

Dedicated to the 90th Anniversary of Academician M.G. Voronkov

From Organosilicon Precursors to Multifunctional Silicon Carbonitride

N. I. Fainer

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,
pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
e-mail: Nadezhda@niic.nsc.ru*

Received June 23, 2011

Abstract—Films of silicon carbonitride of variable composition are prepared by the method of plasmachemical decomposition of tetramethyldisilazane, hexamethyldisilazane, and hexamethylcyclotrisilazane in the mixture with helium in the temperature range of 373–973 K. The chemical composition of the low temperature films (373–673 K) is described by the formula $\text{Si}_x\text{N}_y\text{O}_z\text{H}$, whereas that of high temperature films, by the formula Si_xN_y . The films of silicon carbonitride are found to be a nanocomposite material containing an amorphous part and nanocrystals, whose structure is close to the phase $\alpha\text{-Si}_3\text{N}_4$. Films of the composition $\text{Si}_x\text{N}_y\text{O}_z\text{H}$ are promising as low-k interlayer dielectrics in ultra-large scale integrated circuits of new generation, as well as protecting antireflective coatings and light-emitting diodes.

DOI: 10.1134/S1070363212010070

Nowadays more severe requirements are imposed on the quality of construction materials used in many fields of science and technology. New materials are necessary stable to high temperatures, mechanical wear, abrasion, corrosion and oxidation [1]. That is why various methods are intensively developed for the synthesis of refractory superhard coatings (hardness > 20 GPa), which have long lifetime, enhanced hardness, and are relatively cheap [2]. For example, coatings are made of materials alternative to the expensive diamond coatings. Binary solid compounds like SiC, TiC, TiN can provide an enhanced wear stability, but hardly can possess a wide variety of functional properties.

Recent research has shown that coatings on the basis of ternary compounds exceed in their functional properties the coatings based on binary compounds [3]. One of promising ternary materials is silicon carbonitride. It possesses new properties as compared with crystalline binary compounds Si_3N_4 and SiC. Films of silicon carbonitride possess an exclusive combination of physicochemical properties like high thermal conductivity, thermal stability (up to 1500°C), resistance to oxidation, high hardness, chemical inertness, that makes them ideal wear- and corrosion-

stable materials for applications in aggressive media, for high-temperature industrial and strategic applications [4–10]. It is assumed that a high thermal, chemical, and mechanical stability is achieved due to the absence of boundaries between the grains and of the oxides as secondary phases in these coatings. Besides, such properties as low density and good thermal shock resistance, are very important in the future for aerospace, automobile, and other fields of industry. It is known that stainless steel possessing high corrosive stability is rusted when stored for a long time in the open air because of acid rains. To prevent this process, the steel must be coated, for example, with a transparent solid film, like the film of silicon carbonitride [11]. In general, films of silicon carbonitride can be used in various applications, not only as barrier isolating layers, films for protection of flat panel displays, but also for general industrial application.

Adjustable characteristics of the width of the forbidden zone [12–15], regulated transparency in the visible and IR regions [16–19], and high thermal stability [20] make the films of silicon carbonitride attractive for micro- and optoelectronics. Silicon carbonitride is also an important material in sensor

technologies due to its excellent mechanical and electric properties. It possesses good optical properties: a high transmission coefficient ($> 90\%$) in the UV, visible, and IR regions of the spectrum. This is very useful for membrane applications, which require the combination of these properties.

Films of silicon carbonitride are grown by different methods, including both physical vapor deposition (PVD) (various modifications of magnetron sputtering [21–27], ionic implantation [28–29], etc.), and chemical deposition from vapor phase (CVD) [30–35]. The properties of the obtained layers depend on specific features of the used method of synthesis and on the conditions of the process: its temperature and the composition of the reaction medium. The CVD method is universal and is widely used in practice, because it provides the possibility to achieve high productivity with high quality of the layers. At present, various modifications of the CVD method exist: deposition of the compound due to thermal decomposition of the starting volatile compounds [7, 33], photoinduced (laser) LICVD [34, 35] and plasma-enhanced PECVD deposition from vapor phase [36–40]. Conventional CVD methods require high temperatures of growth (> 1173 K). The use of laser and plasma activation of the gas phase allows decreasing the temperature of the growth of layers to 373–473 K.

In the processes of chemical deposition of the silicon carbonitride layers complex gas mixtures are usually used: $[\text{SiCl}_4 + \text{NH}_3 + \text{C}_3\text{H}_8 + \text{H}_2]$, $[\text{Si}(\text{CH}_3)_4 + \text{NH}_3 + \text{H}_2 \text{ (or Ar)}]$, $[\text{SiH}_4 + \text{NH}_3 + \text{CH}_4 \text{ (or C}_2\text{H}_4) - \text{H}_2 \text{ (or Ar)}]$, $[\text{CH}_4 + \text{H}_2 + \text{N}_2 + \text{SiH}_4]$ [7, 33]. These compounds are highly toxic and explodable, therefore, to increase the safety of the synthesis, a search for new starting compounds is performed.

The preparation of silicon carbonitride films with the use of volatile low toxic organosilicon compounds of different composition and structure, including all required elements (Si, C, and N) in one molecule, is an alternative method of synthesis [41]. It is noteworthy here that the molecular structure of the starting organosilicon compounds affects the chemical and phase composition, as well as the microstructure of the deposited films of silicon carbonitride. The main part of compounds used for preparation of silicon carbonitride belonged to the class of silazanes: hexamethyldisilazane [11, 39, 42–54], hexamethylcyclotrisilazane [55–59], polysilazanes, etc.

