ФИЗИКА ПЛАЗМЫ/PLASMA PHYSICS

INVESTIGATION OF THE PLASMA COMPOSITION OF HOLLOW CATHODE ARC DISCHARGE WITH ACTIVE AL ANODE IN HEXAMETHYLDISILAZANE/TETRAETHOXYSILANE VAPORS

Research article

Bryukhanova Y.A.[1], *, Skorinina P.A.[2], Makarov E.V.[3]
[1] ORCID : 0009-0002-8352-3570;
[2] ORCID : 0000-0002-8904-7600;
[3] ORCID : 0000-0003-1596-3777;
[1, 3] Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russian Federation
[1] Ural Federal University named after the first President of Russia B.N. Yeltsin, Yekaterinburg, Russian Federation
[2] Institute of Engineering Science of the Ural Branch of the Russian Academy of Sciences, Yekaterinburg, Russian Federation

* Corresponding author (yuliya.bryuhanova.96[at]mail.ru)

Abstract

Optical emission spectroscopy was used to analyze the plasma composition during reactive evaporation of Al in an arc discharge with a self-heating hollow cathode (SHHC) in a gas mixture of $Ar+N_2/Ar+O_2$ in vapors of organosilicon compounds (OSC) hexamethyldisilazane (HMDS) and tetraethoxysilane (TEOS) at a pressure of $\sim10^{-4}$ Torr. The density of the total ion saturation current per sample, with a fraction of metal ions up to 50%, reached 10 mA/cm^2, which is an important condition for the formation of high-quality dense coatings. The influence of fluxes of organosilicon precursors, reactive gases, the current of the main discharge gap and the flow of Al vapors on the degree of decomposition of HMDS and TEOS and on the plasma composition has been studied. High rates of decomposition of the initial HMDS and TEOS molecules were achieved, as well as high values of the degree of dissociation of N_2 (up to 0,07) and O_2 (up to 0,4). Trial coatings of SiAlCN and SiAlCO with a homogeneous structure and good adhesion to stainless steel substrates were obtained. The hardness of the SiAlCN test films reached 30 GPa, and the hardness of SiAlCO reached 12 GPa. Thus, it is shown that this method of activation of a vapor-gas mixture provides an intensive flow and a high degree of ionization of Al vapors, and also allows for deep decomposition of organosilicon precursors of HMDS and TEOS to form coatings of the desired composition, good quality with high deposition rates.

Keywords: hollow cathode arc discharge, ion assistance, organosilicon compounds, PVD, PECVD.

ИССЛЕДОВАНИЕ СОСТАВА ПЛАЗМЫ ДУГОВОГО РАЗРЯДА С ПОЛЫМ КАТОДОМ И АКТИВНЫМ AL АНОДОМ В ПАРАХ ГЕКСАМЕТИЛДИСИЛАЗАНА/ТЕТРАЭТОКСИСИЛАНА

Научная статья

Брюханова Ю.А.[1], *, Скорынина П.А.[2], Макаров Е.В.[3]
[1] ORCID : 0009-0002-8352-3570;
[2] ORCID : 0000-0002-8904-7600;
[3] ORCID : 0000-0003-1596-3777;
[1, 3] Институт электрофизики Уральского отделения Российской академии наук, Екатеринбург, Российская Федерация
[1] Уральский федеральный университет имени первого президента России Б. Н. Ельцина, Екатеринбург, Российская Федерация
[2] Институт машиноведения Уральского отделения Российской академии наук, Екатеринбург, Российская Федерация

* Корреспондирующий автор (yuliya.bryuhanova.96[at]mail.ru)

Аннотация

Оптическая эмиссионная спектроскопия использовалась для анализа состава плазмы при реактивном испарении Al в дуговом разряде с самонагревающимся полым катодом (СПК) в газовой смеси $Ar+N_2/Ar+O_2$ в парах кремнийорганических соединений (КС) гексаметилдисилазана (ГМДС) и тетраэтоксисилана (ТЭОС) при давлении $\sim10^{-4}$ Торр. Плотность суммарного ионного тока насыщения на образец при доле ионов металла до 50% достигала 10 мА/см^2, что является важным условием для формирования высококачественных плотных покрытий. Исследовано влияние потоков кремнийорганических прекурсоров, реакционных газов, тока основного разрядного промежутка и потока паров Al на степень разложения HMDS и TEOS и на состав плазмы. Достигнуты высокие скорости разложения исходных молекул HMDS и TEOS, а также высокие значения степени диссоциации N_2 (до 0,07) и O_2 (до 0,4). Получены пробные покрытия SiAlCN и SiAlCO с однородной структурой и хорошей адгезией к субстратам из нержавеющей стали. Твердость пробных пленок SiAlCN достигала 30 гПа, а SiAlCO — 12 гПа. Таким образом, показано, что данный способ активации парогазовой смеси обеспечивает интенсивное течение и высокую степень ионизации паров Al, а также позволяет проводить глубокое разложение кремнийорганических прекурсоров HMDS и TEOS с получением покрытий требуемого состава, хорошего качества и с высокой скоростью осаждения.

Ключевые слова: дуговой разряд с полым катодом, ионная поддержка, кремнийорганические соединения, PVD, PECVD.

Introduction

The development of ion-plasma methods for the synthesis of films and coatings for various purposes is one of the relevant areas of research in the field of surface modification and the production of new materials. Currently, methods based on the plasma decomposition of organosilicon compounds (OSC) are being developed for the deposition of multicomponent films with unique properties. The use of liquid organosilicon precursors is due to one of the most affordable methods of obtaining silicon in the gas phase, their low cost, as well as a wide range of precursors with different chemical compositions and the content of elements Si, C, N, O etc. At the same time, the advantage of using OSC to obtain multicomponent films is also the presence of Si-C, Si-N, etc. bonds in the molecule, the incomplete decomposition of which upon activation in plasma facilitates the formation of the desired chemical structure of coatings. As a rule, films obtained from such precursors have the same elemental ratio as in the initial precursor molecules [1]. The elemental composition of the synthesized films can be adjusted by adding reactive components to the gaseous medium, for example, gases CH_4, N_2 and O_2, which significantly corrects the chemical composition of the coatings obtained and, accordingly, their properties. In addition, a metal component can also be added to such a combined-gas mixture and multicomponent metal-ceramic coatings with a unique combination of properties can be obtained. For example, one of such promising materials are compounds based on SiAlCN and SiAlCO, which have replaced ceramic materials based on SiCN and SiCO. As technologies have improved, for example, in the nuclear power industry or the gas turbine industry, the task has become to develop more efficient materials capable of operating under extreme conditions with increased loads. SiAlCN and SiAlCO [2] have a unique set of properties. SiAlCO has a high coefficient of piezo sensitivity (strain sensitivity), so they can be used to create smaller sensor systems. SiAlCN have abnormal oxidation resistance at temperatures up to 1400°C [3] due to the addition of Al [4]. In addition, such coatings have high temperature resistance [5], high hardness and wear resistance [6]. Therefore, such coatings are ideal for protecting components that are subject to wear at elevated temperatures, as well as for creating sensitive, compact sensors for extreme applications.

