Materials Science Forum
ISSN: 1662-9752, Vol. 876, pp 14-24
doi:10.4028/www.scientific.net/MSF.876.14

Submitted: 2016-07-21
Revised: 2016-08-30
Accepted: 2016-08-30
Online: 2016-10-10

New Method for Synthesis of Hard Coatings Using Pulsed Bombardment with High-Energy Gas Atoms

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Keywords: magnetron sputtering, metal atoms, fast gas atoms, coating synthesis, surface layer, adhesion improvement.

Abstract. For deposition of hard coatings is used a source of metal atoms accompanied by high-energy gas atoms. The metal atoms are produced due to sputtering a flat rectangular target in low pressure magnetron discharge. The gas atoms with energy up to 30 keV are produced due to charge exchange collisions of accelerated ions in space charge sheaths near the surfaces of a grid parallel to the target. The ions are extracted from the discharge plasma and accelerated by high-voltage pulses applied to the grid. The metal atoms pass through the grid and deposit on the products. Conjunction of their trajectories with those of gas atoms bombarding the growing coating allows synthesis of the coatings on rotating dielectric products. Mixing by high-energy gas atoms of the coating atoms and atoms of the product material in its surface layer improves the coating adhesion.

Introduction

Plasma- and beam-assisted deposition methods are widely used for production of various functional thin films on the surface of machine parts and tools [1]. Properties of a growing film depend on the energy transferred to the atoms condensing on its surface. This energy may be supplied, for instance, through the substrate heating. In thermal equilibrium conditions it controls activation of its surface, which is critical to the film adhesion, as well as the growing film morphology. Another way to supply the energy is bombardment of the film with accelerated ions. In the latter case the equilibrium heating of the film and the substrate is replaced by the non-equilibrium atomic scale heating [2]. It is more controllable through electrical parameters and universal, because in this case the energy is independent of the substrate temperature. This enables the film deposition on heat sensitive materials and a wide-range regulation of the film properties, which are very sensitive to the ion energy.

For instance, the density of Mg films deposited using a Mg^+ ion beam grows with the ion energy from 83% of the bulk material density at the energy of 24 eV to its maximal value (about 100% of the bulk material density) at the ion energy of 48 eV and then falls down to 50% and 15% with the energy increasing to, respectively, 120 eV and 300 eV [3]. In the same time the Mg film adhesion rises with the ion energy monotonically due to deeper penetration of accelerated particles into the substrate.

When slow atoms are condensing on the substrate and the growing film is bombarded by accelerated ions, the film properties depend not only on the energy of ions, but also on the ratio of their flow density on the substrate surface to that of condensing atoms.

At the ion energy 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 film modification with high-energy ions is usually carried out in pulsed regimes. Due to recoil-induced

atom transport and ion mixing of the substrate and film materials the width of the substrate-to-film interface may be comparable with the film thickness thus ensuring a perfect adhesion [4-6]. Pulsed bombardment by high-energy ions enables production of sputtered nanocomposite films [6] hardly relating to known structure zone models.

When a conductive film is deposited on a conductive substrate, they both are usually bombarded with ions extracted from the magnetron discharge plasma and accelerated by a negative DC or pulsed bias voltage applied to the substrate. Pretreatment with ions enables an appreciable improvement of the film adhesion to the substrate. The ion bombardment of growing film enables a wide-range regulation of the film properties by means of variation of the ion energy and the ratio of the ion current density to the flow density of condensing atoms. Nevertheless to regulate properties of dielectric films or of any films on dielectric substrates broad beam sources of accelerated ions [7, 8] or fast atoms [9-11] are needed, because it is impossible to apply a high negative voltage to dielectrics.

While coating a complex shaped product rotating inside a vacuum chamber, some parts of the product surface shadow the other. At some time intervals, the accelerated particles do not bombard the growing coating at all. Because accelerated particles from a beam source, such as that used in [12], and metal atoms taking part in the synthesis, such as those from the source of metal atoms sputtered from a conductive target [13], converge on the product from different directions. There is no shading only when a source is used, where metal atoms and fast gas atoms start from one and the same emissive grid and move to the product along the same trajectories [14].

