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In situ probe measurements of plasma parameters during the deposition of boron coatings by the magnetron method

© V.I. Gushenets,[1] A.S. Bugaev,[1] A.V. Vizir,[1] E.M. Oks,[1,2] A.G. Nikolaev,[1] G.Yu. Yushkov[1]

[1] Institute of High Current Electronics, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia
[2] Tomsk State University of Control Systems and Radioelectronics, Tomsk, Russia
e-mail: nik@opee.hcei.tsc.ru

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The features of the probe technique are described and the results of measuring the parameters of plasma generated by a planar magnetron sputtering system with a pure boron target during coating deposition are presented. A feature of probe measurements was the use of heating the collecting surface of a single Langmuir probe. Heating led to a decrease in the electrical resistance of the boron film on the surface, which made it possible to carry out *in situ* probe measurements of the magnetron discharge plasma parameters during the entire process of boron coating.

Keywords: plasma parameters, probe method, planar magnetron, boron films.

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Introduction

Creation of boron layers on surfaces of materials is widely used to modify metal and alloy surfaces for the purpose of their hardening, improvement of wear resistance and corrosion resistance [1,2]. Traditionally boriding is a process in which the surface is diffusion-saturated by boron from a boron-containing medium at high temperature. Depending on the physical state of this medium, three main methods of boriding are distinguished: gas boriding [3], liquid boriding [4], and solid state boriding [5]. More recently, traditional methods of boriding are being rivaled by plasma-assisted methods, there the fourth physical state of matter, i.e. plasma generated in low-pressure electrical discharges, is used as a boron-containing medium. The plasma-assisted methods allow not only diffusive saturation of surface with boron, but also creation of boron coating on it [6], as it is implemented, for example, with the use of magnetron discharge [7].

At the same time, the magnetron method in its traditional implementation is not completely suitable to apply boron coatings on surfaces. Pure boron at normal conditions has high specific electrical resistance at a level of units of $\mathrm{M\Omega\cdot cm}$ [8], which impairs functioning of the magnetron discharge with a cathode (target) made of boron with currents acceptable for process application. To address this problem, we have proposed and implemented a design of planar magnetron with thermally isolated target made of pure crystal boron pre-heated in high-voltage magnetron discharge [9]. Since boron is a semiconductor material and has negative temperature coefficient of electrical resistance, with the target heated up to several hundreds degrees its resistance decreases down to a level where stable burning of the magnetron discharge with direct current of hundreds milliampere becomes possible. Another difficulty for the use of boron target in magnetron was the formation of non-conductive boron coating on the anode impairing the discharge current closure. This problem was resolved through application of a special anode design with part of its surface not subjected to intensive sputtering. All this allowed ensuring boron coatings application on the surface at rates of about 5 nm/min.

Since boron has more than 10 allotropic modifications [10], which are significantly different in their physical and chemical properties, the properties of boron coatings are defined by conditions of their application. In turn, the conditions of coatings formation are defined by parameters of the plasma in which they grow. Thus, when applying boron coatings, it is necessary to control parameters of the plasma. Since application of coatings using a magnetron dc sputter is a continuous process with typical durations from tens of minutes to several hours, it is necessary to provide for measurement and control of plasma parameters throughout the entire cycle of coating application. To measure parameters of plasma, the probe method suggested by I. Langmuir as early as in 1926 [11] is widely used. However, non-conductive boron coating is deposited on the working surface of probe and it distorts current-voltage curve of the probe then plasma parameters are measured by the probe method. Cleaning of the probe surface from non-conductive boron coatings does not solve the problem, because typical times of coating formation causing significant distortions of probe characteristics are 5–10 min. To address the problem, we have developed a single probe with its working surface heated up to a temperature, at which the boron coating becomes conductive. This allowed us to provide for continuous *in situ* measurement and control of plasma parameters throughout the entire process of boron coating application with a duration of up to 10 h.