A great contribution to the development of the synthesis and application of organosilicon compounds in different fields of science, technology, and medicine was made by M. G. Voronkov. Under his leadership, in the 70–80-th of the last century dielectric films close in composition to silicon nitride were obtained in the processes of plasmochemical decomposition of hexamethylcyclotrisilazane in the mixtures with nitrogen or ammonia [55]. It turned out that the properties of the films were strongly dependent not only on the composition but also on the structure of organosilicon precursors, namely, the structure and properties of the silicon carbonitride films could be modified and regulated by selection and creation of suitable precursors and by choosing the conditions of synthesis of the films [60].

The present work summarizes the results of the systematic study of optical, mechanical and electro-physical properties of thin films of silicon carbonitride of the general formula $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ or SiC_xN_y , prepared on the basis of 1,1,3,3-tetramethyldisilazane (TMDS), 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and 1,1,3,3,5,5-hexamethylcyclotrisilazane (HMCTS). The correlation is found between physicochemical, functional properties, chemical composition, and the design of the molecule of compounds-precursors.

Determination of Chemical, Phase Compositions, and Types of Chemical Bonds in the Silicon Carbonitride Films

To increase the validity of the results obtained by different methods of research, films of silicon carbonitride of various thickness have been synthesized: from 200–300 nm to several μm . For the same purpose, supports made of silicon, gallium arsenide, and quartz glass were used. It turned out that the main parameters determining the physicochemical properties of the layers were the temperature of the synthesis and the nature of the compound-precursor. The influence of the plasma power on the properties of the layers was less pronounced, so, most experiments were carried out with the fixed plasma power (30 W).

Investigation of the chemical composition and the types of chemical bonds in compounds of variable composition, like silicon carbonitride, is not a simple task, which is complicated when studying thin films. Therefore, to get most complete information about the investigated films, we have used a set of spectroscopic methods like IR, Raman, X-ray photoelectron and energy dispersive spectroscopy.

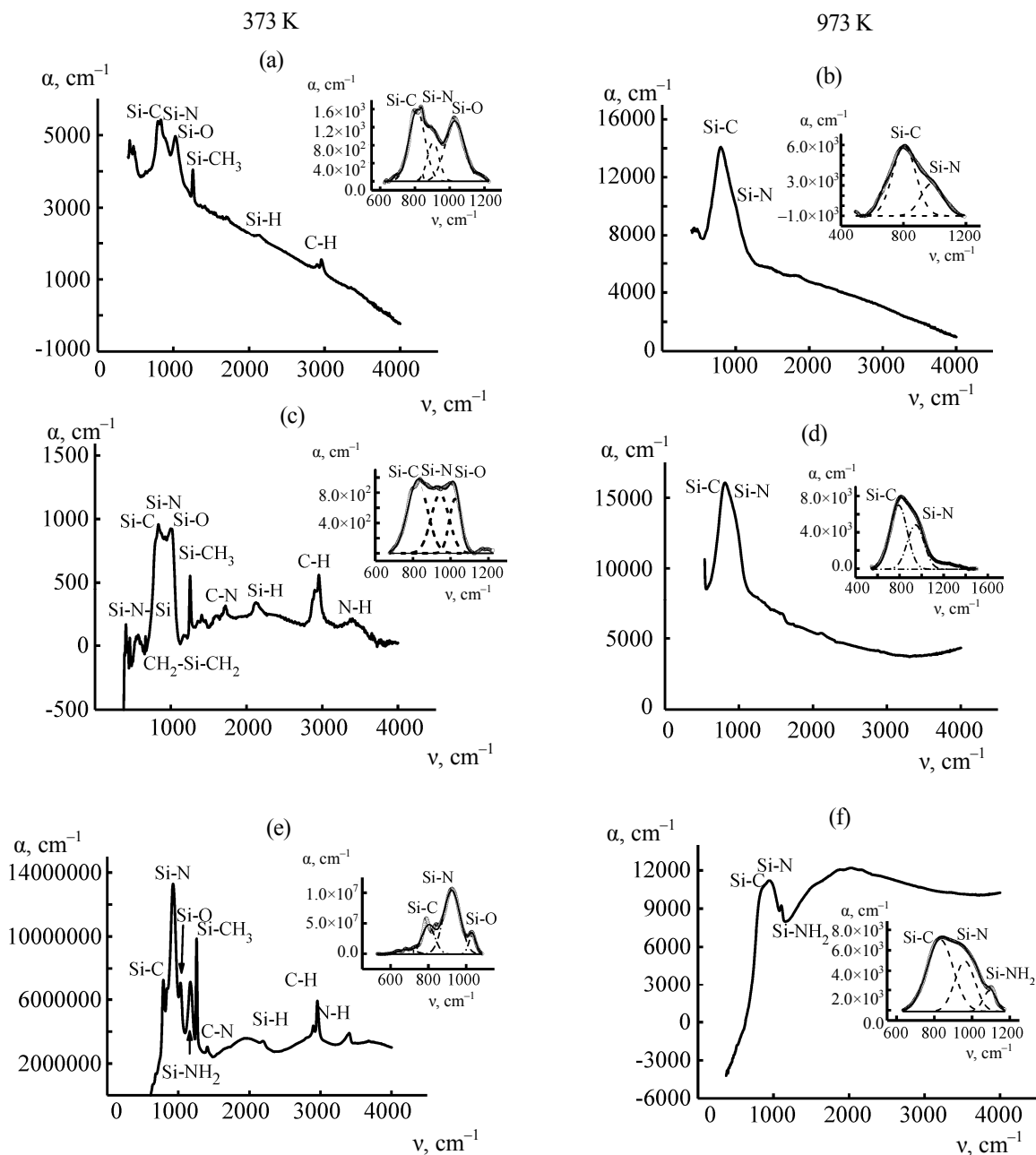


Fig. 1. Change of IR spectra of silicon carbonitride films depending on the temperature of synthesis and design of compound-precursor. (a, b) (TMDS+He); (c, d) (HMDS+He); (e, f) – (CHMTS+He).