A source with common emissive surface for both metal atoms and accelerated gas ions has significantly improved adhesion of thin copper films deposited on dielectrics when the growing film was bombarded by pulsed beams of fast argon atoms with energy of several keV. However, in order 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 [4-6]. Therefore, the energy of fast neutral gas atoms must be increased up to ~ 25 keV and more.

From the source [14] through its grid enter the chamber accelerated ions. As to the fast neutral gas atoms and molecules, they are produced during flight of the ions to the product due to charge exchange collisions with gas molecules inside the chamber. The ions are accelerated in the space charge sheath between the emissive grid and plasma emitter of the source produced using hollow cathode glow discharge. The negative potential of the grid, which limits the flow of electrons from the chamber to the source, is equal to about 100 V, and the voltage of up to a few kilovolts accelerating the ions is applied to the discharge anode. The anode potential is almost equal to the potential of the plasma emitter.

To produce high-energy ions using the same source [14], high voltage pulses must be applied to its anode as well. In this case, the pulses with an amplitude of ~ 30 kV will be applied to the hollow cathode, to the target located on the cathode bottom and being sputtered by ions from the plasma emitter, to the discharge power supply connected between the anode and the cathode, as well as to the source of bias voltage of 2 kV connected between the cathode and the target [14]. These circumstances, as well as problems with the hollow cathode glow discharge ignition at a high voltage[15] significantly complicate the task.

It was shown in [9] that the beams of fast neutral atoms and molecules can be produced due to charge exchange collisions of accelerated ion in space charge sheaths near negatively biased grids 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 an ion emitter. Applying high-voltage pulses to the grid parallel to the planar magnetron target, it is possible to produce pulsed beams of high-energy gas atoms bombarding the growing coating. Herewith atoms of the target material taking part in the coating synthesis enter the chamber through the same grid. This work is dedicated to development of a magnetron sputtering system, generating pulsed beams of high-energy gas atoms bombarding the growing coating.

Experimental setup

Figure 1 presents scheme of the experimental setup for the deposition of coatings bombarded with pulsed beams of high-energy gas atoms. On vacuum chamber *1* is installed rectangular 130-mm-deep hollow case *2* with an inner cross-section of 600x200 mm² At the case bottom, a planar magnetron is mounted with water-cooled 9-mm-thick, 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 anode-target voltage up to 650 V.