A promising method for the synthesis of such coatings is the hybrid plasma-chemical PVD+PECVD method [7], based on the evaporation of metal by a stream of electrons from an arc charge with a hollow cathode in a medium containing vapors of organosilicon precursors. The advantage of this method is the ability to change almost all deposition conditions in a wide range to select the optimal synthesis mode to obtain the desired coating properties. Also, the use of a gas discharge can provide an intense ion flux necessary for the formation of a dense qualitative coating structure [8], and low-temperature plasma decomposition of precursors, in contrast to thermal activation [9] carried out at temperatures of ~1000°C, will allow the synthesis of coatings on a wider range of materials.

The purpose of this work is to study the conditions for the formation of an active vapor-gas medium by the method of anodic evaporation of Al in an arc discharge plasma with a self-heating hollow cathode (SHHC) in an $Ar+N_2/Ar+O_2$ medium containing pairs of organosilicon compounds HMDS/TEOS for the deposition of promising PDC coatings based on SiAlCN and SiAlCO. The paper presents the results of a study of the effect of various discharge parameters with a self-heating hollow cathode and a sectional anode, including the discharge current, the type of precursor, the amount of precursor consumption and reactive components of the gaseous medium, on the plasma composition, including the degree of dissociation of various plasma components and its ionic composition.

Experimental methods

Experimental studies of plasma-chemical activation of a vapor-gas mixture were carried out in a gas-discharge system, the scheme of which is shown in Figure 1. The design of such a system is described in detail in [7].

A special feature of this scheme is the use of an arc discharge with a self-heating hollow cathode and a sectional anode to ensure independent control of the metal evaporation rate and the current density of gas ions [7]. One section was a water-cooled hollow cylinder made of stainless steel (12X18H10T), the second section was not water-cooled and consisted of a hollow crucible made of refractory material, closed on the end and sides with screens made of molybdenum and ceramic tube for better thermal insulation.

At the initial stage, before switching to the thermionic mode, the SHHC was heated in a glow discharge in a pulsed-periodic gorenje mode. Then the discharge switched to the arc mode, the Ar flow was 30 cm^3/min. To independently adjust the flow of Al vapors, the ion current density, the degree of activation of the vapor-gas mixture, and the current to the cooled anode (I_d) varied in the range of 5–30 A, the current in the crucible circuit (I_{cr}) in the range of 1–10 A, the flows of reactive gases N_2/O_2 5–45 cm^3/min, and the flows of HMDS/TEOS 0–2 g/h.
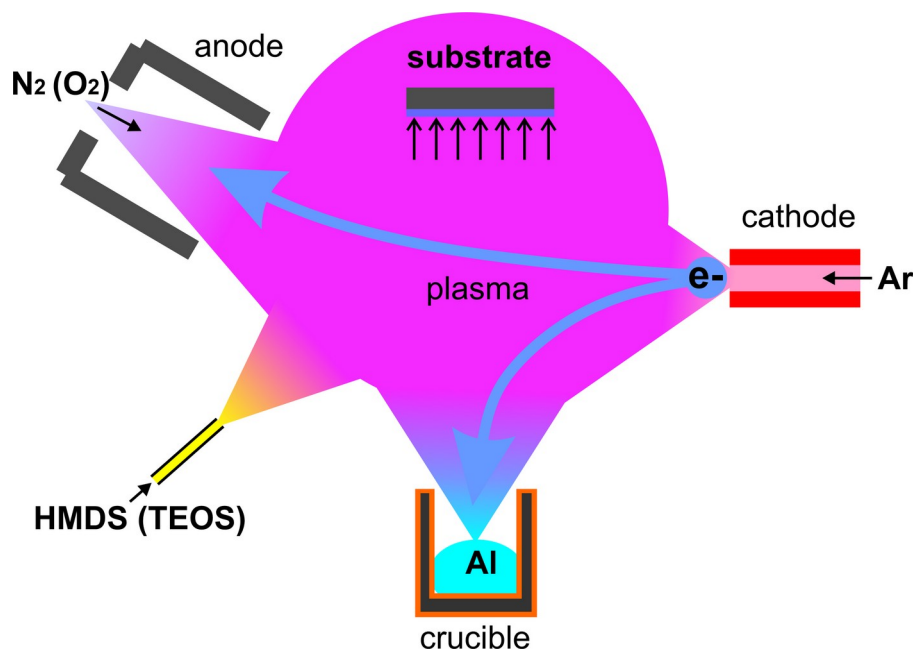
Figure 1 - Electrode scheme of the experimental facility
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Organosilicon precursors hexamethyldisilazane ($[(CH_3)_3Si]_2NH$) and tetraethoxysilane (($C_2H_5O)_4Si$) were chosen because they are non-toxic, environmentally friendly, affordable and cheap. They contain all the necessary elements for the formation of coatings based on SiCN and SiCO. Since accurate adjustment of the chemical composition is necessary to create coatings with the required set of physico-chemical properties, additional reactive gases N_2/O_2 were introduced into the combined-cycle gas mixture containing carbon dioxide and metal vapors.

The composition of low-pressure arc discharge plasma (0,5–1 mTorr) with SHHC in gas mixtures of $Ar+N_2+Al$ and $Ar+O_2+Al$ with vapors of organosilicon precursors hexamethyldisilazane (HMDS) and tetraethoxysilane (TEOS), respectively, was analyzed by optical emission spectroscopy using an OceanOptics HR2000 spectrometer in the wavelength range from 200 up to 1100 nm (resolution 0,84 nm).

Results and discussion

The processes of activation of all components of the vapor-gas mixture, including the dissociation of reactive gas molecules and the decomposition of organosilicon precursors, are important factors influencing the formation of coatings based on PDC ceramics by plasma chemical deposition in a reactive vapor-gas medium. The plasma was analyzed by optical emission spectroscopy to identify its constituent components, as well as to assess the degree of dissociation of reactive gases N_2 and O_2 and the intensity of the decomposition of organosilicon precursors HMDS and TEOS.

