Charge and elemental composition of plasma generated by sputtering of powder target from amorphous boron

Y F Ivanov, V V Shugurov, O V Krysina and V E Prokopiev
Institute of High Current Electronics SB RAS, Tomsk, 634055, Russia

E-mail: yufi55@mail.ru

Abstract. One of the effective and widespread methods of surface hardening of metal products is an ion-plasma saturation of the surface of machine parts and mechanisms with various elements (nitrogen, oxygen, carbon). Less investigated method is the process of ion-plasma saturation of the metals and alloys surface with boron. The purpose of the present work is to develop a method for the formation and study of parameters (electron temperature, plasma potential and concentration), elemental and charge composition of plasma generated at sputtering of a target from amorphous boron powder. To achieve the stated goal, a discharge system with a hot anode made of powder boron, as well as a pulse arc evaporator with a hot cathode made of sintered boron powder, was developed, designed, created and tested. Charge and elemental composition of boron-containing plasma generated during powder target sputtering from amorphous boron are defined by optical spectrometry method. It is shown that the generated plasma contains mainly neutral atoms and single-charge boron ions, as well as iron, silicon, copper and argon particles.

1. Introduction
Chemical-thermal treatment (CTT) is widely used in industry to modify the surface of metals and alloys [1]. One method of CTT is boriding [2-5]. Solid-phase, liquid-phase and gas-phase boriding are used. These methods are characterized by large labor and energy costs, low level of environmental friendliness and high explosion hazard at gas-phase boriding. One of the effective and widespread methods of surface hardening of metal products is ion-plasma saturation of the material with various elements. These are nitrogen, carbon, oxygen and their various combinations [6]. Less investigated method is the process of ion-plasma saturation of the surface of metals and alloys with boron.

The purpose of the present work is to develop a method for the formation and study of parameters (electron temperature, plasma potential and concentration), elemental and charge composition of plasma generated at sputtering of an amorphous boron powder target.

2. Material and methods
The target was amorphous boron, powder graded A with TU 2112-001-49534204-2003 of the following composition: B - 96.2 wt.%; Fe - 0.3 wt.%; Si - 0.2 wt.%; H₂O - 0.3 wt.%. Experiments were carried out on the COMPLEX setup [7]. In the vacuum chamber 9 (figure 1) of the setup there is an input of high-frequency (HF) radiation with an electrode-holder of boron powder hinge 8. Electrode diameter is
120 mm, distance to treated samples is 60 mm. RF discharge was supplied from the high-frequency OEM12B-01/03 generator by Artesyn Embedded Technologies with a maximum power of 1250 W at a load of 50 Ohms and an operating frequency of 13.56 MHz. On the upper flanges of the vacuum chamber there is a window with quartz glass 2 for spectroscopic measurements and a flange with a cylindrical Langmuir probe 4 for measurements of plasma parameters. Gas plasma was created using a PINK plasma source with thermionic and hollow cathodes. Argon was used as the working gas at a pressure of (0.5-0.6) Pa. The samples to be treated were fixed on the satellite of the manipulator unit, which was able to rotate in a horizontal plane to increase the uniformity of sample processing. The temperature of the samples was measured using a chromel-aluminum thermocouple located in the cavity of the samples holder and isolated from it using a quartz cup.

The principle of the system operation is follows: the vacuum chamber was previously pumped out to a pressure less than $5 \times 10^{-3}$ Pa, then argon was introduced into the chamber through the PINK plasma generator to pressure of 0.5-0.6 Pa and a non-self-sustained arc discharge was ignited with a thermionic and hollow cathode with a discharge current up to 100 A. After that, RF power was supplied on the electrode-holder 8 through the matching device and a non-self-sustained RF discharge was ignited on the target from boron powder. In the absence of PINK plasma generator discharge, the RF discharge did not ignite. With a discharge current of the PINK plasma generator of 100 A, the RF discharge power reached 800 W. Under such conditions, the deposition rate of the boron film on the samples surface reached to 500 nm/h.

Pulsed negative bias voltage was used to clean and heat the samples, which led to their intense bombardment with argon and boron ions. The bias voltage was within (300-500) V, pulse duty factor was (0.25-0.85), and pulse repetition frequency was 50 kHz.

To effectively use the boron powder as a material for film deposition and carrying out of ion-plasma borating of the metals and alloys surface, it is necessary to achieve its electrical conductivity, as well as to conduct maximum compaction of the powder target. The most effective method in both cases is to heat the

![Figure 1. The scheme of the experiment: 1 - spectrometer with a light guide; 2 - window with quartz glass; 3 - PINK gas plasma generator; 4 - a Langmuir cylindrical probe; 5 - treated samples; 6 - RF generator with matching device; 7 - thermocouple; 8 - RF electrode with boron powder hinge; 9 - working vacuum chamber.](image)
target from the boron powder to high temperatures. At room temperature, boron is a dielectric, but at temperatures above (823-973) K, its conductivity is unity of Ohm·cm [8] and it is possible to effectively effect on it by an electric field. At heating to 1600°C and higher, boron evaporates intensively and it becomes possible to deposit the boron in the form of a film on the materials surface.

