Silicon Carbonitride Films as a Promising Material Synthesized from New Sources

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Abstract

Silicon carbonitride films were synthesized by means of the chemical vapour deposition (CVD) process in the scheme with remote plasma. Initial compounds were the silyl derivatives of 1,1-dimethyl hydrazine: dimethyl(2,2-dimethylhydrazino)silane and dimethyl-bis-(2,2-dimethylhydrazino)silane. The molecules of the monomers contain the bonds Si–N, Si–C and C–N which are necessary for the formation of silicon carbonitride.

According to the data of X-ray photoelectron XPS and IR spectroscopy, it was stated that the synthesized films are different types of composite compounds in which silicon atom is connected with nitrogen and carbon atoms, or nitrogen atom forms chemical bonds with silicon and carbon. Films synthesized at $T <$ 673 K are partially hydrogenated. Electron microscopic studies showed that nanocrystals 50–200 nm in size are formed in the amorphous matrix of films. It was discovered by diffraction of synchrotron radiation (DSR) method that the formation of crystals and their crystalline forms are independent of the substrate temperature. This gives grounds to assume that the formation of nanocrystals can happen in the gas phase, or be initiated by strain in the film increasing as its thickness grows. The films exhibit high thermal stability till 1273 K.

INTRODUCTION

Interest to the composite layers of silicon carbonitride, which has increased in the recent years, is first of all connected with a favourable combination of the properties of silicon carbide, silicon nitride, and carbon nitride, and with the opening possibilities to govern the characteristics of the final material by varying its synthesis conditions. Depending on the ratio of Si–C and Si–N bonds, the optical band gap changes. The material, with the structure formed due to Si–N and C–N bonds, should possess high hardness, in comparison with silicon nitride and carbide; it can be used as superhard coatings [1–7].

At the same time, composite films of silicon carbonitride are complicated compounds of non-periodic structure, and their proper-ties are unusual, which attracts substantial fundamental interest. Having no analogs in nature, this material is a unique subject to investigate the metastable state of the substance and the processes of its transformation into new forms, incuding crystalline and composite nanostructures with the characteristic size of separate phases up to 100 nm, and the structures of isolated clusters of different phases in the amorphous matrix. The last two years are pronounced with the increase of the number of publications dealing with the search for new synthesis processes and with the investigations of the characteristics of silicon carbide, silicon nitride, carbon nitride films and composites based on them.

At present, the opinions on the structure and phase composition of silicon carbonitride are ambiguous. Some authors [1, 8] investigating this material obtained under the equilibrium condi-

tions assume that it is a mixture of SiC and Si_3N_4 phases (in some cases with graphite admixture). Films synthesized under non-equilibrium conditions are, as a rule, mainly amorphous; they are solid solutions of carbon in Si_3N_4 and contain Si–N–Si and Si–C–Si bonds, or silicon in C_3N_4 and contain Si–N–Si and Si–N–C bonds. The latter version was reported in [2, 4]; the authors synthesized $Si_xC_yN_z$ films by heating the silicon substrate in a mixture of gases CH_4, N_2 and H_2 at a temperature above 1073 K. No C–N bond was detected in films synthesized from hexamethyldisilazane [6] and in ceramics obtained from polysilazanes [9, 10]. It was demonstrated that the phase composition of films depends on the molecular structure of the initial compound [3–6].

Explosive and flammable gaseous mixtures containing methane (or other hydrocarbons), nitrogen, hydrogen and monosilane are most often used in the synthesis of silicon carbonitride films [2, 3, 7]. Volatile organosilicon compounds, for example silazanes (hexamethyldisilazane and hexamethylcyclotrisilazane) containing Si–N and Si–C bonds in the initial molecule are used as alternative, more safe initial compounds [6, 11]. A series of silyl derivatives of 1,1-dimethylhydrazine, including dimethyl(2,2-dimethylhydrazino)silane – $(CH_3)_2HSiNHN(CH_3)_2$ (DMDMHS) and dimethyl-bis-(2,2-dimethylhydrazino)silane – $(CH_3)_2[SiNHN(CH_3)_2]_2$ (DM-bis-DMHS) was recently synthesized in the Irkutsk Institute of Chemistry, SB RAS. These volatile compounds seem more promising than silazanes for the deposition of silicon carbonitride films because the N/Si ratio in their molecules varies from 2 to 4, while in silazanes this ratio varies from 0.5 to 1. Besides, DMDMHS and DM-bis-DMHS are molecular precursors of silicon carbonitride because the initial molecules of these monomers already contain the appropriate Si–N, Si–C and C–N bonds. In [12] we demonstrated the principal possibility of the efficient deposition of silicon carbonitride films using one of the mentioned precursors, DMDMHS, in CVD process initiated by remote plasma.