In Fig. 1 the IR spectra of low-temperature and high-temperature films obtained by the use of three gas mixture (TMDS+He), (HMDS+He), and (HMCDS+He) are shown. All spectra are normalized to the thickness of the film. The assignment of the absorption bands was performed by the use of the available published data [61, 62]. It is seen that the IR spectra of the low-temperature films contain, along with the main wide band, a lot of peaks belonging to hydrogen-containing

bonds. In contrast, these bands are lacking in the spectra of high-temperature specimens. The assignment of the bands is given in Table 1.

The IR spectra of silicon carbonitride films were analyzed using the computer program Origin 7.0 “fit multiple peak Gaussian function.” For this, the bands in the IR spectra of all films of silicon carbonitride were deconvoluted into components using Gauss

Table 1. Parameters of IR spectra (ν , cm^{-1}) of films of silicon carbonitride prepared in the temperature ranges 373–673 and 673–972 K

Mixture	373–673 K	673–972 K
TMDS+He	800 (Si–C), 950 (Si–N), 1030 (Si–O–Si), ~1250 (Si–CH ₃), ~2200 (Si–H), ~2900–2960 (C–H)	800 (Si–C), 950 (Si–N)
HMDS+He	450 (Si–N–Si), 800 (Si–C), 950 (Si–N), 1030 (Si–O–Si), 1400 (C–N), 1030–1040 (CH ₂ –Si–CH ₂), ~1250 (Si–CH ₃), ~2200 (Si–H), ~2900–2960 (C–H), 3390 (N–H)	800 (Si–C), 950 (Si–N)
CHMTS+He	800 (Si–C), 950 (Si–N), 1030 (Si–O–Si), 1400 (C–N), ~1100 (δ_{NH} , Si ₂ NH), ~1250 (Si–CH ₃), ~2200 (Si–H), ~2900–2960 (C–H), 3390 (N–H)	800 (Si–C), 950 (Si–N), ~1100 (δ_{NH} , Si ₂ NH)

curves and their integral intensities were calculated. The analysis has shown that the increase in the temperature from 373 to 973 K results in a monotonous increase in the ratio of integral intensities $I_{\text{Si–C}}/I_{\text{Si–N}}$ for all films. With the increase in the temperature of the synthesis the concentration of Si–C bonds increases, in spite of the fact that the chemical composition of films prepared from HMCTS is close to silicon nitride, from TMDS, to silicon carbide, from HMDS is between them. This coincides with the results of thermodynamic calculations for the system Si–C–N–H with the use of the starting gas mixtures (TMDS+He), (HMDS+He), and (CHMTS+He) [46, 58].

Note that IR spectroscopy is one of few methods allowing the detection of the presence of hydrogen in films. The relative content of hydrogen-containing bonds in films was estimated as the ratio of the sum of the areas of the corresponding bands to the sum of areas of all bands in the IR spectrum. With increase in the temperature of the synthesis the concentration of the hydrogen-containing bonds decreases or fully disappears. In the films prepared from TMDS, their concentration is minimal, and in those prepared from HMCTS, maximal. Note also that the content of the hydrogen-containing bonds, determined from the analysis of IR spectra, correlates with the concentration of hydrogen in the films obtained by plasma-chemical decomposition of HMCTS and studied by the ^1H NMR spectroscopy method [56].

As follows from Table 1, the main band in the IR spectra of low-temperature films is a superposition of stretching vibrations of the Si–C, Si–N, and Si–O bonds. Besides, the spectra contain bands corresponding to hydrogen-containing bonds. The main band in the IR spectra of high-temperature films is a superposition of the stretching vibrations of the Si–C and Si–N bonds, the hydrogen-containing bonds practically lacking. Therefore, the chemical composition of low-

temperature films of silicon carbonitride more precisely corresponds to the formula of hydrogenated silicon oxycarbonitride, $\text{SiC}_x\text{N}_y\text{O}_z\text{H}$, whereas that of high-temperature films, to the formula SiC_xN_y .

The chemical composition and the types of chemical bonds were determined by the method of X-ray photoelectron spectroscopy (XPS). The analysis of the Si2*p*-lines has shown that the composition of low-temperature films is closer to silicon oxycarbonitride, whereas that of high-temperature films, to silicon carbonitride. Besides, it is noteworthy that in high-temperature films and in the majority of low-temperature films the Si–C bond with the electron bond energy of 100.6 eV is lacking, and the bonds are formed with the energy of ~101.1–101.3 eV. This value is an intermediate between the values of the Si–C and Si–N bonds (101.8–102.1 eV); in the literature it is assigned to the Si–C–N bond [33, 63]. The presence of the Si–C–N bond is indicative of the presence of polysubstituted tetrahedrons ($\text{C}_n\text{SiN}_{4-n}$) due to the partial substitution of the nitrogen atoms of the Si–N bonds by carbon atoms. The high-temperature films prepared from HMCTS are shown to be close to silicon nitride, whereas those from HMDS or TMDS correspond to silicon carbonitride.

In view of appearance of charging of the surface of dielectric films during the XPS measurements, we have used the method of determination of the Auger parameter of silicon (α), which is the difference between the energies of the Auger lines SiKLL and Si2*p*-lines. This provides an additional opportunity to determine the chemical state of the silicon atom. It is known that $\alpha(\text{Si}) = 1716.1$, $\alpha(\text{SiO}_2) = 1712.2$, $\alpha(\text{Si}_3\text{N}_4) = 1714.45$, $\alpha(\text{SiC}) = 1715.4$ [54]. The Auger parameters of silicon were determined for the layers of silicon carbonitride grown in the temperature range 373–973 K with the use of different organosilicon precursors. The obtained results prove the conclusions

made from the analysis of the data of the XPS and IR spectroscopy. The low-temperature films prepared from HMCTS are closer to silicon oxynitride, and from HMDS, to silicon oxycarbonitride. The composition of high-temperature films synthesized from TMDS approaches silicon carbide, the films from HMDS correspond to silicon carbonitride, and those from HMCTS are close in composition to silicon nitride. Chemical bonds are formed between all principal (Si, C, N) and impurity (O and H) elements.