Optical emission spectra of gas discharge plasma in mixtures of $Ar+Al+N_2+HMDS$ and $Ar+Al+O_2+TEOS$ are shown in Figure 3. In the UV region and in the visible range, there are mainly intense lines of excited Ar atoms (700-1000 nm), an Al line of 396.2 nm corresponding to the $3s^23p–3s^24s$ transition, as well as lines C (484,2 nm, $2s^22p^3p–2s^22p(2P°1/2)16d$) and H (656,3 nm, 2s–3p). The presence of the latter two indicates a sufficiently deep decomposition of the initial HMDS and TEOS molecules. The difference between the spectra in Figures 3 *(1)* and 3 *(2)* is the presence of atomic components resulting from the dissociation of reactive gases N_2 and O_2, respectively. Thus, N atoms (746.8 nm, $2s^22p^3(2D°)3s–2s^22p^3(2D°)s3p$) were detected in $Ar+N_2+Al+HMD$, in $Ar+O_2+Al+TEOS$ - O (794,8 nm, $2s^22p^3(2D°)3s–2s^22p^3(2D°)3p$). In addition to the neutral component of the plasma, lines of ionic components were detected on the spectra: Ar^+ (400–450 nm), and in the vapor-gas mixture $Ar+O_2+Al+The$ lines Al^+ (390,1 nm, $3s^23p–3p^2$) and N_2^+ (391,9 nm, $2s^22p^3(2D°)3s–2s^22p^3(4S°)3p$) were also present in the TEOS. Of the molecular components, the singuletes N_2 (337,1 nm, $C^3\Pi_u–B^3\Pi_g$) and O_2 (759,37 nm, $b^1\Sigma_g^+–X^3\Sigma_g^-$) were detected in the spectra.

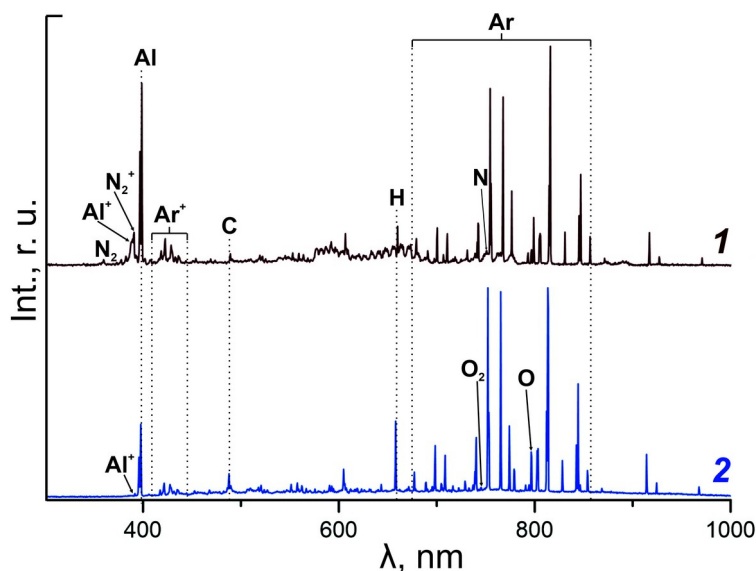Figure 2 - Optical radiation spectrum of Ar+N$_2$+Al+HMDS *(1)* and Ar+O$_2$+Al+TEOS *(2)* arc plasma
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To quantify the degree of dissociation and the ratio of ion concentrations in plasma, a kinetic equation describing the process of the appearance and disappearance of particles in plasma and the Einstein ratio were used. The concentration ratio is as follows: $N_i/N_k = (I_i/I_k)\cdot(A_k\cdot h\nu_k\cdot\tau_k\cdot\sigma_k/A_i\cdot h\nu_i\cdot\tau_i\cdot\sigma_i.)$, where $N_{i/k}$ is the concentration of particles in the ground state, $I_{i/k}$ is the intensity of the spectral line, $A_{i/k}$ is the Einstein coefficient, $h\nu_{i/k}$ is the transition energy, $\tau_{i/k}$ is the lifetime of the state, $\sigma_{i/k}$ is the excitation cross section of the energy state. The constants for the calculation are shown in Table 1.

The dependences of the degree of dissociation of reactive gases N$_2$ and O$_2$ on various conditions of discharge combustion are shown in Figure 3. As can be seen, with this method of activation of a vapor-gas medium, the degree of nitrogen dissociation in a mixture of Ar+N$_2$+Al+HMDS is quite high compared, for example, with RF methods used to generate nitrogen atoms [10]. Since such systems are dominated by ionic components formed in corona and glow discharges, which require a high concentration of ions to maintain.

Table 1 - Data used in calculation

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Particle grade	λ, nm	$A\times10^7$, s^{-1}	$h\nu$, eV	$\tau\times10^{-9}$, s	σ, cm^2	$A\times\tau$
N	746,8	1,96 [11]	11,99 [12]	26,3 [12]	$6,2\times10^{-16}$ [13]	-
N$_2$	337,1	-	11,1 [12]	-	$5,5\times10^{-18}$ [13]	0,52 [12]
O	794,8	0,58 [14]	12,5 [14]	4 [14]	3×10^{-18} [14]	-
O$_2$	749,4	-	1,63 [15]	-	$4,6\times10^{-18}$ [15]	0,33 [15]
H	656,3	4,41 [11]	12,09 [14]	1,6 [14]	$9,3\times10^{-17}$ [14]	-
Ar	811,5	3,3 [11]	13,07 [14]	3,1 [14]	5×10^{-18} [14]	-