The goal of the present investigation is to develop the understanding of the nature of chemical bonds, molecular structure and phase composition of silicon carbonitride films synthesized under non-equilibrium conditions in remote plasma-induced CVD process from new volatile organosilicon compounds.

EXPERIMENTAL CONDITIONS AND METHODS OF FILM CHARACTERIZATION

Chemical vapour deposition with the remote plasma of radio-frequency (rf) discharge described in detail in [13] was used for the synthesis of films. The plasma was formed during the excitation of the rf-discharge 013.56 MHz) in the carrier gas flow (helium or hydrogen). The vapour of volatile monomer was added at some distance from the plasma downstream near the heated substrate on which the film was deposited. Silicon substrates were preliminarily treated in organic solvents, polishing etchant, and in HF solution to remove the oxide from the surface. Film synthesis conditions were as follows: total pressure, P = 200 Pa; rf-discharge power, W = 0.02 W cm^{-3}, gas/monomer pressure ratio, R = 0.5. The substrate temperature T_s was stabilized at an accuracy of ~1 °C within the range 298–873 K. Boiling points of DMDMHS and DM-bis-DMHS are 353 and 434 K, respectively. The temperature of the source of initial compound was kept at a level of about 298 K. The thickness and refractive index of films were determined using the LEF-3M ellipsometer (λ = 633 nm). IR spectra of films deposited on silicon or germanium substrates were recorded using the FTIR 8300 Shimadzu spectrometer. Spectra were interpreted on the basis of literature data [6, 14, 15].

XPS measurements were performed using a VG Microtech spectrometer with non-monochromatized MgK_a radiation ($h\nu$ = 1253.6 eV). All spectra were taken in a constant analyser energy (20 eV) regime with a resolution of about 1 eV. Before measurements the spectrometer was calibrated against Au $4f_{7/2}$ peak with a binding energy of 80.0 eV from the golden film deposited onto the surface of samples. The contour of the peaks was approximated by the Doniach – Sundjic function.

The microstructure of the films was examined by scanning electron microscopy (SEM) and diffraction of by synchrotron radiation methods. The X-ray Diffraction measurements were performed with High Resolution Powder Diffrac-

tometer of Siberian Synchrotron Radiation Center (beam-line No. 2 of VEPP-3, storage ring). The sample was placed at a small glancing angle to incident beam (q ~1°) to irradiate the whole surface of the film and this position had been kept while the analysis was performed. The sample was rotated around the normal to the surface to average the crystallites' orientation. The X-ray Diffraction patterns of the films were monitored at wavelength $l = 1.5330$ Å within angular range $2q = 20–70°$ and at scan step $D(2q) = 0.05°$.

RESULTS

Deposition rate

The dependencies of the film deposition rates for DMDMHS (system I) and DM-bis-DMHS (system 2) are shown in Fig. 1. One can see that the growth rate in the system I decreases with increasing substrate temperature and is independent (within the experimental error) on the type of the excited gas. In the system II, starting from T_s ³ 473 K, the deposition rate is practically independent of temperature. However, the dependence of the growth rate on the excited gas is observed: the film grows faster when excited hydrogen is used as carrier gas.

