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GENERATION OF BORON IONS FOR BEAM AND PLASMA TECHNOLOGIES

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The urgency of the study of generation of beams and plasmas containing boron ions is caused by their application in ion-beam and plasma technologies of modification of the surface properties of not only semiconductors, but also structural materials. This is due to the fact that boron compounds are hard and chemically resistant materials that can be used to create hardening and protective surface coatings for a wide nomenclature of details. The operating principle and the characteristics of the experimental setup developed for generation of plasma and boron ion beams intended for creation of such coatings are presented, including an ion source based on vacuum arc with separation of boron isotopes in a magnetic field intended for high-dose ion implantation, a plasma generator with boron target intended for obtaining coatings by magnetron sputtering, and a forevacuum electron source intended for synthesis of surface boron-containing coatings by electron beam evaporation.

Keywords: boron ions, plasma, ion implanter, electron beam evaporation, thin boron films.

INTRODUCTION

The urgency of the study of generation of plasma containing boron ions is caused not only by the interest to this problem of plasma physics, but also by practical application of plasma and boron ion beams for ion-plasma technologies. To generate the plasma containing boron ions, ionization of gaseous boron compounds or flows of materials containing boron are conventionally used. It is obvious that in these cases, to obtain pure boron ion beams, they must be preliminary separated from impurity ions, which is realized in ion implanters. The boron ion implanters are widely used in technologies of obtaining semiconductor wafers, and the ion sources used in them are the most perfect, but technically complex devices. Nowadays the modern modifications of the Freeman source are most often used in implanters to generate the boron ion beams [1]. For example, gaseous boron trifluoride (BF_3) is used as a plasma-forming substance in such sources. There are two problems in this method of boron plasma generation. First, the incandescent cathode of the source corrodes in the atmosphere of this aggressive gas, and second, boron trifluoride is sufficiently toxic. These special features complicate the use of such ion implanters for solving a wide range of problems of surface modification of structural materials. Previous studies [2] have shown that the use of the vacuum arc with pure boron cathode is promising. However, since boron is a wide band-gap semiconductor having specific resistance of about 2 MΩ·cm under normal conditions, for stable initiation and burning of the arc, the cathode heating

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to about 800°C is required, after which the specific boron resistance decreases to 1 Ω·cm. Such method of boron plasma generation in the vacuum arc has been used in [3, 4]; it is promising for ion-plasma technologies of material surface modification.

Generation of flows of sputtered boron atoms to obtain boron-containing coatings can be obtained in a high-frequency magnetron discharge with pure boron target [5]. However, the coating speed in this case is low and does not exceed several fractions of nanometers per minute. Over the last decade, considerable interest has been observed to investigations of the magnetron discharge in the mode of target *self-sputtering* [6, 7] in which the coating speed is significantly higher, and the fraction of ions of the target material in the arc plasma considerably exceeds the fraction of ions in the working gas. Realization of the magnetron discharge with heated boron target provided generation of boron ion plasma and its subsequent sputtering on the surface of details, including in the self-sputtering mode [8].

A flow of boron atoms and ions can be generated by evaporation of a pure boron target or a ceramic target on its basis by electron beam with subsequent ionization of the target material in this beam. The problem here is high electric resistance of the target. Its surface is charged by the electron beam that makes impossible the beam focusing and hence, effective heating. The developed electron source, operating in the forevacuum range of pressures up to 1 Torr [9, 10] allows the problem of charging of the target surface to be solved, because its electron charge is effectively neutralized by ions of the dense beam plasma with density of 10^{10}–10^{11} cm^{-3}. This makes it possible to use electron beams to deposit boron-containing coatings by the electron beam.

In the present work, the operating principle and the characteristic of the experimental setup intended for generation of boron plasmas and ion beams for surface modification and creation of boron-based hardening coatings are presented. The developed equipment comprises a vacuum arc source of ions with separation of boron ion isotopes in a magnetic field intended for high-dose ion implantation, a plasma generator with crystal boron target intended for deposition of coatings by magnetron sputtering, and a forevacuum plasma source of electrons intended for synthesis of the boron-containing surface coatings by electron beam evaporation.