An increase in the discharge current in the range of 5–25 A leads to a slight (5–10%) increase in the degree of dissociation. To a much greater extent, the degree of nitrogen dissociation in the sample location is influenced by the current in the crucible circuit, which can be explained by a combination of a high concentration of electron flux near the crucible and a high pressure of metal vapors in the area of their drift from the crucible towards the substrate. As is known [11], nitrogen dissociation in plasma in the presence of a stream of fast electrons occurring in a discharge with SHHC [7] occurs mainly as a result of a two-step process of dissociative recombination of molecular nitrogen ions: $e^-+N_2\rightarrow N_2^++2e^-$, $e^-+N_2^+\rightarrow 2N$. The presence of a dense vapor stream of a more easily ionized metal probably intensifies the process of formation of molecular ions by recombination with the participation of metal ions.
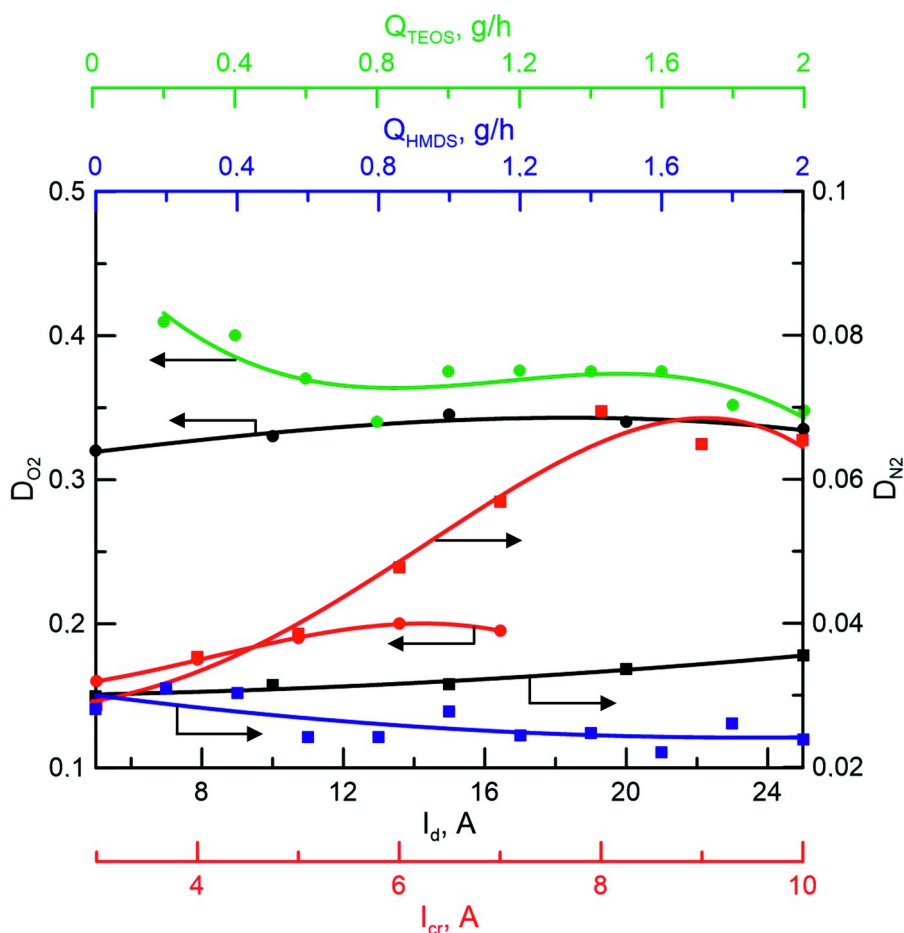
Figure 3 - Dependences of the degree of dissociation of nitrogen D_{N2} and oxygen D_{O2} on the discharge current (I_d), crucible current (I_{cr}), and precursor flux
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The binding energy in the N_2 molecule is almost twice as high as the binding energy in O_2, so the degree of dissociation of oxygen differs significantly from nitrogen. The calculation results showed [16] that the dissociation of oxygen molecules in the plasma of an arc discharge with SHHC is extremely difficult, and it is difficult to achieve a high degree of oxygen dissociation above 0,5 even with high arc discharge power, but this is an order of magnitude higher than for nitrogen. As can be seen, the oxygen dissociation process slows down both with an increase in saturated aluminum vapor pressure and with high O_2 and TEOS fluxes, which may be due to an increase in the overall pressure in the chamber. As a result, the free path of electrons decreases, their average energy decreases, and thus the intensification of the process of ionization and dissociative recombination by electron impact decreases. An increase in the degree of oxygen dissociation with an increase in the current of the main discharge gap may be due to an increase in the concentration of fast electrons interacting with the vapor-gas medium.

Figures 4 and 5 show the dependences of the intensities of the hydrogen line H (656,3 nm) on various plasma conditions. The course of HMDS decomposition reactions occurring in a gas-discharge plasma is determined by the binding energies between the atoms in the initial molecules, as well as the discharge power. The decomposition of the hexamethyldisilazane molecule in plasma occurs as a result of a stepwise reaction: first, the Si-C bond breaks and the methyl group is lost, then the Si-N single bond breaks. As a result, fragments of a molecule with a Si=N double bond appear in the plasma, which are involved in the formation of coatings. In the following stages, the stronger N-H and C-H bonds and the Si=N double bond are destroyed, resulting in the appearance of H, C, and Si atoms in the plasma, the content of which can be used to determine the degree of decomposition of HMDS.

It can be seen that the current in the crucible circuit most significantly affects the decomposition of the initial precursor molecules in the Ar+N_2+Al+HMDS medium, which can be explained by an increase in pressure in the local region near the crucible, where intensive activation processes of all plasma-forming components occur due to an increase in the frequency of particle collisions in the plasma. The influence of other parameters turned out to be less significant. A slight decrease in the decomposition rate of the HMDS molecule with an increase in the N_2 flux may be due to an increase in the overall pressure in the vacuum chamber and a corresponding decrease in the average electron energy.

Just as in the case of HMDS, the decomposition of the TEOS molecule occurs stepwise: first, the Si-O bond breaks to form C_2H_2-O, followed by the loss of the C_2H_5 methyl group, but to date little is known about the intermediate products of the decomposition reaction of the TEOS molecule. It is reported that the decomposition of TEOS and the formation of SiCO-based films are affected by the addition of O_2, which accelerates the decomposition of organosilicon molecules [17]. Atomic oxygen has a significant effect on the quality of the coatings obtained, since there is a relationship between the substrate temperature and the deposition rate, which strongly depends on the presence of O: the deposition rate increases with increasing substrate temperature in the presence of oxygen. However, the formation of coatings of the desired chemical composition with a certain

set of properties depends not only on the introduction of a reactive gas, but also on the decomposition process of the TEOS molecule, which also contains oxygen. As can be seen in Figure 5, an increase in the magnitude of the TEOS flow leads first to an increase in the intensity of H, and then to its decrease. The gas-phase decomposition reaction of the TEOS molecule can also be enhanced by atomic oxygen, as in [17], which can be observed in our case.
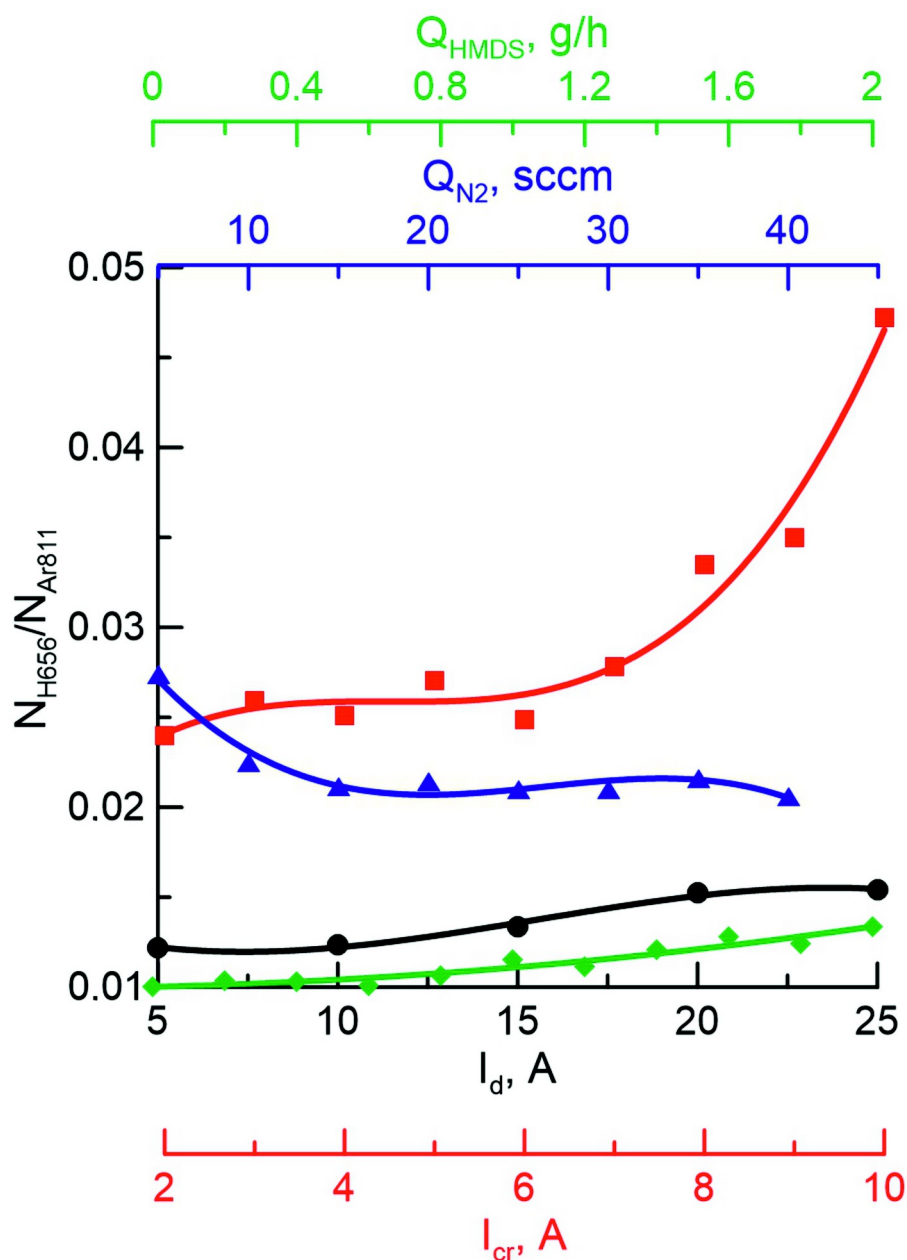

