Comparative study of the conditions for SiCN-coatings deposition in a electron beam generated plasma and in a discharge with a self-heated

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Silicon Carbonitride

SiCxNy (SiCxNy:H)

Properties:

-High values of hardness (up to 42 GPa) and Young's modulus

-Low values of the coefficient of friction

-Resistance to oxidation in air up to 1600°C

-Low values of dielectric constant (up to 3)

-High optical bandgap (3-4 eV) and transmittance (up to 95%)

-High thermal conductivity

Application:

- Protective coatings for a wide range of applications

-Optical coatings

-Dielectric coatings, etc.

Basic physical and chemical properties of massive SiC and Si3N4	Si3N4	SiC
Density, g/cm3	3,192	3,21
Refractive index	2,02 (588 nm)	2,55
Band gap, eV	4,0	2,2-3,3
Hardness, GPa	35-45	15-34
Young's modulus, GPa	298	357-392
The dielectric constant	6,3-7,1	semiconductor

Basic methods of obtaining SiCN coatings

Physical Vapor Deposition (PVD)

Magnetron sputtering of targets (Si, SiC, graphite) in a nitrogen-containing gas medium (N2, Ar, C2H2, CH4, etc.)

Advantages: Possibility to obtain films of a given composition by varying the target sputtering parameters and the composition of the gas medium, high mechanical characteristics of the coatings

Disadvantages:

Impossibility of homogeneous processing of products of complex shape and low coating rates.

Chemical Vapor Deposition (CVD)

using multicomponent gas mixtures or organosilicon compoundsений

Types of gas medium activation:

UV activation (UVCVD)

Thermal Activation (HWCVD)

Plasma activation (PECVD)

Advantages of the method:

-High application rates

-Ability to process products of complex shape

-Ability to obtain coatings with high performance at low temperatures

Gaseous media types

Multicomponent gas mixtures

For example, ($SiCl_4 + NH_3 + N_2 + CH_4$) or ($SiCl_4 + C_3H_8 + NH_3 + H_2$)

Organosilicon compounds (OSC)

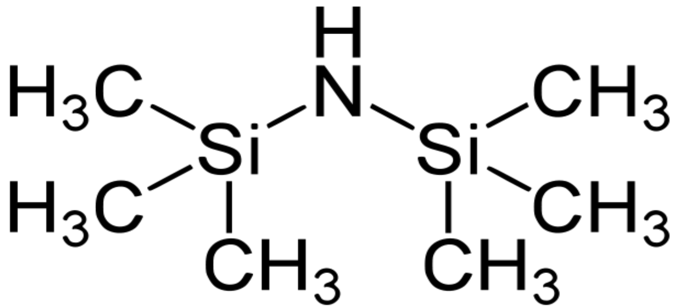
precursor compounds with a branched molecular structure and containing Si-C bonds (organosilanes)

Disadvantages:
- Ecology and explosion hazard
- Often it was not possible to synthesize films with a high carbon contentда

Benefits:
- Environmental safety, low fire and explosion hazard
- The presence of all necessary elements (Si, C, N) and bonds between them in the precursor molecule

The advantage of using such compounds, among other things, is that to obtain a film with the required properties, you can use CBS with the desired ratio of elements and the required types of bonds between elements..

Hexamethyldisilazane — chemical compound, an alkyl- and amino derivative of monosilane with the formula [(CH3) 3Si] 2NH, a colorless liquid with a pungent odor, rapidly hydrolyzed by water.



