Magnetron sputtering system for coatings deposition with activation of working gas mixture by low-energy high-current electron beam

N V Gavrilov, A S Kamenetskikh, A I Men’shakov, O A Bureyev

Institute of Electrophysics, 106 Amundsen str., Yekaterinburg, 620016, Russia

E-mail: gavrilov@iep.uran.ru

Abstract. For the purposes of efficient decomposition and ionization of the gaseous mixtures in a system for coatings deposition using reactive magnetron sputtering, a low-energy (100–200 eV) high-current electron beam is generated by a grid-stabilized plasma electron source. The electron source utilizes both continuous (up to 20 A) and pulse-periodic mode of discharge with a self-heated hollow cathode (10-100 A; 0.2 ms; 10-1000 Hz). The conditions for initiation and stable burning of the high-current pulse discharge are studied along with the stable generation of a low-energy electron beam within the gas pressure range of 0.01 – 1 Pa.

It is shown that the use of the electron beam with controllable parameters results in reduction of the threshold values both for the pressure of gaseous mixture and for the fluxes of molecular gases. Using such a beam also provides a wide range (0.1-10) of the flux density ratios of ions and sputtered atoms over the coating surface, enables an increase in the maximum pulse density of ion current from plasma up to 0.1 A, ensures an excellent adhesion, optimizes the coating structure, and imparts improved properties to the superhard nanocomposite coatings of (Ti,Al)N/a-Si3N4 and TiC/-a-C:H. Mass-spectrometric measurements of the beam-generated plasma composition proved to demonstrate a twofold increase in the average concentration of N⁺ ions in the Ar-N2 plasma generated by the high-current (100 A) pulsed electron beam, as compared to the dc electron beam.

1. Introduction
In the development of coating deposition technology, a significant milestone was reached with the design of magnetron sputtering systems (MSS) with unbalanced magnetic field [1], which have provided an increase in the ion current density on the surface of workpieces and, as a consequence, an increase in the strength of adhesive bonds between coating and substrate and an improved control over the nucleation processes, morphology, chemical composition, and microstructure of coatings as well as over the level of internal stress and the recrystallization processes occurring in the coatings [2]. Also, in order to increase the degree of plasma ionization, initiation of additional discharges in the MSS effective volume has been applied widely [3]. In such ionized physical vapor deposition systems, most frequently used a thermionic cathode discharges, a high-frequency discharges, and a microwave discharges. In the coating deposition technology of magnetron sputtering, an important advance has been made by the application of a high-power impulse discharge mode (HiPIMS mode), which ensures a steep increase in the degree of ionization of sputtered atoms of the cathode materials [4].
The use of a low-energy electron beam for plasma generation, properties of the beam-generated plasma and some applications for material surface modification have been reported in a number of studies, e.g., in [5]. An electron beam (2 keV, 50–100 mA) was generated in a high-voltage glow discharge with a hollow cathode at a pressure of 2–13 Pa in pulse-periodic mode (2 ms, 10–20% duty factors). The ribbon electron beam (25x1 cm²) is drifting in a longitudinal magnetic field, thus forming a ‘plasma sheet’. Ions arrive at the samples disposed at a distance of 4–5 cm away from the plasma with the energy to be determined by the bias voltage on the samples. A plasma model is reported [6] to have been developed, wherein plasma is generated by an electron beam in low-pressure nitrogen, and a conclusion has been made that the properties and composition of the plasma differ considerably from those of the plasma generated in the gas discharge. An electron source, with a thermionic cathode and an electron optic system, which generates dc electron beam (3.6 A, 140 V) at a pressure of 0.15 Pa, is reported in [7] for steel nitriding application.

The present paper reports about some features of using a broad electron beam in a MSS application, with the beam having a round cross-section (100 cm²) at an energy 100–200 eV, and a pulse current of 1–100 A. The beam is generated in a plasma source of electrons, which is based on a self-heated hollow cathode discharge. The paper reports on the results of studying the conditions of stable generation of electron beam at elevated pressures (up to 1 Pa) and low accelerating voltages (100 V) in a high-current pulse-periodic mode, on the results of mass-spectrometry of the beam-generated argon-nitrogen plasma, and on the results of using MSS in combination with an electron beam source for the purpose of superhard nanocomposite coatings deposition.

