

# Investigation of a New Method of the Organosilicon Compounds Activation by a Low-energy Electron Beam for SiCN-coatings Deposition

Andrey Menshakov,<sup>a, b, †</sup> Seif Cholakh<sup>b</sup>

<sup>a</sup> Institute of Electrophysics of the Ural Branch of the Russian Academy of Sciences, 106 Amundsen St., Yekaterinburg, 620016, Russia

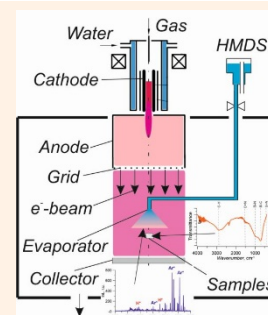
<sup>b</sup> Ural Federal University, 19 Mira St., Yekaterinburg, 620002, Russia

<sup>†</sup> Corresponding author: [menshakovandrey@mail.ru](mailto:menshakovandrey@mail.ru)

Received: 29 January, 2020; Accepted: 12 February, 2020; Published: 29 February, 2020

The article describes a new method of organosilicon compounds activation by low energy electron beam for SiCN coatings deposition. The composition of the beam plasma in a hexamethyldisilazane-containing gas medium was studied, and it was shown that the precursor molecules decomposition degree increases with the beam current and nonmonotonically depends on the electron beam energy. The application of a low-energy electron beam for the plasma-chemical vapor decomposition of hexamethyldisilazane and for samples heating up by electron beam to 600°C makes it possible to obtain SiCN-based coatings with a hardness up to 18 GPa and thickness ~1 μm for 1 h.

**Keywords** SiCN coating; Polymer derived ceramic; Low-energy electron beam



One of the ecological, effective and productive modern methods for silicon carbonitride (SiCN) coatings production is a chemical vapor deposition in organosilicon compounds (OSC) vapors medium by its decomposition in plasma (PECVD) [1]. The main factor determining the unique characteristics of SiCN-coatings (such as high hardness, oxidation resistance, chemical inertness, etc.) are the conditions of its synthesis, so the possibility of a controlled change of various processing parameters is crucial for coatings with desired properties obtaining. Usually a radio frequency discharge is used for plasma activation of the precursor vapors [2]. It is important to control the precursor molecules decomposition degree in order to facilitate the formation of films containing both Si–C and Si–N bonds and, as a result, having high mechanical characteristics. However, when using gas discharges, in fact, the only controlled parameter is the discharge current (or power). An alternative way to generate plasma is to use low-energy electron beams [3]. The advantage of this method is that in the range of electron energies 100–200 eV, which is close to the maximum of electron impact ionization cross section of gas molecules and atoms, the frequency of plasma processes increases, resulting in the formation of ionized and excited particles. In addition, an important advantage of the sources

used [4] is the independent control of the emission current and electron energy, pressure and gas medium composition over a wide range, which provides flexible control of the plasma parameters. This method was not previously used for the OSC decomposition.

This approach was realized in an electrode system with a two-stage source of a wide (~100 cm<sup>2</sup>) low-energy electron beam based on a self-heating hollow cathode discharge (SHHC), the design of which was described in detail in [5] (Figure 1). The beam current  $I_b$  was varied up to 5 A by changing the discharge current in the first stage, electron beam energy varied in the range 50–500 eV. Hexamethyldisilazane [(CH<sub>3</sub>)<sub>3</sub>Si]<sub>2</sub>NH (hereinafter HMDS) was taken as an OSC precursor. The precursor vapor flow was 2 g h<sup>-1</sup>. Argon was used as the plasma-forming gas, which flow was kept constant (40 sccm), the pressure in the chamber was 0.2–0.3 Pa.

The OSC molecules decomposition process is determined both by the binding energies between the atoms in the initial molecule and by the energy of particles in the plasma. According to Ref. 6, the HMDS molecule decomposition proceeds according to the following scheme: the molecule is excited in the first stage, the Si–C bond is broken (binding energy 3.3 eV), and separation of the methyl group occurs:

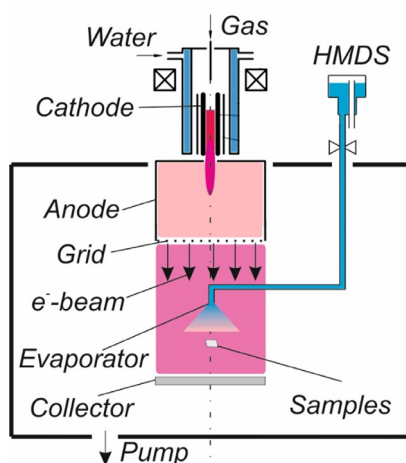


Figure 1: Electrode scheme of experimental facility.