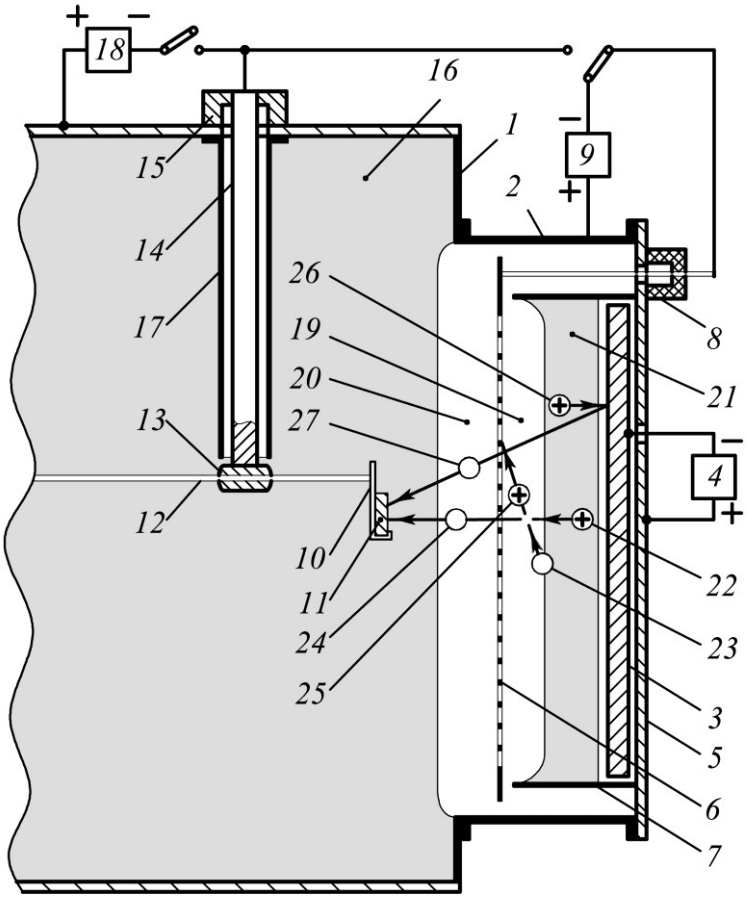

Figure 1: Scheme of experimental setup. 1 - vacuum chamber, 2 - hollow case, 3 - target, 4 - magnetron power supply, 5 - flange, 6 - grid, 7 - screens, 8, 15 -feed-through, 9 - high-voltage pulse generator, 10 - holder, 11 - substrate, 12 – rod, 13 – guide bush, 14 - cylindrical electrode, 16 - plasma,17 - cylindrical screen, 18 - DC power supply, 19, 20 - space charge sheaths, 21 - magnetron discharge plasma, 22, 25, 26 - ions, 23 - gas molecule, 24 - high-energy molecule, 27 - atoms of the target material

On ceramic insulators (not shown in Fig. 1) inside case *2* is fixed grid *6* with 7-mm-diameter holes the distance between their centers amounting to 8 mm, which is produced of 1.5-mm-thick titanium sheet. Above and below target *3* two flat screens *7* electrically connected with flange *5* prevent from deposition of metal films on the insulators installed behind them. 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. The maximum amplitude of the current pulse amounts to 15 A.

Holder *10* of substrates *11* is mounted on horizontal rod *12* passing through guide bush *13*, which rotates on cylindrical electrode *14* of high-voltage feed-through *15*. If the substrate *11* is made of a

conductive material, it is possible to connect the generator *9* to electrode *14* and to apply high-voltage pulses directly to substrate *11*. To reduce the ion current in the circuit of electrode *14* from plasma *16* filling the chamber the electrode surface is covered by grounded cylindrical screen *17*. The holder design allows variation of the distance between substrate *11* and target *3* from zero to 300 mm. A negative voltage ranging from 100 to 1200 V can be applied to substrate *11* from source *18*.

The vacuum chamber is evacuated by a turbo-molecular pump to 0.001 Pa pressure. Before opening the door of the chamber, it is heated with hot water. Stability of the operating pressure ranging from 0.1 to 2 Pa and of the predetermined percentage of nitrogen in mixture with argon is supported by a dual-channel supply system with gas flow controllers. The vacuum pumping system, the gas supply system and parameters of the power supplies *4*, *9* and *18* are controlled from a control panel.

After evacuation of the chamber and filling it with the working gas, the power supply *4* is switched on. After the discharge is ignited, the chamber is filled with glow of the discharge plasma (Fig. 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 the mixture of argon and nitrogen (15%) and a current in the magnetron target circuit of 8 A

When a high-voltage pulse is supplied to grid *6*, sheaths *19* and *20* of positive space charge are formed near the grid surface thus separating the discharge plasma into two parts. Plasma *16* filling chamber *1* is not involved in the discharge during the pulse. It is cut off from plasma *21* located between target *3* and grid *6* of the ongoing magnetron discharge. The ions *22* from plasma *21* are accelerated by the grid, and during collisions in sheaths *19* or *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*.

Experiment results

The studies have shown that in the current stabilization mode, the magnetron discharge in argon, nitrogen and mixtures of these gases is stable at current in the target circuit exceeding 1 A and gas pressure of above 0.2 Pa. At lower currents and pressures, oscillations of the voltage and the discharge plasma glow are observed.

