Surface & Coatings Technology 325 (2017) 327–332

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Products pre-treatment and beam-assisted deposition of magnetron sputtered coatings using a closed cylindrical grid inside a planetary rotation system

A. Metel *, M. Volosova, S. Grigoriev, Yu. Melnik

*Moscow State University of Technology "STANKIN", 1 Vadkovsky per., Moscow 127055, Russian Federation*

ARTICLE INFO

*Article history:*
Received 25 April 2017
Revised 21 June 2017
Accepted in revised form 27 June 2017
Available online 28 June 2017

*Keywords:*
Products heating
Etching
Fast gas atoms
Magnetron sputtering
Coating deposition
Adhesion

ABSTRACT

For pre-treatment of dielectric and conductive products planetary rotating inside a process vacuum chamber and beam-assisted deposition on the products of magnetron sputtered coatings, a closed cylindrical grid is placed inside the planetary rotation system. When magnetron targets are disconnected from power supplies, the chamber is filled with plasma of glow discharge at argon pressure of 0.2–1 Pa. Application to the grid of negative voltage up to 3 kV results in production of fast neutral argon atoms with energy up to 3 keV, which bombard the rotating products heating and etching them. When magnetrons are switched on, and high-voltage pulses are applied to the grid, mixing by high-energy gas atoms of the product and coating atoms results in appreciable improvement of adhesion and other properties of the coatings.



## 1. Introduction

Synthesis of protective or wear-resistant coatings is a well-established technique for the quality improvement of engineering products. The coating properties strictly depend on the energy of atoms depositing on its surface. When this energy is supplied by means of the coating bombardment by accelerated ions, the ion-assisted coating deposition takes place, and the equilibrium heating of the product and coating is replaced by non-equilibrium surface heating in atomic scale [1]. In this case, the energy transferred to the atoms condensing on the product surface is independent of the product temperature. This allows the coating synthesis on products made of low-temperature materials and improvement of the coating adhesion. The adhesion grows monotonically with the ions energy due to deeper penetration of accelerated particles into the substrate [2].

The accelerated particles can sputter all deposited atoms, when their energy rises up to 1–3 keV [3]. For this reason, the growing coating can be modified by high-energy ions only in pulsed regimes. Due to mixing of the substrate and coating materials by accelerated particles with energy up to 50 keV, the interface width can exceed 1 μm and ensure a perfect adhesion of titanium nitride coating with thickness up to 50 μm [4–6]. Pulsed bombardment by high-energy ions substantially modifies properties of sputtered titanium nitride coatings resulting in production of nc-$Ti_2N$/nc-TiN nanocomposite with microhardness up to 5000 HV0.04 [6].

In order to bombard coatings growing on conductive products by accelerated ions the products are mainly immersed in plasma of a gas discharge and a negative bias voltage is applied to them. However, the magnetron sputtering of the coatings is characterized by a comparatively low plasma density near the negatively biased product surface [7]. The plasma density grew up many times only with the use of unbalanced magnetrons [8–10], which ensure an adequate ion current density on the product surface.

Using an RF power supply connected to a flat conductive holder of a flat dielectric substrate, negative potential of the substrate surface can amount to hundreds of volts [11] thus enabling an effective sputtering of the substrate by argon ions. However, complex shaped dielectric products with deep cavities cannot be uniformly etched using this expensive and unhealthy RF technique. For this reason, regulation of the coating properties on complex shaped dielectric products requires the use of broad beam sources of accelerated ions [12,13] or fast neutral atoms [14–17].

Incidences to the product surface of slow metal atoms arriving from the magnetron target and fast gas atoms arriving from the beam source and bombarding the growing coating are determined by the product shape and its position relative to the magnetron and the beam sources. When the product is positioned on planetary rotation system inside a process chamber [10], some parts of its surface can shadow the other parts. To ensure an uninterrupted bombardment of the growing coating

* Corresponding author.
*E-mail address:* a.metel@stankin.ru (A. Metel).

http://dx.doi.org/10.1016/j.surfcoat.2017.06.071
0257-8972/

by fast atoms it was proposed to combine the sources of metal atoms and fast gas atoms in the same device with a common emissive grid for both kinds of particles [14]. A combined source was developed with a target placed at the hollow cathode bottom and sputtered by ions from the plasma emitter produced by the hollow cathode glow discharge [18]. Through orifices of an emissive grid placed opposite to the target, the target material atoms enter the process chamber together with ions accelerated from the same plasma emitter. To decrease the rate of the coating sputtering by 3-keV argon atoms, the ratio of the ion current in the target circuit to the current of accelerated up to 3 keV ions entering the chamber has been substantially increased using a non-uniform magnetic field [19]. The combined source allowed deposition on alumina and glass substrates of standard TiN coatings with a good adhesion.

However, in order to synthesize on dielectric products the superhard nanocomposite coatings as on the metal substrates subjected to high-voltage pulses and bombardment by high-energy ions [4], pulsed beams of neutral atoms with energy of 20–30 keV are needed. Due to electrical breakdowns, the combined source [18] does not allow application of 20-kV accelerating pulses. To create physical conditions for the coating synthesis, which are similar to those in [4], a magnetron sputtering system generating pulsed beams of high-energy gas atoms was developed [20]. The system is mounted in a hollow rectangular case on the chamber wall and contains a $0.15 \times 0.36$ m$^2$ magnetron target at the case bottom and a flat grid inside the case at the distance 60 mm from the target. When a 30-kV negative pulse is applied to the grid, ions from the magnetron discharge plasma are accelerated in the space charge sheath between the plasma and the grid, pass through the grid orifices and are decelerated in the second sheath between the grid and secondary plasma in the chamber. Due to the charge exchange collisions in the sheaths with the gas atoms, the ions turn into fast gas atoms, which bombard products in the chamber. As the fast atom energy corresponds to potential of the point where the charge exchange collision took place, the energy of fast atoms is distributed continuously from zero to ~30 keV. Sputtered atoms of the target material fly to the products through the same grid orifices. They deposit on the product, and the growing coating is bombarded by pulsed beams of high-energy atoms. It was experimentally proved that pulsed bombardment by high-energy atoms appreciably increases hardness of titanium nitride coating on dielectric substrates and improves its adhesion [20].

