Coating synthesis on dielectric substrates assisted by pulsed beams of high-energy gas atoms

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Abstract. Titanium nitride and aluminum nitride coatings have been deposited on glass and aluminum oxide substrates in a flow of metal atoms accompanied by high-energy gas atoms. The metal atoms are produced due to sputtering of a flat rectangular magnetron target. The gas atoms with energy up to 25 keV are produced due to charge exchange collisions of ions extracted from the magnetron discharge plasma and accelerated by high-voltage pulses applied to a flat grid parallel to the target. The metal atoms pass through the grid and deposit on the substrate. Conjunction of their trajectories with those of gas atoms bombarding the growing coating enables the coating synthesis on complex-shape dielectric products planetary rotating inside the vacuum chamber. Mixing high-energy gas atoms of the coating and substrate atoms substantially improves the coating adhesion.

1. Introduction
Plasma- and beam-assisted deposition methods are widely used for production of various functional coatings on the surface of machine parts and tools [1]. Properties of a growing coating depend on the energy transferred to the atoms condensing on its surface. This energy may be supplied due to the product heating. When the energy is supplied by accelerated ions bombarding the product, the equilibrium heating of the coating and the product is replaced by non-equilibrium atomic-scale heating [2]. In this case, the energy is independent of the substrate temperature. It enables coating deposition on heat-sensitive materials and wide-range regulation of the coating properties.

Under energy of ions rising up to hundreds and thousands of volts, their sputtering efficiency monotonically rises, and the ions are able to sputter all deposited atoms. For this reason, the coating modification by high-energy ions is usually carried out in pulsed regimes. Due to ion mixing of the product and coating atoms, the width of the interface may be comparable with the coating thickness, thus ensuring perfect adhesion [3-5].

When a conductive coating is deposited on a conductive product, it can be bombarded with ions extracted from the discharge plasma and accelerated by a negative DC or pulsed bias voltage applied to the product. Nevertheless, the modification of dielectric coatings or any coatings on dielectric products can be carried out only with the use of broad beam sources of accelerated ions [6] or fast atoms [7-9], because it is impossible to apply high negative voltage to dielectrics.

When a complex shaped product is being coated, some parts of the product surface shadow the others during its rotation inside the chamber, and at some time intervals, the accelerated particles do not bombard the growing coating at all. This is because accelerated particles from a beam source [10] and metal atoms, for instance those from the source of metal atoms [11], converge on the product from...
different directions. There is no shadowing only when the source [12] has common emissive grid for both metal atoms and accelerated gas ions moving to the product along the same trajectories. This source significantly improves adhesion of thin films deposited on dielectrics when the growing film is bombarded by pulsed beams of fast gas atoms with energy of several keV. To ensure adhesion of 0.1-mm-thick superhard coatings on dielectric ceramic products, it is necessary to create the same physical conditions of their synthesis, as in [3-5]. Therefore, the energy of fast neutral gas atoms must be heightened up to ~25 keV and more.

It is impossible to produce high-energy ions using the source [12], because of electrical breakdowns at 20-kV amplitude of pulses applied to the anode of hollow cathode glow discharge used for generation of plasma emitter, and problems with the discharge ignition at high voltage [13].

It was shown in [7] that the beams of fast neutral atoms and molecules can be produced due to charge exchange collisions of accelerated ions in space charge sheaths near negatively biased grid immersed in low-pressure gas discharge plasma. In this case, the beam parameters depend mainly on the pressure and do not depend on the gas discharge type. It is possible, for instance, to use the magnetron discharge plasma as ion emitter and to produce pulsed beams of high-energy gas atoms bombarding the growing coating due to application of high-voltage pulses to the grid parallel to the planar magnetron target. Similarly to [12], the target material atoms taking part in the coating synthesis will enter the chamber through the same grid together with high-energy gas atoms. This work is dedicated to the development of the magnetron sputtering system, generating pulsed beams of high-energy gas atoms bombarding the growing coating.

2. Experimental setup

Figure 1 depicts the scheme of the experimental setup used for the deposition of coatings bombarded by pulsed beams of high-energy gas atoms.