At the argon pressure 0.3 Pa the discharge voltage *U* monotonically increases from 265 to 319 V when the current rises from 1 to 8 A. With the pressure increasing up to 1 Pa, the voltage decreases to 240 V at the current 1 A and to 290 V at 8 A. When nitrogen is added to argon, the voltage rises. In pure nitrogen it exceeds the voltage in pure argon by 30-50 V.

In the absence of grid *6*, a 120-mm-high and 160-mm-wide flat electrode was installed parallel to the target surface at different distances from it. The electrode was attached to rod *12* instead of the substrates holder *10*. Stabilized negative voltage amounting to 50 V was applied to the electrode from power supply *18*. Currents in the electrode circuit at a distance to the target h = 50 mm at argon pressure of 0.3 Pa and currents in the target circuit of 3 A, 5 A and 8 A amounted, respectively, 0.5 A, 0.95 A and 1.4 A (solid curves in Fig. 3). When the distance h increase to 100 mm, these currents nearly linearly decrease to 0.06 A, 0.14 A and 0.24 A. When the distance rises to h = 150 mm, the currents amounts to 0.02 A, 0.04 A and 0.08 A, respectively, and are only slightly reduced with the further increase of the distance.

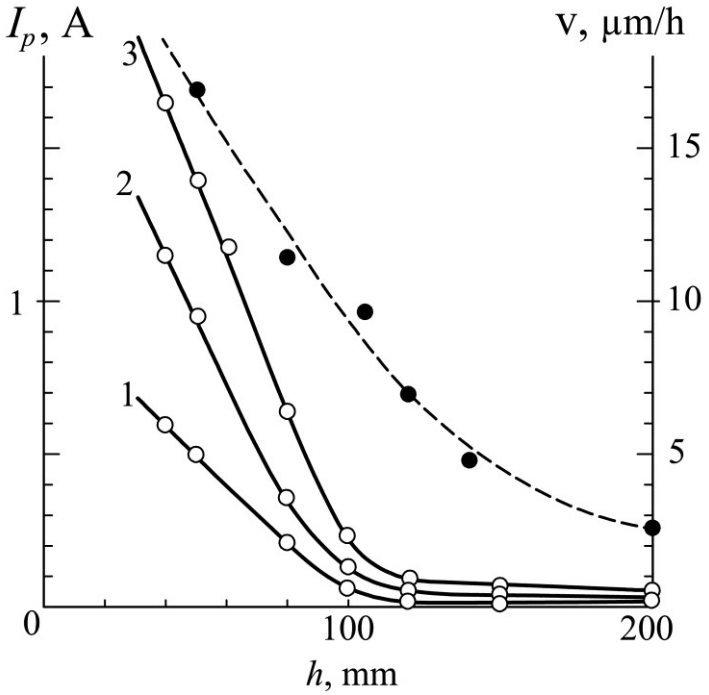

Figure 3: Dependencies on the distance h from the target of titanium coating deposition rate v at current of 8 A in the target circuit (dashed line) and current in the probe circuit I_p (solid lines) at the current in the target circuit of 3 (1) 5 (2) and 8 A (3)

The dashed curve in Fig. 3 presents dependence on the distance to the target of the titanium coating deposition rate in the absence of grid *6* on flat substrates made of high speed steel. Substrate *11* was placed on holder *10*, and on its surface facing target *3*, a titanium 0.5-mm-thick mask was fixed. After 5-minute-long etching of the substrate and the mask with argon ions, extracted from the magnetron plasma and accelerated by negative voltage of 1200 V applied to the holder, titanium coatings were deposited on their surfaces. During the deposition process, the bias voltage of the substrate amounted to 100 V. After the coating deposition for 20-60 minutes 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 (manufactured by Bruker Nano, Inc., USA). The titanium deposition rate was determined by dividing the height of the step by the deposition time. At the current in the target circuit of 8 A, it amounts to 2.5 μm/h at the distance from the target of 200 mm, increases to 9.5 μm/h at the distance of 100 mm and to 17 μm/h at the distance of 50 mm. Measurements have shown that at the distance of 120 mm from the target, the titanium deposition rate amounts to 7 μm/h and is independent of the argon pressure in the range from 0.2 to 2 Pa. When reducing the current in the target circuit, the deposition rate is decreasing proportionally to the current.