$(\text{CH}_3)_3\text{-Si-NH-Si-(CH}_3)_3^* \rightarrow (\text{CH}_3)_3\text{-Si-NH-Si-(CH}_3)_2 + \text{CH}_3$ . Then the single Si–N bond is broken (3.5–3.7 eV). As a result, fragments of the molecule with the Si=N double bond, which participate in the formation of the SiCN coating, are formed. At the next stages, the bonds of N–H (4–4.1 eV), C–H (4.3–4.8 eV), and Si=N are destroyed; as a result, H, C, and Si atoms appear in the region of coating deposition, the content of which allows one to judge the decomposition degree of HMDS. In the obtained optical emission plasma spectra, both the lines of the plasma-forming gas and the lines of atoms from the precursor molecules were detected (Figure 2). In particular, weak lines of the Si atom at 252.85 nm and 288.16 nm are observed as well as intense H atom lines belonging to the Balmer series—486.1 nm and 656.3 nm. Since the intensity at 656.3 nm ( $I_{\text{H}656}$ ) is proportional to the concentration of the corresponding element in the plasma, its change can be used to judge the change in the H content, and, as a result, with a constant precursor vapor stream, its decomposition degree.

An increase in the beam current leads to an increase in the HMDS decomposition degree (Figure 2), which can be explained by the intensification of plasma processes with increasing plasma concentration. At the same time, the initial energy of the beam electrons nonmonotonically affects the HMDS decomposition degree:  $I_{\text{H}656}$  increases with increasing accelerating voltage to ~100 V, with a further increase in the electron energy, whereas the degree of decomposition of HMDS practically does not change.

Typically, the electron temperature in a gas discharge plasma is 1–4 eV, and the electron energy at the initial stage is only enough to excite a precursor molecule, so its fragmentation takes place only with the neutral particle participation. A feature of a beam plasma is the presence of two groups of electrons in it: the fast electrons with an energy up to several hundred eV and the plasma electrons with a temperature of 0.3–1 eV [7]. The ionization potential of the HMDS molecule is 8.8 eV [8]; therefore, in the presence of the fast electrons in the plasma, the fragmentation process can be intensified to be due to an additional mechanism that

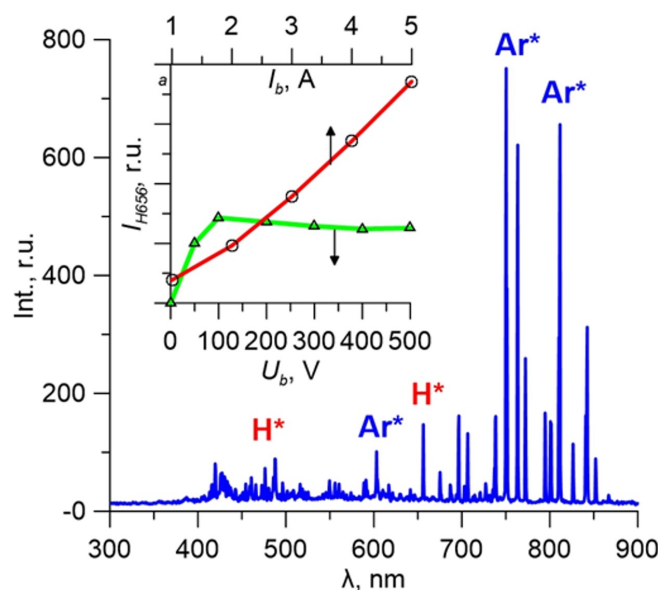


Figure 2: Optical emission spectra of e-beam plasma in Ar + HMDS gas mixture. Dependences of the H\* (656.3 nm) line intensity on the current  $I_b$  (at  $U_b = 200$  V) and the energy  $U_b$  (at  $I_b = 5$  A) of the electron beam are shown in the inset.

starts from the formation of  $(\text{CH}_3)_3\text{-Si-NH-Si-(CH}_3)_3^+$  by electron impact ionization and weakening of chemical bonds in the molecule, which can explain the increased decomposition degree of the precursor molecules with increasing electron energy.