The elemental composition of the films was determined by the method of energy dispersive spectroscopy. For more validity of the results of elemental analysis only those values of the electron beam energy (~5–7 keV) and thickness of the film (500–600 nm) were used, which we found to be optimal in the course of the performed investigation [64]. The data obtained are given below.

Compound-precursor	Si:C:N	Elemental composition, at %			
		Si	C	N	O
TMDS	2:4:1	28.22	55.26	14.26	2.26
HMDS	2:6:1	20.15	64.94	13.60	1.31
CHMCTS	1:2:1	18.15	44.46	32.68	4.72

Apart from the main elements, films of silicon carbonitride contained oxygen as an impurity. Since the method of energy dispersive spectroscopy does not make it possible to determine hydrogen, a comparison was made of the elemental composition of the films grown from different compounds-precursors at a high temperature, when the content of hydrogen is small. As follows from the data above, the films from TMDS have the highest concentration of silicon as compared to the films synthesized from HMDS and HMCTS, and the films from HMCTS have high concentration of nitrogen and minimal concentration of carbon, which is nicely consistent with the chemical composition of the starting compounds.

The investigation by the method of Raman spectroscopy revealed the absence of graphite inclusions in the low-temperature and their presence in the high-temperature films as nanocrystals of the size 1–2 nm. The lowest amount of the nanocrystals was found in the films grown from HMCTS, the largest, in those grown from HMDS, which is in compliance with the content of carbon in the starting compounds-precursors.

Therefore, the performed studies of the chemical composition using a number of spectroscopic methods

have shown that, regardless of the organosilicon precursors, the composition of the low-temperature films more precisely corresponds to the formula of hydrogenated silicon oxycarbonitride $\text{SiC}_x\text{N}_y\text{O}_z\text{H}$, and that of high-temperature films, to the formula SiC_xN_y .

Applying the procedure of nondestructive X-ray phase analysis using the X-ray beam produced by synchrotron radiation we had elaborated, we studied the phase composition of the films synthesized in the temperature range 373–973 K [50, 59]. As a result, in the films nano-crystals have been found having the size from 20 to 80 nm and the phase composition close to the standard phase $\alpha\text{-Si}_3\text{N}_4$. Their presence is also confirmed by high performance transmission electron microscopy. The method of Selected Area Electron Diffraction (SAED) revealed the presence of amorphous zones in the films and proved the presence of nanocrystals having the structure close to the phase $\alpha\text{-Si}_3\text{N}_4$ [65]. Therefore, the films of silicon carbonitride synthesized by plasmochemical decomposition of volatile silazanes, are nanocomposite, with nanocrystals close to the phase $\alpha\text{-Si}_3\text{N}_4$ distributed in the amorphous phase.

Investigation of the surface of all films by means of atomicraster electron microscopy revealed its nanograin character, as well as high uniformity and planarity. The mean-square roughness of the surface of the films of composition $\text{SiC}_x\text{N}_y\text{O}_z\text{H}$ is equal to 0.2–0.6 nm, and of the films of composition SiC_xN_y , 0.7–2.3 nm.

Investigation of Physicochemical and Functional Properties of Silicon Carbonitride Films

Optical properties. To measure the optical characteristics, the deposition of the films of silicon carbonitride was performed on transparent melted quartz supports. The optical properties were investigated by the methods of ellipsometry and spectrophotometry. In Fig. 2, the temperature dependence of the refractive index of films grown from different compounds-precursors is shown. The increase in the temperature of the synthesis results in the increase in the refractive index of the films of silicon carbonitride synthesized from different starting compounds from 1.45 to 3.15. Note lower values of the refractive index of the films synthesized from the cyclic compound HMCTS. Apparently, this is due to the presence in them of a large content of hydrogen and their chemical composition close to silicon nitride. The values of the refractive index of the films deposited from TMDS is

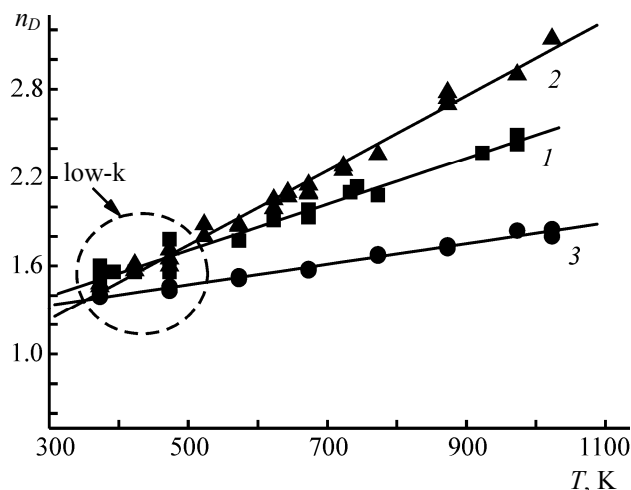


Fig. 2. The dependence of the refractive index of silicon carbonitride films on the temperature of synthesis and design of compound-precursor. (1) (TMDS+He), (2) (HMDS+He), and (3) (CHMTS+He).

lower than of those grown from HMDS, which is due to a larger concentration of carbon in the latter [19]. The refractive indices of the films used as low- k dielectrics vary within the values 1.4–1.6.

