Synthesis of silicon carbonitride films by activation gas flow in laser power optical pulsating discharge plasma

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Abstract. A new method has been developed for the plasmochemical deposition of hard protective silicon carbonitride coatings from a hexamethyldisilazane (HMDS) Si₂NH(CH₃)₆ vapor and HMDS + benzene activated by a powerful optic pulse discharge (POPD) in a high-velocity gas flow of argon. The method allows depositing silicon carbonitride coatings with a rate of 0.5–1.2 μm·min⁻¹ that is (1–5)·10² times higher than in conventional CVD processes. It has been found that coating deposition rate and structure of coatings depend on the process parameters: flow rates of HMDS and HMDS+benzene and plasma generating gas (argon). The method allows depositing SiCN coatings containing Si–C, Si–N and Csp³–N bonds with high velocity and microhardness 24 GPa.

1. Introduction

Silicon carbonitride is a unique multifunctional material, which successfully combines the best properties of silicon carbide and nitride. Silicon carbonitride layers are traditionally prepared either at increased temperatures \(T \geq 1000°C\) by the chemical vapor deposition (CVD) method or at relatively low temperature using radio frequency, microwave, or glow discharge plasma (PECVD) [1]. The decreased pressure in the reactor and the relevant low deposition rates hamper the preparation of layers and coatings. These methods with thicknesses above one micron are necessary for solving application problems.

The powerful optical pulsating discharge (POPD) in a high-speed gas flows is a new form of an optical discharge [2]. POPD is obtained in the gas under the impact of the pulsating periodic radiation of 10–100 kHz and the peak energy of laser pulsations of 500–1000 kW. At the plasma chemical synthesis of coatings the radiation is focused in the high-speed 100 – 300 m·s⁻¹ gas fluxes providing the high cooling rate of the gas phase after the laser pulse, a decrease in the sizes of the formed solid phase centers of nucleation, and fast delivery of reagents to the processed surface [3]. In this paper, we present the results of studying the kinetic and physicochemical properties of the silicon carbonitride films synthesized from hexamethyldisilazane (HMDS) and HMDS + benzene as precursors using POPD plasma.
2. Experimental

A new type of POPD in combination with the high speed $100–200\,\text{m}\cdot\text{s}^{-1}$ flow of the gas stream was applied for the laser plasma chemical deposition’s hard coatings in the atmospheric pressure reactor.

The deposition of layers was performed in non-chamber modes of the plasma-chemical synthesis. The non-chamber mode of a laser plasma-chemical synthesis is based on the efficient protection of a reaction zone by a cooling gas (Ar) which spreads through a circular gap between the nozzle section and substrate surface [4]. This mode opens up great opportunities to widely apply this method, as it allows covering the large and different configuration surfaces. Hexamethyldisilazane $(\text{CH}_3)_3\text{SiNHSi(CH}_3)_3$ was chosen as a precursor because it contains all chemical fragments (Si–N, Si–C) required for forming of silicon carbonitride. Addition of benzene enlarges the concentration of C atoms in the gas phase that can be useful for the formation of Si–C bonds.

The film deposition was carried out on substrates: stainless steel (Cr = 12–14 wt. %, Si, Mn, Ni ≤ 0.8 wt. %). The process parameters were: a substrate temperature was varied from 550° to 850°C by the outside heater, flow rate of a gas-carrier (argon) was $100–200\,\text{m}\cdot\text{s}^{-1}$. The energy of the laser beam was 1.6 kW at a frequency of 120 kHz.

Before deposition, Ar was mixed with liquid HMDS or HMDS+ benzene (a precursor) vapor. Liquid precursors were injected with the rate of $20–80\,\mu\text{l}\cdot\text{min}^{-1}$ into the system by Precision Pump (Model LSP01). The mixture of liquid precursor with argon was then mixed with the main argon flow in a reactor. The deposition time was 1-3 min. The deposition rate varied within $0.1–2.0\,\mu\text{m}\cdot\text{min}^{-1}$ and depended on the process parameters. The thickness of the coatings was determined by measurements of reflection spectra of the coatings and calculation by the known formulas, taking into account the refractive index determined from the ellipsometric data.

To characterize synthesized coatings a set of modern methods was used: Fourier IR spectrometer IFS-85 (Bruker), scanning electron microscope JSM 6700F and atomic-force microscope (NT MDT “Solver-Pro”).

3. Result and Discussion

The composition, structure, and properties of the silicon carbonitride coatings and their dependence on the parameters of the synthesis have been studied in detail.