1. Procedure and technique of the experiments

The experiments, which results are reported in this work, were performed with the use of a planar magnetron with a thermally insulated target of 99.99 at.% pure boron heated in a discharge. The target had a diameter of 51 mm, thickness of a 4 mm, and was manufactured by the method of hot-pressing of crystal boron with a grain size of $1-20\,\mu$m in vacuum. Design of the magnetron used in the experiments is shown in Fig. 1, *a* and its parameters and characteristics are detailed in [9,12]. The magnetron was placed on the end flange of a cylinder vacuum chamber with a diameter of 30 cm and a length of 40 cm made of stainless steel. Anode of the magnetron was electrically connected to the vacuum chamber body. The chamber was fore-vacuumed by a 2NVR-5DM rotary vane vacuum pump and high-vacuumed by a Varian TM101 turbomolecular pump down to a pressure of 0.2 mPa.

The magnetron discharge was powered from two stabilized power supply sources by Spellman: SL150 and SL300 with adjustable maximum voltages of 6 and 3.2 kV and currents of 25 and 200 mA, respectively. Both sources were functioning in the mode of current stabilization. The SL150 source was used to initially warm up the target in a relatively weak-current high-voltage magnetron discharge, while the SL300 was turned on after the target was heated, to provide a magnetron discharge current of 25 to 90 mA DC in the process of boron coating application. The instability of the discharge current in the process of coating application and probe measurements of plasma parameters of the magnetron discharge was less than 0.1 mA. The lower range of the discharge current was selected to ensure sufficient rate of the boron coating application onto the substrate, and the upper current range was limited by the possible thermoelastic destruction (cracking) of the relatively brittle boron target. The experiments were carried out at a pressure of working gas — argon — from 0.3 to 1 Pa. With lower gas pressures the magnetron discharge evolved to the weak-current high-voltage mode of burning with a current of a few milliamperes and a voltage of a few kilovolts. With higher pressures the rate of coating application decreased due to elastic collisions of boron atoms sputtered from the target surface and atoms of the working gas.

The electrode configuration of the single Langmuir probe used in the experiment and schematic diagram of its power supply sources connection are shown in Fig. 1, *b*. The *U*-shaped probe with a length of 20 mm was made of tungsten wire with a diameter of 1.0 mm. The diameter of wire was selected based on the condition of its exceedance over the thickness of the space charge layer near the collecting surface of the probe in all ranges of discharge current and voltages of the current-voltage curve of the probe to be measured. When measuring plasma parameters, the probe was positioned at a distance of 50 mm from the surface plane of the magnetron target (Fig. 1, *a*). The distance from the target to the probe was selected based on the condition that it should be much less than the thickness of the negative space charge layer of the probe in comparison with the typical dimension of the Larmor radius of plasma electrons in the scattered magnetic field of the magnetron. In [13] results of magnetic field measurements are reported depending on the distance to the target, from which it can be seen that the field strength at the point of probe is negligible (less than 0.5 mT), therefore the effect of magnetic field on the current-voltage curve of the probe can be neglected.

The choice of *U*-shaped configuration of the probe is caused by the necessity to compensate for the self-magnetic field of the probe when an up to 10 A direct current flows through the probe providing its warming up to a temperature of up to 500°C. Without the probe warming the high resistance of the boron coating on the collecting surface of the probe caused a decrease in the current measured by the probe, a change in slope of the current-voltage curves of the probe and their shift towards the region of lower voltages. Thus, after 30 min of magnetron operation with a boron cathode, the ion saturation current of the probe decreased by $3-5$ times. Since boron is a wide-bandgap semiconductor, it has a negative temperature resistance coefficient. Thus, with a temperature increase from 20 to 300°C, the specific electrical resistance of crystal boron decreases by five orders of magnitude: approximately from $3\,\mathrm{M\Omega\cdot cm}$ down to $20\,\Omega\cdot\mathrm{cm}$ [8]. With a heating current over 9 A flowing through the probe and heating its surface and, respectively, forming a boron film, the current-voltage curve of the probe remained almost unchanged throughout the entire duration of the measurements. The time to obtain the current-voltage curve of the probe in the process of plasma parameters measurement was about 3 min. It was multiple times less than the typical measurement time of plasma parameters of the discharge related to the depositing of boron coating on electrodes. In the process of measurements, the plane of *U*-shaped probe was oriented parallel to the magnetron target surface. At the same time, the plasma flux of the magnetron discharge was directed predominantly perpendicular to the probe plane. This ensured maximum ion current into its collecting surface, which allowed decreasing the signal-to-noise ratio when measuring current-voltage curve of the probe and thus ensuring required accuracy of the current-voltage curve measurement near the floating potential of the plasma at low discharge currents.

