Investigation of the plasma composition of a discharge with a self-heating hollow cathode and an active anode in a gas mixture with titanium and hexamethyldisilazane vapors

A I Menshakov¹,², Yu A Bruhanova¹, Yu S Surkov¹ and P A Skorynina³

¹Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, 106 Amundsen St., Yekaterinburg, 620016, Russia
²Ural Federal University, 19 Mira St., Yekaterinburg, 620002, Russia
³Institute of Engineering Science UB RAS, 34 Komsomolskaya str., Yekaterinburg, 620049, Russia

E-mail: aim@iep.uran.ru

Abstract. The analysis of composition of low-pressure (~0.1–1 mTorr) hollow cathode arc plasma in Ar+N₂ gas mixture with Ti+hexamethyldisilazane vapors was carried out by optical emission spectroscopy. The influence of HMDS flow rate (1–10 g/h), discharge current (10–50 A) and Ti-vapors flow on hexamethyldisilazane decomposition degree and plasma composition and was investigated. The proposed plasma activation method provides both an intense flow and a high activation degree of metal vapors, and a sufficient decomposition degree of precursor vapors for the formation of solid TiSiCN coatings at a high deposition rate. Test coatings with a thickness of 6 microns and a hardness of 31 GPa were obtained in 1 hour at 400ºC.

1. Introduction

A number of studies have been devoted to the deposition of nanocomposite (nc) TiSiCN coatings due to its perfect tribological and mechanical properties [1-4]. This allowed them to be used in such extreme areas as high-speed cutting [5] and protection of components from aggressive environments [6]. Nc-TiSiCN coatings can be obtained using both chemical (CVD) [2] and physical (PVD) vapor deposition methods [1,6]. The approaches often used either do not satisfy the requirements for environmental friendliness and safety, as, for example, when using explosive and poisonous gases [7], or they are too complex, or do not allow independently control the conditions that can affect the properties of obtained coatings.

At the same time, methods are currently being intensively developed based on the thermal or plasma decomposition of liquid organosilicon compounds (OSC), which contains the elements necessary for the SiCN-coatings formation. The use of such precursors is due to both their low cost and a rather wide choice of OSC with different relative contents of Si, C, N components. Moreover, which is especially important, the Si-C, C-N, Si-N bonds that are necessary are already present in the used precursors for the formation of TiSiCN coatings, therefore, to facilitate the formation of films containing these bonds, it is important to control the decomposition degree of the initial molecules. The most common method is reactive magnetron sputtering of a Ti target in a mixture of a plasma-
forming gas (Ar, N2) with an organosilicon precursor [8]. To activate the precursor vapors in such systems, a non-self-sustained discharge with a direct-heating cathode is used. The use of an additional electron source made it possible to increase the intensity of ion tracking [9], however, a drawback of the direct glow cathode is its short service life in the environment of reactive gases. In addition to the relatively low deposition rate, the use of magnetron sputtering to obtain this type of coating in most cases is accompanied by a number of difficulties due to the need to create optimal deposition conditions and to provide the required percentage of the components of the formed coating in the sputtering targets. In addition, the poisoning of targets in the environment of chemically active gases and, as a consequence, the difficulty of burning a magnetron discharge can be attributed to significant disadvantages of this method. Promising for these purposes is a self-heated hollow cathode discharge (SHHC) [10], which advantages are stability, wide working pressures range (~0.1-10 mTorr), a wide discharge currents range (~5-100 A), low degree of plasma pollution with cathode erosion products. This discharge was used to generate a large volume plasma during the deposition of various types of coatings by the PECVD method, including CrN, Al2O3, SiCN, etc. At the same time, the idea of using a discharge with a self-heating hollow cathode (SHHC) simultaneously to activate an organosilicon precursor vapors and to heat the evaporated anode and create an ionized stream of titanium vapor, as well as for ionization of a vapor-gas medium and intensive ion accompaniment is attractive and promising. The activation of OSC vapors is carried out upon their inlet directly into the area of the sample location. The advantages of this approach are, first, the absence of direct contact between the OSC vapor and the cathode cavity and, as a result, the absence of the need for additional etching of the surface from the forming dielectric films, and more stable discharge burning, and, secondly, the presence of in a discharge plasma with SHHC a sufficiently large fraction (up to ~ 80%) of fast electrons with energies up to ~100 eV [11], which can excite and ionize components of vapor-gas mixture in a large volume, and also provide sufficient power density on the crucible to evaporate necessary metal.