The diagram of the electrode discharge system for heating and evaporating the target from boron powder based on a non-self-sustained arc discharge with a thermionic and hollow cathodes and an uncooled combined anode is presented in figure 2. The anode of the discharge system of non-self-sustained arc discharge with a thermionic and hollow cathodes was made in the form of a cylindrical graphite crucible with a diameter of 40 mm and a height of 20 mm. On the upper end surface of the crucible, a recess with a diameter of 30 mm and a depth of 8 mm was made for hinge of boron powder. The crucible was located at the distance of 100 mm from the outlet of the cathode cavity of the gas plasma generator. In the gap between the anode crucible and the cathode cavity of the gas plasma generator there was a holder with treated samples, the temperature of which was controlled by a chromel-aluminum thermocouple. The principle of the system operation: argon is fed in the working chamber up to a pressure of (0.6-0.8) Pa, power is supplied to the thermionic cathode. The filament current of three tungsten cathodes with a diameter of 0.8 mm and a length of 100 mm was (160-170) A, the magnetic coil current was set at 1.5 A. Then, a voltage was supplied between the hollow cathode and the crucible anode, which led to the ignition of a non-self-sustained arc discharge. Initially, the discharge current was closed through a graphite anode crucible. As its temperature increases, the specific resistance of boron decreases and the specific resistance of graphite increases, which, at temperatures above (823-973) K, leads to the switching of the discharge to the boron surface and a further increase in its temperature. This ensures a high rate of boron evaporation. The ionization of boron vapors occurs under the influence of electrons of gas plasma.

3. Results and discussion
The process of generation of gas plasma formed during combined operation of high-frequency boron sputter and gas discharge plasma source based on non-self-sustained arc discharge with combined thermionic and hollow cathodes obtained by probe method (electron temperature, plasma potential and concentration, floating potential of generated gas plasma) has been investigated. Probe measurements were carried out using a cylindrical Langmuir probe with a diameter of 0.4 mm and a length of 5 mm, connected to an automated probe measurement system [9], developed in the laboratory of plasma emission electronics of the IHCE SB RAS. Measurements were carried out at the following parameters: argon pressure 0.6 Pa, discharge current of the PINK plasma generator of 100 A, RF discharge power of 800 W. Figure 3 shows the typical volt-ampere characteristic of the probe. To average the parameters, 10 volt-ampere characteristics of the probe were taken for 2000 measurements per each one. The moment of measurement was tied to the minimum filament current of the cathode of the PINK plasma generator. The following parameters of the plasma were determined: plasma potential of 2.9 V; plasma concentration of $8.5 \times 10^{17}$ m$^{-3}$; electron temperature of 1.4 eV; floating potential of –6.8 V.

**Figure 3.** The typical volt-ampere characteristic of the probe.

![Volt-Ampere Characteristic](image3.png)

**Figure 4.** The optical spectrum of plasma radiation generated at sputtering a powder target from amorphous boron in the wavelength range of (205-305) nm. Parameters: gas - Ar, $p = 0.2$ Pa, $P = 600$ W.

Determination of charge and elemental composition of boron-containing plasma generated during sputtering of powder target from amorphous boron was carried out by spectrometry method. Optical spectra of boron-containing plasma radiation were captured using the Ocean Optics HR 4000 spectrometer. Plasma radiation in the area of the target sputtering from boron was recorded through a quartz window located on the flange of the working setup (figure 1). The integration time was selected in the range of (1-30) s to increase the intensity of the boron emission lines. The survey was carried out in four wavelength ranges. In a wide range (No. 1 - (200-1100) nm), due to the relatively low resolution (0.75 nm), the large number of observed spectral lines and the high intensity of the emission lines of argon, oxygen, hydrogen and water, it was not possible to correctly interpret and separate the radiation lines of interest of atoms and ions contained in the plasma under investigation. In this regard, the main survey of radiation spectra for a qualitative study of the composition of the formed boron-containing plasma was carried out in three narrower ranges No. 2 - (350-425) nm, No. 3 - (250-350) nm and No. 4 - (200-300) nm with a higher resolution (0.01-0.03 nm). It should be noted that the most intense emission
lines of boron atoms are in the range of (200-300) nm, therefore, more detailed identification of peaks was carried out in this range. In selected wavelength ranges, identification of spectral lines was carried out using reference data from universally recognized sources [10-12].

As a result of the studies, it was found that the generated plasma is multicomponent and, along with boron atoms and ions (neutral boron atoms (B I), single-charge and double-charge boron ions (B II and B III)) (figure 4) contains neutral iron atoms (Fe I), single-charge iron ions (Fe II), neutral copper atoms (Cu I), single-charge copper ions (Cu II), neutral silicon atoms (Si I), single-charge silicon ions (Si II). The presence of iron atoms and ions is due to its presence in the sputtering target (0.3 wt.%), as well as the fact that most of the elements in the system (the holder of the sputtering target, the walls of the chamber, the hollow cathode of the gas plasma source) are made of AISI 304 stainless steel, the main element of which is iron. The presence of silicon particles is explained by their presence in the composition of the sputtering target (0.2 wt.%). Copper is the material of the current-carrying parts of the setup, which are located directly in the vacuum chamber and can be slightly sputtered with gas ions. Neutral atoms, one- and two-charge argon ions (Ar I, Ar II, Ar III), which were used as a working gas, are also observed.

4. Conclusion
A discharge system with a hot anode made of boron powder has been developed, constructed, manufactured and tested. Optimization was carried out and samples of sintered boron powder in graphite crucibles with a diameter of 35 mm and a powder filling thickness of up to 8 mm were obtained. This system is used to obtain sintered cathodes from boron powder for an arc evaporator with a hot cathode. A pulsed arc evaporator with a hot cathode made of sintered boron powder was developed, designed, manufactured and tested. Charge and elemental composition of boron-containing plasma generated during powder target sputtering from amorphous boron are determined by spectrometry method. It is shown that the generated plasma contains mainly neutral atoms and single-charge boron ions, as well as that of iron, silicon, copper and argon.

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