To measure current-voltage curve of the probe, two sources of stabilized voltage were used, *B1* and *B2* (Fig. 1, *b*). Source *B2* provided a constant reference voltage, for example, +30 V, and source *B1* was used to change the prove potential by voltage with an adjustable step of 0.1 V. This configuration allowed measurements of ion and electron branches of the current-voltage curve without

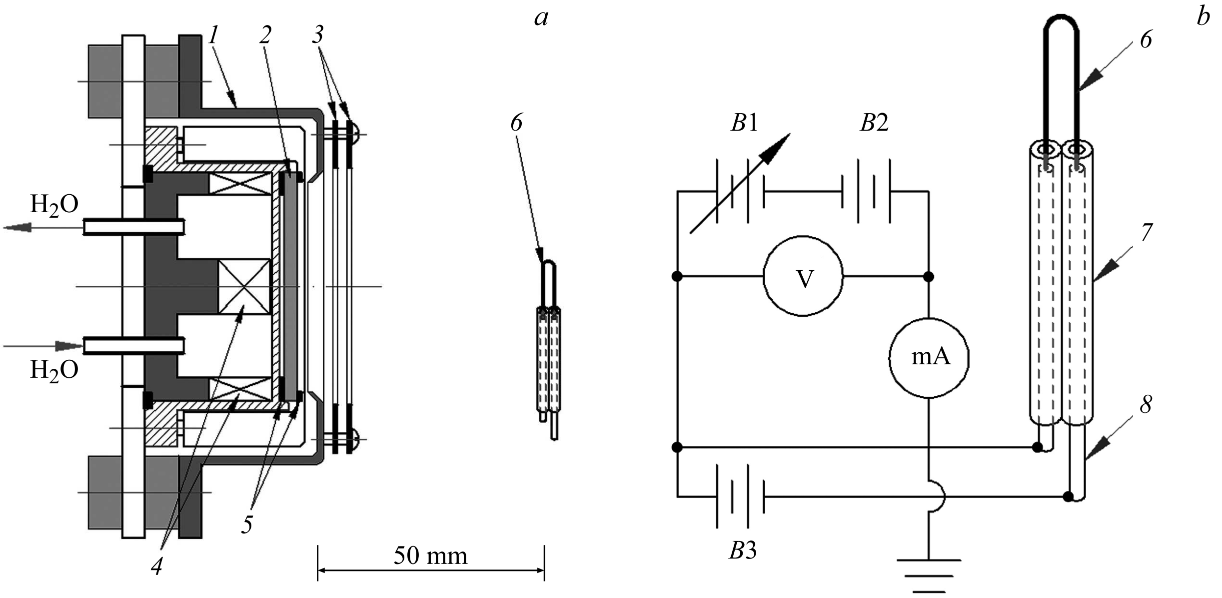

Figure 1. Planar magnetron (*a*) and single probe with power supply sources connection circuit diagram (*b*). *1* — anode, *2* — boron target, *3* — additional anode rings, *4* — NBFe-magnets, *5* — thermal-insulating gaskets of GraFoil, *6* — probe, *7* —- quartz tube, *8* — current leads, *B1 B2* and *B3* — stabilized power supply sources.

switching over the power supply source polarity. Current and voltage of the probe in relation to the earthed vacuum chamber were measured by Fluke-287 digital multimeters with an impedance of 10 MΩ. All this allowed us to ensure high stability and reproducibility of plasma parameters measurement results in the process of their *in situ* monitoring when applying boron coating by the magnetron method.