The article presents the results of an investigation of the plasma composition in discharge with a self-heating hollow cathode in a nitrogen-argon gas medium containing hexamethyldisilazane and titanium vapors obtained by anodic evaporation within a single-discharge system, and also shows the influence of various plasma generation parameters on its composition, including the activation degree of metal and precursor vapors.

2. Experimental methods

The studies were carried out in a gas discharge system based on a discharge with a self-heating hollow cathode made of titanium nitride [10]. The peculiarity of the studied configuration, in comparison with [10], was that the discharge current was closed to two independent anodes at once: a cooled steel anode of the main discharge and an uncooled graphite anode—a crucible in which a titanium crumb was placed.

First, a glow discharge was ignited in the argon medium between the hollow cathode and the cooled anode. As the cathode was heated by ion bombardment, the discharge switched to thermionic mode, while the discharge voltage decreased from ~400 to 60-200 V depending on the discharge current \(I_d\), which was regulated in the range of 5-50 A. After that, voltage was applied to the anode-crucible, and the electron stream closing on it heated it to the melting point of titanium (1670°C) in 1-2 minutes. The current in the crucible circuit \(I_c\) was regulated within 0-10 A, while its temperature reached 2100°C. As is known, at high temperatures in a nitrogen medium on the surface of titanium a refractory titanium nitride is formed, which has a higher melting point and a significantly lower saturated vapor pressure, and, accordingly, blocks the entry of titanium vapors into the processing area, therefore nitrogen was injected into the vacuum chamber only after heating the crucible above the titanium melting point. Hexamethyldisilazane ([(CH3)3Si]2NH, HMDS) was selected as a precursor, firstly, because of its wide availability and low cost. In addition, there is data [12] that when using HMDS, it is possible to obtain TiSiCN-coatings with a lower friction coefficient, in comparison
with other organosilicon precursors. The precursor vapor flow was regulated within 0–10 g/h by Mini Cori-Flow digital mass flow controller (Bronkhorst). For spectral measurements, the ISP-30 spectrograph was used, equipped with a MORS-6 photoelectronic cassette manufactured by MORS LLC (Troitsk, Russia). The photodetector consists of 6 charge-coupled devices (CCD lines) of the TSD 1304 DG type manufactured by Toshiba (Japan). The spectral range of the measuring complex ranged from 196 nm to 930 nm, and the spectral resolution of the prism device depends non-linearly on the wavelength and in this range increased from 0.005 to 0.2 nm.

Figure 1. Experimental scheme.

Figure 2. Optical emission spectrum of the discharge plasma.

3. Results and discussion
Optical emission spectra of the discharge plasma in the coatings deposition region is shown in figure 2. The discharge spectrum contains areas characteristic of the components present in the discharge. The UV region and the visible range mainly consist of bright lines of an atom and a single-charged titanium ion. In the near-IR range, strong lines of the argon atom and its ion predominate, as well as bands characteristic of the vibrational levels of the first positive system of molecular nitrogen $\text{B}^3\Sigma \rightarrow \text{A}^3\Sigma$. In the absence of Ti vapors, the current flow in the discharge is provided by charged particles of buffer gases generated in the hollow cathode. This is confirmed by the presence of bands of the molecular nitrogen ion $\text{B}^2\Sigma_u^+ \rightarrow \text{X}^2\Sigma_g^+$: 391.4 nm, 427.8 nm, etc. There are also low-intensity Ar$^+$ lines, for example, 461 nm and 487 nm. When the titanium vapor source, which is the anode, is heated, titanium vapors begin to play the role of an easily ionized additive. This is indicated by the low ionization potential of 6.82 eV, while the ionization potential of the buffer gases Ar is 15.76 eV and for the N$_2$ molecule is 15.6 eV. The same process leads to a significant increase in the current density in the discharge. Also in the spectrum there are lines of hydrogen atoms H (the strongest of which is 656.3 nm), which indicates a stepwise and sufficiently deep decomposition of the precursor molecules.