After addition to argon of 15%nitrogen,the blue discharge plasma glow changes its color to pink, and the coating deposition rate is reduced by 2 times. Increasing the nitrogen content in the gas mixture up to 20%reduces the deposition rate by 2.5 times, and addition of 25% nitrogen reduces the rate by 3 times. In all cases, a golden hard coating of titanium nitride is synthesized on the substrates. With the reduction of the nitrogen content in the gas mixture to 10%, synthesis of titanium nitride stops and on the substrate is deposited titanium coating. In this case, the color of the discharge plasma is again light blue, and the deposition rate increases to the values measured during the discharge in argon without nitrogen addition (dashed curve in Fig. 3). When the current in the target circuit amounts to 8 A and the pressure of argon mixed with 15% nitrogen is equal to 0.4 Pa on the substrate made of high speed steel and distanced from the target at 90 mm is deposited within 1 hour in absence of the grid 5.6-μm-thick titanium nitride coating with microhardness of 2200 HV25.

In contrast to the above coating deposition at the negative voltage of 100 V following the substrate pretreatment by ions with energy up to 1200 eV, no pretreatment has been carried out before the deposition assisted by pulsed bombardment of the substrate by high-energy ions. At the pressure of argon and nitrogen mixture ranging from 0.2 to 0.8 Pa, first to the substrate were applied high-voltage pulses with specified amplitude, width and repetition rate, and only after that the magnetron discharge with specified current of 2 to 8 A was activated. The substrate with initial temperature equal to the room temperature immediately became immersed in the gas discharge plasma. Titanium atoms arrived to its surface and synthesis of the nitride coating started, the growing coating being bombarded by argon and nitrogen ions accelerated by high-voltage pulses. Only a few minutes later the substrate temperature measured by IP 140 IMPAC pyrometers (manufactured by LumaSense Technologies, Inc, USA) grew to 200-400 °C due to the substrate bombardment by high-energy ions and heating by the discharge radiation.

When to the substrate are applied high-voltage pulses the coating deposition rate is a little lower compared to the deposition at the bias voltage of 100 V. At the argon pressure of 0.4 Pa, current in the target circuit of 8 A, width of 25-kV pulses amounting to 40 μs and their repetition rate amounting to 50 Hz, the titanium coating deposition rate at a distance h = 90 mm from the target amounted to 10 μm/h. At the same pressure and current, addition to argon of 15% nitrogen reduced the coating deposition rate to 5 μm/h.

In contrast to the golden coatings synthesized on the substrate at a constant voltage of 100 V, titanium nitride coatings produced using high-voltage pulses are dark brown. Measurements with the POLYVAR-MET durometer (manufactured by Reichert-Jung, Austria) showed that the microhardness of 5-μm-thick coatings on hard alloy substrates, synthesized using 25-kV pulses grows from 2100 HV25 to 2900 HV25 with increase in the nitrogen content from 15% to 20%. With further increase in the nitrogen content to 25% and 30%, it slightly diminishes to, respectively, 2800 HV25 and 2700 HV25. However, the increase in microhardness of coatings with an increase in the nitrogen content occurs not regularly. Analysis of the gas medium and plasma composition in the vacuum chamber by means of the EQP energy-mass analyzer (manufactured by Hiden Analitical Ltd., England) revealed that increase of the microhardness requires a sufficiently low content of water vapor and, accordingly, of hydrogen and oxygen ions.

Evaluation of adhesion using a scratch tester, showed that critical loads for the coatings synthesized using 25-kV pulses were 4 times higher than for conventional nitride coatings synthesized at constant bias voltage. When however the pulse amplitude diminishes from 25 to 5 kV, the critical loads and microhardness decrease to conventional values.

