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Research article

Vacuum devices and ion-assisted processes for forming functional coatings

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ABSTRACT

In this study, processes of vacuum formation of the coating-substrate structure with the effect of ion purification and atomic transfer were studied. The processes of vacuum formation of the coating-substrate structure with the influence of ion treatment and atomic transfer in this system are of a complex nature. When irradiated with ion flows and simultaneous deposition of coatings, several processes occur: heating, sputtering, desorption, ion insertion, mixing, and chemical reactions. Estimates show that for effective modification of coatings, a deposition regime is required that provides an energy impact of the order of 100 eV per atom of the coating. To solve the problems of ion (ion-stimulated) deposition of metal coatings, in addition to vacuum-arc devices, relatively simple evaporator designs from a crucible-anode in a hollow cathode, an electron beam evaporator with an additional electrode, and several systems with plasma generation units that complement the devices can be used magnetron sputtering.

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KEYWORDS

Vacuum forming
Coating structure
Heating
Sputtering
Desorption
Ion insertion

1. Introduction

The parameters of materials are largely determined by the properties of the surface, so coating as a method of creating surface layers of the required composition is important. The development of equipment and technology in functional coatings and surface treatment of materials is associated with improving the quality of coatings, increasing the efficiency of technological processes, and their unification. Growing requirements for products in mechanical engineering, optics, electronic engineering, instrument making, and other industries necessitate the creation of new methods and devices for processing materials [1].

Vacuum electron-ion, plasma, beam, and photonic processing methods are promising in this regard. Of great scientific and practical interest is the study of the effects of ion flows in a vacuum in combination with the deposition of coatings on the elemental composition, structure, and properties of materials and coating-substrate systems. It should be noted the relatively high efficiency of the impact of flows of "heavy" ions on materials, the specific combination of thermal, radiation, and chemical processes occurring, and atomic interactions in the properties of processed materials and coatings. Various vacuum methods for producing coatings are known [1–5], mainly based on the evaporation and sputtering of materials. Quite well-studied operations are thermal evaporation, ion-plasma sputtering, and sputtering, condensation with ion bombardment based on vacuum-arc treatments, and ion-beam treatment of the surface of materials [6–10]. Of interest is ion (ion-assisted) deposition of coatings [11–15], in which the coating being formed is treated with ions. For the work purpose, processes of vacuum formation of the coating-substrate structure with the effect of ion purification and atomic transfer were studied using vacuum devices and ion-assisted processes to form functional coatings.

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Table 1. Characteristics of vacuum coating deposition methods.

Coating deposition methods	Principles of materials evaporation	Characteristic modes of coating deposition	Vacuum degree, Pa
Thermoresistive evaporation	Heating the material until its saturating vapor appears at about 1 Pa	Filament current 50–500 A, evaporator heating up to 2300 K, deposition rate up to 100 nm/s	10^{-7}–10^{-1}
Evaporation from refractory crucibles	Heating in a crucible with an RF inductor or electrons	Released power up to 5–10 kW/h, deposition rate up to 50 nm/s	10^{-5}–10^{-2}
Electron beam evaporation	Surface heating by focused flow	Beam current up to 5 A, voltage up to 20 kV deposition rate up to 200 nm/s	10^{-4}–10^{-2}
cathode sputtering	Spraying a surface with a stream of ions	Cathode voltage up to 4 kV, current up to 1–2 A, deposition rate 1 nm/s	10^{-1}–10
Magnetron sputtering	Sputtering of a cathode in a magnetic field	Discharge current up to 50 A, voltage up to 10^3 V, deposition rate up to 100 nm/s	10^{-1}–5×10^{-1}
Precipitation from compounds under reduced pressure	Decomposition of compounds with surface reaction	Heating the base to 500–1500 K with the supply of reagents, deposition rate up to 1–2 nm/s	1–300

2. Parameter estimates and experimental part

Typical characteristics of some basic methods of vacuum deposition of coatings (except vacuum arc) are given in Table 1.