Figure 3 shows the dependences of the line intensities H$^*$ (656 nm), Ar$^*$ (811 nm), Ar+ (461 nm), Ti+ (334.9 nm) and Ti$^*$ (453 nm) on the current in the crucible circuit at constant values of the discharge current $I_{d}=30$ A and the vapor flow of the precursor $Q_{HMDS}=3$ g/h. An increase in the current in the crucible circuit, and, accordingly, the flow of titanium vapor, leads to an increase in the intensities of all plasma components, including argon ions. The increased pressure of the vapor-gas mixture near the crucible and, as a result, a decrease in the voltage drop and an increase in the current density lead to a decrease in the electron temperature. The low ionization potential of Ti contributes to the formation of a large number of secondary electrons involved in avalanche reproduction processes.
Most likely, the increase in the intensity of the glow of the argon ion lines is associated with the
processes of stepwise ionization of buffer gases or with the processes of titanium ions recharging.

**Figure 3.** The dependences of the intensities of the plasma component lines on the current in the
$I_{cr}$ crucible circuit.

**Figure 4.** The dependences of the intensities of the plasma component lines on the HMDS vapour flow.

In contrast to the work [13], where the average charge of ions coming from a low-pressure cathode arc
was 2.1, the lines of two-charged Ti$^{2+}$ ions in the plasma of the anode arc could not be
distinguished against the background of intense Ti$^+$ and Ti$^+$ lines: it can be assumed that single-
charged ions mainly arise in the anode region of the plasma, due to the ionization of titanium atoms by
a stream of fast (up to ~100 eV) electrons [11], coming from the SHHC to the crucible. The results of
probe measurements indicate that an increase in the current in the crucible circuit also leads to a
significant increase in the density of the ion current on the treated surface. At a discharge current of 25
A in the absence of a current to the crucible, the saturation current density of ions $j_i$ from the plasma
was 5 mA/cm$^2$. Connecting a crucible with a current of 10 A on it increased the $j_i$ value to 20 mA/cm$^2$.
Since the results of plasma spectroscopy show (Figure 3) that the increment of the ion current with an
increase in the current per crucible is accompanied not only by an increase in the metal component in
the plasma, but also by an intensification of the ionization processes of plasma-forming gases, it is
difficult to judge the degree of ionization of metal vapors and the relative content of metal ions on the
treated surface.

An increase in the vapor flow of the precursor at constant values of the metal vapor flow ($I_p=3$ A)
and the discharge current ($I_d=30$ A) (figure 4) leads to a corresponding decrease in the content of
active components of the vapor-gas mixture in the coatings deposition region, which is apparently due
to the intensification of their scattering processes on the precursor molecules with an increase in the
vapor concentration. At the same time, the content of hydrogen atoms, and as a consequence, active
fragments of precursor molecules, changes nonmonotonically with an increase in the HMDS vapor
flow: at first, an increase in $Q_{HMDS}$ leads to a corresponding increase in the concentration of these
components, but with a further increase in the vapor pressure, the processes of scattering of the
electron flow on the molecules of the vapor-gas mixture begin to prevail, and the vapors activation
degree in the area of coating deposition decreases.

With an increase in the total discharge current at constant values of the vapor fluxes of titanium and
the precursor, the degree of their activation increases. At the same time, the plasma concentration in
the main discharge gap has a greater effect on the degree of decomposition of precursor vapors than on
the activation of metal vapors (figure 5). Obviously, this is due to the fact that the intensity of
excitation and ionization of titanium vapors is mainly determined by processes in the region with the maximum metal vapor pressure and the maximum electron flux density near the crucible, while the degree of activation of precursor molecules and buffer gases is determined by their pressure and energy distribution and the intensity of the electron flux in the region of vapor flow drift.

Figure 5. The dependences of the intensities of the plasma component lines on the current in the $I_{cr}$ crucible circuit.