2. Experimental results and discussion thereof

Probe measurements consisted in determining of the current-voltage curve of the probe, i.e. the dependence of current in the probe circuit on the probe voltage in relation to the reference electrode (in this case - the earthed vacuum chamber). Current-voltage curves of the probe measured at a magnetron discharge current of 75 mA in linear and semilogarithmic scales are shown as an example in Fig. 2. The shape of current-voltage curves of the probe can be qualitatively explained as follows. With a high negative potential only ions are fed from the plasma to the collecting surface of the probe, while electrons are reflected by the probe potential. When a positive potential in relation to the plasma is applied to the probe, only electrons are fed to its surface, and their current is considerably higher than that of ions because of the greater mobility of electrons. Further increase in positive potential of the probe results in growth of the electron current due to the increase in collecting surface of the plasma boundary with the increase in space charge layer thickness near the probe surface. With a probe potential close to the floating potential in the plasma, the probe current is composed of the currents of electrons and ions onto the probe surface, with current polarity being defined by predominance of either of the particles. Temperature of plasma electrons was determined by the slope of electron branch of the current-voltage curve of the probe in semilogarithmic scale (Fig. 2, *b*) before the saturation section I_{sat}. There are two linear sections on the presented current-voltage curve: I_{cold} and I_{hot}, which occurrence can be explained by the presence of two groups of electrons with different temperatures in the magnetron discharge plasma. The presence of these two groups of electrons in the magnetron discharge with a metal conductive target was registered earlier in [14–17]. In the processing of the current-voltage curve of the probe, the beginning of the saturation current section of the electron branch was used to determine the plasma potential, then the above-mentioned procedure was used to determine temperatures of two electron groups, and then the plasma concentration was determined. Mean temperature of hot electrons in the plasma is about 5 eV, which is approximately 3 times higher than the temperature of cold electrons.

Note, that Debye radius for mean values of temperature and concentration is approximately equal to 0.11 mm, while the probe radius is 0.5 mm, i. e. several times greater than the Debye radius. Since we used argon as a working gas, and taking into account that with these parameters of the discharge current, the plasma is composed mainly of argon ions, then path length of argon ions in their gas for a pressure of 0.4 Pa is at least 1.6 cm. Free path length of electrons in argon is 5.6 times longer. Thus, free path lengths of particles are considerably greater than the probe radius.

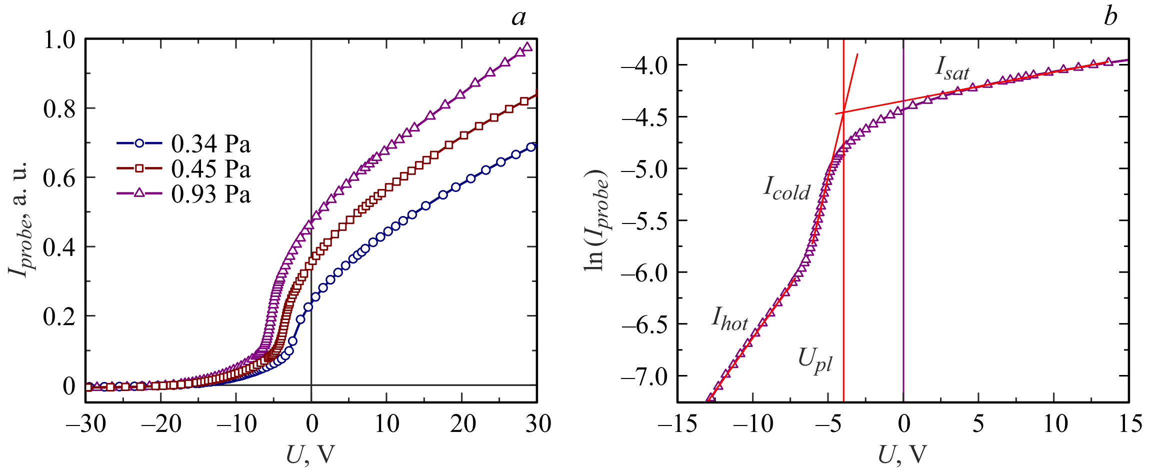

Figure 2. Current-voltage curves of the probe for the magnetron discharge with a boron target and a current of 75 mA at different argon pressures (*a*) and current-voltage curve of the probe in semilogarithmic scale at an argon pressure of 0.93 Pa (*b*).