It should be noted that the above methods of coating deposition do not create relatively high energy of particles in the flow of the deposited material, and the degree of ionization remains below the range of 1 in Fig. 1 (less than 1%). This limits the adhesive strength and some other coating parameters. Additional ionic exposure significantly changes the deposition process. During ion stationary deposition of coatings, the effect on the parameters of the coating-substrate structure can be described by such parameters as the type and energy of ions (m_i, E_i), ion flux density (j_i), coating deposition rate (V_{oc}), the ratio of the ionized component to the total flux of deposited atoms (F_i/F_i+F_a) and specific energy of ion impact ε_i per one deposited particle (E_iF_i/F_i+F_a). If during conventional deposition ε_i is the energy imparted to one particle and can vary from 1 to 1000. During magnetron sputtering, it explains the energy that a single ion can knock out when it hits a particle (Fig. 2). Table 2 shows some processes under ion exposure.

It should be noted that the vast area (2–4) of the energy diagram which is distinguished by a variety of process parameters, is of significant interest and is least studied in terms of its technological capabilities and the operating physical mechanisms of modification of materials. Surface treatment mainly comes down to the physical processes of atomic condensation, their introduction, and sputtering. If part of the flow of atoms is condensed, part is introduced, and sputtering occurs simultaneously, then depending on the results of these processes, growth of the coating, doping of the surface layer or its sputtering with coefficient S should be observed. The diagram (Fig. 2) shows the main areas of ion treatment during the condensation of functional coatings in a high vacuum, explaining the processes that occurred including deposition and etching (sputtering).

The diagram explains the predominance of various effects during ion deposition of coatings depending on the parameters of the specific energy and the particles' resulting flux (deposition rate). In the different specific energy regions shown in the diagram, different physical effects of ionic influences predominate. In principle, ion exposure to the substrate can be carried out preliminary, simultaneously with the deposition of coatings, after the deposition of coatings, and combined,

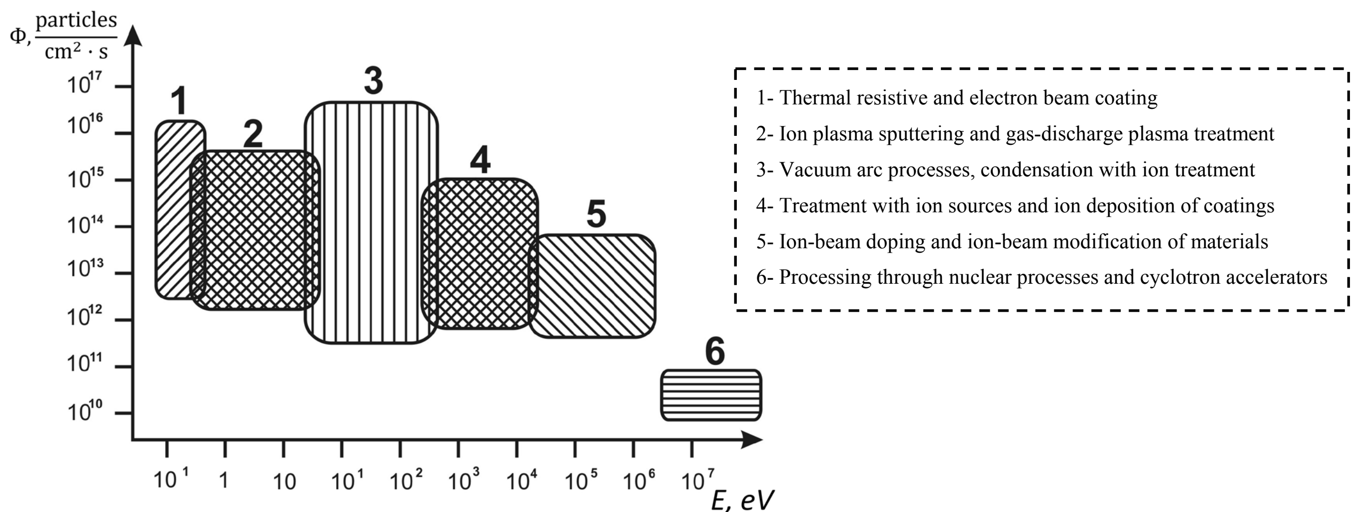

Fig. 1. Energy and intensity of surface treatment of materials.