2. Experimental Technique

A schema of a magnetron sputtering system with the gas working medium activated by an electron beam, (MSS EB) is displayed in Figure 1. An electron source is mounted on the working chamber (340 mm in dia, 270 mm in height) and comprises a hollow cathode 1 and a hollow anode 2, with a grid electrode 3 being a part of it. Once a discharge is initiated and an accelerating voltage is applied between the grid 3 and the walls of a chamber 4, there appeared a double layer of space charge in the grid area, wherein an electron beam is formed. Four flat magnetrons 5 with a sputtered targets diameter of 75 mm, operating in a pulse-periodic mode (50 kHz, 10 μs) are disposed on the side surface of the chamber. Pulsed discharge current for each of the magnetrons is controlled independently (0.1–2 A). Samples are placed at a manipulator 6 with a planetary gear. A gas flux required for burning the discharge is fed through the hollow cathode made of a tube with an internal

![Figure 1. The diagram of magnetron sputtering system. 1 – hollow cathode, 2 – hollow anode, 3 – grid, 4 – working chamber, 5 – magnetrons, 6 – manipulator, 7 – samples.](image-url)
diameter of 8 mm and a wall thickness of 1 mm. To obtain nitride coatings, a TiN cathode is used, in which case a reaction gas is fed through the cathode. To obtain carbide coatings, acetylene is fed directly into the working chamber.

MSS operating in combination with an electron beam source is featured with a reduction in the threshold value of the working gas pressure and the discharge voltage (Figure 2). When a pulsed beam at a current of 100 A is used, the magnetron discharge current during the beam pulse is approximately twice as great. The described MSS has a specific that, with the use of sputtered cathodes made of different materials, it is necessary to ensure a speed of sample rotation that could eliminate the heterogeneity in the contents of sputtered elements on the coating surface. In our conditions, this was achieved at a sample rotation speed of 10 rpm. The distance between the surfaces of MSS sputtered targets and the samples was 60 mm at an average.

![Figure 2](image)

**Figure 2.** Dependences of magnetron discharge voltage vs Ar flow rate (a) and electron beam current (b). Electron beam current: $I = 0$, $2 - 2$ A. Ar flow rate: $b = 5$ sccm.

The use of an MSS combined with an electron beam source based on a glow discharge with a hollow cathode was reported in [8]. The maximum beam current of this electron source did not exceed 5 A due to glow-to-arc transition, and the maximum ion current density was reported not to exceed a few mA/cm$^2$. The creation of an electron beam source based on a self-heated hollow cathode discharge (SHHC) has made it possible to increase the beam direct current up to 20 A and to rise the ion current density up to $\sim$10 mA/cm$^2$ [9]. Further development of MSS EB is associated with the use of a pulse-periodic mode of SHHC discharge. Once a low-current discharge is initiated to provide heating and transition of the hollow cathode into the thermionic emission mode ($4-5$ A, 50 V), a voltage pulse of 200-600 V in amplitude is applied to the electrodes, which leads to an increase in the discharge current up to a few hundred amperes over a time of about 0.1 ms. By matching the values of pulse repetition rate and current pulse amplitude, such discharge can be sustained in the pulse-periodic mode[10].

### 2.1. High current electron beam generation

The conditions for stable generation of a high-current electron beam at low accelerating voltages were determined using a double Langmuir probe technique [11]. One of the probes was disposed in the emitting plasma of the electron source, and the other was placed in the beam-generated plasma of the working chamber. Under stable electron beam generation, there exists a double layer of space charge between the plasmas, and the probes’ floating potential difference occurs, which value is, to an accuracy of the electron temperature, equal to the potential difference of the plasmas, i.e., is close to the voltage drop on the double layer. Figure 3 displays waveforms recorded under the stable mode of the electron beam generation. Growth of the beam current $I_b$ is delayed relative to the discharge current $I_d$ and reaches saturation in 0.15–0.2 ms, with the floating potential difference $U_{dl}$ being comparable to the accelerating voltage value. In the unstable mode, the voltage drop on the double
layer is modulated with oscillations of a frequency of 400 kHz and with the amplitude approaching the sum of the accelerating voltage and the pulse voltage on the discharge gap.

![Figure 3](image)

**Figure 3.** Characteristic waveforms of: 1-$I_d$ (50 A/div), 2-$U_{dl}$ (50 V/div), 3-$I_b$ (40 A/div), 50 μs/div.

Figure 4 shows the curves which divide the regions of stable mode and unstable mode of the electron beam generation; and it becomes evident from the results that the accelerating voltage of at least 160 V is required for stable generation of the electron beam with a current of 100 A, using a fine-grain grid with a mesh size of 1x1 mm. It was established that along with the electron beam instability there occurs the instability of discharge, which is associated with gaseous conditions in the cathode region. To attain the maximum discharge current, it is necessary that a relationship be maintained between the discharge current and the gaseous flux through the cathode, which relationship amounts to $~3 \text{ A} \cdot \text{min/cm}^3$, with the discharge burning in nitrogen at a pulse duration of 0.1 ms.