The process under investigation is multi-parametric, and its rate depends on precursor concentration in a gas flow, gas flow rate, and laser beam energy introduced into the gas flow.

It follows from figure 1 that the dependence of a growth rate on the flow rate of hexamethyldisilazane $(F_{\text{HMDS}})$ and HMDS+ benzene is non-monotonic: it enlarges with the increase of $F_{\text{HMDS}}$ and $F_{\text{HMDS+benzene}}$ and reaches maximum at this experimental parameter at $F_{\text{HMDS}} \approx 50\,\mu\text{l}\cdot\text{min}^{-1}$ and $F_{\text{HMDS+benzene}}$ at $40\,\mu\text{l}\cdot\text{min}^{-1}$ and then it goes down.

![Figure 1. The growth rate of SiCN film deposition on precursor flow rate.](image-url)
We have found that the growth rate of the coating depends on the substrate temperature. Therefore, the limiting steps are assumingly the processes occurring on the substrate surface (adsorption, chemical reaction, desorption of reaction products). During decomposition of hexamethyldisilazane, on solid, gaseous products (NH$_3$, CH$_3$, CH$_2$, CH) are generated [5]. With increasing HMDS flow, their concentration in the gas phase increases, which shifts the equilibrium of the reaction in the direction of primary product formation. As a result, we observe a decrease in the coating rate growth.

The parameters of the process determine the composition, structure and functional properties of coatings. A complex investigation is performed to establish the composition, structure, and properties of silicon carbonitride coatings depending on synthesis parameters.

The IR spectra of the coatings characterizing their chemical structure are given in figure 2. Figure 2 shows the comparison of the IR spectra of films prepared in the HMDS (1) and HMDS+benzene as a precursor (2). There are main absorption bands corresponding to oscillation modes Si–C ($\omega$ = 750 cm$^{-1}$), Si–N ($\omega$ = 960 cm$^{-1}$) and Csp$^3$–N ($\omega$ = 1106 cm$^{-1}$) in spectra. Csp$^3$–N bonds are typical of the material based on carbon nitride. The ratio of Si–C / Si–N calculated from IR spectra by Gaussian peak fitting gives values 1.24 for (1) and 2.1 for (2).

Figure 3 shows the dependence of the ratio of Si–C / Si–N bonds calculated from IR spectra in the SiCN films produced at different velocity of HMDS feed rate in the gas flow of argon. The ratio Si–C / Si–N increases from 0.5 to 3 with increasing HMDS feed rate from 20 to 80 μl·min$^{-1}$ at the gas flow of argon 27 l·min$^{-1}$. The structure and morphology of the surface of coatings were determined using the X-ray diffraction and atomic force microscopy methods. The X-ray diffraction data of the prepared films show that they are amorphous.

![Figure 2](image.png)

**Figure 2.** IR spectra of the coatings and Gaussian peak fitting. Precursor 1) HMDS; 2) HMDS+benzene; $F_{ar}$ = 27 l/min; precursor flow rate 20 μl min$^{-1}$. 

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The study of morphology with AFM microscope has shown that the surface roughness increases with increasing feed rate of HMDS in the argon gas flow. Figure 4 shows the average size of the surface particle on the input HMDS flow in the reactor.

To determine the microhardness of coatings obtained, a scanning nanohardness tester (NanoScan) was used. To define the real hardness of the coating (excluding a softer substrate influence), the nanoindentation results were treated taking into account the substrate hardness to the techniques suggested in [6]. Figure 5 presents the results of coating microhardness measurements for SiCN films produced at different gas flow of argon 25 (a) and 33 (b) L·min\(^{-1}\). Decreasing hardness at the high gas flow of argon is connected with decreasing temperature of the substrate at increasing total gas flow at equal input power in the laser beam.
4. Summary
A new method has been developed for the plasmochemical deposition of hard protective silicon carbonitride coatings from a hexamethyldisilazane (HMDS) Si$_2$NH(CH$_3$)$_6$ and (HMDS+benzene) vapors activated by a powerful optic pulse discharge (POPD) in a high-velocity gas flow of argon.

The method allows depositing silicon carbonitride coatings with a rate of 0.5–1.2 μm·min$^{-1}$ that is (1–5)10$^2$ times higher than in conventional CVD processes.

It has been found that coating deposition rate and structure of coatings depend on the process parameters: flow rates of HMDS and HMDS+benzene and plasma generating gas (argon).

The method allows depositing SiCN coatings containing Si–C, Si–N and Csp$^3$–N bonds with high velocity and microhardness of 24 GPa.

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