Table 2. Processes in vacuum and solids under ion influence and their results.

Vacuum chamber	Solid	Results
Elastic collisions with their gas's excitation and ionization	Charging the surface	Removing the surface layer
Recharging part of the ion flow	Excitation and ionization of atoms	Formation of new compounds
Cathode surface sputtering	Surface heating	Change in structure and composition
Ion-ion emission	Introduction of ions into the surface layer	Phase transformations
Secondary electron and photon emission	Formation of point radiation defects	
	Atomic displacement	
	Stimulation of surface chemical reactions	

for example, before the deposition of coatings and in the initial stage of its formation.

Calculations using the Monte Carlo method show that for effective action (modification of parameters) of coatings during ion deposition, ion action modes are required to ensure the release of energy in atomic collisions of 100 eV per atom of the deposited coating.

Considering that almost any elements in different charge states and at different energies can be used as accelerated particles, vacuum ion processing is a convenient means of influencing objects and allows one to change the properties of the surface regions of materials and coatings within a wide range.

The most effective methods and devices for ion deposition (condensation with ion bombardment) are vacuum-arc processes and numerous installations that implement this method [15, 16]. However, in most cases, such methods are not used to form coatings in microelectronics, optics, and some other fields due to high temperatures and the presence of a droplet fraction in the flow.

For other methods of material evaporation, effective ionization of the resulting vapor and treatment of the growing coating with accelerated ions is a difficult task. So, when using a conventional materials evaporator (Fig. 3), when currents of up to 200 A are passed through the boat, the emerging flow of metal vapors (Cu, Ag, Ti) has a degree of ionization of no more than 0.1%. There is a need for a separate vapor ionizer installed between the evaporator and the substrate (substrate holder to which a negative potential is applied). At the same time, the complexity of the design increases many times over.

The design of a device with an extended evaporator and a separate vapor ionizer is shown in Fig. 4.

This design has a vapor ionization rate of up to 1% and allows obtaining a current density of up to 0.1 mA/cm^2 at a negative voltage of up to 500 V, which is also quite efficient. A noticeably more efficient design is the electric discharge device with a hollow cathode, shown in Fig. 5. For the deposition of coatings of Al, Al-Si alloy, Cu, Ag, Au, Ni, Ti, SiO and coatings from other materials with a maximum evaporation temperature of up to 2000 °C and a large (more than 0.1 m^2) processing area, an electric discharge device of a simple design has been used with a cylindrical crucible evaporator. The device uses the effect of igniting a discharge in a hollow cathode with a hot evaporating anode electrode.

An electric-discharge device for ion deposition includes the following main elements: a hollow cathode, an anode crucible, a filament cathode, a shutter, and an insulated substrate holder, inputs, control, and power units. The design of an electric discharge device with a hollow cathode and a hot crucible-anode showed the ion deposition device acts as follows. After obtaining a vacuum degree of ~10^{-4} Pa in the vacuum working chamber, the power supply of the device is