Benefits of using as a precursor:

- The presence in the composition of all the necessary elements for the synthesis of the SiCN coating and the presence of bonds between them (Types of bonds: Si-C (318 kJ/mol), Si-N (333-355 kJ/mol), NH (386-391 kJ/mol) , CH (411-460 kJ/mol)

- High pressure of saturated vapor (17.2 mm Hg at 300 K)

- Availability and relative cheapness

Decomposition of hexamethyldisilazane*

Primary plasma reaction - loss of methyl group:

$$(CH_3)_3Si - NH - Si(CH_3)_3^{\#\#\#} \rightarrow (CH_3)_3Si - NH - Si(CH_3)_2^{\cdot} + \dot{C}H_3$$

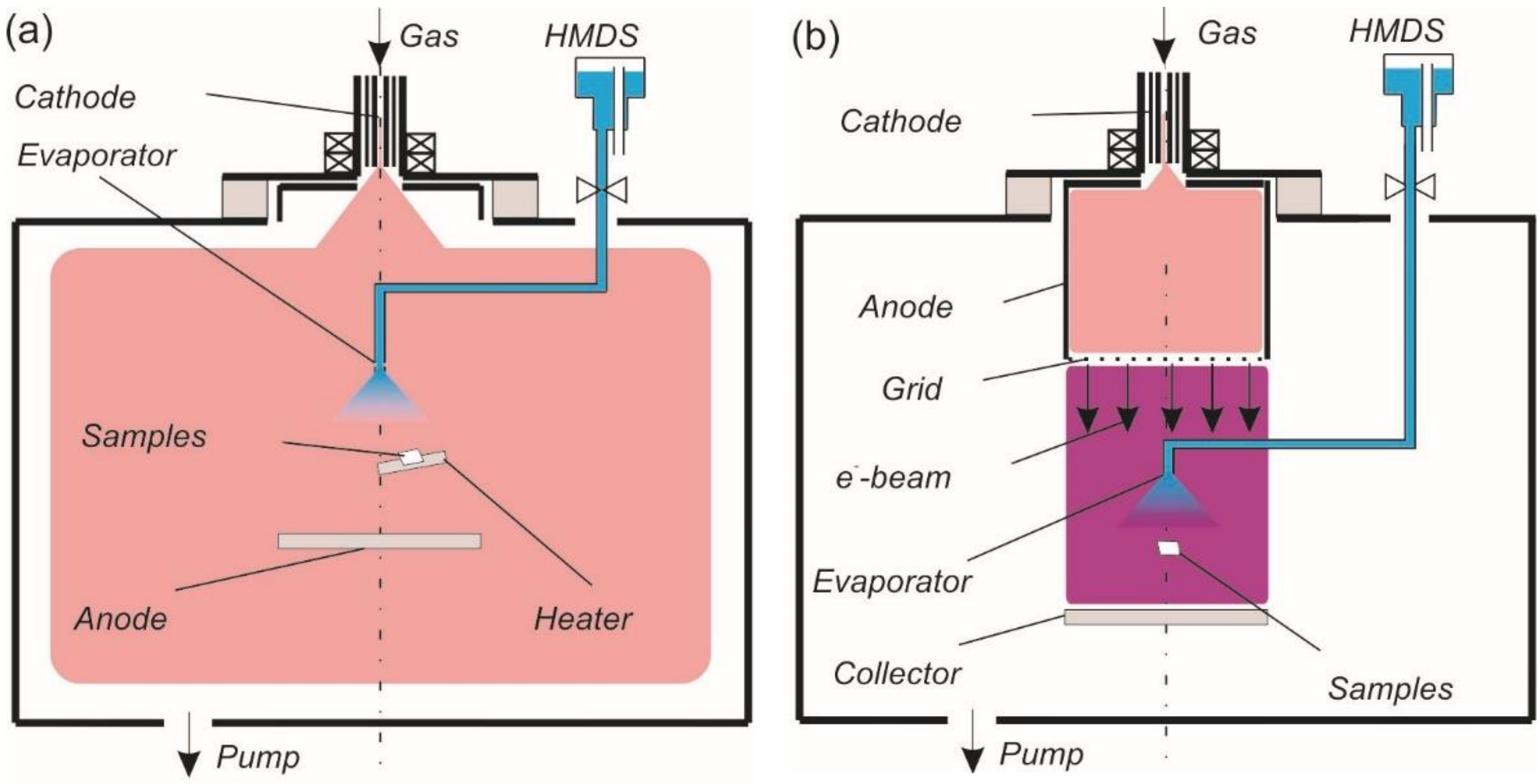
The next step is breaking the single Si-N bond:

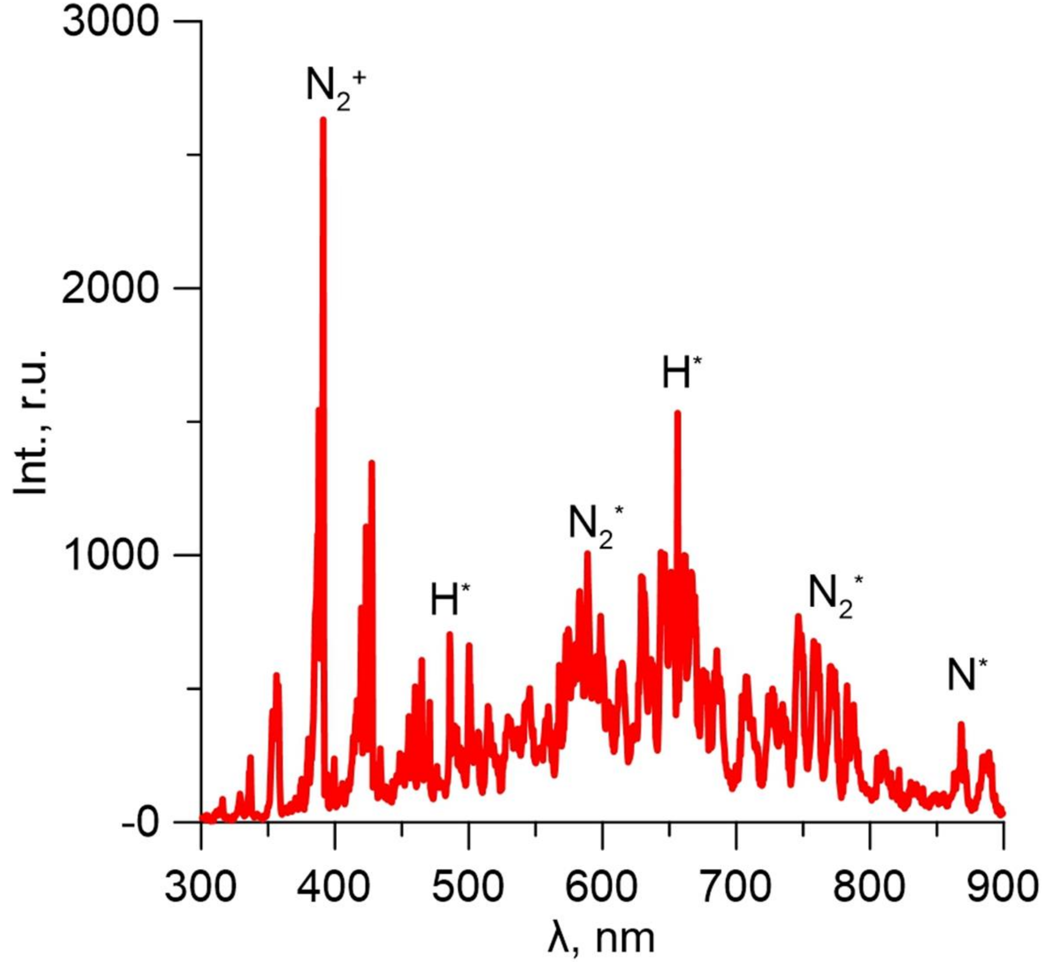
$$(CH_3)_3Si - NH - Si(CH_3)_2^{\cdot} \rightarrow (CH_3)_3Si^{\cdot} + HN{=}Si(CH_3)_2$$

As a result, particles with a Si = N double bond appear in the plasma, which are involved in the formation of a SiCN coating

*Th. Stelzner et al. / Surface & Coatings Technology 200 (2005) 372–376

Electrode schemes of experimental systems based on a: discharge with a SHHC and a remote anode (a) and source of a low-energy electron beam based on a discharge with a SHHC.

