Investigation of the conditions for the formation of SiCN-based coatings in arc discharge with self-heated hollow cathode

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Abstract. Method for low-temperature (<200°C) deposition of SiCN-based coatings in a large volume chamber (0.3 m$^3$) by decomposition of organosilicon precursor in nitrogen-argon plasma of discharge with self-heated hollow cathode and remote anode (40 cm) at pressure of ~1 mTorr was investigated. The analysis of the composition of coatings by IR spectroscopy and the analysis of plasma composition are carried out by optical emission spectroscopy. The influence of discharge current (10-40 A) and the flow of gas mixture (5-15 sccm hexamethyldisilazane and 60 sccm Ar-N$_2$ mixture) on plasma composition and elemental composition of coatings was investigated. It is shown that the degree of decomposition of precursor molecules is increased with growth of the current and with increase of Ar content in the gas mixture.

1. Introduction

Among the modern methods for production of SiCN coatings, the methods of chemical vapor deposition (CVD), where volatile organosilicon compounds (OSC – low-toxic liquids in whose molecules all the necessary SiCN elements and connections are present) are used as a component of the working medium, are the most safe, environmentally friendly and productive ones. At the same time, the activation of the gaseous medium (production of active components involved in the formation of a coating on the required surface and containing Si-C, Si-N, C-N bonds) occurs most often either by thermal decomposition of the initial compounds [1] or by a low-temperature method using plasma stimulation (PECVD).

While the traditional (thermal) methods of CVD require high temperatures (> 900°C), use of plasma activation of the gas phase can reduce the growth temperature of layers to 100-200°C [2], which opens the possibility of deposition to the low-temperature materials, for example, polymers. As sources of plasma for production of SiCN coatings by PECVD method, radio frequency generators are most often used [3], which is due, firstly, to the effective excitation and decomposition of OSC molecules in RF discharge, and, secondly, to the simplicity of the method: samples are located under RF potential, the vapors of OSC are projected near their surface, the total area of the treated surface in this case being determined by the area of the electrode-antenna. In order to facilitate the formation of films containing simultaneously Si-C and Si-N bonds, it is important to control the degree of decomposition of the initial molecules. However, in fact, when using RF generator, the only changeable discharge parameter is its power, and there is no possibility of independent change of the...
current density and energy of the active particles, which narrows the possibilities for controlling the degree of decomposition of the OSC molecules and plasma composition, and also does not allow one to investigate the effect of these parameters on the characteristics of obtained coatings. In addition, radio frequency generators introduce additional impurities (up to 25 at.% in the volume of the coating) consisting of the antenna material [4]. Solution of the problem associated with contamination of the coatings requires a more complicated construction of RF generator or significant limitation of the operating parameters' range.

In this connection, a problem has arisen in the development and investigation of alternative methods for activation of gaseous medium containing organosilicon components, with low degree of plasma contamination and at the same time providing high efficiency and productivity and enabling a controlled change in the composition of gaseous medium and in the degree of decomposition of initial components.

For the processing of products with large total surface area, it is advisable to use devices that generate large volumes of spatially uniform plasma, for example, by ignition of gas discharge in a working chamber. Promising for this purpose is a discharge with a self-heated hollow cathode (SHHC) [5], whose advantages are the wide range of discharge currents (from units to hundreds of amperes) and working pressures of gaseous medium (0.1-10 mTorr), stability of burning and low degree of plasma contamination products of cathode erosion. This type of discharge was successfully used to generate large volumes of plasma when producing protective CrN coatings by the PECVD method for products with total area of the order of 1 m² [6], and also for creating emission plasma in the electron source used for ion-plasma nitriding of structural materials [7] and ion assisting in magnetron sputtering systems [8]. This paper is devoted to the study of the features of SiCN-based coatings obtained by decomposition of OSC vapors in discharge plasma with SHHC.

2. Experimental technique

The experiments were carried out in a gas-discharge system, the scheme of which is shown in figure 1. Flat anode 2 was located opposite to the self-heated cathode 1 at a distance of 40 cm. The organosilicon precursor vapor was supplied through the evaporator 3 located on the axis of the discharge system at a distance 17 cm from the cathode. Samples 4 (20 x 10 mm², AISI430, glass) were located on a insulated flat electrode (whose potential was floating relative to the discharge system electrodes) at a distance 16 cm from the evaporator. Hexamethyldisilazane \([(CH_3)_3Si]_2NH\) (HMDS) was used as precursor in production of SiCN coatings, its advantages being the presence of all the necessary elements and bonds between them, high volatility, availability and low cost. The gas (Ar, N₂ or N₂+Ar) was supplied to cathode cavity \(Q = 60 \text{ sccm}\) and after heating of cathode by ion bombardment in glow discharge and igniting of diffuse arc discharge between cathode 1 and remote anode 2, the evaporator 3, located in the center of the plasma jet, was heated to a temperature above HMDS boiling point (126°C). As a consequence, the vapor flow was determined solely by the feed rate of HMDS. The vapor flux \(Q_{HMDS}\) varied from 5 to 15 sccm.

