located at a distance of 10 cm from the target to be evaporated. In this case, the surface temperature of the samples did not exceed 200°C. It was controlled by a high-speed optical pyrometer. To control the composition of the working atmosphere of the vacuum chamber during coating deposition, an RGA-100 analyzer was used. The mass-charge composition of the beam plasma was controlled by a quadrupole mass spectrometer. The deposition rate of boron coatings was significantly higher than in the case of using the magnetron sputter and reached 1 µm / min.

4. Summary
Equipment for the deposition of pure boron coatings on surfaces was created based on the method of magnetron sputtering and electron beam evaporation. The deposition rate of coatings on surfaces based on the first method was 20 nm / min, and that of the second, reached 1 µm / min. The described equipment will be used to obtain pure boron coatings, promising for use in modern electronic devices and extreme ultra-violet optics, and boron nitride coatings with high hardness, which are in demand for surface hardening tasks in the industry. The considered methods for obtaining pure boron coatings using magnetron discharge [20] and forevacuum electron source [21] are original and first implemented by the authors of the article. The analog of the first method can be considered a high-frequency magnetron discharge with a dielectric target [19]. In this case, the surface positive charge of the sputtering ions on the boron target is neutralized by the electron flux from the plasma with a pulse of reverse polarity. However, the rate of deposition of boron coatings in this case is several times lower than that obtained in this article. As for the method of deposition of boron during its evaporation by heating an electron beam, this method has not been used before, since beam focusing is impossible due to surface charging. This became possible only when using the fore-vacuum pressure range.

Since both pure boron and its compounds can have different crystal structures that form a large group of solid refractory compounds with very different physical, chemical, and mechanical properties, control of the structural-phase composition during the formation of boron-based coatings is of fundamental importance. To obtain coatings with high consumer properties, it is planned to conduct research using the deposition equipment presented in this work with in situ controls the film deposition process using synchrotron radiation of an anomalous scattering station of the Siberian Synchrotron and Terahertz Radiation Centre at Budker Institute of Nuclear Physics of Siberian Branch Russian Academy of Sciences.
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