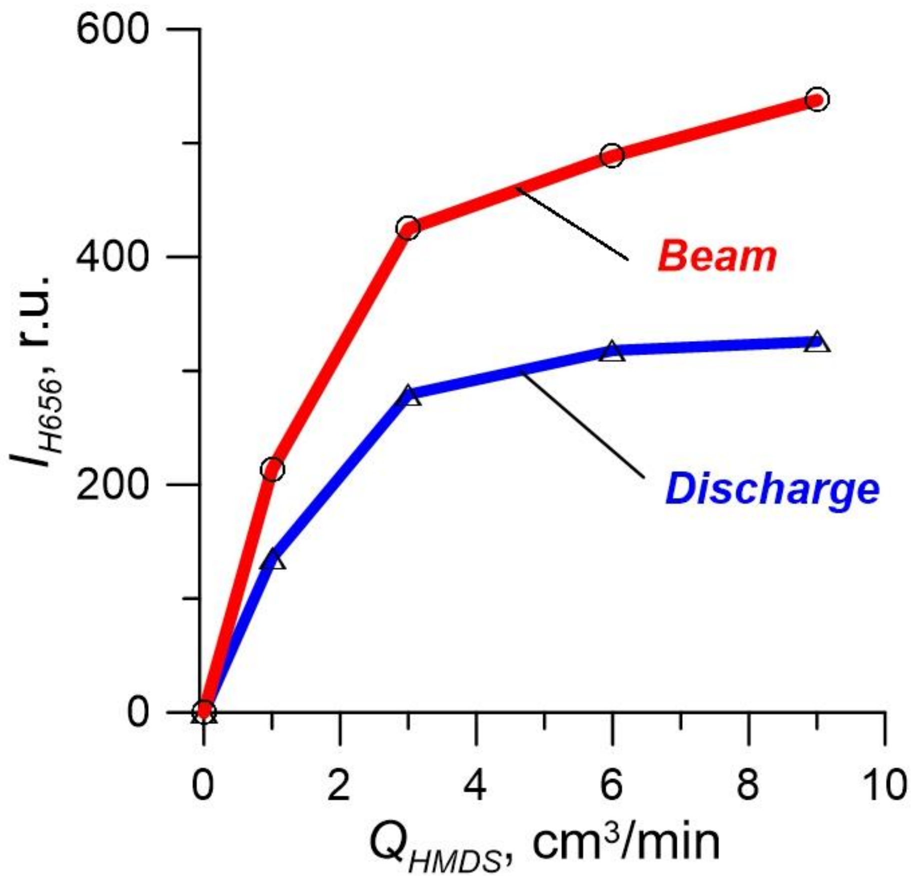




The optical spectrum of the electron beam plasma in a mixture of N2+HMDS. Beam current 5 A, electron energy 200 eV, Q(HMDS)=3 g/h

In the obtained plasma spectra, both the lines of the plasma-forming gas and the lines of atoms from the precursor molecules were detected. In particular, weak lines of the Si* atom 251.92, 252.85 nm (corresponding to transitions to the ground state 3P0 - 3P), a Si* line 288.16 nm (1P0 - 1D), as well as intense lines of the H* atom, belonging to the Balmer series - 486.1 nm and 656.3 nm are observed.