After grid *6*(Fig. 1) was installed at a distance of 60 mm from the 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%.It can be explained by losses of titanium atoms on the grid with a transparency of 70%. When nitrogen (15%)was added to argon, the deposition rate diminished more 2 times, and within 2 hours a 6.5-μm-thick golden titanium nitride coating with a microhardness of 2200 HV25 was synthesized on the substrate.

In order to bombard the growing coating with high-energy gas molecules, the high-voltage pulses were applied to grid *6* (Fig. 1) immersed in the magnetron discharge plasma and substrates were floating. Within each pulse near both surfaces of the grid are formed two sheaths of positive space charge, where ions are accelerated and high-energy atoms are formed due to charge exchange collisions of the ions with gas molecules. The sheaths width depends on the pulse amplitude and the ion current density from the plasma. To determine the current density of ions *22* from plasma *21* (Fig. 1) located between grid *6* and target *3*, dependencies of the grid current I_g on the grid voltage U_g were obtained (Fig. 4).

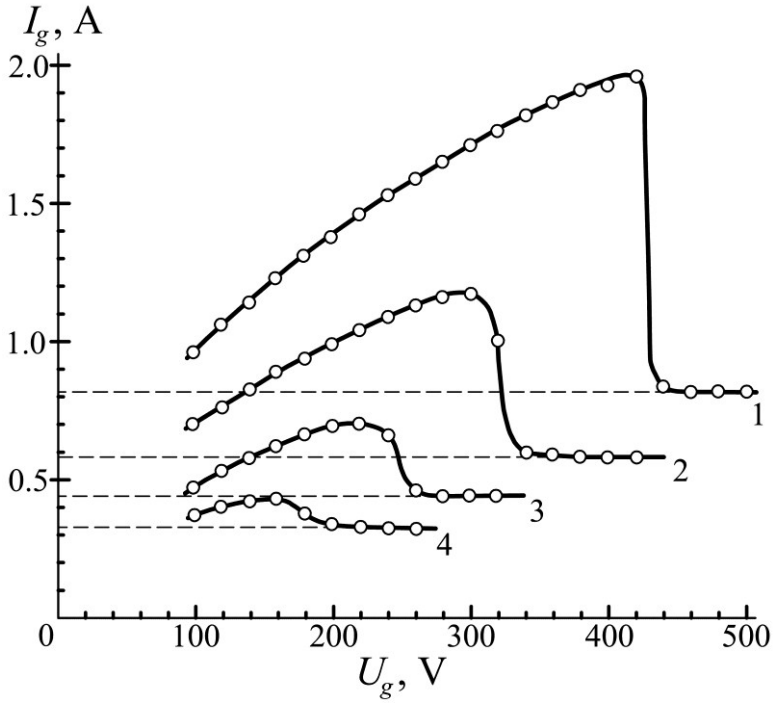

Figure 4: Dependencies on voltage U_g between the chamber and the grid of current I_g in the grid circuit at argon and nitrogen (15%)mixture pressure of 0.4 Pa, current in the target circuit of 4 A and distance between the grid and the target of 70 (curve 1), 80 (2) 90 (3) and 100 mm (4)

At first the current in the grid circuit rises when the grid voltage increases. But at a voltage of hundreds of volts it dramatically reduces approximately 2 times and with a further increase in the voltage it keeps the constant value I_{gi}. After the fall in the current, 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 (Fig. 5). It can be explained by the fact that the grid prevents penetration of electrons from discharge plasma *21* into chamber *1*. In this case, the current in the grid circuit I_{gi} is equal to the 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 [16], the secondary electron current can be neglected, and I_{gi} may be considered as average current of ions arriving from plasma *21* to the grid *6*.Fig. 6 shows dependencies of the current I_{gi} 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.

In the case of coating deposition with application of high-voltage pulses to the grid, no activation and heating of the substrates by accelerated ions has been carried out before the deposition, hence the transitional layer between the substrate and the coating was also formed at room temperature, the same as in previous experiments with application of high-voltage pulses to the substrates.