Plasma density was estimated on the basis of ion saturation current. The ion saturation current was calculated from the equation of approximating straight line of the ion branch of the probe characteristic in the point where the probe potential is greater (in absolute value) than the space potential or the plasma potential by a value of $kT_{\text{eff}}/2$, when the prelayer near the probe is completely formed [18,19]. The plasma potential was determined in the region of bend of the transient and electron branches of the current-voltage curve of the probe plotted in semilogarithmic scale (Fig. 2, *b*). Although in our experiments the electron saturation current was not used to determine the plasma density, this current can be determined from the approximating straight line $I_{\text{el}}(U)$ in the point of its intersection with the straight line $I_{\text{cold}}(U)$. The plasma density n_0 was determined by the Bohm formula for the ion current from the plasma to the negative cylinder electrode [20]:

$$n_0 = \frac{I_i}{0.61eA_{\text{coll}}} \times \sqrt{\frac{m_{\text{eff}}}{T_{\text{eff}}}},$$

where I_i — ion saturation current, e — electron charge, A_{coll} — collector area, T_{eff} — effective electron temperature, m_{eff} — effective mass of plasma ions. From the results of [17] it follows that value of T_{eff} is close to the temperature of the cold component of the plasma, and therefore, in determining the n_0 it was assumed that $T_{\text{eff}} \approx T_{\text{cold}}$. Since, according to [12], at a current of magnetic discharge with boron target less than 100 mA, boron in the discharge plasma is represented mainly as non-ionized atoms sputtered from the target surface and concentration of boron ions is approximately 50 times less than that of single-charged ions of argon, then m_{eff} was assumed equal to the argon mass. The calculated density of plasma is in the range from $3 \cdot 10^9$ to $6 \cdot 10^9\,\text{cm}^{-3}$. Dependencies of parameters of magnetron discharge plasma with boron target on the working gas pressure obtained as a result of processing of current-voltage curves of the probe are shown in Fig. 3.

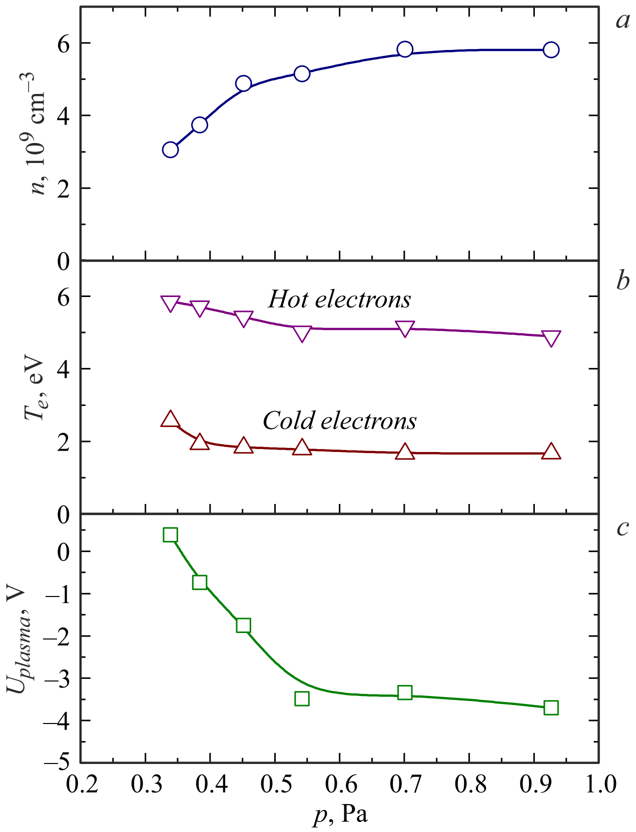

Figure 3. Plasma density (*a*), temperature of electrons (*b*), and plasma potential (*c*) as functions of the working gas pressure. Discharge current — 75 mA.