Samples were washed with a solvent in an ultrasonic bath and then purified by etching in a pulse-periodic discharge (50 kHz, \(I_d = 20 \text{ A}, 200 \text{ V}\)) in argon \(Q_{Ar} = 40 \text{ sccm}\) for 20 min.

Figure 1. The scheme of the experimental setup for the deposition of SiCN coatings. 1 – self-heated hollow cathode, 2 – anode, 3 – evaporator, 4 – samples.
The value of the floating potential of the samples in relation to anode was – (50-100) V. The pressure of gas mixture in the chamber was 1 mTorr. The discharge current was regulated in the range 10-40 A. The deposition time of the coatings was 2 hours. The temperature of the samples didn’t exceed 200°C during the deposition process.

Plasma analysis by the method of optical emission spectroscopy (OES) was carried out using ISP-30 spectrophotometer integrated with the multichannel photodetector MORS-6, the operating spectral range of which was 200-950 nm. Investigations of the elemental composition of the coatings were carried out on LEO 982 electron microscope with attachment of energy dispersive X-ray analysis (EDS) Oxford instruments X-Max. Transparency of the samples was measured on UV Shimadzu-1700 spectrophotometer in wavelength range of 370-1100 nm. IR spectra of the coatings were recorded using Vertex 70 FTIR spectrometer in wavenumber range from 400 to 4000 cm\(^{-1}\) with resolution up to 1 cm\(^{-1}\). The spectra were averaged over 16 frames. Microhardness of the obtained coatings was measured by Shimadzu DUH-211s dynamic microhardnesser with load of 10 mN. Averaging of microhardness values was carried out for 6-8 measurements. Thickness of the coatings was measured on a Calotest instrument.

3. Experimental results and discussion
The mechanism of reactions taking place in plasma upon precipitation of silicon carbonitride films is determined by binding energies between the atoms in precursor compound. According to [9], where the composition of radiofrequency plasma containing vapors of organosilicon precursors was studied, decomposition of the hexamethyldisilazane molecule in plasma proceeds according to the following scheme. The reaction is stepwise – first Si–C bond (binding energy 3.3 eV) is broken, then methyl group is lost: (CH\(_3\))\(_3\)-Si-NH-Si-(CH\(_3\))\(_3\) → (CH\(_3\))\(_3\)-Si-NH-Si-(CH\(_3\))\(_2\) + CH\(_3\), which agrees with the known data on binding energies in the molecule. Then single bond Si–N (3.5-3.7 eV) is broken: (CH\(_3\))\(_3\)-Si-NH-Si-(CH\(_3\))\(_2\) → (CH\(_3\))\(_3\)-Si + HN = Si-(CH\(_3\))\(_2\). As a result, fragments of molecule with double bond Si=N that participate in the formation of SiCN coating appear in the plasma. This scheme of decomposition of HMDS is also confirmed by the results of mass spectrometry. On the following stages, N–H (4.4-1 eV), C–H (4.3-4.8 eV) and Si=N bonds are destroyed, resulting in the appearance of H, C, and Si atoms in the plasma; their content can indicate the degree of HMDS decomposition.

Figure 2 shows the characteristic emission spectra of discharge plasma with SHHC in mixtures of argon and nitrogen with HMDS. In the observed spectra, in addition to the lines belonging to plasma-forming gas, strong lines of hydrogen atom are found, belonging to Balmer series – 486.1 nm and 656.3 nm. These lines are present in plasma spectra of discharge with HMDS both in pure argon and nitrogen, and in their mixture. In HMDS + Ar medium, along with the lines related to Ar and Ar\(^+\), silicon lines 251.43, 251.61, 251.92, 252.41, 252.85 nm are observed that correspond to transitions to basic state \(^1\)P\(_0\) – \(^3\)P. Relative intensities of the lines are in good agreement with the tabulated data. In addition to them, the \(^1\)P\(_0\) – \(^1\)S transition lines are observed: 263.13 nm (weak luminescence) and 390.55 nm. In all experiments there is a silicon line 288.16 nm (\(^1\)P\(_0\) – \(^3\)D).
The presence in the plasma of silicon atoms, for the appearance of which, according to the scheme considered above, the destruction of double bond Si=N is necessary, indicates deep decomposition of the original HMDS molecule.