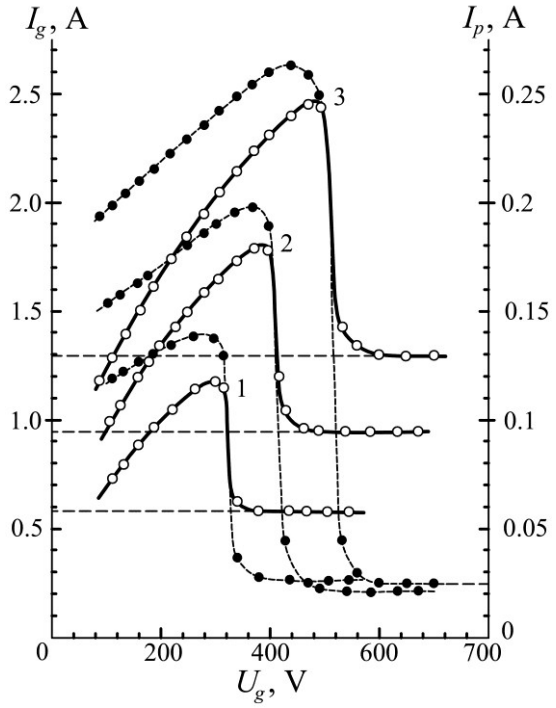

Figure 5: Dependencies on U_g of current I_g in circuit of the grid distanced at 80 mm from the target (solid curves) and current I_p in the circuit of a flat probe distanced at 5 cm from the grid (dashed curves) at currents in the target circuit of 4 A (curve 1), 6 A (2) and 8 A (3)

At pressure 0.7 Pa of the argon and nitrogen (15%) mixture, current 8 A in the target circuit and amplitude 20 kW of the voltage pulses applied to the grid, a dark brown 5.8-μm-thick nitride coating with microhardness of 2700 HV25 was synthesized within 2 hours on the initially cold substrate made of hard alloy.

Critical loads characterizing its adhesion are about 3.5 times higher than in the case of nitride coatings, synthesized at a constant bias voltage 100 V of the substrate. When amplitude of the pulses applied to the grid is reduced to 15 kV, the coating parameters remain virtually unchanged. However, at voltages lower than 10 kV, microhardness decreases to 2200 HV25, the adhesion is considerably reduced, and at the amplitude of 5 kV delamination of the coating is already observed. Decrease in microhardness and adhesion is also observed with the gas pressure reduction.

Discussions

When we deposited titanium coating without pre-heating and activation of the substrate [17] by argon ions with energy of 1200 eV it was always delaminated. To ensure an admissible adhesion of titanium nitride coating it was also necessary to deposit before the coating synthesis an adhesive titanium sublayer. The most striking difference of coatings deposited using high-voltage pulses applied to the substrate is formation of the transitional layer (interface) ensuring a perfect adhesion at room temperature without any preheating and activation. The adhesion was improved due to bombardment of the metal substrate by ions with an energy ranging from 5 to 25 keV, which cross its surface in the form of neutral atoms. In the surface layer with a thickness, respectively, from 20 to 100 nm, each of these ions triggers dislodgement of 300 to 1500 atoms, respectively, from the crystal lattices of the substrate and coating synthesized on it. As a result, atoms of the substrate and atoms of the coating are mixing together. With the number of deposited atoms of the target material increasing, percentage of the coating atoms near the surface gradually rises. This is the reason of the interface width increase and the adhesion improvement.