With increase in the discharge current the floating potential and the plasma potential decrease linearly (Fig. 4, *a*). This is probably connected to the presence of a nonconductive boron film on the magnetron discharge anode and walls of the vacuum chamber, which formation results

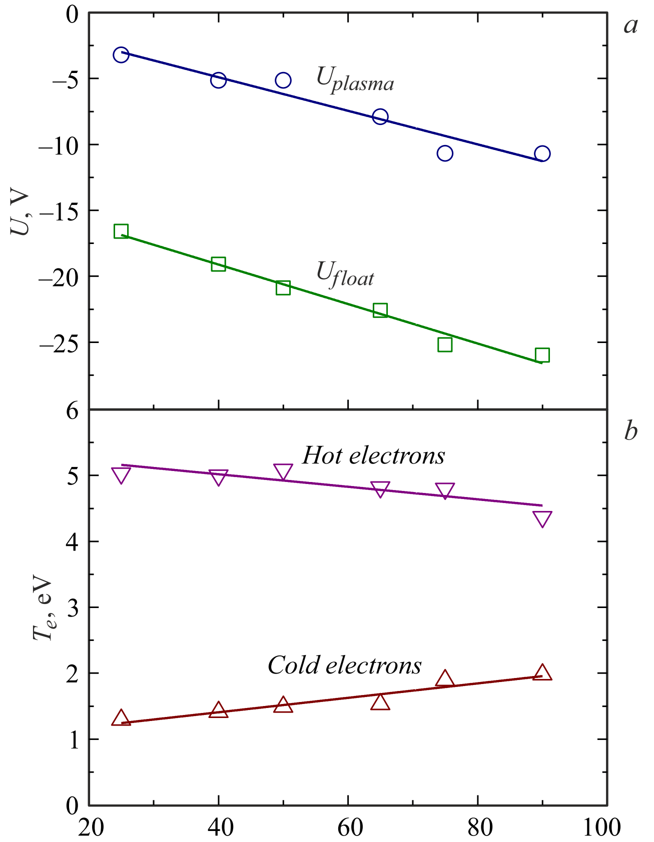

Figure 4. Floating potential and plasma potential (*a*) and temperatures of two groups of electrons (*b*) as functions of the magnetron discharge current. Argon pressure — 0.68 Pa.

in an additional resistance in the discharge circuit. Dependencies of Fig. 4, *a* are measured after 5 h of the total time of the coating application process. It was noted that due to the growth of thickness of the non-conductive boron film these potentials decrease over time, which means that electrical resistance of the coating increases. In the process of measurement of current-voltage curves of the probe, these changes in potentials were compensated by change in the reference voltage of the source *B2* (Fig. 1, *b*), and thus current-voltage curves of the probe can be measured *in situ* throughout the entire process of the boron coating application.

With increase in the discharge current the temperature of hot electrons decreases and the temperature of cold electrons increases in contrast (Fig. 4, *b*). This is probably a result of electrons scattering in the process of their interaction with oscillations of the plasma electric field, because drift electron velocity of the magnetron discharge is an order of magnitude higher than the thermal velocity of ions. As the plasma concentration increases, these oscillations are attenuated faster, hence the kinetic energy exchange between two groups of electrons becomes more intensive, which leads to their temperatures equalization.