Figure 4 - Dependence of the ratio of hydrogen to argon (N_{H656}/N_{Ar811}) on the discharge current (I_d), crucible current (I_{cr}), nitrogen flux (Q_{N2}) and hexamethyldisilazane flux (Q_{HMDS}) in a mixture of Ar+N$_2$+Al+HMDS
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As can be seen, with an increase in the O$_2$ flux and the TEOS flux, the ratio of H/Ar concentrations changes nonmonotonously and reaches saturation, which probably indicates the complete decomposition of the precursor molecule in the Ar+O$_2$+Al+TEOS medium. Apparently, this is due to the presence of atomic oxygen in the plasma. Its concentration increases not only due to the introduction of reactive gas, but also during the decomposition of the TEOS molecule. As the O$_2$ and TEOS fluxes increase, the H/Ar concentration ratio increases significantly at first. As the authors of [18] have shown, films obtained without oxygen retain the structures of the initial molecules, which indicates that the molecules practically did not decompose during the process. The film formation is primarily caused by the adsorption and surface reaction of monomer molecules and radicals. That is, without oxygen, the surface reaction is dominant in the formation of films. On the other hand, when oxygen is added, it is excited and enhances the gas-phase decomposition reaction of the molecule with the formation of intermediate compounds in the gas phase (that is, the oxidation reaction, which is exothermic, occurs in the gas phase). The effect of the main discharge current and the crucible current on the TEOS decomposition rate turned out to be insignificant, which is probably due to the fact that when measuring this dependence, the O$_2$ and TEOS fluxes were at the level of 10 sccm

and 1 g/h, respectively, which is sufficient for complete decomposition of the precursor, and a further increase in I_d and I_{cr} does not affect this indicator.
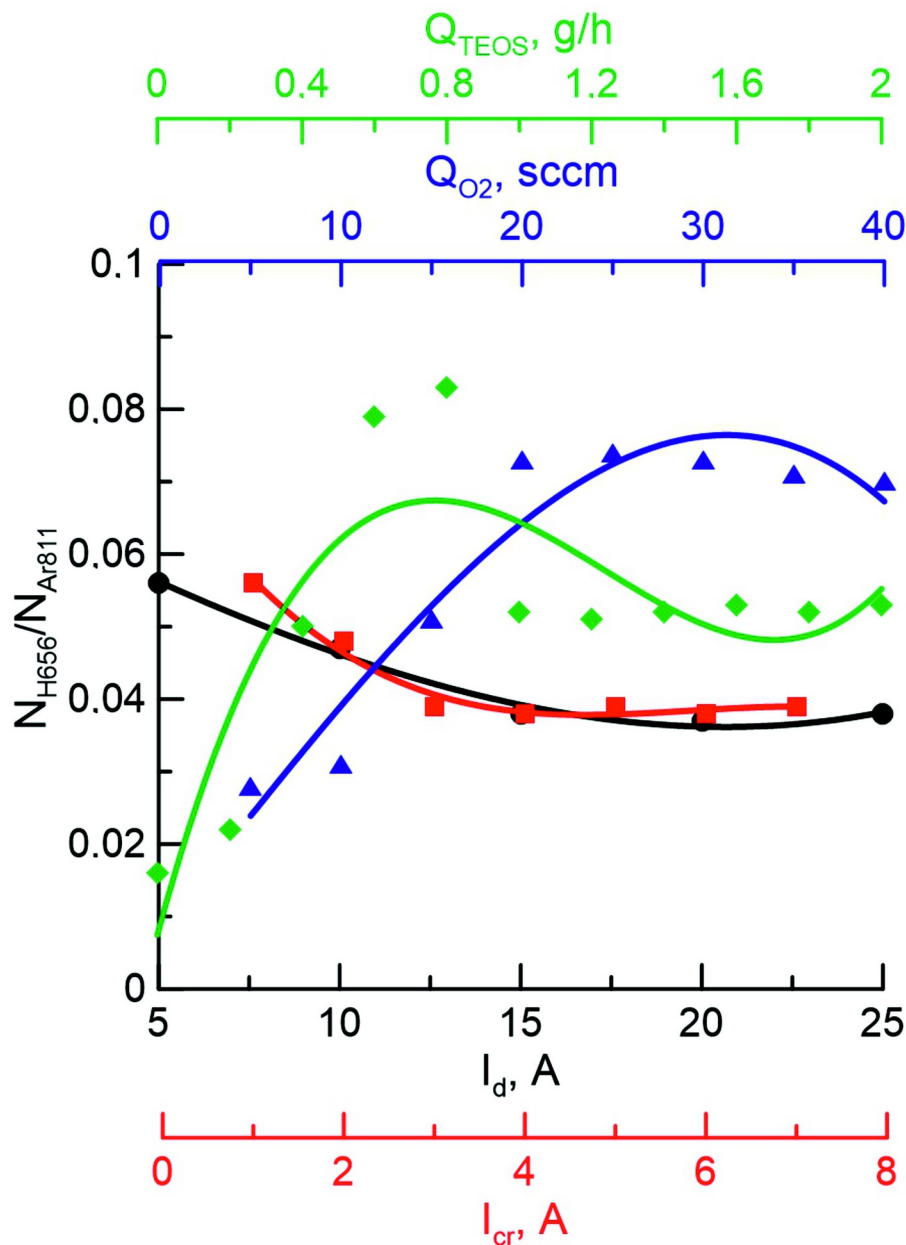