Using the method of spectrophotometry the optical transmission of the films was measured in the wave length range 200–2500 nm. The low-temperature films of composition $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ prepared from different organosilicon compounds possess an outstanding transmission in the visible and IR regions of the spectrum. Thus, films grown from the gas mixture (TMDS+He) have the best transmission coefficient (~98%) in a wide range of wave lengths, from 300 to 2500 nm. The films grown from the gas mixture (HMCTS+He) have the transmission coefficient of 95–96% in the wave length range 330–2500 nm, and those from the gas mixture (HMDS+He), 90–92% in the range 450–2500 nm. High-temperature films of the composition SiC_xN_y are less transparent, they show a shift of the edge of the absorption band toward the red region of the spectrum, apparently, due to the formation of inclusions of free graphite at high temperatures of the synthesis. SiC_xN_y films synthesized from the gas mixture (HMCTS+He) have the transmission coefficient of 87–90% in the range 580–2500 nm; those grown from the mixture (TMDS+He), 80–88% in the range 480–2500 nm, and from the mixture (HMDS+He), 80% in the range 1400–2500 nm. Therefore, variation of the chemical composition of the films as a function of the temperature of

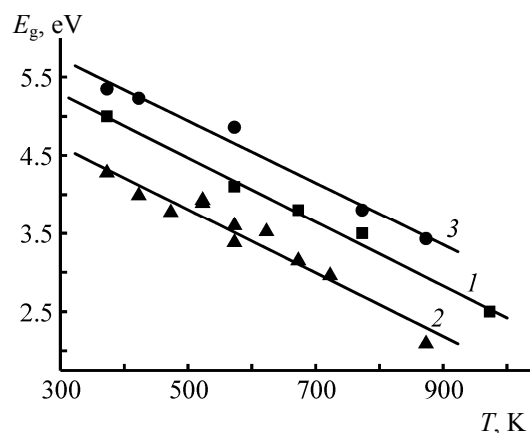


Fig. 3. the dependence of the optical width of the forbidden zone on the temperature of synthesis and design of compound-precursor. (1) (TMDS+He), (2) (HMDS+He), and (3) (CHMTS+He).

the synthesis and the structure of compound-precursor results in a variety of the obtained optical properties.

From the transmission spectra using the Tauc method [66] the optical width of the forbidden zone was calculated. In Fig. 3 the dependence of the optical width of the forbidden zone on the temperature of synthesis for the films prepared from HMCTS (E_g variation range from 5.4 to 3.4 eV), from TMDS (E_g 5.0–2.5 eV) and from HMDS (E_g 4.3–2.0 eV) is presented. The values of E_g decrease with the increase in the temperature of the synthesis, which can be connected with the increase in the concentration of graphite in the films.

Therefore, the synthesized films have different chemical composition, from that close to silicon nitride to that close to silicon carbide, with large variation of the optical width of the forbidden zone regulated by the transparency in the visible and IR regions. This allows using the films of silicon carbonitride in optoelectronic devices, like detectors of UV radiation or low-voltage electroluminescent diodes for the blue spectral region.

Electrophysical characteristics. The measurements of the C–V and I–V characteristics of the structures metal–dielectric–semiconductor Al– $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ –Si(100) have shown that low-temperature films of the hydrogenated silicon oxycarbonitride are good dielectrics. The volt-Farad (C–V) and volt-Ampere (I–V) dependencies for the films grown from HMDS

have been studied. The dependencies for this series of specimens have a classical shape: clearly defined plateau of ($C-I$), the run of the ($I-I$) dependence, and a clearly defined breakdown voltage.

The low-temperature films are low- k dielectrics with the values of k equal to 2.5–3.8. Below the electrophysical parameters of films $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ are given depending on the design of compound-precursor. It is evident that the films obtained from HMCTS possess the lowest dielectric constant, apparently, due to a high concentration of hydrogen in them and a substantial admixture of oxygen.

Compound-precursor	Si:C:N	ϵ	ρ , Ω cm	E_{tr} , V cm ⁻¹
TMDS	2:4:1	3.8–4.2	1.3×10^{11}	9.3×10^5
HMDS	2:6:1	3.0–4.0	10^{13} – 10^{16}	1.0×10^6
CHMTS	1:2:1	2.5–4.5	10^{10} – 10^{13}	10^6 – 10^8

Mechanical characteristics. The measurements of microhardness and the Young's modulus of the specimens $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ and SiC_xN_y , grown from the aforementioned compounds-precursors and having the thickness of ca. 1 μm have been performed. For this, the loading and unloading curves were recorded in the coordinates load–the depth of penetration of the indenter using the diamond Berkovich indenter. The measurements were performed for the loads of 1 and 0.5 μN and the depth of penetration of the nanoindenter from 50 to 160 nm. The analysis of the curves by the Oliver–Pharr method makes it possible to determine the values of microhardness and the elastic modulus of the films. The dependences of the microhardness and the Young's modulus of the silicon carbonitride films on the temperature of their synthesis and the design of the molecules of compounds-precursors are obtained. The mechanical properties of all films grown from the organosilicon compounds under consideration are shown to be improved with the increase of the temperature of synthesis due to lower hydrogen concentration in them and increased concentration of the Si–C or Si–C–N bonds [54], since it is known that silicon carbide (32 GPa) is harder than silicon nitride (20 GPa). The films from HMCTS have the lowest microhardness and the Young's modulus, apparently, due to a higher concentration of hydrogen as compared to the films from TMDS and HMDS, as well as due to their chemical composition close at low temperatures to silicon oxynitride, and at high temperature, to silicon nitride. The films from TMDS

Table 2. Dependence of the hardness and Young's modulus of silicon carbonitride films on their chemical composition and design of compound-precursor

Compound-precursor	$\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$		SiC_xN_y	
	Hardness, GPa	Young's modulus, GPa	Hardness, GPa	Young's modulus, GPa
TMDS	3.8–15	21–90	18–36	125–190
HMDS	2–15	12–88	18–28	120–186
CHMTS	0.3–6	2.4–50	7–13	50–80

and HMDS are hard since they have an enhanced concentration of the Si–C or Si–C–N bonds. The hardest are the films prepared from TMDS at any temperature, because they have the lowest concentration of the hydrogen-containing bonds and the largest concentration of the Si–C or Si–C–N bonds.