Conclusion

This work presents the results of probe measurements of parameters of the plasma formed by a magnetron discharge with a plane thermally insulated target made of pure boron. The probe measurements of such discharge plasma applied to form boron coatings on surfaces feature the depositing of non-conductive boron film on the collecting surface of the probe that makes impossible measurement of current-voltage curve of the probe with high reliability and accuracy. In this work we have proposed the use of the probe with heated collecting surface. Heating of the surface makes to decrease the resistance of boron coating with a negative temperature resistance coefficient, and this allows probe measurement of such discharge. As a result of analysis of current-voltage curves of the probe, the presence of two groups of electrons with different temperatures was identified in the plasma of the discharge column. The experimental data was obtained regarding the plasma characteristics: plasma density, electron temperature of two groups of electrons, floating potential and plasma potential in the range of discharge currents of a planar magnetron with boron target from 25 to 90 mA and argon pressures in the vacuum chamber from 0.5 to 1 Pa. All this allowed *in situ* monitoring of parameters of the magnetron discharge plasma when it is used to apply boron coatings onto surfaces.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] I. Campos, M. Palomar, A. Amador, R. Ganem, J. Martinez. Surf. Coat. Technol., **201**, 2438 (2006). DOI: 10.1016/j.surfcoat.2006.04.017
[2] C.V. Robino, M.J. Cieslak. Metall. Mater. Trans. A, **26** (7), 1673 (1995). DOI: 10.1007/BF02670754
[3] M. Kulka, N. Makuch, A. Piasecki. Surf. Coat. Technol., **325**, 515 (2017). DOI: 10.1016/j.surfcoat.2017.07.020
[4] A.N. Simonenko, V.A. Shestakov, V.N. Poboinya. Metal Science and Heat Treatment, **24** (5), 360 (1982). DOI: 10.1007/BF00782814
[5] B. Sarma, N. Tikekar, K.S. Ravi Chandran. Ceramics International, **38** (8), 6795 (2012). DOI: 10.1016/j.ceramint.2012.05.077
[6] E. Rodríguez Cabeo, G. Laudien, S. Biemer, K.-T. Rie, S. Hoppe. Surf. Coat. Technol., **116–119**, 229 (1999). DOI: 10.1016/S0257-8972(99)00116-4
[7] E.M. Oks, A. Anders, A.G. Nikolaev, Yu.G. Yushkov. Rev. Sci. Instrum., **88**, 043506 (2017). DOI: 10.1063/1.4980149

[8] E.S. Greiner, J.A. Gutowski. J. Appl. Phys., **28** (11), 1364 (1957). DOI: 10.1063/1.1722660

[9] V.I. Gushenets, E.M. Oks, K.P. Savkin, A.V. Vizir, G.Yu. Yushkov, A. Hershcovitch, T.V. Kulevoy. Rev. Sci. Instrum., **81**, 02B303 (2010). DOI: 10.1063/1.3258029

[10] Xu Sun, Xiaofei Liu, Jun Yin, Jin Yu, Yao Li, Yang Hang, Xiaocheng Zhou, Maolin Yu, Jidong Li, Guoan Tai, Wanlin Guo. Adv. Functional Mater., **27** (19), 1603300 (2017). DOI: 10.1002/adfm.201603300

[11] H.M. Mott-Smith, I. Langmuir. Phys. Rev., **28** (4), 727 (1926). DOI: 10.1103/PhysRev.28.727

[12] A.V. Vizir, A.G. Nikolaev, E.M. Oks, V.P. Frolova, A.A. Cherkasov, M.V. Shandrikov, G.Yu. Yushkov. Russ. Phys. J., **64** (12), 2177 (2022). DOI: 10.1007/s11182-022-02574-9

[13] P.V. Kashtanov, B.M. Smirnov, R. Hippler. Physics-Uspekhi, **50** (5), 455 (2007). DOI: 10.1070/PU2007v050n05ABEH006138

[14] T.E. Sheridan, M.J. Goeckner, J. Goree. J. Vac. Sci. Technol. A, **9** (3), 688 (1991). DOI: 10.1116/1.577344

[15] V. Karzin, V. Smirnov. J. Phys.: Conf. Ser., **729**, 012021 (2016). DOI: 10.1088/1742-6596/729/1/012021

[16] D.J. Field, S.K. Dew, R.E. Burrell. J. Vac. Sci. Technol. A, **20** (6), 2032 (2002). DOI: 10.1116/1.1515800

[17] Bon-Woong Koo, Noah Hershkowitz, Moshe Sarfaty. J. Appl. Phys., **86** (3), 1213 (1999). DOI: 10.1063/1.370873

[18] W. Lochte-Holtgreven (Editor) *Plasma Diagnostics* (North-Holland, Amsterdam, 1968)

[19] R.L. Merlino. Am. J. Phys., **75** (12), 1078 (2007). DOI: 10.1119/1.2772282

[20] D. Bohm Chap. *3 in book The Characteristics of Electrical Discharges in Magnetic Fields* A. Guthrie, R.K. Wakerling (Eds.), (McGraw-Hill, 1949)