Figure 5 - The dependence of the ratio of hydrogen to argon (N_{H656}/N_{Ar811}) on the discharge current (I_d), crucible current (I_{cr}), oxygen flux (Q_{O2}) and tetraethoxysilane flux (Q_{TEOS}) in a mixture of Ar+O$_2$+Al+TEOC
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Figure 6 shows the dependences of the ratio of concentrations of aluminum ions (N_{Al+}) and argon ions (N_{Ar+}) obtained in the Ar+N$_2$+Al+HMDS medium on the discharge parameters. Data analysis shows that the N_{Al+}/N_{Ar+} ratio is significantly affected by the magnitude of the N$_2$ flux. The effect of the discharge current, the current in the crucible circuit, and the HMDS flow turned out to be less significant. The monotonous growth of N_{Al+}/N_{Ar+} with an increase in the flow of reactive gas from 5 to 35 sccm may be due to an increase in the total pressure in the chamber, which may have a significant effect on the temperature of the anode crucible [19], which, in turn, leads to increase in melt temperature and saturated vapor pressure of aluminum. As the pressure increases, the temperature in the vacuum increases with increasing nitrogen flow due to Charles' law: with a constant mass of gas and its volume, the gas pressure is proportional to its absolute temperature. The temperature increases due to an increase in the pressure of the reactive gas: the higher the temperature, the higher the evaporation rate of aluminum, which means that the temperature of the crucible in the combined-cycle mixture has become higher.
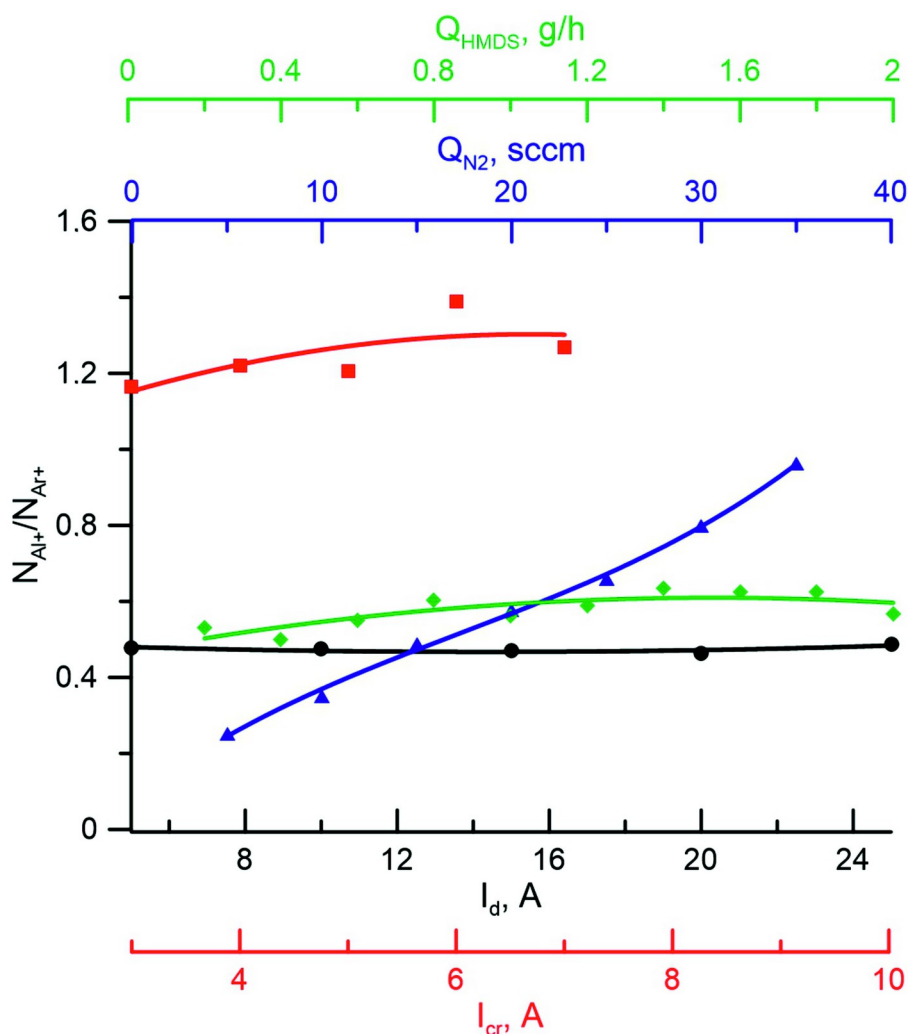
Figure 6 - Dependences of the ratio of concentrations of aluminum ions and argon ions (N_{Al+}/N_{Ar+}) on the discharge current (I_d), crucible current (I_{cr}), nitrogen flux (Q_{N2}) and hexamethyldisilazane flux (Q_{HMDS}) Ar+N_2+Al+HMDS
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However, as reported in [20], depending on which reactive gas is introduced into the combined-cycle mixture, the temperature-pressure dependence may differ significantly. The reason for this difference may be the different interaction of particles in a vapor-gas environment, but the effect of these mechanisms on such a temperature change depending on the type of gas has not yet been fully studied. Therefore, in an environment containing oxygen, the behavior of the dependence of N_{Al+}/N_{Ar+} on the O_2 flux can be radically different. The low ionization potential of Al (5,99 eV) leads to a faster ionization process of metal atoms compared to Ar (15,76 eV). In addition, the flow of reactive gas and pressure do not significantly affect the electron temperature, which strongly affects the ionization process by secondary electrons, as an increase in the current in the crucible circuit, as was shown in [7].