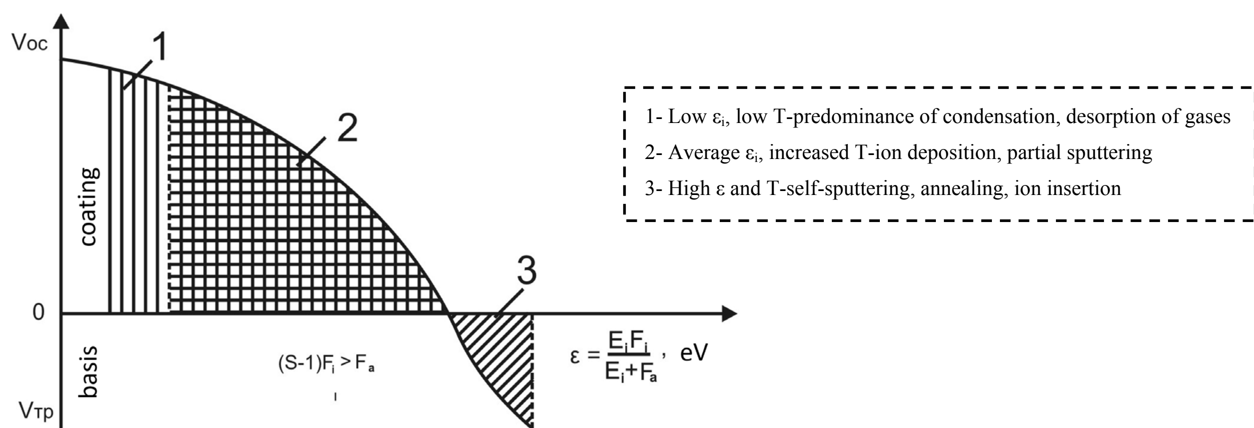

Fig. 2. Effects of ion exposure during coating deposition.

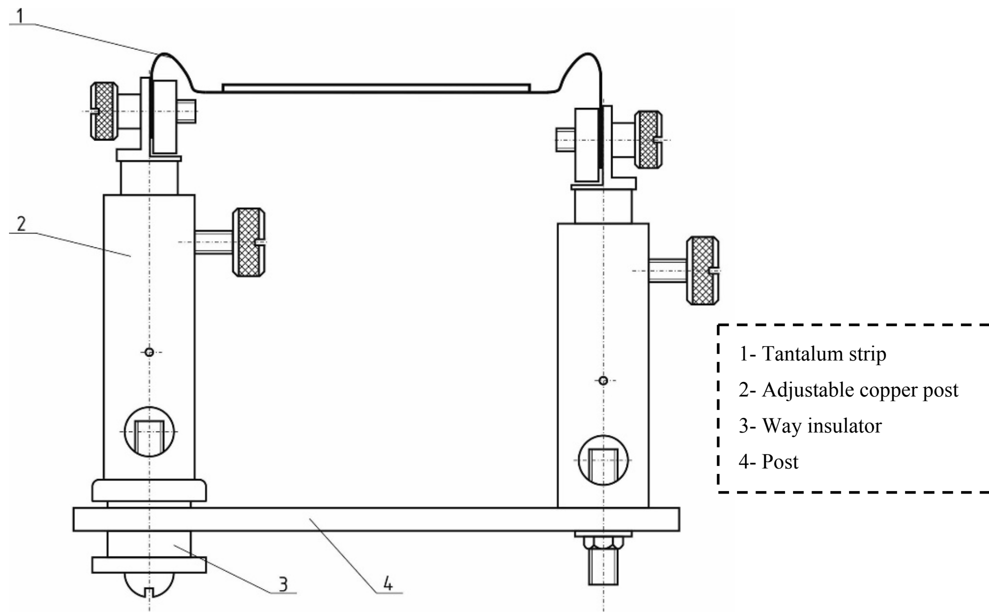

Fig. 3. Design of thermal evaporator.

turned on, the maximum high voltage (~5 kV) is supplied to the anode crucible with the working material, and a filament current of up to 30 A is supplied to the cathode, ensuring the emission of current from the cathode from 20–30 mA to 250–300 mA. This ensures the heating of the crucible to the temperature of formation of a noticeable flow of solid-phase vapor. A transition is observed from a vacuum discharge with a current of up to 300 mA at voltages up to 4 kV to a discharge at currents of about 2.0 A with voltages of up to 500–700 V. Then the filament tungsten cathode is turned off and the shutter is opened, after which coatings are deposited in the selected mode at a negative voltage on a rotating substrate holder until the working material was completely evaporated.