![Figure 1. Scheme of the experimental setup.](image-url)

On vacuum chamber 1, rectangular 130-mm-deep hollow case 2 is installed with an inner cross-section of 600×200 mm. At the case bottom, a planar magnetron is mounted with water-cooled 150-mm-wide and 370-mm-long titanium target 3. Magnetron power supply 4 is connected between target 3 and grounded flange 5, which serves as the magnetron discharge anode. The power supply ensures stabilized current in the target circuit ranging from 1 to 8 A at voltage of up to 650 V between the
anode and the target. Inside case 2 grid 6 is placed. The width of the gaps between grid 6 and the inner surfaces of case 2 amounts to 10 mm. The system design allows variation of the distance between target 3 and grid 6 from 60 to 100 mm. Using feed-through 8 the grid is connected to high-voltage pulse generator 9. The generator allows regulation of the pulse amplitude from 3 to 30 kV, the pulse width from 5 to 50 μs, and the repetition rate from 5 to 50 Hz. Holder 10 of substrates 11 is mounted on horizontal rod 12 passing through guide bush 13, which rotates on cylindrical electrode 14 of feed-through 15. The holder design allows varying the distance between substrate 11 and target 3 from zero to 300 mm.

After the power supply 4 is switched on, the discharge is ignited and the chamber is filled with glow of the discharge plasma (Figure 2), which is most intense near the target surface.

Figure 2. Photograph of the discharge plasma glow inside the chamber at pressure 0.3 Pa of argon and nitrogen (15%) mixture and current in the magnetron target circuit of 8 A.

When a high-voltage pulse is applied to grid 6, near its surface sheaths 19 and 20 of positive space charge are formed separating the discharge plasma into two parts. During the pulse, plasma 16 filling chamber 1 is not involved in the discharge. It is cut off from plasma 21 of the ongoing magnetron discharge located between target 3 and grid 6. The ions 22 from plasma 21 are accelerated by the grid; due to collisions in sheaths 19 and 20 with gas molecules 23, they turn into fast neutral molecules 24. All ions 25 resulting from the charge exchange collisions are collected by grid 6.

3. Experimental results
Substrate 11 was placed on holder 10, and on its surface a 0.5-mm-thick titanium mask was fixed. After the coating deposition, the mask was removed, and height of the step between the open surface of the substrate and its surface covered with the mask was measured using the DektakXT profilometer (Bruker Nano Inc., USA). The titanium deposition rate was determined by dividing the height of the step by the deposition time. In the absence of grid 6 and at the current in the target circuit of 8 A, it amounted to 2.5 μm/h at the distance from the target of 200 mm; to 9.5 μm/h, at the distance of 100 mm and to 17 μm/h, at the distance of 50 mm.

After grid 6 (Figure 1) with the transparency of 70 % was installed at the distance of 60 mm from target 3, the titanium coating deposition rate—at argon pressure of 0.4 Pa and current in the target circuit of 8 A—on a substrate distanced from the target at 90 mm diminished from 10 to 7 μm/h, i.e. by 30%. When nitrogen (15%) was added to argon, the deposition rate diminished more than 2 times,
and within 2 hours a 6.5-µm-thick golden titanium nitride coating with the microhardness of 2200 HV was synthesized on the substrate.

When high-voltage pulses were applied to grid 6, near both surfaces of the grid sheaths of positive space charge were formed, where ions were accelerated and high-energy atoms were produced. The sheaths width depends on the pulse amplitude and the ion current density. To determine the current density of ions 22 from plasma 21 (Figure 1) located between grid 6 and target 3, dependencies of the grid current $I_g$ on the grid voltage $U_g$ were obtained (Figure 3).

**Figure 3.** Dependencies of current $I_g$ on voltage $U_g$ between the chamber and the grid in the grid circuit at the pressure of argon and nitrogen (15%) mixture of 0.4 Pa, current in the target circuit of 4 A and distance between the grid and the target of 70 mm (1), 80 mm (2) 90 mm (3) and 100 mm (4).

The current in the grid circuit rises when the grid voltage increases. But at a voltage of hundreds of volts it dramatically reduces approximately by 2 times and with a further increase in the voltage it keeps the constant value $I_{gi}$. After the current drop, glow intensity of plasma 16 in the chamber sharply diminishes, and the ion current in the circuit of the probe installed in the chamber reduces by ten times. It can be explained by the fact that the grid prevents electrons of discharge plasma 21 from penetrating into chamber 1. In this case, the current in the grid circuit $I_g$ is equal to the total current of ions extracted from plasma 21 and secondary electrons emitted by the grid. Since at voltages lower than 600 V, the coefficient of ion-electron emission does not exceed 0.1 [14], the secondary electron current can be neglected, and $I_g$ may be considered as average current of ions arriving from plasma 21 to grid 6. Figure 4 shows the dependencies of current $I_g$ in the grid circuit on the distance $h$ between the grid and the target at currents in the target circuit ranging from 4 to 8 A.