Figure 7 shows the dependences of the ratio of concentrations of aluminum ions (N_{Al+}) and argon ions (N_{Ar+}) on various discharge parameters obtained in the medium Ar+O_2+Al+TEOC. The current in the crucible circuit has the most significant effect on this ratio. As can be seen, the dependence has a nonmonotonic character: the decrease in N_{Al+}/N_{Ar+} from 0,8 to 0,6 with an increase in current from 1 to 4 A is due to the constant intensity of the Al$^+$ line, which indicates a low concentration of aluminum atoms evaporating from the surface of heated aluminum. At the same time, there is an increase in the intensity of the Ar$^+$ line as the discharge power increases. A further increase in N_{Al+}/N_{Ar+} is associated with an increase in the temperature of the crucible and a significant increase in the concentration of Al vapors and their subsequent ionization. This nonmonotonic behavior is explained by the nonlinear dependence of the saturated vapor pressure on the metal temperature, therefore, in the 1–4 A region at lower temperatures and, consequently, saturated vapor pressures, the concentration of aluminum atoms remains low. Probe diagnostics of the plasma showed that the ion current density in the sample location region at maximum currents in the studied ranges can reach 10–12 mA/cm^2.
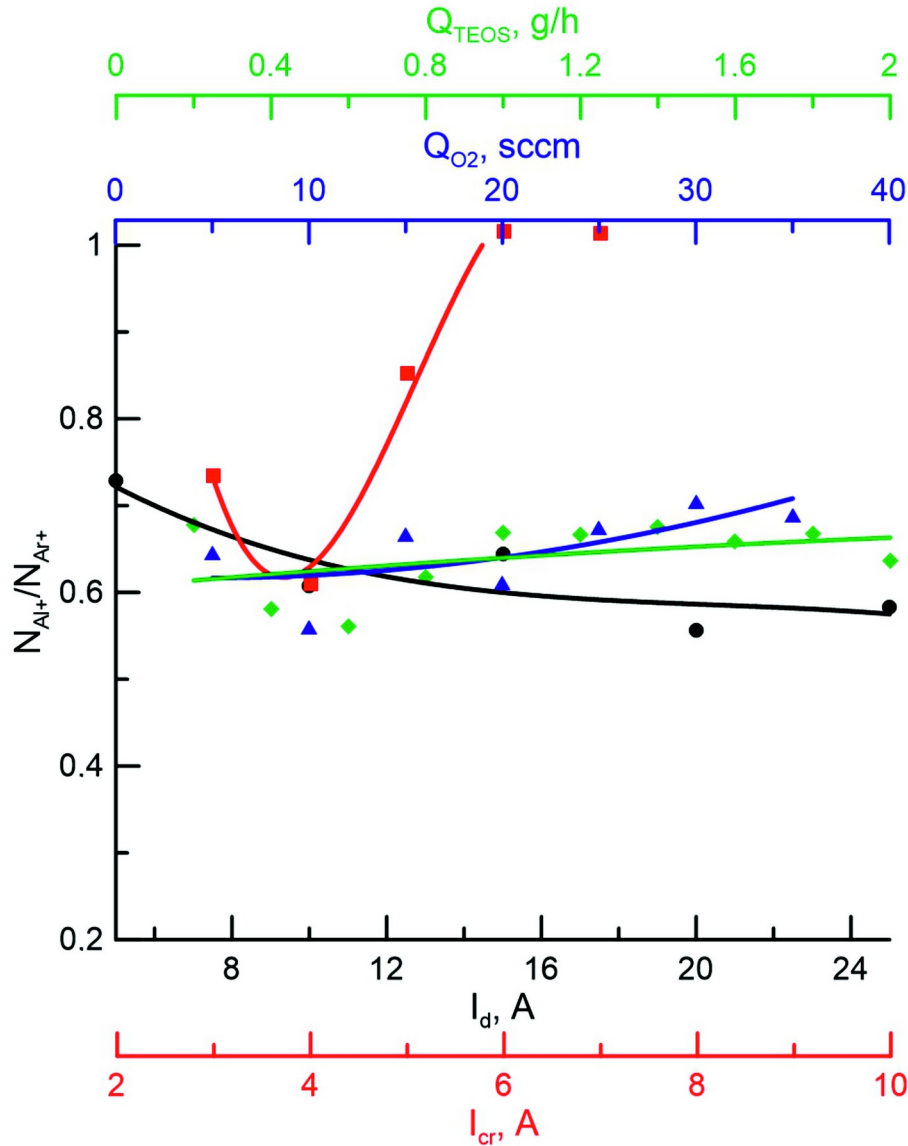
Figure 7 - Dependences of the ratio of concentrations of aluminum ions and argon ions (N_{Al+}/N_{Ar+}) on the discharge current (I_d), crucible current (I_{cr}), nitrogen flux (Q_{O2}) and hexamethyldisilazane flux (Q_{TEOS}) Ar+O₂+Al+TEOS
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Test coatings of SiAlCN and SiAlCO with a homogeneous structure and good adhesion to the sprayed substrates were obtained. Figure 8 shows SEM images of the film surface. It can be seen that the surface of the coatings is smooth, without visible defects in the form of chips, cracks or microdrops. The SiAlCO films obtained at Q_{O2} = 10 sccm, Q_{TEOS} = 0,5 g/h, and I_{cr} = 4 A had the following chemical composition: 18,8 at.% Si, 22,7 at.% Al, 2 at.% C, and 54 at.% O, and a hardness of 12 GPa. SiAlCN films obtained at Q_{N2} = 10, Q_{HMDS} = 1 g/h and I_{cr} = 5 A: 26,8 at.% Si, 23,1 at.% Al, 19,1 at.% C and 27,4 at.% N, their hardness was 25 GPa. Despite the fact that the coatings were obtained of good quality, the problem of determining the optimal element ratio remains open, so further research will be aimed at determining the optimal modes of synthesis of coatings with the desired chemical composition and set of properties.
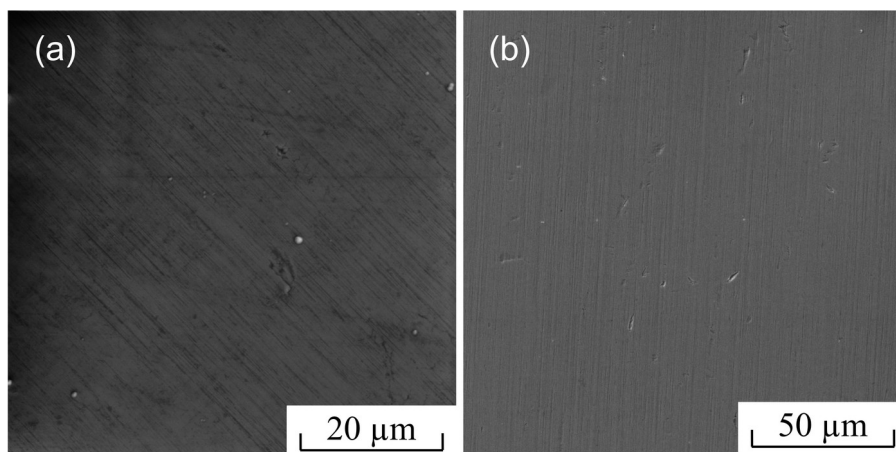
Figure 8 - SEM images of the surface of SiAlCN *(a)* and SiAlCO *(b)* films
DOI: https://doi.org/10.60797/IRJ.2025.155.33.9

Conclusion

Thus, the method of activation of a vapor-gas mixture containing organosilicon precursors and additional reactive components N_2 and O_2 in an arc discharge with a hollow self-heating cathode and a sectional anode under aluminum evaporation conditions, as well as the effect of combustion modes on the dissociation of reactive gases N_2 and O_2 and the degree of decomposition of HMDS and TEOS, was investigated. The results of spectral plasma diagnostics showed the presence in the studied media of the necessary elements for the synthesis of SiAlCN and SiAlCN coatings. High rates of decomposition of the initial HMDS and TEOS molecules, high values of the degree of dissociation of N_2 up to 7% and O_2 up to 40% were achieved. The investigated method of activation of a vapor-gas medium provides an intense ion flow to the treated surface with a fraction of metal ions in excess of 50%, which is important for the formation of dense, high-quality coatings. Trial SiAlCN and SiAlCO coatings were obtained in combined-cycle mixtures of Ar+N_2+Al+HMDS and Ar+O_2+Al+TEOS, respectively. Thus, the results of the study showed the prospects of using this synthesis method to obtain PDC coatings with the necessary elemental composition and the required set of physico-chemical properties.