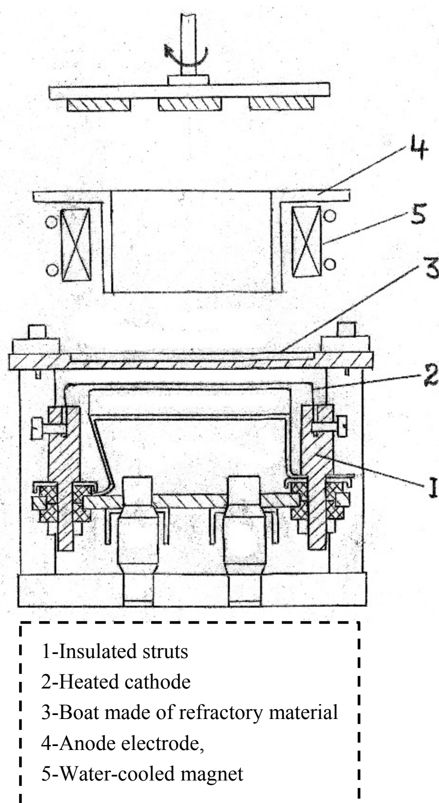

Fig. 4. Coating deposition device with a separate vapor ionizer.

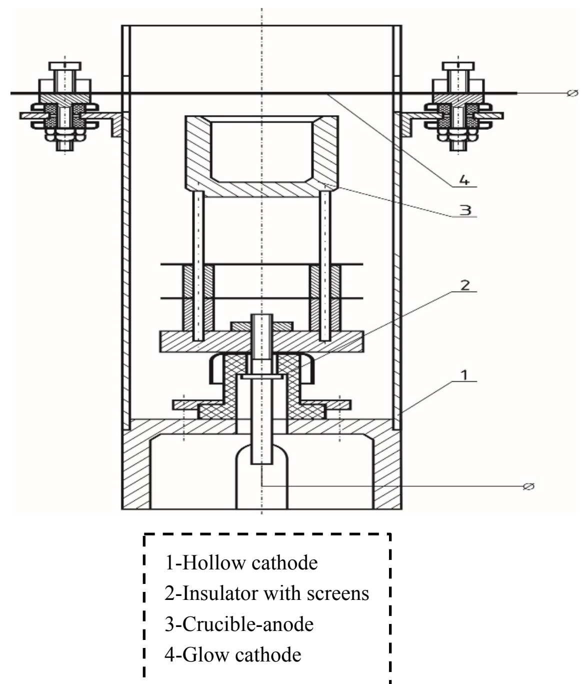

Fig. 5. Electric discharge evaporator with hollow cathode.

The hollow cathode crucible anode deposition device has been used to deposit copper and silver coatings on molybdenum substrates and has the following main characteristics:

- Degree of vacuum in the "starting" mode of the device, 10^{-3} Pa;
- Temperature of the crucible-anode with the working material, up to 2000 °C;
- Mass of working material evaporated in one cycle, up to 20;
- Deposition rate of metal coatings, up to 50 nm/s;
- Treated area (without rotation of substrates), 3–10 dm^2;
- Ion current density on the substrate holder, 0.1–0.5 mA/cm^2;
- Degree of ionization of metal vapor flow, 1–5 %.

To implement the method of ion deposition of metal coatings (Al, Al-Si, Ni) and some oxides in a system with electron beam evaporation from a copper water-cooled crucible, a modernized UELI-1 evaporator and a material vapor flow ionizer were used. The beam-plasma type ion deposition device included an electron beam evaporation system, a cooled copper crucible with a heated ring discharge electrode, a rotating steel insulated substrate holder, and control and power units. The discharge electrode was a cylindrical (diameter 40–50 mm) tantalum or tungsten strip electrode up to 1 mm thick with a cut, located above a copper crucible and connected to electrical inputs (two inputs for voltages up to 1 kV and currents up to 100 A).

A beam-plasma-type ion deposition device with an electron beam evaporator is shown schematically in Fig. 6.

The ion deposition device with a beam evaporator worked as follows. After creating a vacuum degree of 10^{-3}–10^{-4} Pa in the vacuum working chamber, the power supplies were turned on and a stable voltage at the cathode was established (12 kV). Then the electromagnetic coils and cathode heating were turned on. In this case, the emission current was set to about 30–50 mA and the focused electron beam was scanned over the working material located in a copper-cooled crucible. The device remained operational even at a vacuum degree of the order of 1 Pa. The working material, for example, an Al-Si alloy, gradually melted and took the form of a copper crucible. To effectively evaporate the material, beam scanning is turned off, the operating point is selected, usually in the center of the crucible, and by increasing the cathode heat, the beam current (load current) is set within 200–400 mA. As a rule, the electron beam is focused into a central zone with an area of 1–4 mm^2. After, the cathode emits a high-energy (1 kV) beam of electrons focused by a magnetic field, which hits the material in the crucible and carries away the sputtered material from the crucible, deposited on the substrate.