Chemical structure of films: IR spectroscopy

IR absorption spectra of the films synthesized in the systems I and II are shown in Fig. 2. For comparison, the spectrum of the initial
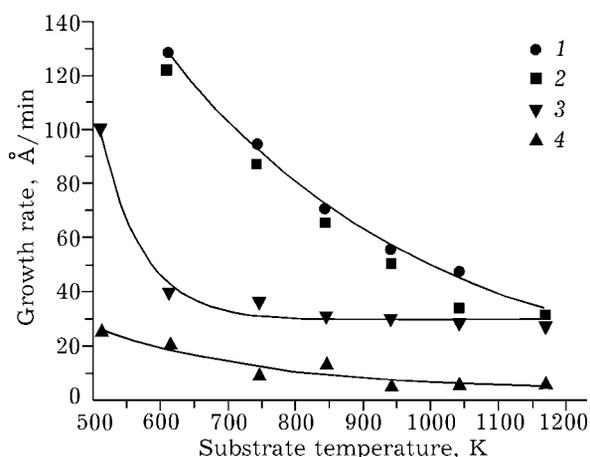

Fig. 1. The dependence of film growth rate on the substrate temperature: 1, 2 — films grown from DMDMHS with H_2^* (1) and with He⁎ (2); 3, 4 — from DM-bis-DMHS with H_2^* (3) and with He⁎ (4).
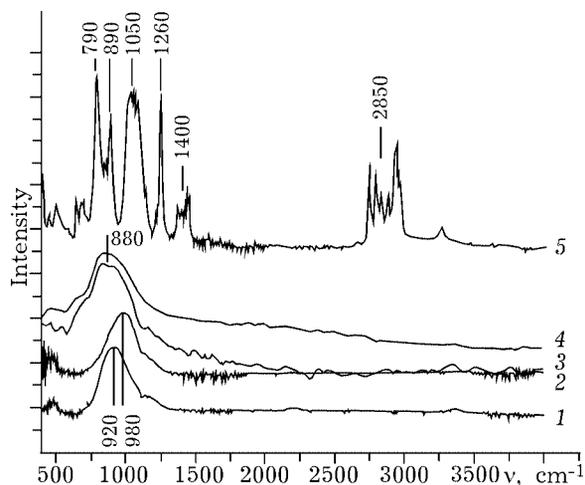

Fig. 2. IR spectra of the films synthesized with He⁎ in the systems: DM-bis-DMHS (1, 2) and DMDMHS (3, 4) at $T_s = 673$ (1, 3) and 873 K (2, 4); 5 — the spectrum of the initial DM-bis-DMHS.

monomer DM-bis-DMHS is shown in the same Fig.; its absorption bands are identified as follows. The peak at 790 cm^{-1} relates to the deformation vibrations of the $-CH_3$ and Si–C groups; the bands at 2900–2970, 1400 and 1260 cm^{-1} correspond to the symmetric C–H, asymmetric C–H, $-CH_3$ symmetric and asymmetric deformation vibrations, respectively. The absorption at 1050 cm^{-1} corresponds to C–N(sp^3) vibrations. The peaks at 3270 and 890 cm^{-1} are due to the stretching N–H and asymmetric Si–N–Si vibrations, respectively. The spectra of films obtained in both systems contain only one broad absorption band in the region 700–1200 cm^{-1}. This band may be the superposition of the vibrations of several different oscillators, namely: Si–C (800 cm^{-1}), Si–N (900–940 cm^{-1}), C–N (1000–1100 cm^{-1}), Si–CH_n–Si (1010–1050 cm^{-1}), and Si–O–Si (1070–1100 cm^{-1}) [6, 14, 15]. The positions of the maximum of this band for the films obtained in the systems I, II + He⁎ at different substrate temperatures differ in frequency substantially. At $T_s = 873$ K, the band is shifted to larger wavenumbers, which is the evidence that the material is enriched with nitrogen; thus, the probability of the formation of C–N bonds is higher. It should be noted that in the spectra of the films synthesized in the systems I, II + H_2^* (not shown in the Fig. 2) the positions of the maximum of the mentioned band is independent of substrate temperature and corresponds to the fre-

quency 850 cm^{-1}. The absence of noticeable absorption in the region 450 cm^{-1} points to the absence of Si–O–Si groups in the films. Large refractive index (1.8–2.0) of the films deposited at 673 and 873 K is also the evidence of the absence of noticeable amount of Si–O bonds. A weak signal at 1170 cm^{-1} shows that hydrogen forms a bond with nitrogen.