However, it is too hard to control the energy distribution of fast atoms, because it depends on the pulse amplitude, the gas pressure and the magnetron discharge current. It was shown in [15] that application of a negative bias voltage up to 4 kV to a closed cylindrical grid immersed in low-pressure gas-discharge plasma results in production of monoenergetic fast atoms. Energy of the atoms corresponds exactly to the applied voltage in a wide range of plasma density and gas pressure. This can substantially facilitate control of the coating deposition process and improve reproducibility of the results. It seems that application to the closed grid of high-voltage pulses also can result in production of monoenergetic fast atoms with the energy corresponding to the pulse amplitude.

When thickness of the coating layer deposited on a rotating product within its one revolution is less than the depth of the fast atoms penetration into the coating, periodical mixing by the fast gas atoms of the product and coating atoms can results in the same improvement of the coating adhesion as it was in the case of uninterrupted mixing. However this assumption has yet to be proved. The present work is devoted to investigation of the products pre-treatment by fast atoms produced using a closed cylindrical grid placed inside the planetary rotation system and deposition of magnetron sputtered coatings periodically bombarded by those fast atoms.

## 2. Experimental

Fig. 1 presents a coating deposition system equipped with four planar magnetrons mounted on 850-mm-high vacuum chamber shaped as a hexagonal prism with the incircle diameter of 600 mm. The chamber volume amounts to $V = 0.265$ m$^3$ and area of its inner surface amounts to $S = 2.39$ m$^2$. Two pairs of $90 \times 360$-mm$^2$ magnetron targets are connected to AC 50-kHz power supplies and form two dual magnetron sputtering systems [21] mounted on both doors of the chamber. At any moment, one of the system targets acts as a sputter cathode on negative potential, while the second target acts as an anode on potential of the plasma filling the chamber. Additional anode connected to positive pole of a DC power supply can increase the plasma potential, which enables a non-self-sustained glow discharge with electrons trapped inside the chamber. When the magnetron targets are disconnected from their power supplies, the additional anode allows filling of the chamber with homogeneous plasma of self-sustained hollow cathode glow discharge the chamber itself being used as the hollow cathode.

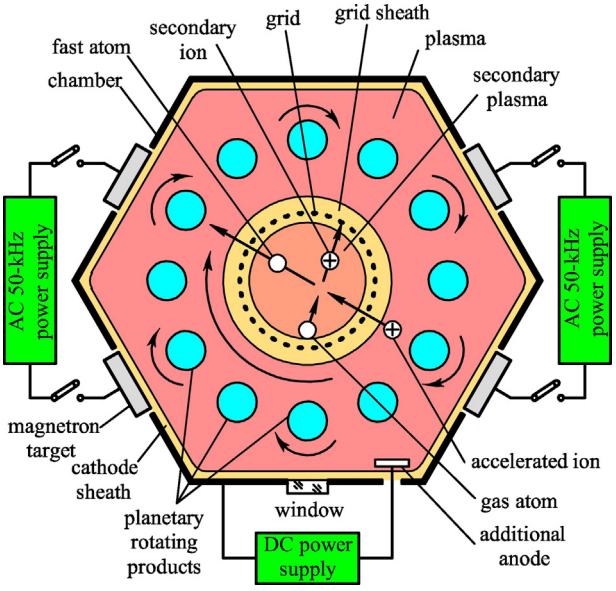


**Fig. 1.** Schematic diagram of the coating deposition system.

Axes of the products planetary rotating inside the chamber are distant from the chamber axis at 0.21 m. Inside the planetary rotation system is mounted a 0.3-m-high and 0.2-m-diameter cylindrical grid covered by end discs. It is made of 0.8-mm-thick titanium sheet with 0.75-mm-diameter orifices, the distance between their centers amounts to 0.8 mm. The grid is fixed to a feedthrough on the top of the chamber.

An additional DC power supply (not shown in Fig. 1) connected between the chamber and the grid allows application to the grid of negative voltage ranging from 0.1 to 3 kV. The grid can be disconnected from the DC power supply and connected to a high-voltage pulse generator (not shown in Fig. 1). The latter allows application to the grid of negative pulses with amplitude ranging from 3 to 30 kV, the pulse width ranging from 5 to 50 μs, and repetition rate ranging from 5 to 50 Hz. The maximal amplitude of the current pulse in the load circuit amounts to 15 A. In order to minimize the ion current in the grid circuit the end discs of the grid as well as the current lead between the upper disc and the feedthrough are coved with screens electrically connected to the chamber.

A turbo-molecular pump ensures the residual gas pressure of 0.001 Pa, and the gas supply system allows regulation of the working gas pressure from 0.01 to 5 Pa. A quartz window allows observation of the grid and products rotating in the chamber as well as measurement of the products temperature by pyrometer IMPAC IP 140 produced by the LumaSense Technologies GmbH (Germany). A movable disc probe negatively biased to 40 V relative to the additional anode allows measurement of the ion current density on the probe surface in the space between the window and the grid.