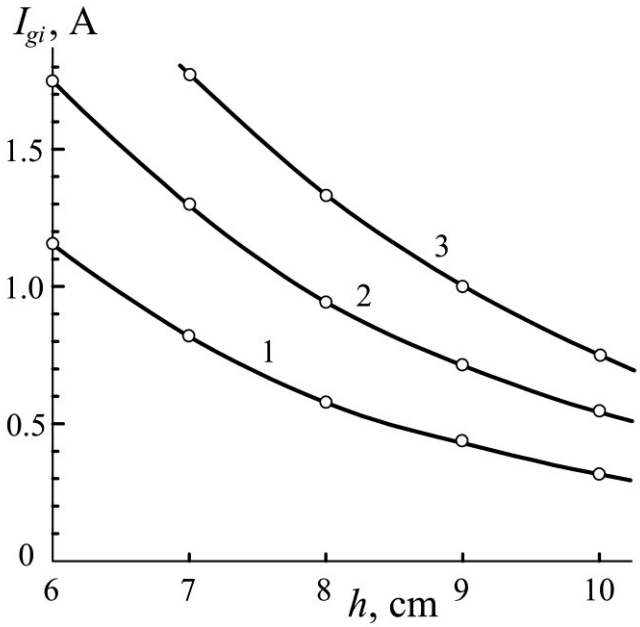

Figure 6: Dependencies on the distance h between the grid and the target of current I_{gi} in the grid circuit, when the grid prevents penetration of the magnetron discharge plasma in the chamber, at the current in the target circuit 4 (curve 1), 6 (2) and 8 A (3)

The energy of atoms produced due to charge exchange collisions of ions accelerated in sheaths *19* and *20* (Fig. 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 4 A, the current of ions *22* in the grid circuit is equal to I_{gi} = 1.15 A (Fig. 4). It rises to I_{gi} = 2.3 A with increase in the target current to 8 A, and the average ion current density j on the grid with a surface area of over 0.072 m² becomes equal to 32 A/m².

Within the pulse width of 10 to 50 microseconds, the magnetron discharge plasma density and the current of ions extracted from the plasma to the grid are virtually unchanged. At the pulse amplitude amounting to U =10 kV, amplitude of the current pulse in the grid circuit is equal to 7 A. The threefold increase in the current compared with the current I_{gi} = 2.3 A is due to the kinetic emission of secondary electrons as a result of the grid bombardment by high-energy ions. From the Child-Langmuir law it follows that the width of the sheath is equal to d = 1.6 cm. With the pulse amplitude increasing to 25 kV, the sheath width rises to 3 cm. However, with the distance h to the target decreasing, density of plasma *21* rises significantly. According to dependence on h of the ion current in the probe circuit at current in the target circuit of 8 A (solid curve 3 in Fig. 3), it increases 1.3 times at the boundary of the 1.6-cm-wide sheath *19*. Therefore, the estimates of the average width of the sheath overestimate the real values by 15-25%.

The fast molecule energy corresponds to the potential of the point, where the charge exchange collision took place [18]. Therefore, it is distributed continuously from zero to the value eU corresponding to the pulse amplitude. At room temperature and a pressure of p = 0.1 Pa, the density of the gas molecules is equal to $n = 2.5\text{x}10^{19}\text{m}^{-3}$. The charge exchange cross section of 10-keV argon ions is equal to $\sigma = 1.4\text{x}10^{-19}$ m² [19]. Therefore, the charge exchange length of these ions $\lambda = 1/(n\sigma) \sim 0.3$ 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 ~ eU. The number of such molecules rises with pressure increase to $p \sim 0.5$ Pa, when the charge exchange length $\lambda \sim 0.06$ m exceeds the sheath width approximately by 2 times [20]. At $p \sim 1$ Pa λ is less than the width of the layer ~ 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 with 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.

Conclusions

1. Bombardment of growing coating by neutral molecules with energies up to 20 keV creates the same physical conditions for its synthesis on the products made of metal and dielectric ceramics, as bombardment by ions with equal energy. It makes it possible to synthesize coatings with enhanced adhesion and microhardness on rotating inside the chamber products made both of conductive and dielectric materials.

2. Coating adhesion is improved due to increase in the interface width, caused by mixing in the surface layer atoms of the product and atoms of synthesized thereon coating due to the product bombardment with ions or fast gas atoms with an energy up to 25 keV.

Acknowledgements

This project was supported by Grant No. 14-29-00297 of the Russian Science Foundation.
The work is carried out on the equipment of the Center of collective use of MSTU "STANKIN".

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