In Table 2 the values of microhardness and the Young's modulus are given for the films of the composition $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ and SiC_xN_y . Noteworthy is the fact that high values of microhardness and the Young's modulus are observed for the films of the composition $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$, which can be used as low- k dielectrics in microelectronics. These values exceed the corresponding characteristics of the other known low- k materials, like Dow Chemical SiLK (H 0.4 GPa, E 3.8 GPa), technical diamond (black diamond) (H 0.13–3.6 GPa, E 7.76 GPa), Oxazola dielectric (H 0.4 GPa, E 2.6 GPa), porous SiLK (H 0.16–0.19 GPa, E 1.5 GPa), etc. Combination of a low value of dielectric constant and good mechanical properties of the synthesized dielectric films $\text{SiC}_x\text{N}_y\text{O}_z\text{:H}$ allows for their competition with the other low- k materials for the use in modern microelectronics.

Films of the SiC_xN_y composition have high values of microhardness and the Young's modulus. The record films are those synthesized from TMDS; they have the microhardness of 36 GPa, which is comparable with the values of microhardness of other hard materials, for example, cubic boron nitride [67]. Besides, these films are transparent, refractory [68] and corrosion-stable, so, the coatings on their basis can find a wide application.

Therefore, the methods are elaborated for preparation of films of a multifunctional material, silicon carbonitride of variable composition, by plasmochemical deposition from organosilicon compounds,

belonging to the class of silazanes: tetramethyldisilazane, hexamethyldisilazane, and hexamethylcyclotrisilazane in the mixture with helium in the temperature range 373–973 K. The layers synthesized in the temperature range 373–673 K correspond to the chemical composition $\text{SiC}_x\text{N}_y\text{O}_z\text{H}$, and in the range 773–973 K, to composition SiC_xN_y . All films are nanocomposite materials, in the amorphous part of which nanocrystals are distributed close in the composition to the standard phase $\alpha\text{-Si}_3\text{N}_4$, whereas the high-temperature films of the composition SiC_xN_y additionally contain the impurity inclusions of nanocrystalline graphite. The obtained refractory films having high hardness, transparency, and corrosion stability, are promising as protecting coatings for a wide range of industrial applications, as well as for optoelectronic, micro- and nanoelectronic devices.

EXPERIMENTAL

The films of silicon carbonitride of variable elemental composition were obtained by plasma-chemical deposition of the vapors of TMDS, HMDS, HMCTS and helium as an additional gas at lowered pressure in a reactor ($4\text{--}6 \times 10^{-2}$ Torr) in the temperature range 373–973 K. The above compounds have different atomic ratio Si:C:N, equal to 2:4:1, 2:6:1, and 1:2:1, respectively. The experimental installation and the procedure are described in [58]. As a support, monocrystalline silicon(100), gallium arsenide (100), and melted quartz were used. The supports underwent standard chemical treatment for removal of a violated layer and surface impurities, their quality was controlled by the method of ellipsometry.

Chemical composition and the types of chemical bonds in the obtained silicon carbonitride films were studied by the use of IR, Raman, X-ray photoelectron, and energy dispersive spectroscopy. The instruments and procedures used are described in [58]. The structure and phase composition of the films were investigated using a nondestructive technique RFA-SI (Siberian Synchrotron and Terahertz Radiation Center, Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences), high resolution transmission, and raster electron microscopy, atomic force microscopy [50, 54]. Optical properties of the films were investigated on ellipsometers LEF-2, LEF-3 and spectrophotometer SF-18 (λ 400–750 nm). The optical transmittance and the values of optical width of the forbidden zone for the films deposited on transparent supports were determined on a Shimadzu UV-3101PC

spectrophotometer in the range 190–3200 nm with the resolution of 5 nm. For investigation of mechanical properties of the films of ~ 1 μm thickness a nanotester CSZM Nano Hardness was used equipped with the Berkovich diamond indenter. The measurements were performed with the maximum load of 0.5–1.0 μN and the depth of penetration of the nanoindenter of 50–160 nm. The instrument was calibrated and the data analyzed using the Oliver–Pharr method [69]. For electrophysical measurements the structures metal–dielectric–semiconductor (MDS) were made, in which as a gate dielectric the film of silicon carbonitride was used.

ACKNOWLEDGMENTS

This work was performed with the financial support from the Russian Foundation for Basic Research (grant no. 10-07-00274a) and Siberian Branch of Russian Academy of Sciences (Project no. 97).

REFERENCES

1. Bai, X., Zhang, C., and Tao, A., *Proc. Nat. Sci.*, 2005, vol. 105, p. 97.
2. Riedel, R., Kleebe, H., J., Schoenfelder, H., and Aldinger, F., *Nature*, 1995, vol. 374, p. 526.
3. Mishra, S.K., *Int. J. Appl. Ceram. Technol.*, 2009, vol. 6, p. 45.
4. Chen, L.C., Chen, C.K., Wei, S.L., Bhusari, D.M., Chen, K.H., Chen, Y.F., Jong, Y.C., and Hunag, Y.S., *Appl. Phys. Lett.*, 1998, vol. 72, p. 2463.
5. Liu, Y. and Cohen, M.L., *Science*, 1989, vol. 245, p. 841.
6. Chang, H.L. and Kuo, C.T., *Mater. Chem. Phys.*, 2001, vol. 72, p. 236.
7. Badzian, A., Badzian, T., Drawl, W., and Roy, R., *Diamond Relat. Mater.*, 1998, vol. 7, p. 1519.
8. Chang, H.L., Kuo, C.T., *Diamond Relat. Mater.*, 2001, vol. 10, p. 1910.
9. Fu, Y., Sun, C.Q., Du, H., and Yan, B., *Surf. Coat. Technol.*, 2002, vol. 160, p. 165.
10. Bill, J., Seitz, J., Thurn, G., Durr, J., Canel, J., Janos, B.Z., Jalomecki, A., Santez, D., Schempp, S., Lamparter, H.P., Mayer, J., and Aldinger, F., *Phys. Stat. Solidi, A*, 1998, vol. 166, p. 269.
11. Nakayamada, T., Matsuo, K., Hayashi, Y., Izumi, A., and Kadotani, Y., *Thin Solid Films*, 2008, vol. 516, p. 656.
12. Badzian, A., Badzian, T., Roy, R., and Drawl, W., *Thin Solid Films*, 1999, vol. 354, p. 148.
13. Zhang, D.H., Gao, Y., Wei, J., and Mo, Z.Q., *Thin Solid Films*, 2000, vols. 377–378, p. 607.