Thermal conditions of the hollow cathode in the pulse mode were estimated with an allowance made for the fact that, during a pulse time, a surface layer of the cathode is heated up, which thickness is small as compared to the cathode wall thickness, and radiation from the surface is absorbed fully by the walls of the closed cathode cavity. Then heat is removed into the cathode bulk and is radiated off the cathode surface. The changes in the surface temperature increment over a pulse at a variable repetition rate and at the same average discharge current were calculated (Figure 5). The lower the frequency, the higher the pulse current is required to sustain stable discharge in the pulse-periodic mode. Calculations carried out for a TiN cathode demonstrate that the thickness of the surface layer, heated during a pulse of 0.1 ms duration, amounts to 30 μm approximately, and the temperature of the cathode emitting surface may rise a few hundred degrees at a pulse power density of $~2 \times 10^4 \text{ W/cm}^2$.

![Figure 4](image)

**Figure 4.** Dependences of maximum electron beam current on accelerating voltage. Gas pressure: 1-$1 \times 10^{-3}$, 2-$5.4 \times 10^{-3}$ Torr.

![Figure 5](image)

**Figure 5.** Calculated curves of cathode surface temperature increment in pulse-periodic mode at frequency: 1-100 Hz, 2-200 Hz, 3-800 Hz.
2.2. Mass spectrometry of beam-generated plasma

The experimental technique was described elsewhere [12]. A modified dynamic monopolar mass-spectrometer MX-7304A was used, which had an ion-optic system installed instead of an ionizer. A potential of ~300 V was applied on the ion extractor. Accelerated ions arrived into the equipotential space inside the drift tube, and at the input of the analyzer were slowed down to energy of 30 eV ensuring a high resolution of the analyzer. The small size (2 mm) of the aperture at drift tube input and the use of a differential vacuum pumping made it possible to maintain a pressure of 0.03 Pa in the analyzer. Nevertheless, the large lengths of the drift tube and the mass-analysis region entailed the necessity for correction of the measurement results in view of the difference in the charge-exchange cross-sections for atomic and molecular nitrogen ions [12].

Figure 6 shows the resultant curves showing the relative contents of atomic nitrogen ions in the argon-nitrogen beam-generated plasma (at a flux ratio of $Q_{N_2}/Q_{Ar}=1:1$) as a function of the frequency of pulsed electron beam under constant value of average beam current. As compared to the DC electron beam, the high-current pulse electron beam provides approximately twice as great the $N^+$ ion content in plasma. Measurements of the emitting plasma composition proved the contents of atomic $N^+$ ions at a level of 8–12% as in the pulsed discharge as in the dc discharge. The content of ions of the hollow cathode material in the beam-generated plasma was below the measurement detection level.

2.3. Coating deposition in MSS EB

Properties of TiN coatings formed in MSS EB have been studied in [13]. Electron beam (100 eV, 0-8 A) was injected into Ar-$N_2$ gaseous mixture, with the pressure being maintained within 0.15–0.28 Pa by altering the nitrogen flow rate (1-25 sccm). Hardness of TiN coatings deposited without the electron beam reaches maximum value (25 GPa) at nitrogen flow rate of 12 sccm. As the beam current increases up to 5 A, the nitrogen content grows in the coatings and the hardness increases to 30–35 GPa at low nitrogen flow rates (~5 sccm). The effect of the electron beam on the gaseous mixture results in increased lattice parameter and the level of microstress, in a reduction of the grain size, and in a change in the coating texture.

Nanocomposite coatings of TiC/a-C:H of 5 μm in thickness were obtained by the reactive magnetron sputtering of Ti in a gaseous mixture of Ar-$C_2H_2$ which was additionally irradiated with an electron beam (100 eV, up to 1 A). The coating composition was controlled by altering the $C_2H_2$ flow rate within the range of 1–16 sccm at a constant Ar flow rate of 40 sccm and a constant magnetron current (2 A, 10 μs, 50 kHz). Hardness of the coatings depends nonmonotonically on the $C_2H_2$ flow rate. The maximum hardness of ~30 GPa was attained at Ti content of ~38 at.% in the coating. It was established that irradiation of the gaseous mixture during the coating deposition with electron beam facilitates accelerated acetylene decomposition and allows multiple (from 10 down to 2 sccm) reduction of the $C_2H_2$ flow rate at which the maximum hardness of the coating can be achieved.