SOURCE OF BORON ION BEAMS BASED ON THE VACUUM ARC

A circuit diagram of the vacuum arc source of boron ions is shown in Fig. 1. The vacuum arc was triggered at a residual gas pressure on a level of 10^{-6} Torr between pure crystal boron cathode *1* – the cylinder 10 mm in diameter and length of 8 mm – and hollow aluminum alloy anode *2* with internal diameter of 12 cm and length of 15 cm. The cathode spots of the vacuum arc were initiated on the surface of ceramic insert *4* by a high-voltage breakdown between cathode *1* and triggering tungsten electrode *3* with diameter of 1.6 mm. Spiral heater *5* made of tungsten wire 0.7 mm in diameter surrounding molybdenum cathode holder *6* was used for heating of cathode *1* to a temperature of 600°C to provide its sufficient conductivity during discharge triggering. Unlike the discharge initiation in vacuum arc ion sources with Mevva-type metal cathode [11], two discharges from independent power supply units *8* and *9*, connected in parallel, were used for triggering of the arc discharge on the boron cathode and maintenance of its stable burning during the entire arc pulse. Source *8* of discharge triggering had an output voltage of 15 kV, a pulse duration of 20 μs, and a pulse amplitude of 40 A. It was used to initiate the high-voltage breakdown between electrodes *1* and *3*. The breakdown current was subsequently supported by the pulse of an auxiliary supporting discharge from power supply unit *9*. The duration of this pulse (≈100 μs) was equal to the duration of the main vacuum arc pulse set by power supply unit *10* representing a forming *LC*-circuit. The voltage on source *9* was 3 kV for a pulse amplitude of 100 A on a load of 15 Ω. The pulse amplitude of the main vacuum arc was also 100 A at a charging voltage of 1.4 kV of the source forming network *10*. The use of the system with triggering and auxiliary discharges provided stable initiation of the arc with pure boron cathode and stable burning of the main arc during the entire pulse. A special feature of plasma generation in the vacuum arc with pure boron cathode is the formation of a significant number of macroparticles during arc burning. The fraction of macroparticles in the boron arc plasma decreased due to *multipoint* arc initiation using a tungsten fine-mesh grid instead of dielectric insert *4* and initiation of cathode spots in places of grid contact with the cathode surface.

The ion beam was formed using a three-electrode slot-hole accelerating-decelerating system. Diaphragm *7* placed at the input of the magnetic separator (see Fig. 1) *cut out* a portion of the ion beam with sizes 6 × 40 mm from

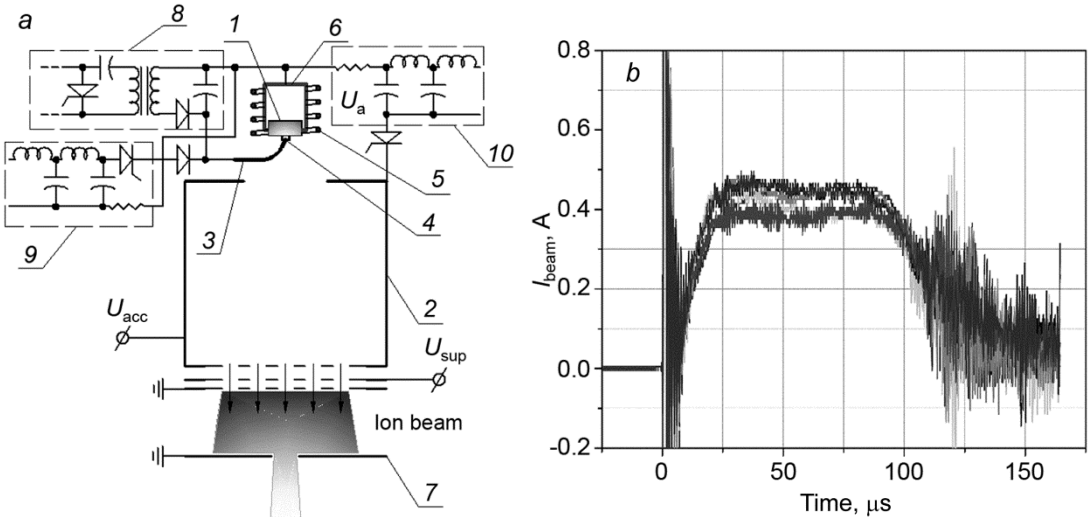

Fig. 1. Circuit diagram of the boron ion source (*a*) comprising cathode *1*, hollow anode *2*, trigger *3*, ceramic insert *4*, heater *5*, cathode holder *6*, diaphragm *7* at the magnet input, source *8* of high-voltage triggering, source *9* of the supporting discharge, and vacuum arc source *10*; and waveforms of its five subsequent ion beam pulses (*b*).