An electron beam evaporation ion deposition device with a discharge electrode has been used to deposit aluminum coatings up to 0.8 µm thick on silicon substrates and provides the following main characteristics:

- The initial degree of vacuum during device operation, 10^{-3} Pa;
- Maximum loading of working material into the crucible, 50 cm^3;
- Deposition rate of aluminum coatings, 2–50 nm/s;
- Maximum discharge current during evaporation, 1.5 A;
- Area treated when applying coatings, 1–5 dm^2;
- Ion current density on the substrate, 0.1–0.5 mA/cm^2;
- Degree of ionization of material vapor flow, 1–2%.

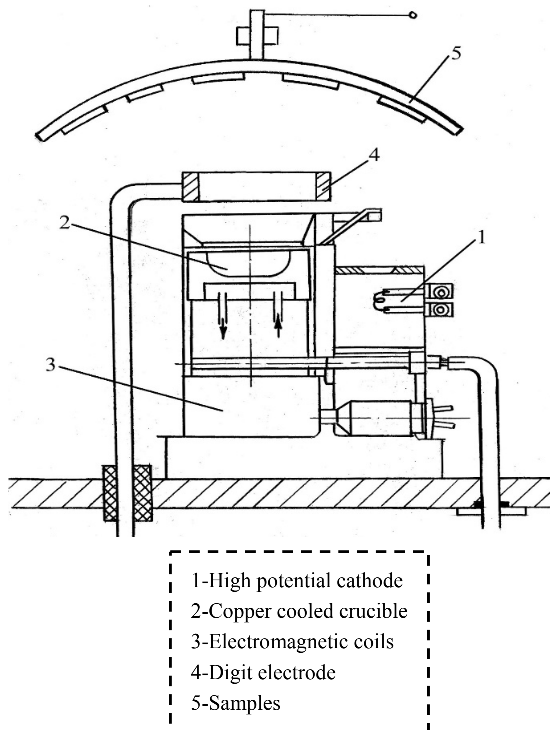

Fig. 6. Ion deposition device with electron beam evaporator.

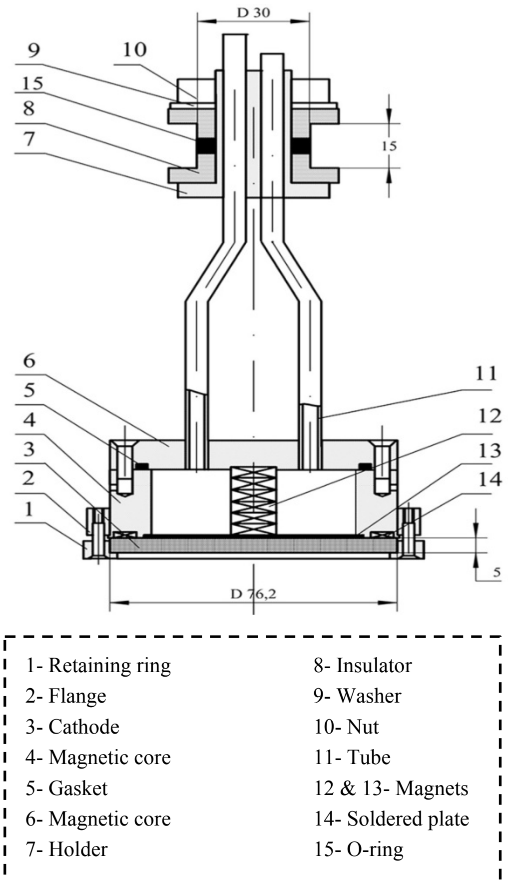

Fig. 7. Magnetron sputtering device with replaceable cathode.