X-ray photoelectron spectroscopy of films

The results of X-ray photoelectron spectroscopic studies (XPS) of the films synthesized in the system DMDMHS + H$_2^*$ are discussed in detail in [12]. The spectra were interpreted on the basis of the known data [3, 4, 16–25]. It was revealed unambiguously that Si–C and Si–N are the main types of bonds in the film obtained in the system DMDMHS + H$_2^*$. Comparison of the XPS and IR spectroscopic data allows us to assume that this material cannot be considered as a mixture of silicon nitride and silicon carbide phases but is a compound in which silicon atom is bonded with nitrogen and carbon atoms.

X-ray photoelectron spectra of C 1s, N 1s levels for the films synthesized in the system DMDMHS + He* are shown in Fig. 3, a, b,
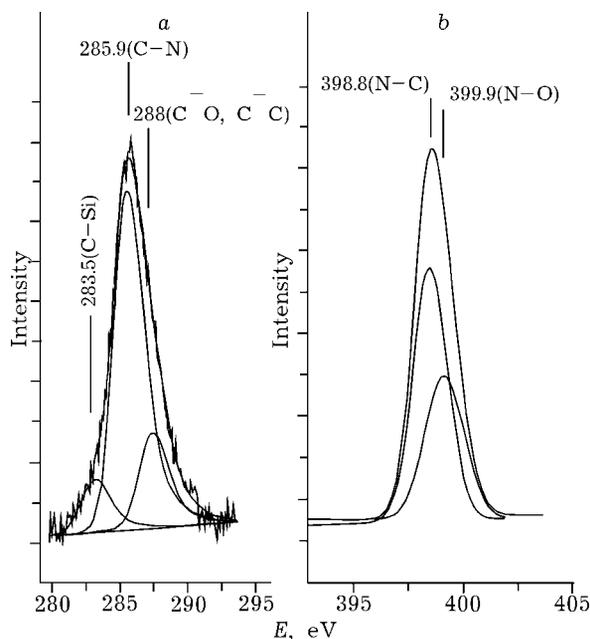

Fig. 3. XPS of the core levels C 1s (a) and N 1s (b) of the film synthesized in the system DMDMHS – He* at T_s = 673 K.

respectively. The contour of the C 1s line has a typical shape of wings, so it was reasonable to de-convolute it into three individual substituents with the energies 288.0, 285.9 and 283.5 eV. The peak at 288.0 eV can be attributed to the manifestation of C–O and C–H bonds. The presence of C–C bonds cannot also be excluded. The C–H bonds are formed at switching rf-discharge off at the last stage of film growth as a result of the adsorption of partially non-decomposed monomer on the surface. It can be assumed that the presence of oxygen is due to water or molecular oxygen adsorbed on the film surface when exposed to air. The position of the second component C 1s (285.9 eV) and the existence of photoemission from the N 1s level (398.8 eV) are the evidences of the presence of C–N bond. For comparison: the major part of the known values for the C 1s and N 1s levels in CN$_x$ films are 284–285 and 398–399 eV, respectively [4, 22].

The microstructure of films

The investigation of films by means of scanning electron microscopy showed that the films have good adhesion and smooth surface (Figure 4). In their essence, the films are amorphous; however, nanocrystalline insertions 50–200 nm in size are observed in the amorphous matrix. Figure 5 shows the X-ray diffraction patterns of the films synthesized at 473, 673, 873 K in the system DMDMHS + He*. The lattice spacing calculated from the X-ray spectra is listed in Table 1. Since the dimensions of the unit cell in Si$_x$N$_y$C$_z$ are close to those for the
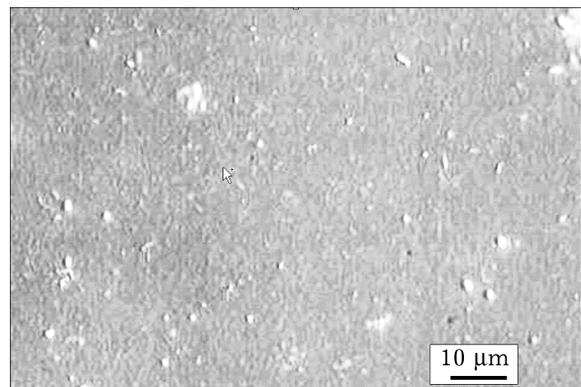

Fig. 4. Microphotograph of the film surface.