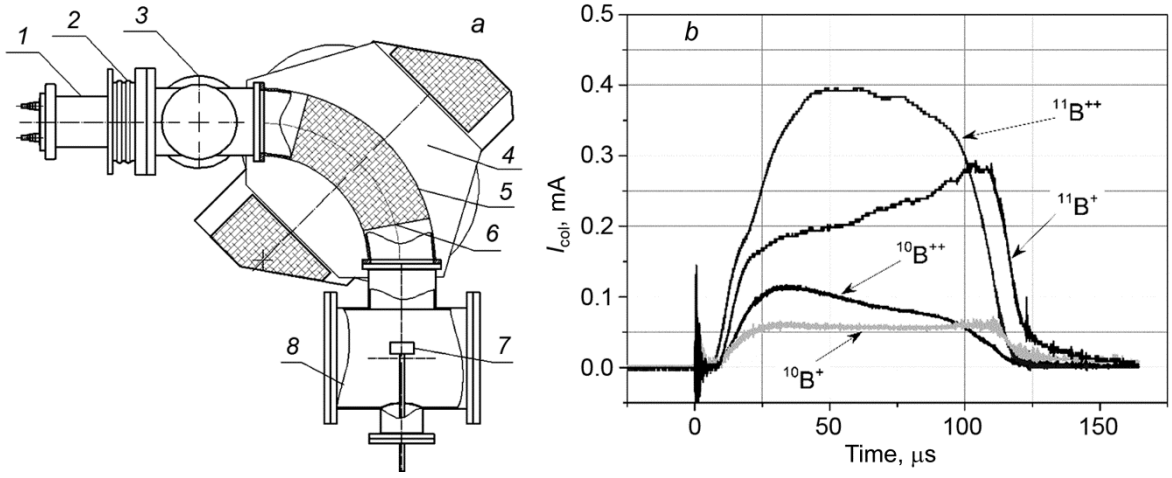

Fig. 2. Outline of the magnetic separator of the beam of boron ions (*a*) comprising ion source *1*, high-voltage insulator *2*, test chamber *3* of the ion source, separator magnet *4*, ion conductor *5*, central ion beam axis *6*, ion collector *7*, and output chamber *8*; and waveforms of current of isotopes of boron ions after the separator (*b*).

the total ion beam generated and accelerated by voltage up to 20 kV with current on a level of 400 mA. Then the beam passed through the deflecting magnetic field of the separator (Fig. 2*a*) in which ions moving along the Larmor radii deviated in accordance with their charge-to-mass ratios. The magnetic system of the separator provided separation of ions of boron isotopes ^{10}B and ^{11}B with charge states +1 and +2 and masses of 10 and 11 u, respectively. The pulses of these isotopes of boron ions are shown in Fig. 2*b*.

The alternative approach to generation of beams of boron isotopes in the vacuum arc is the use of the lanthanum hexaboride (LaB_6) cathode [12] instead of the pure boron cathode. Since LaB_6 possesses the conductivity comparable with that of metals, no preliminary heating of the cathode and no additional supporting discharge are

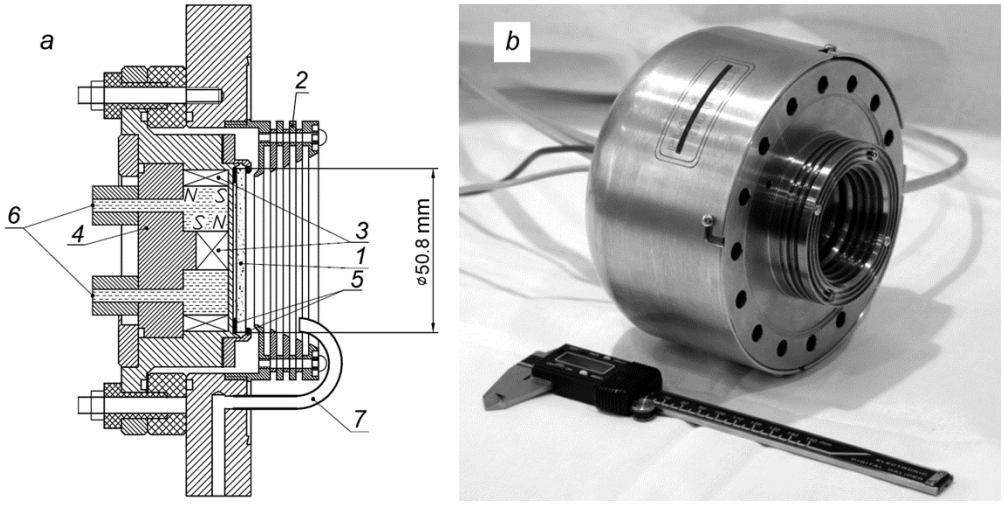

Fig. 3. Planar magnetron with crystal boron target comprising target *1*, multiple plate anode *2*, cylindrical permanent magnets *3*, magnetic circuit *4*, heat insulating gaskets *5*, water cooling channels *6*, and working gas inlet *7* (*a*); and external view of the setup (*b*).