In practice, DC magnetron sputtering devices are widely used, which are based on the use of crossed magnetic and electric fields to increase the efficiency of ionization of the working gas and create a dense plasma region above the surface of the cathode target. A voltage of 400 to 700 V is usually applied to the magnetron cathode. One of the urgent tasks is to simplify the design and the ability to quickly change target cathodes. In addition, several targets made of alloys and compounds are supplied in the form of disks with a diameter of 76 mm, which requires the creation of a sputtering device specifically for this cathode size and with the ability to integrate the sputtering device into any vacuum working chamber. Such a device can be used for additional ion-plasma processing of substrates if a negative voltage of 50 to 500 V is applied to the substrate holder located at a distance of 50–100 mm from the cathode. In this case, the current to the substrate holder increases from 50 to 100 V and then changes slightly (by 20–30%) with an increase in voltage to 500 V. The device allows you to treat the surface of materials with a tubular diverging ion-plasma flow (discharge current up to 50 mA, discharge voltage up to 5 kV). This current depends on the magnetron discharge current and the current density on the conductive substrate reaches 1–2 mA/cm^2. The design of a magnetron sputtering device with a small-sized replaceable cathode is shown in Fig. 7.

Ion sources with closed electron drift are of practical interest for ion deposition devices. In an ion source with closed electron drift, containing a hollow body that serves as a cathode. The end walls contain an emission slot and channels for injecting working gas, magnetic tips, an anode installed in the housing cavity opposite the slot, and sources of magnetomotive force. Magnetic tips are equipped with removable plates installed in compliance with the geometric relationships between the plates and the emission slit aperture. For practical implementation of processes of vacuum-plasma (ion) surface treatment of materials (flat products), several new options for sources of beam-plasma flows were developed and tested. A stream of gas ions can be directed onto the substrate simultaneously with the deposition of coatings for additional energy impact. The design of one beam-plasma processing device placed on the flange of a vacuum chamber is shown in Fig. 8.

To solve the problem of processing several objects in a vacuum chamber, it turned out to be possible to construct a system including a magnetron sputtering device and a moving plasma generation unit (ion source) with the ability to process the sputtered cathode and/or the processed substrate. In this case, it becomes possible to beam-plasma treat the surface of the target cathode of a magnetron device to facilitate the formation of an anomalous glow discharge, as well as cathode sputtering and substrate treatment.

At the same time, an increase in the productivity of sputtering the cathode surface is observed, and the possibility of using beam-plasma (ion) processing is expanding. Fig. 9 shows an embodiment of the developed movable structure.

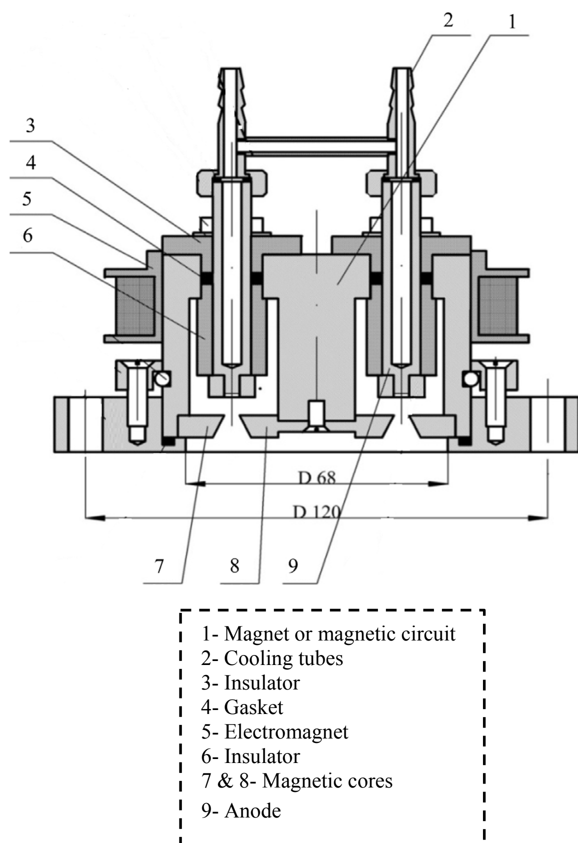

Fig. 8. Beam-plasma surface treatment device.