Test coatings were deposited to the AISI304 stainless steel samples. During deposition in the trial mode, the discharge current $I_d$ was 25 A, the current $I_{cr}$ per crucible was 3 A, the displacement potential determining the ion energy on the surface of the samples was -100 V. First, ionic cleaning of the surface of the samples took place in an argon medium at a displacement potential of -500 V, then a titanium sublayer with a thickness of 150-200 nm was obtained, after which a precursor ($Q_{HMDS} = 1$ g/h) was injected into the chamber and the coating was formed within 1 hour. The temperature of the samples measured by the thermocouple did not exceed 400°C. At the end of the cycle, the samples were cooled in vacuum to room temperature, after which microhardness was measured on a Shimadzu DUH-211s microhardness meter, and the elemental composition was studied on a Tescan VEGA II XMU scanning electron microscope with an INCA ENERGY 450 X-ray energy dispersive microanalysis system. Figure 6 shows a micrograph of the surface of the obtained sample, and it is clear that the coating is solid and even, it is worth noting separately the absence of microdrops on the surface, the presence of which is characteristic, for example, for a high-performance method based on cathode sputtering of a metal target. The microhardness of the obtained coatings with a thickness of 6 microns was 28-31 GPa. In the composition of the coating, the main element is Ti (38.7 at.%), the content of N and C is 13.2 and 15.2 at.%, respectively. At the same time, an increased Si content (32.1 at.%) is observed in the coating for this type of coatings, in comparison with the known literature data, which indicates a suboptimal ratio of the fluxes of active plasma components. This will be the subject of further research.

4. Conclusion
The presented method of forming an active vapor-gas medium for obtaining promising multicomponent coatings allows simultaneously creating a dense gas plasma in a sufficiently large volume, decomposing molecules of volatile organosilicon compounds, as well as forming an intense flow of metal vapors. Also, this method allows you to independently change the vapor flows of the
precursor and metal and their degree of activation within a fairly wide range, while providing intensive (up to 20 mA/cm\(^2\)) ion support of the coating formation process. This makes it possible to vary widely such parameters as the deposition rate, the ratio of elements, the degree of ion exposure. This method provides deposition of solid TiSiCN-based coatings at a high deposition rate (6 µm/h) without the formation of microdrops on the treated surface.

**Acknowledgement**
The work was supported by the Russian Science Foundation (grant no. 20-79-10059).

**References**
[1] Thangavel E, Lee S, Nam K S, Kim J K and Kim D G 2013 *Appl. Surf. Sci.* 265 60–5
[2] Qiu L, Du Y, Wu L, Wang S, Zhu J, Cheng W, Tan Z, Yin L, Liu Z and Layyous A 2019 *Surf. Coat. Tech.* 378 124956
[3] Movassagh-Alanagh F, Abdollah-zadeh A, Aliofkhazraei M and Abedi M 2017 *Wear* 390 93–103
[4] Dayan M, Shengli M and Xu K 2005 *Surf. Coat. Tech.* 200 382–6
[5] Imamura S, Fukui H, Shibata A, Omori N and Setoyama M 2007 *Surf. Coat. Tech.* 202 820–5
[6] Swminiathan V P, Wei R and Gandy D W 2007 *Turbo Expo: Power for Land, Sea, and Air* 5 7–16
[7] Kuo D H and Huang K W 2001 *Thin Solid Films* 394 71–9
[8] Lin J, Wei R, Bitsis D C and Lee P M 2016 *Surf. Coat. Tech.* 298 121–31
[9] El-Rahman A M and Wei R 2014 *Surf. Coat. Tech.* 241 74–9
[10] Menshakov A I, Emlin D R, Surkov Yu S and Cholakh S O 2018 *J. Phys.: Conf. Ser.* 1134 012039
[11] Hershcovitch A I 1996 *Appl. Phys. Lett.* 68 464
[12] Wei R, Rincon C, Langa E and Yang Q 2010 *J. Vac. Sci. Technol.* A. 28 1126
[13] Yushkov G Y, Anders A, Oks E M and Brown I G 2000 *J. Appl. Phys.* 88 5618