14. Chen, K.H., Wu, J.-J., Wen, C.Y., Chen, L.C., Fan, C.W., Kuo, P.F., Chen, Y.F., and Huang, Y.S., *Thin Solid Films*, 1999, vols. 355–356, p. 205.
15. Gomez, F.J., Prieto, P., Elizalde, E., and Piqueras, J., *Appl. Phys. Lett.*, 1996, vol. 69, p. 773.
16. Soto, G., Samano, E.C., Machorro, R., and Cota, L., *J. Vac. Sci. Technol., A*, 1998, vol. 16, p. 1311.
17. Jedrzejowski, P., Cizek, J., Amassian, A., Klemberg-Sapieha, J.E., Vlcek, J., and Martinu, L., *Thin Solid Films*, 2004, vols. 447–448, p. 201.
18. Xie, E., Ma, Z., Lin, H., Zhang, Z., and He, D., *Optical Mater.*, 2003, vol. 23, p. 151.
19. Chen, C.W., Huang, C.C., Lin, Y.Y., Chen, L.C., Chen, K.H., and Su, W.F., *Diamond Relat. Mater.*, 2005, vol. 14, p. 1010.
20. Chen, W., Huang, C.C., Lin, Y.Y., Chen, L.C., and Chen, K.H., *Diamond Relat. Mater.*, 2005, vol. 14, p. 1126.
21. Zhou, F., Yue, B., Wang, X., Wu, X., and Zhuge, L., *J. Alloys Compd.*, 2010, vol. 492, p. 269.
22. Hoche, H., Pusch, C., Riedel, R., Fasel, C., and Klein, A., *Surf. Coat. Technol.*, 2010, vol. 205, p. S21.
23. Du, X.-W., Fu, Y., Sun, J., Yao, P., and Cui, L., *Mater. Chem. Phys.*, 2007, vol. 103, p. 456.
24. Tomasella, E., Rebib, F., Dubois, M., Cellier, J., and Jacquet, M., *J. Phys. Conf. Ser.*, 2008, vol. 100, p. 082045.
25. Hoche, H., Allebrandt, D., Bruns, M., Riedel, R., and Fasel, C., *Surf. Coat. Technol.*, 2008, vol. 202, p. 5567.
26. Mishra, S.K. and Bhattacharyya, A.S., *Mater. Lett.*, 2008, vol. 62, p. 398.
27. Li, W.L., Yang, J.L., Zhao, Y., and Fei, W.D., *J. Alloys Compd.*, 2009, vol. 482, p. 317.
28. Ishimaru, M., Naito, M., Hirotsu, Y., and Sickafus, K.E., *Nucl. Instrum. Meth. Phys. Res., B*, 2003, vol. 206, p. 994.
29. Suvorova, A.A., Nunney, T., and Suvorov, A.V., *Nucl. Instrum. Meth. Phys. Res., B*, 2009, vol. 267, p. 1294.
30. Hirai, T. and Goto, T., *J. Mater. Sci.*, 1981, vol. 16, p. 17.
31. Bae, Y.W., Du, H., Gallois, B., Gonsalvest, K.E., and Wilkens, B.J., *Chem. Mater.*, 1992, vol. 4, p. 478.
32. Schonfelder, H., Aldinger, E., and Riedel, R., *J. Phys. IV France*, 1993, vol. 3, no. C7, p. 1293.
33. Bendeddouche, A., Berjoan, R., Beche, E., Merle-Mejean, T., Schamm, S., Serin, V., Taillades, G., Pradel, A., and Hillel, R., *J. Appl. Phys.*, 1997, vol. 81, p. 6147.
34. Suzuki, M., Maniette, Y., and Okutani, T., *J. Am. Ceram. Soc.*, 1993, vol. 76, p. 1195.
35. Besling, W.F.A., Vanderput, P.J.J.M., and Schoonman, J., *J. Phys. IV France*, 1995, vol. 5, no. C5, p. 953.
36. Ting, S.-F., Fang, Y.-K., Hsien, W.-T., Tsair, Y.-S., Chang, C.-N., Lin, C.-S., Hsieh, M.-C., Chiang, H.-C., and Ho, J.-J., *J. Electron. Mater.*, 2002, vol. 31, p. 1341.
37. Awad, Y., El Khakani, M.A., Aktik, C., Mouine, J., Camire, N., Lessard, M., Scarlete, M., Al-Abadleh, H.A., and Smirani, R., *Surf. Coat. Technol.*, 2009, vol. 204, p. 539.
38. Latrasse, L., Lacoste, A., Sanchez-Lopez, J.C., Bes, A., Rayar, M., and Pelletier, J., *Surf. Coat. Technol.*, 2009, vol. 203, p. 2343.
39. Bulou, S., Le Brizoual, L., Miska, P., de Pouques, L., Hugon, R., and Belmahi, M., *J. Phys. Conf. Ser.*, 2010, vol. 12, p. 012002.
40. Zhang, H., Gao, Y., Wei, J., and Mo, Z.Q., *Thin Solid Films*, 2001, vols. 377–378, p. 607.
41. Kroke, E., Li, Y.-L., Konetschny, C., Lecomte, E.L., Fasel, C., and Riedel, R., *Mater. Sci. Eng.*, 2000, vol. 26, p. 97.
42. Izumi, A. and Oda, K., *Thin Solid Films*, 2006, vol. 501, p. 195.
43. Limmanee, A., Otsubo, M., Sugiura, T., Sato, T., Miyajima Sh., Yamada, A., and Konagai, M., *Thin Solid Films*, 2008, vol. 516, p. 652.
44. Dez, R., Ternergall, F., Reynaud, C., Mayne, M., and Armand X Her-lin-Boime, N., *J. Eur. Ceramic Soc.*, 2002, vol. 22, p. 2969.
45. Vassallo, E., Cremona, A., Ghezzi, F., Dellera, F., Laguardia, L., Ambrosone, G., and Coscia, U., *Appl. Surf. Sci.*, 2006, vol. 252, p. 7993.
46. Fainer, N.I., Kosinova, M.L., Rumyantsev, Yu.M., and Kuznetsov, F.A., *J. Phys. IV. France*, 1999, vol. 9, no. PR8, p. 769.
47. Fainer, N.I., Kosinova, M.L., Yurjev, G.S., Rumyantsev, Yu.M., and Asanov, I.P., *NIMA*, 2000, vol. 448, p. 294.
48. Fainer, N.I., Kosinova, M.L., and Rumyantsev, Yu.M., *Russ. Khim. Zh.*, 2001, vol. 45, p. 101.
49. Fainer, N.I., Maximovskii, E.A., Kosinova, M.L., and Rumyantsev, Yu.M., *Mater. Sci. Forum.*, 2001, vols. 378–381, p. 493.
50. Fainer, N.I., Maximovskii, E.A., Rumyantsev, Yu.M., Kosinova, M.L., and Kuznetsov, F.A., *NIMA*, 2001, vol. 470, p. 193.
51. Fainer, N.I., Rumyantsev, Yu.M., Golubenko, A.N., Kosinova, M.L., and Kuznetsov, F.A., *J. Cryst. Growth*, 2003, vol. 248, p. 175.
52. Fainer, N.I., Kosinova, M.L., Rumyantsev, Yu.M., and Kuznetsov, F.A., *Zh. Strukt. Khim.*, 2004, vol. 45, p. 66.
53. Fainer, N., Rumyantsev, Y., Kosinova, M., Maximovskii, E., and Kesler, V., *Surf. Coat. Technol.*, 2007, vol. 201, p. 9269.
54. Fainer, N.I., Kosinova, M.L., Rumyantsev, Yu.M., Maximovskii, E.A., and Kuznetsov, F.A., *J. Phys. Chem. Solids*, 2008, vol. 69, p. 661.