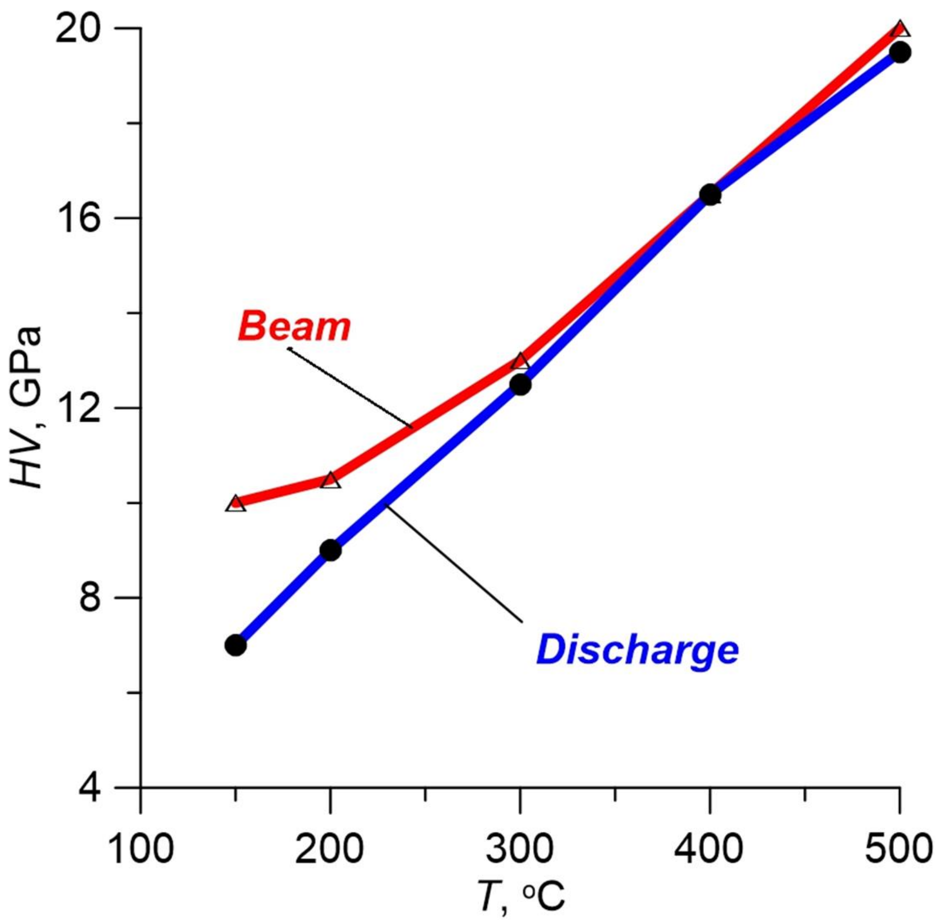
Since the intensity $I_{H(656)}$ of the H* line is proportional to the concentration of the corresponding element in the plasma, its change can be used to judge the change in the hydrogen content, and, as a result, with a constant vapor stream of the precursor, its decomposition degree.



Dependences of the H*(656.3 nm) line intensity on the HMDS flux in the discharge plasma with SHHC and in the beam plasma, ji=1 mA/cm2.

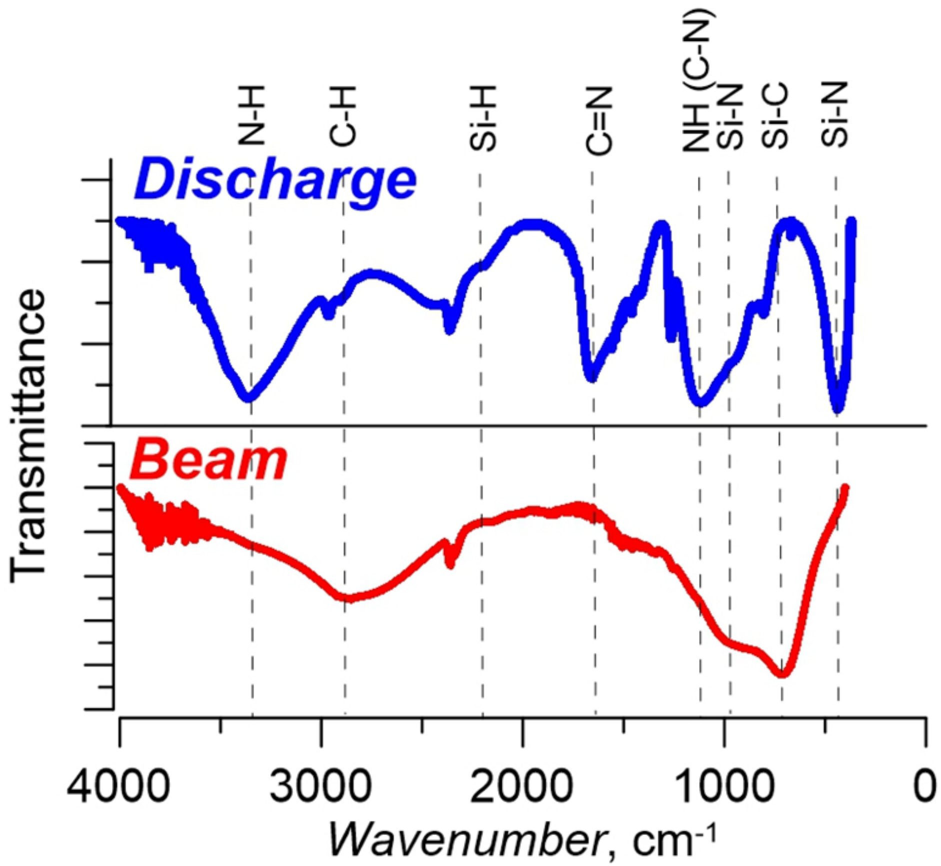
It was found that the vapor decomposition degree of HMDS in the beam plasma is higher than in the anode plasma of the discharge with SHHC.