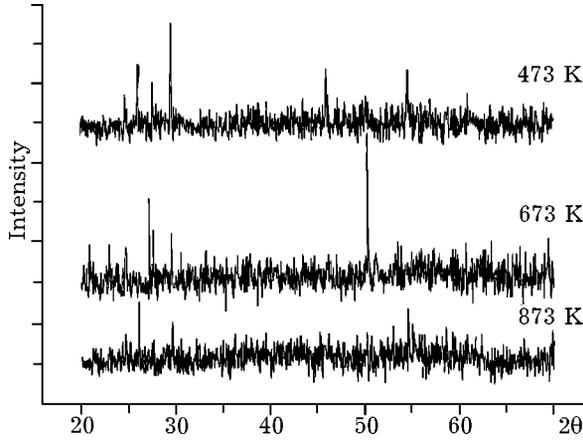Fig. 5. XPA spectra of the films synthesized in the system DMDMHS — He* at different temperatures.

phases a-Si_3N_4 and C_3N_4 [23, 25], the data for these phases are included in the Table 1 for comparison. It can be concluded that the major part of reflections corresponds to the a-Si_3N_4 phase; however, some of them can reasonably be attributed to the C_3N_4 phase or to both

phases. Silicon carbide and graphite were not detected. It should be noted that the occurrence of crystals, their dimensions and crystal forms are independent of the substrate temperature during the synthesis of the films.

Film properties

1. The refractive index of films varied within the range 1.5–2.4 depending on the synthesis conditions.

2. The optical band gap varied from 2 to 5 eV, depending on the ratio of Si—C/Si—N bond concentrations in the films. UV spectra used to estimate the optical band gap are shown and discussed in [12].

3. Films synthesized at T ³ 673 K did not change their chemical composition and optical properties during the annealing at temperatures till 1273; they were insoluble in the buffer HF solution.

ÒÀBLE 1

The d-spacing obtained from the data of X-ray phase analysis, and literature data for the phases: a-Si_3N_4, C_3N_4, graphite

DSR	a-Si_3N_4			b-C_3N_4			a-C_3N_4			C		
d, Å	d, Å	hkl	I	d, Å	hkl	I	d, Å	hkl	I	d, Å	hkl	I
				5.50	100	m	5.50	100	m			
4.20	4.32	101	m									
3.84	3.88	110	m									
3.57							3.55	101	s			
3.40	3.37	200	m									
3.25												
3.21				3.17	110	m	3.17	100	s			
3.01	2.89	201	s	2.75	200	s	2.75	200	m			
										2.669		s
	2.599	102	s									
	2.54	210	s							2.51	002	s
	2.32	211	s	2.25	101	s	2.37	201	s	2.35	101	s
	2.158	202	s									
	2.083	301	m	2.08	201	s	2.08	210	m			
1.95	1.937	220	w	1.95	111	m	1.90	211	s			
	1.884	212	w				1.87	112	s			
	1.864	310	w									
1.80	1.806	103	m							1.83	102	m
	1.771	311	m				1.77	202	w			
	1.751	302	w									
1.67	1.637	203	w				1.70	301	m			
										1.54	301	m

DISCUSSION

It follows from the experimental results obtained that the initial composition of the gas-phase mixture has a substantial effect on the growth rates and chemical composition of the films. For the system I, the type of the excited gas has practically no effect on the rate of film deposition. Film growth rate depends on the substrate temperature; hydrogen concentration in films decreases with the increase of temperature. It can be concluded on the basis of these data that the limiting stage of the process is hydrogen desorption from the surface of the growing film. In the system II, the type of the excited gas has a substantial effect on the growth rate. With H_2^*, the growth rate is higher than with He^*; however, at $T_s \geq 473$ K the rate becomes independent of temperature: as the susbtrate temperature increases, the rate of hydrogen desorption increases and gas-phase processes become the limiting stage.