The electron beam also ensures significant heating of the samples: at a beam current of 1 A and accelerating voltage 500 V, the temperature of samples reached 600°C. Test coatings were deposited to AISI430 stainless steel samples at an electron beam energy of 500 eV, a beam current at 1.3 A, and the sample temperature of 600°C. The coating thickness was ~1 μm in 1 h, and its microhardness reached 16–18 GPa. An analysis of the coating composition by the FTIR method showed that Si–C and Si–N bonds are present in both coatings (Figure 3). In the IR spectra obtained, the intensity of the absorption peaks of hydrogen-containing

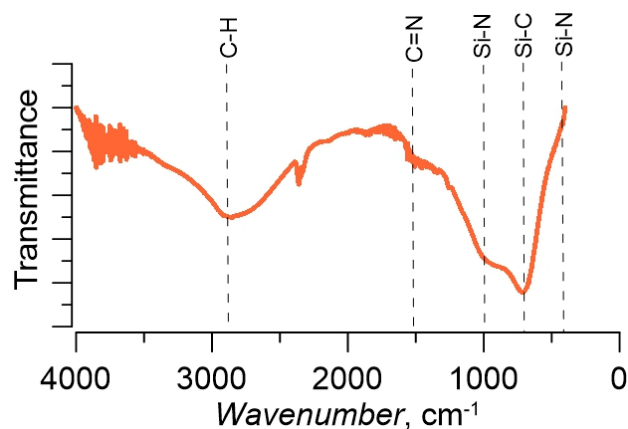


Figure 3: IR spectra of SiCN-coating.

bonds of the initial HDMS molecules is lower than in the coatings deposited in an arc discharge [9]. It may also confirm more intense decomposition of the precursor in beam plasma.

### Acknowledgments

The study was financially supported by the Russian Science Fund, grant No. 18-79-00233.

### References

- [1] V. R. Shayapov, Yu. M. Rumyantsev, A. A. Dzyuba, B. M. Ayupov, and N. I. Fainer, *Appl. Surf. Sci.* **265**, 385 (2013).
- [2] A. M. Wrobel, P. Uznanski, A. Walkiewicz-Pietrzykowska, and K. Jankowski, *Appl. Organomet. Chem.* **31**, e3871 (2017).
- [3] S. G. Walton, C. Muratore, D. Leonhardt, R. F. Fernsler, D. D. Blackwell, and R. A. Meger, *Surf. Coat. Technol.* **186**, 40 (2004).
- [4] N. V. Gavrilov, D. R. Emlin, and A. S. Kamenetskikh, *Tech. Phys.* **53**, 1308 (2008).
- [5] N. V. Gavrilov and A. I. Men'shakov, *Instrum. Exp. Tech.* **54**, 732 (2011).
- [6] Th. Stelzner, M. Arolda, F. Falka, H. Stafasta, D. Probstb, and H. Hoche, *Surf. Coat. Technol.* **200**, 372 (2005).
- [7] E. H. Lock, R. F. Fernsler, S. P. Slinker, I. L. Singer, and S. G. Walton, *J. Phys. D* **47**, 425206 (2014).
- [8] K. A. O. Starzewski, H. T. Dieck, and H. Bock, *J. Organomet. Chem.* **65**, 311 (1974).
- [9] A. I. Menshakov, D. R. Emlin, Yu. S. Surkov, and S. O. Cholakh, *J. Phys.: Conf. Ser.* **1134**, 012039 (2018).



All articles published on e-J. Surf. Sci. Nanotechnol. are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0). You are free to copy and redistribute articles in any medium or format and also free to remix, transform, and build upon articles for any purpose (including a commercial use) as long as you give appropriate credit to the original source and provide a link to the Creative Commons (CC) license. If you modify the material, you must indicate changes in a proper way.

Published by The Japan Society of Vacuum and Surface Science