Using the reactive magnetron sputtering with an additional electron beam treatment of the gaseous mixture, nanocomposite coatings of (Ti, Al)/a-Si$_3$N$_4$ were obtained. Two cathodes made of Ti (VT1-0, 98.61 – 99.7 %), a Si (99.999 %) cathode, and an Al cathode (A999) were used in the MSS EB. The bias voltage on the samples (50 kHz, 10 μs) amounted to -100 V. In the electron source, a combined mode of discharge was utilized: a low-current mode at a dc (up to 8 A) in combination with a pulsed mode (250 Hz, 0.2 ms, up to 100 A). The pressure of gaseous mixture in the chamber was 0.14 Pa, with the flow rate of argon and nitrogen through the hollow cathode changing in the range of 22 – 34 sccm and 6 - 18 sccm, respectively. The average current density and the pulse current density of ions on the sample were 6 mA/cm$^2$ and 60 mA/cm$^2$, respectively.

With the optimal values of element contents in the coating (Si ~5, Al ~15, Ti ~27 at %), the maximum value of hardness $H = 41$ GPa was obtained, with the elastic modulus $E$ being 590 GPa. Figure 7 shows $H$ and $H/E$ ratio as a function of the discharge current amplitude of the electron source, with the average electron-beam current maintained constant at 7 A. Reducing the average current with decreasing the current amplitude was compensated by an increase in the dc component of the discharge current. As the discharge current amplitude increased from 0 to 100 A, the hardness of
coating increased by 10 GPA, with the $H/E$ ratio increased by 12 % (up to 0.069). A high pulse ion current density (60 mA/cm$^2$) did not lead to the growth of internal stresses in the coatings.

3. Conclusion
Additional ionization and excitation of a gaseous medium with an electron beam during coating deposition using reactive magnetron sputtering makes it possible to attain to high pulsed values of ion current density (up to 0.1 A/cm$^2$) on the coating surface, which considerably affects adhesion and properties of the coatings.

A plasma source of electrons based on pulse discharge with a self-heated hollow cathode generates an electron beam with a current of 10-100 A and an electron energy of 200 eV at pressures ranging from 0.01 to 1 Pa in a pulse-periodic mode (1000 – 100 Hz, 0.2 ms).

Mass-spectroscopy of Ar-N$_2$ beam plasma demonstrated that the high-current pulsed electron beam provides twice as great a content of atomic nitrogen ions (up to 18%) as compared to the dc electron beam and gaseous discharge, which can be used in order to improve efficiency of the metals nitriding.

Acknowledgement
The study was carried out within a state program task No. 0389-2014-0006 and was partially supported by the Russian Foundation for Basic Research, project No. 14-08-00249-a.

References
[1] Window B, Savvides N 1986 J. Vac. Sci. Technol. 4(3) 453
[2] Thornton J A 1974 J. Vac. Sci. Technol. 11 666
[3] Musil J, Kadlec S, Münz W D 1991 J. Vac. Sci. Technol. A 9(3) 1171
[4] Kouznetsov V et al. 1999 Surf. Coat. Technol. 122(2-3) 290
[5] Leonhardt D, Walton S G, Fernsler R F 2007 Physics of Plasmas 14 057103
[6] Lock E H, Fernsler R F, Slinker S, Walton S G 2014 J. of Phys. D: Appl. Phys. 47(42) 425206
[7] Abraha P, Yoshikawa Y, Katayama Y 2009 Vacuum 83 497
[8] Gavrilov N V, Mamaev A S 2009 Technical Physics Letters 35(8) 713
[9] Gavrilov N V, Men'shakov A I 2011 Instruments and Experimental Techniques 54(5) 732
[10] Gavrilov N V et al. 2014 Izvestia VUZov. Fizika 57(11/3) 209
[11] Gavrilov N V, Kamenetskikh A S 2013 Technical Physics 58(10) 1426
[12] Bureyev O A, Gavrilov N V 2010 Proc. of 16th SHCE, Tomsk, Russia, 35
[13] Kamenetskikh A S, Gavrilov N V, Chukin A V 2014 Izvestia VUZov. Fizika 57(10) 161