Before the deposition with application to the grid of high-voltage pulses, no activation and heating of the substrates has been carried out, hence the formation of the transitional layer between the substrate and the coating started at room temperature. At the pressure of the argon and nitrogen (15%) mixture of 0.7 Pa, the current of 8 A in the target circuit and the amplitude of 20 kV of the voltage pulses applied to the grid, a brown 5.8-µm-thick nitride coating with the microhardness of 2700 HV was synthesized within 2 hours on the initially cold substrate made of hard alloy. Evaluation of its adhesion using a scratch tester, showed that critical loads for the coatings synthesized using 20-kV pulses are several times higher than that of conventional nitride coatings, synthesized at a constant bias voltage of 100 V of the substrate.
Figure 4. Dependence of current $I_{gi}$ on the distance $h$ between the grid and the target in the circuit of the grid preventing the magnetron discharge plasma from penetrating into the chamber, at the current in the target circuit 4 (1), 6 (2) and 8 A (3).

When the amplitude of pulses applied to the grid is reduced to 15 kV, the coating parameters remain virtually unchanged. However, at voltages lower than 10 kV, the microhardness decreases down to 2200 HV, the adhesion is considerably reduced, and at the amplitude of 5 kV, delamination of the coating is already observed.

4. Discussion
The most striking difference of coatings deposited using high-voltage pulses applied to the grid is their perfect adhesion despite the interface formation at room temperature without any preheating and activation. The adhesion is improved due to bombardment of the substrate by high-energy gas atoms. In the surface layer with a thickness ranging from 20 to 100 nm, each of these atoms triggers dislodgement of hundreds of atoms from the crystal lattices of the substrate and the growing coating. As a result, atoms of the substrate and the coating are mixing together. This is the reason of the interface width increase and the adhesion improvement.

The energy of atoms produced due to charge exchange collisions of ions accelerated in sheaths 19 and 20 (Figure 1) is determined by the ratio of the ion charge exchange length, depending on their energy and gas pressure, to the width of the sheath, which depends on the voltage applied to grid 6 and the current density of ions 22 accelerated from plasma 21. When current in the target circuit is equal to 8 A, the current of ions 22 in the grid circuit is equal to $I_{gi} = 2.3$ A, and the average ion current density $j$ on the grid with the surface area of 0.072 m² is equal to 32 A/m².

From the Child-Langmuir law [15], at $j = 32$ A/m² and the pulse amplitude $U = 25000$ V, the sheath width is equal to 0.03 m. The fast molecule energy corresponds to the potential of the point, where the charge exchange collision took place [7]. Therefore, it is distributed continuously from zero to the value $eU$ corresponding to the pulse amplitude. At room temperature and pressure of $p = 0.1$ Pa, the density of the gas molecules is equal to $n = 2.5 \times 10^{19}$ m⁻³. The charge exchange cross section of 25-keV argon ions is equal to $\sigma = 10^{-19}$ m² [15, 16]. Therefore, the charge exchange length of these ions $\lambda = 1/(n\sigma) \approx 0.4$ m exceeds by ten times the width of the sheath. When they pass through the sheath, only a few of accelerated ions are converted into neutral molecules with an energy $\sim eU$. The number of such molecules rises with pressure increase to $p \sim 0.5$ Pa, when the charge exchange length $\lambda \sim 0.08$ m exceeds the sheath width approximately by 2 times [20]. At $p \sim 1$ Pa $\lambda$ is less than the width of the layer $\sim 0.3$ m and the maximum energy of molecules is reduced, since most of the ions are converted into fast molecules, even before they reached the grid. The experimentally observed deterioration in
adhesion of the coatings at the gas pressure lower than 0.7 Pa can be explained by a decrease in the energy and the number of high-energy gas molecules.

5. Conclusion
1. Bombardment of growing coating by neutral molecules with energy up to 20 keV creates the same physical conditions for its synthesis on the products made of metals and dielectric ceramics, as bombardment by ions with equal energy. This enables the synthesis of coatings with enhanced adhesion and microhardness on products rotating inside the chamber and made of both conductive and dielectric materials.
2. The reason of the coating adhesion improvement can be the interface width increase, caused by mixing of the product with atoms of the growing coating by gas atoms with energy up to 25 keV in the very beginning of the coating deposition.

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