The ionization potential of the HMDS molecule is 8.8 eV, therefore, in the presence of fast beam electrons in the plasma, the fragmentation process can be intensified due to an additional mechanism starting from the formation of the ion $(CH_3)_3$-Si-NH-Si-$(CH3)_3^+$ by electron impact ionization, and the weakening of chemical bonds in the molecule, which may explain the increased decomposition degree of the precursor molecules in comparison with the gas discharge plasma, as well as the increase in the decomposition degree with increasing electron energy.



It was found that at low deposition temperatures T (<200°C) the microhardness of the coatings obtained in the beam plasma turned out to be slightly higher (8–10 GPa) than in the discharge plasma with SHHC (7–8 GPa).

Dependences of microhardness of SiCN coatings obtained in the discharge plasma with SHHC and in the beam plasma on temperature. PN2+HMDS=1 mTorr, QHMDS=3 g/h, ji=1 mA/cm2.



In contrast to the coatings obtained in an arc discharge plasma, in the IR spectra of the coatings deposited in beam plasma, even in the low-temperature mode, the absorption peaks of hydrogen-containing bonds of the initial HMDS molecules which decrease the hardness of the coatings, are rather low, which can also indicate a more intense decomposition of the precursor in beam plasma, and can explain elevated microhardness of coatings obtained in beam plasma.

IR spectra of coatings obtained in a discharge plasma with SHHC and in an electron beam plasma. PN2+HMDS=1 mTorr, QHMDS=3 g/h, T = 200°C.

Conclusions

- Upon vapor decomposition of the organosilicon precursor in the beam and anode plasmas coatings with a thickness of up to 2 μm and a hardness of up to 20 GPa were obtained.

- Increased decomposition degree of OSC in a beam plasma affects the hardness of coatings only at low synthesis temperatures (up to 200°C). With an increase in the deposition temperature, the method of activation of the precursor vapors (by electron beam or in discharge with SHHC) does not significantly affect the properties of the resulting coatings, despite the differences in the plasma composition.

- The investigated plasma generation methods allow the activation of organosilicon precursor vapors successfully. The application of the proposed methods opens up possibilities for independent changes in almost all processing parameters, which allows a wide control of both the mass-charge composition and the degree of decomposition of the components of the gas mixture, and the nature and degree of exposure to the surface of the processed products, which ultimately allows for controlled change the composition and properties of the resulting coatings. At the same time, these methods of plasma generation differ both in the complexity of the devices used and their power schemes, as well as in the ranges of operating characteristics. The method based on the use of a low-energy electron beam is more technically complicated, however, its use can be justified if it is necessary to obtain coatings at low temperatures (lower 200°C), for example, on polymers. To obtain harder coatings, the synthesis of which requires elevated temperatures, it is advisable to use a simpler method of activating OSC vapors in a discharge with a self-heated hollow cathode.