The results of analysis of plasma composition also indicate changes in the degree of decomposition of HMDS molecules with increase of the discharge current and change in the composition of gas mixture (figure 3). The ratio of intensities \( I_{H}/I_{N_{2}} \) of the lines of hydrogen and neutral molecular nitrogen \( N_{2} \) at 357.6 nm, which is proportional to the relative content of these components in the plasma, grows both in pure nitrogen and in its mixture with argon. However the course of dependences differs: while in pure nitrogen the ratio \( I_{H}/I_{N_{2}} \) with increasing current goes to saturation, in the mixture \( Ar + N_{2} \) almost linear behavior of the dependence \( I_{H}/I_{N_{2}} (I_{d}) \) (without saturation) is observed over the entire range of currents, which fact indicates the continued decomposition of precursor molecules. This effect of argon on the plasma composition can be explained both by intensive destruction of the initial molecules by heavier atoms, and by appearance of additional decomposition reactions involving argon.

With decrease of nitrogen content of the gas mixture, an increase in the relative content of atomic Si also occurs, which also testifies for increase of the degree of HMDS decomposition.

At fixed values of HMDS vapor flux (5 sccm) and of total pressure of plasma-forming gas (1 mTorr), coatings up to 4-5 μm thick were obtained with microhardness up to 7-8 GPa, their shade varied from colorless (light yellow) in argon to dark brown in a nitrogen medium.

Analysis of IR spectra of the coatings (figure 4) showed that the main fragments and types of bonds present in the HMDS molecule and characteristic of the SiCN(H) system [10] obtained in the low-temperature regime, remain in all the coatings. But in the coatings precipitated in Ar medium, significantly smaller amount of nitrogen-containing bonds (N–H, Si–N, C–N) is observed, which agrees with the data of elemental analysis (table 1) and may explain lower microhardness of the coatings (4-5 GPa in Ar vs. 7-8 GPa in \( N_{2} \)), since, as shown in [11], the maximum microhardness of coatings was achieved with approximately equal amounts of Si–N and Si–C bonds.

![Figure 3](image1.png) **Figure 3.** Dependencies of intensity ratio \( I_{H}/I_{N_{2}} \) on the discharge current. Total gas pressure 1 mTorr. \( Q_{HMDS} \): 1–15, 2–10, 3–5 sccm.

![Figure 4](image2.png) **Figure 4.** IR-spectra of SiCN-coatings, obtained in argon and nitrogen.
Elemental analysis of the coatings showed (table 1) that when deposited in HMDS + Ar medium, carbon predominates in the coating (up to 50 at.%), most of it, according to IR spectroscopy, is in compound C-H, and the ratio of Si, C and N in the coating is close to their ratio in HMDS molecule. When precipitating in HMDS + N₂ medium, the nitrogen content in the coating reaches 48 at.%, and, apparently, an essential part of this nitrogen is in N–H bond, and the fraction of C and Si is much lower. The difference in oxygen content of the coatings obtained in N₂ and Ar medium can be explained either by increase in sputtering of the surface oxide layers from the discharge system elements by heavier argon atoms or by the binding of oxygen to nitrogen to form volatile NOₓ compounds upon precipitation in nitrogen medium. In HMDS + Ar + N₂ (1:1) gas mixture, Si, C, and N elements content in the coating become close to the stoichiometric SiCN.

The composition of plasma-forming gas mixture significantly influences the optical characteristics of the coatings obtained. Figure 5 shows the transmission spectra of the coatings with respect to 2 mm thick glass substrate. The thickness of coatings in all cases was 4-5 μm. An increase in the nitrogen content in the plasma leads to a decrease in optical transparency of the coatings relative to argon medium. Perhaps the reason for this result is formation, in addition to C–N bonds present in the silicon carbonitride obtained from the HMDS + Ar mixture, of other nitrogen-containing bonds in the course of chemical conversions during the interaction of HMDS and N₂, or a weaker degree of decomposition of the original molecules containing N–H and Si–N bonds, which is confirmed by the data of IR spectroscopy and the results of elemental analysis of coatings.

### 4. Conclusion

Thus, the possibility of depositing a large volume of SiCN-based coatings at low temperature in a chamber is described by decomposition of the organosilicon precursor [(CH₃)₃Si]₂NH in plasma of discharge with a self-heating cathode. At discharge current of 20 A, coatings with good adhesion with hardness up to 7-8 GPa were obtained. The possibility of controlling the composition and properties of the coatings based on SiCN by changing of the composition of gaseous medium is shown. The change in the discharge current, along with a change in argon content in nitrogen-argon gas mixture, leads to a change in the degree of decomposition of the precursor molecules, which is probably the reason for the change in the mechanical characteristics of the coatings. An increase in the nitrogen content of plasma leads to a decrease in the transparency of the coatings.

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