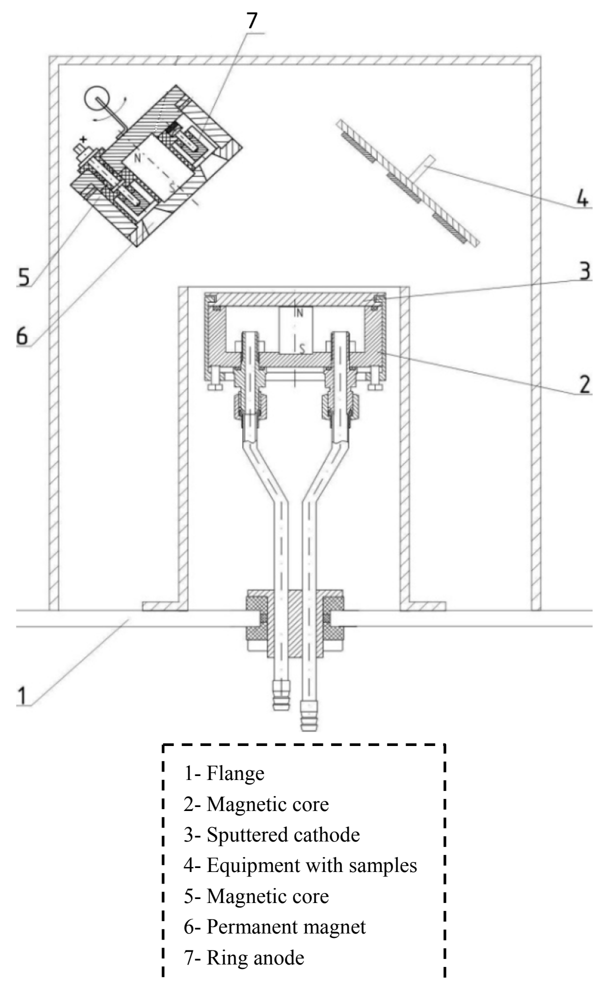

Fig. 9. Plasma treatment design device.

The plasma treatment device contains a chamber in which a magnetron unit with a target cathode is placed to create a flow of sputtered material and at least one movable plasma generation unit with plasma excitation in a discharge with crossed electric and magnetic fields, including a magnetic system made in the form of a hollow magnetic core with a source of a magnetic field, and the magnetic core has a closed annular output channel and a disk anode inside the magnetic core. The plasma generation unit, the substrate, and the magnetron target cathode are located relative to each other in such a way that the plasma generation unit is capable of processing the target cathode or substrate. It is possible to use two or more independent movable plasma generation units for processing the target cathode and the substrate. In practice, the design was tested in the deposition of silicon silicide coatings up to 1 micron thick on dielectric substrates.

3. Conclusions

The processes of formation of a coating-substrate structure in a vacuum under the influence of atomic exchange and ion treatment before obtaining a thin coating of the surface of a dielectric substrate under vacuum conditions are complex. When irradiated with ionic currents and simultaneously applying coatings, several processes occur: heating, shaking, desorption, introduction of ions, mixing, and chemical reactions. In several methods for producing a thin coating in a vacuum, the degree of ionization of particles is as follows. When a current of up to 200 A passes through a thermal evaporator device, metal vapors have an ionization level of no more than 0.1%. In coating deposition with a separate vapor ionizer, ionization of up to 1% is achieved while creating a current density of up to 0.1 mA/cm^2 when applying voltages of up to -500 V to the rotating base holder. The ion deposition device observed ionization up to 5% at a current of 300 mA and voltage up to 4 kV. With magnetron sputtering, it has been established that ionization reaches 2% at voltages up to 500 V and a current density of 1–2 mA/cm^2. As a result of research, it became known that different methods have different levels of ionization.

CRediT authorship contribution statement

I.R. Bekpulatov: Investigation, Writing – original draft, Supervision.
B.D. Igamov: Resources, Writing – review & editing.
G.T. Imanova: Investigation, Writing – review & editing.
A.I. Kamardin: Investigation, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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