55. Voronkov, M.G., Sulimin, A.D., Yachmenev, V.V., Mirskov, R.G., Kokin, V.N., and Chernova, V.G., *Dokl. Akad. Nauk SSSR*, 1981, vol. 259, no. 5, p. 1130.
56. Brooks, T.A. and Hess, D.W., *Thin Solid Films*, 1987, vol. 153, p. 521.
57. Brooks, T.A. and Hess, D.W., *J. Appl. Phys.*, 1988, vol. 64, p. 841.
58. Fainer, N.I., Golubenko, A.N., Rumyantsev, Yu.M., and Maximovskii E.A., *Glass Phys. and Chem.*, 2009, vol. 35, no. 3, p. 274.
59. Fainer, N.I., Rumyantsev, Yu.M., Kesler, V.G., Maximovski, E.A., and Kuznetsov, F.A., *ECS Trans.*, 2009, vol. 25, p. 921.
60. Zhoua, Y., Probst, D., Thissen, A., Kroke, E., Riedel, R., Hauser, R., Hoche, H., Broszeit, E., Kroll, P., and Stafast, H., *J. Eur. Ceram. Soc.*, 2006, vol. 26, p. 1325.
61. Anderson, D.R., *Analysis Silicones*, New York: Willey-Interscience, 1974, p. 100.
62. Mundo, R.D., d'Agostino, R., Fracassii, F., and Palumbo, F., *Plasma Processes and Polymers*, 2005, vol. 2, p. 612.
63. He, X.M., Taylor, T.N., Lillard, R.S., Walter, K.C., and Nastasi, M., *J. Phys. Condens. Matter.*, 2000, vol. 12, p. L591.
64. Rumyantsev, Yu.M., Fainer, N.I., Maximovskii, E.A., and Ayupov, B.M., *J. Struct. Chem.*, 2010, vol. 51, no. 7, p. S179.
65. *JCPDS Int. Center for Diffraction Data*, 1988, vol. 41, no. 360.
66. Tauc, J., Grigorovici, R., and Vancu, A., *Phys. Stat. Solidi*, 1966, vol. 15, p. 627.
67. Jiang, X., Philip, J., Zhang, W.J., Hess, P., and Matsumoto, S., *J. Appl. Phys.*, 2003, vol. 93, p. 1514.
68. Fainer, N.I., Bakovets, V.V., Kosinova, M.L., Rumayntsev, Yu.M., Maximovski, E.A., and Kuznetsov, F.A., Abstracts of Papers, *14th APAM General Assembly and Conference "State of Materials Research and New Trends in Material Science,"* New Delhi, India, 2008, p. 84.
69. Oliver, W.C. and Pharr, G.M., *J. Mater. Res.*, 1992, vol. 7, p. 1564.