required in this case. To initiate the vacuum arc, the triggering high-voltage discharge analogous to that realized in the Mevva sources [13] is sufficient. In this case, the total fraction of boron ions in the beam corresponds to the fraction of their atoms in the cathode material and is about 80%. With the use of the lanthanum hexaboride cathode and an arc current of 140 A [14], the beam boron isotopes with pulse amplitudes comparable with those for the pure boron cathode were obtained at the separator exit.

Separate implantation of ions of boron isotopes ^{10}B or ^{11}B into the target surface that can be performed on the developed equipment can be used to elucidate the influence of different boron isotopes on the change of the surface properties by high-dose ion implantation. The implantation of silicon with ions of isotope ^{10}B having anomalously high capture cross section of thermal neutrons of 200 b (for the isotope ^{11}B, this cross section is 0.005 b [15]) will make it possible to create a neutron flow detector. In this case, neutrons can be recorded by direct electric current measurements in the surface silicon layer arising in the course of the nuclear reaction ^{10}B (n, α) ^{7}Li.

PLANAR MAGNETRON WITH CRYSTAL BORON TARGET

An outline of the electrode and an external view of the planar magnetron with crystal boron target intended for deposition of boron-containing coatings are shown in Fig. 3*a* and *b*, respectively. For target heating, a continuous auxiliary discharge with current of 2 mA and burning voltage on a level of 2 kV were used. Thermal insulation of the boron target 50.8 mm in diameter with a thickness of 3 mm from the water cooling system of the magnetic field based on constant magnets was performed using two graphite foam rings between which the target ends were clamped. A special feature of the magnetron design was the anode with the developed surface made of a set of rings. Such design of the anode provided long lifetime of the setup after formation on its surface of non-conductive boron coating and allowed easily cleaning of the anode. Both the continuous mode of magnetron discharge burning with current up to 0.1 A and the high-current pulse mode of burning with amplitude of arc pulse up to 100 A, pulse duration 10–250 μs, and pulse repetition frequency from 20 Hz to 5 kHz were realized. The pulse repetition frequency was limited by the discharge power equal to 2 kV at which heat can still be removed from the electrodes of the discharge system during prolonged operation of the setup.

In the high-current pulse mode of magnetron discharge burning, the self-sputtering mode was realized [6], characterized by predominance of ions of the cathode material, in this case, boron ions, in the arc plasma. Our measurements of the mass-to-charge plasma fractions with a time-of-flight spectrometer [16] showed that boron ions