Investigations by means of XPS and IR spectroscopy described in [12] for the films synthesized in the system DMDMHS + H_2^* demonstrated that the film is a compound in which the silicon atom is bonded with the N and C atoms. There is no evidence that C–N bonds are present in the films. The maximum of the major absorption band, in the films deposited in the systems I and II with He^*, which is a superposition of Si–C (800 cm^{-1}), Si–N (900–940 cm^{-1}), C–N (1000–1100 cm^{-1}) and Si–CH$_n$–Si (1010–1050 cm^{-1}) vibration modes is substantially shifted into the blue region (880–980 cm^{-1}) in comparison with the films synthesized in the same systems but with H_2^* (850 cm^{-1}). It follows from this observation that in the case of helium used as the excited gas, the synthesized silicon carbonitride contains more nitrogen than in the case of hydrogen excited. This conclusion is also confirmed by the XPS data (see Fig. 3) evidencing the presence of C–N bonds. So, the films synthesized in the system with He^* contain structural fragments in which nitrogen forms chemical bonds both with silicon and with carbon. The fact that no C–N bonds are formed in the films synthesized in the system with H_2^* can be explained by the evolution of CH_3 radicals from the surface of the growing film in the

reaction with the atomic hydrogen formed in plasma, according to the process

$$-CH_3 + H \circledR CH_4$$
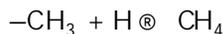
which is more profitable from the energy viewpoint [26]. The detachment of methyl groups from nitrogen results in the destruction of N–C bonds.

Recently, a series of publications appeared in which the structure of films was investigated by means of X-ray diffraction; some of these studies were carried out with bulk samples [10]. It follows from these data that the samples obtained at temperatures below 1273 K are X-ray amorphous. The authors of [4, 27] using ammonia, methane and hydrogen as initial reagents obtained polycrystalline silicon carbonitride films on Si<111> at temperatures above 1273 K using plasmochemical method and carried out a more detailed characterization of these films having concluded that their structure was close tot eh structure of the a-C_3N_4 phase in which a part of carbon positions is occupied by silicon which diffused from the substrate into the film during its growth. When a mixture of hydrogen, methane and nitrogen with a 10 % solution of monosilane in argon was used for the synthesis [27, 28], at $T \pounds 828$ K X-ray amorphous films were deposited; they contained about 4.8 at. % silicon. Two-layer structure composed of the upper nanocrystalline layer and lower amorphous one adjacent to the silicon substrate was obtained from a mixture of H_2N_2 with CH_3NH_2/SiH_4 [29]. The crystal form of the formed nanocrystals was not identified by the authors of the mentioned work.

The results of X-ray phase analysis of the films grown in our system demonstrated that the formation of crystals and their phase modifications are independent of substrate temperature. We assume that this situation is possible when nanocrystal particles are formed in the gas phase during deposition or in the case when the formation of crystals is initiated by the strain in film increasing as its thickness increases. In the latter case, as in [29], a two-layer film structure should be formed.

CONCLUSIONS

Silicon carbonitride films were synthesized by means of chemical vapour deposition in the

system with remote plasma. Initial reagents were silyl derivatives of 1,1-dimethylhydrazine: dimethyl(2,2-dimethylhydrazino)silane and dimethyl-bis-(2,2-dimethylhydrazino)silane, containing different number of nitrogen atoms in the initial molecules. Unlike the known sources used to obtain silicon carbonitride films, the molecules of these compounds contain all the bonds (Si—N, Si—C, C—N) necessary for the formation of silicon carbonitride films.

Investigations by means of XPS and IR spectroscopy demonstrated that the synthesized films cannot be considered as a mixture of silicon nitride and silicon carbide phases but are different types of composite compounds in which silicon atom is bonded to nitrogen and carbon atoms, or nitrogen atom forms chemical bonds with silicon and carbon. The films synthesized at $T < 673$ K are partially hydrogenated.

Electron microscopic studies of the films synthesized in the system with DMDMHS showed that nanocrystals 50—200 nm is size are formed in the amorphous matrix of these films. It was stated by means of the diffraction of synchrotron radiation that the formation of the crystals, as well as their crystal forms are independent of the substrate temperature. This gives us reasons to assume that the formation of nanocrystals can occur in the gas phase or be initiated by the mechanical strain in the film increasing while its thickness increases. Since the close-range order in the structures of films synthesized at temperatures 673—873 K corresponds to the structural units of thermodynamically stable phases — silicon nitride, silicon carbide or carbon nitride, the films possess high thermal stability till temperatures up to 1273 K.

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