Конфликт интересов
Не указан.

Conflict of Interest
None declared.

Рецензия
Все статьи проходят рецензирование. Но рецензент или автор статьи предпочли не публиковать рецензию к этой статье в открытом доступе. Рецензия может быть предоставлена компетентным органам по запросу.

Review
All articles are peer-reviewed. But the reviewer or the author of the article chose not to publish a review of this article in the public domain. The review can be provided to the competent authorities upon request.

Список литературы на английском языке / References in English

1. Chen L. Machining performance of Ti–Al–Si–N coated inserts / L. Chen, S.Q. Wang, Y. Du [et al.] // Surface and Coatings Technology. — 2010. — Vol. 25. — Issue 2. — DOI: 10.1016/j.surfcoat.2010.07.043.

2. Wang Y. Oxidation/Corrosion of Polymer-Derived SiAlCN Ceramics in Water Vapor / Y. Wang, W. Fei, L. An // Journal of the American Ceramic Society. — 2005. — Vol. 89. — Issue 3. — DOI: 10.1111/j.1551-2916.2005.00791.x.

3. Allebrandt D. Oxidation resistance of SiAlCN: H-coatings / D. Allebrandt, H. Hoche, H. Scheerer [et al.] // Surface and Coatings Technology. — 2007. — Vol. 201. — Issue 9–11. — DOI: 10.1016/j.surfcoat.2006.07.204.

4. Liu J. Micro-Machinable Polymer-Derived Ceramic Sensors for HighTemperature Applications / J. Liu, C. Xu, L. An // Proceedings of SPIE. — 2010. — Vol. 7647. — DOI: 10.1117/12.848529.

5. Zhang L. Piezoresistivity of polymer-derived AlSiCN ceramics / L. Zhang, Y. Wang, L. An // Applied Mechanics and Materials. — 2013. — P. 423–426. — DOI: 10.4028/www.scientific.net/AMM.423-426.89.

6. Nakafushi Y. Mechanical properties and microstructure of AlN/SiCN nanocomposite coatings prepared by r.f.-reactive sputtering method / Y. Nakafushi, K. Matsuda, M. Nos // Archives of metallurgy and materials. — 2015. — 2. — DOI: 10.1515/amm-2015-0243.

7. Menshakov A.I. Synthesis of Nanocomposite TiSiCN Coatings by Titanium Evaporation and Organosilicon Compound Activation in Hollow Cathode Arc Discharge / A.I. Menshakov, Y.A. Bruhanova, A.I. Kukharenko [et al.] // Membranes. — 2022. — Vol. 12. — № 3. — 321 p. — DOI: 10.3390/membranes12030321.

8. Menshakov A. Plasma enhanced high-rate deposition of advanced film materials by metal reactive evaporation in organosilicon vapors / A. Menshakov, Y. Bruhanova, P. Skorynina [et al.] // Membranes. — 2023. — Vol. 13. — № 4. — 374 p. — DOI: 10.3390/membranes13040374.

9. Kroke E. Silazane derived ceramics and related materials / E. Kroke, Y.-L. Li, C. Konetschny [et al.] // Materials Science and Engineering R Reports. — 2000. — Vol. 26. — № 4. — P. 97–199. — DOI: 10.1016/S0927-796X(00)00008-5

10. Blant A.V. Nitrogen species from radio frequency plasma sources used for molecular beam epitaxy growth of GaN / A.V. Blant, O.H. Hughes, S.V. Novikov [et al.] // Plasma Sources Science and Technology. — 2000. — Vol. 9. — № 1. — 12 p. — DOI: 10.1088/0963-0252/9/1/303.

11. Electronic database of the Modified National Institute of Standards and Technology. — National Institute of Standards and Technology. — URL: https://www.nist.gov/ (accessed: 06.05.25).

12. Czerwiec T. Nitrogen dissociation in a low pressure cylindrical ICP discharge studied by actinometry and mass spectrometry / T. Czerwiec, F. Greer, D.B. Graves // Journal of Physics D: Applied Physics. — 2005. — Vol. 38. — № 24. — DOI: 10.1088/0022-3727/38/24/003.

13. Itikawa Y. Cross Sections for Electron Collisions with Nitrogen Molecules / Y. Itikawa // Journal of Physical and Chemical Reference Data. — 2005. — Voll. 35. — № 1. — DOI: 10.1063/1.1937426.

14. Grotrian electronic database. — Siberian Branch of the Russian Academy of Sciences. — URL: http://grotrian.nsu.ru/ru (accessed: 06.05.25).

15. Krupenie P.H. The Spectrum of Molecular Oxygen / P.H. Krupenie // Journal of Physical and Chemical Reference Data. — 1972. — Vol. 1 — № 2. — DOI: 10.1063/1.3253101.

16. Tretnikov P.V. Deposition of Al2O3 coatings in Ar-O2 low-pressure discharge plasma under a high dissociation degree of O2 / P.V. Tretnikov, N.V. Gavrilov, A.S. Kamenetskikh [et al.] // Journal of Physics Conference Series. — 2021. — Vol. 2064. — № 1. — 012047 p. — DOI: 10.1088/1742-6596/2064/1/012047.

17. Sawada Y. Synthesis of plasma-polymerized tetraethoxysilane and hexamethyldisiloxane films prepared by atmospheric pressure glow discharge / Y. Sawada, S. Ogawa, M. Kogoma // Journal of Physics D: Applied Physics. — 1995. — Vol. 28. — № 8. — P. 1661–1669. — DOI: 10.1088/0022-3727/28/8/015.

18. Nguyen V.S. Plasma Organosilicon Polymers: Deposition, Characterization, and Application in Multilayer Resist / V.S. Nguyen, J. Underhill, S. Fridmann [et al.] // Journal of The Electrochemical Society. — 1985. — Vol. 132. — № 8. — P. 1925–1932. — DOI: 10.1149/1.2114255.

19. Ahmed A.F. Spectroscopic Analysis of DC-Nitrogen Plasma Produced using Copper Electrodes / A.F. Ahmed, A. Abbas // Iraqi Journal of Science. — 2021. — Vol. 62. — № 1. — P. 3560–3569. — DOI: 10.24996/ijs.2021.62.10.15.

20. Strunin V.I. Simulation of chemical composition nitrogen-argon-aluminum plasma / V.I. Strunin, Z.G. Khudaibergenov // Journal of Physics: Conference Series. — 2021. — Vol. 1901. — № 1. — 012107 p. — DOI: 10.1088/1742-6596/1901/1/012107.