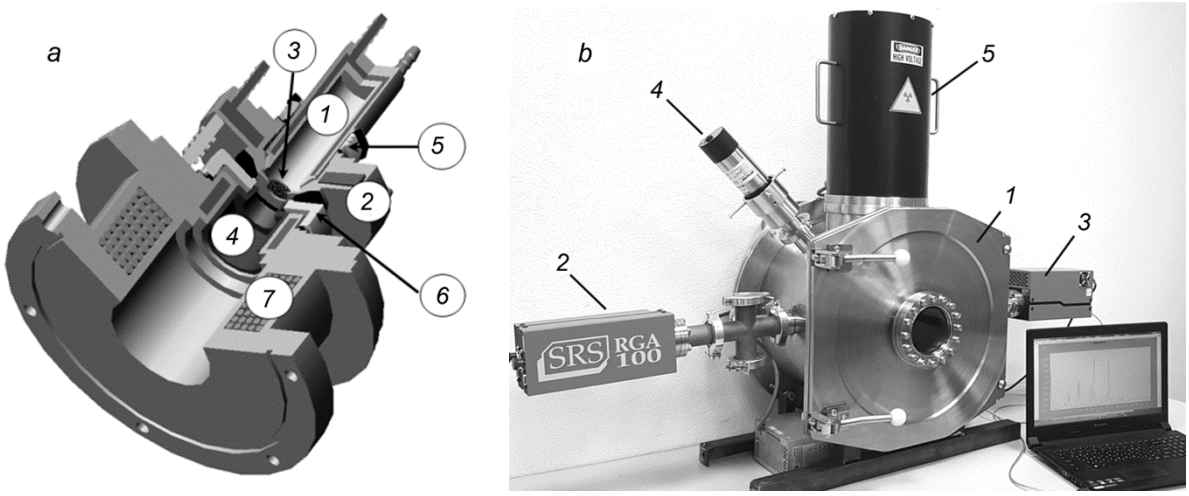

Fig. 4. Schematic of the electron source (*a*) comprising cylindrical hollow cathode *1*, anode *2*, emission electrode *3*, extractor *4*, ceramic high-voltage insulators *5* and *6*, and electromagnetic focusing lens *7*; and external view of the setup for electron beam deposition of boron coatings (*b*) comprising vacuum chamber *1*, RGA-100 analyzer *2* of the composition of the residual atmosphere, plasma mass spectrometer *3*, Raytek optical pyrometer *4*, and electron source *5* in radiating protection casing.

are mostly singly ionized. In addition to the boron ions, a relatively small number of singly and doubly charged ions of the working gas – argon or krypton – were presented in the plasma. The fraction of boron ions integrated over the ion beam pulse reached 85% at a pressure of $2 \cdot 10^{-3}$ Torr, pulse duration of 250 μs, pulse repetition frequency 20 pulses per second, and arc pulse of 50 A.

The magnetron systems with pure boron cathode were used to deposit boron coatings on the surface of structural materials. For a discharge power of 500 W, the coating speed was about 25 nm/min. This is comparable to the productivity of the magnetron with metal target operating in the *classical* continuous mode.

FOREVACUUM SOURCE INTENDED FOR DEPOSITION OF BORON COATINGS BY ELECTRON BEAMS

The electrode system of the forevacuum plasma electron source used for deposition of boron surface coatings by an electron beam and the external view of the setup intended for deposition of coatings based on such source are shown in Fig. 4*a* and *b*, respectively. In this setup, the glow discharge with current up to 1 A was triggered between water-cooled hollow cathode *1* and stainless steel anode *2*. A voltage of 20 kV extracting the arc plasma and accelerating the electrons was applied between emission electrode *3* and extractor *4*. Ceramic insulators *5* and *6* were used to insulate the electrodes of the discharge and accelerating systems. The electron beam with current up to 300 mA was focused onto the boron or boron-containing ceramic target using electromagnetic lens *7*. The diameter of the focal spot of the electron beam on the surface of the target located at a distance of 30 cm from the source was 5–8 mm, and the electron beam power density in the focus reached 10 kW/cm^2. This power density was sufficient for heating and evaporation of the pure boron and boron-containing ceramic targets [17].

The flow of atoms evaporated from the target surface was partially ionized in the beam plasma generated in the area of electron beam transportation and then deposited on the surface of samples placed at a distance of 10 cm from the target. The temperature of the sample surface was controlled by a high-speed optical pyrometer and did not exceed 200°C. The structure of residual atmosphere in the vacuum chamber during coating deposition was controlled by an RGA-100 analyzer (Stanford Research Systems, the USA), and the mass-to-charge fractions of the beam plasma

were measured with a mass spectrometer [18]. The profile of the boron coating surface measured using a three-dimensional contactless Micro Measure 3D-Station profilometer (STIL SAS, France) demonstrated that the coating roughness did not exceed 1 μm. The coating speed was up to 1 μm/min. Our measurements of the coating properties with a Nano Hardness Tester NHT-S-AX-000X (CSEM, Switzerland) revealed that the maximum surface hardness of the coating was obtained by evaporation of the boron target in the nitrogen atmosphere (12 GPa) or of the boron nitride target in the atmosphere of inert gases (17 GPa). It seems likely that this is due to the formation on the sample surface of layers of boron nitride, the hard material having several modifications. Note that the cubic modification of boron nitride can have hardness up to 110 GPa [19] comparable to the diamond hardness. Search for the conditions of obtaining high-quality BN-coatings is an important problem for further use of this electron source to obtain boron-based protective coatings.

CONCLUSIONS

The coatings based on boron and its compounds are promising for surface modification of structural materials. This is due to the high hardness and chemical resistance of such coatings. The development of specialized beam-plasma setup is necessary for a wide use of surface hardening technologies with application of such coatings. Examples of such setups are the devices whose operating principle and characteristic are given in this work. They are the ion source based on the vacuum arc with separation of boron isotopes in a magnetic field for realization of high-dose ion implantation, the plasma generator with crystal boron target for deposition of coatings by the method of magnetron sputtering, and the forevacuum electron source for synthesis of the boron-containing surface coatings by electron beam evaporation. The developed setups are promising for the creation of boron-containing functional, hardening, and protective coatings intended for solving a wide range of practical problems.

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