

Physical and Chemical Transformations in Thin Films of Silicon Carbonitride during Thermal Annealing

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Abstract

Physicochemical transformations that take place in thin nanocrystalline layers of silicon carbonitride as a result of thermal annealing in vacuum at a temperature of 1173 K are investigated. IR, Raman spectroscopy, XPES, ellipsometry and X-ray analysis are applied to study these physicochemical transformations. It is stated that high-temperature annealing of the silicon carbonitride films helps decreasing the amorphous constituent of the film, increasing the density and size of nanocrystals incorporated in the film.

INTRODUCTION

One of the methods used to deposit silicon carbonitride films at relatively low temperatures (473–673 K) is plasma enhanced chemical vapour deposition (PECVD) involving the high-frequency discharge plasma. As a rule, hydrogen-containing compounds are used as initial reagents: silane, silazanes, ammonia [1, 2]. Because of the presence of substantial amounts of hydrogen in the gas phase, it is natural to expect its presence also in the deposited layers as a consequence of incomplete decomposition of the initial compounds. This has been confirmed by experimental results of many researchers who found that the films can contain hydrogen at a level of up to 20 %. According to the IR spectroscopic data, hydrogen is present in the deposited material in the bound state as Si–H and N–H groups. Their concentration is determined by the deposition conditions: synthesis temperature, composition of the gas phase, plasma power, etc. [3–5].

Bound hydrogen that is nearly always present in the layers of low-temperature (PECVD) silicon nitride and carbonitride affects their electrophysical, chemical and mechanical properties. Its presence also deter-

mines physicochemical stability and performance characteristics of the layers, the reliability of devices and equipment utilizing these materials.

One of the methods to remove the bound hydrogen is high-temperature annealing of the deposited layers. Some researchers report dehydrogenation of thin $\text{Si}_x\text{N}_{1-x}:\text{H}$ layers during the annealing [4]. It can be assumed that simultaneously with the removal of hydrogen, the structural changes will also occur, both in these layers and in similar dielectric layers. Unfortunately, the number of investigations of the structure of thin layers containing light elements is very limited. This is likely to be due to the difficulties of their X-ray phase analysis with usual diffractometer because of the small sample mass. The use of XRD using synchrotron radiation opens new possibilities for the structural investigations of these materials.

EXPERIMENTAL

Silicon carbonitride films SiC_xN_y were synthesized by the plasma decomposition of a gaseous mixture of hexamethyldisilazane $\text{Si}_2\text{NH}(\text{CH}_3)_6$ and helium at low pressure (4–

8 Pa) within temperature range 473–873 K according to the procedure described earlier in [3, 6]. Polished single-crystal silicon and gallium arsenide plates were used as substrates.

The thickness and refractive index of the grown layers were measured by means of ellipsometry using LEF-2 and LEF-3M ellipsometers. To determine the character of chemical bonds in layers, we used the IR and Raman spectra in the region 200–4000 cm^{-1} recorded with PHILIPS PU-95 and Triplemate, Spex Raman spectrometer, respectively. To determine the composition and character of chemical bonds in the material, we used Auger spectroscopy and XPS (Surface Science Center (SSC) of RIBER Company). To study the microstructure of the films, the methods of scanning electron microscopy were used (HREM and SAED, JEM2010 instrument). X-ray diffraction studies were carried out at the station “Anomalous scattering” of the accelerator on counterbeams, VEPP-3 of the International Siberian Center of Synchrotron Radiation (Institute of Nuclear Physics, SB RAS, Novosibirsk, Russia). In our experiments, the SR wavelength was a constant parameter 1.5405 Å. To record the diffraction patterns, θ - 2θ scanning was used, as well as 2θ scanning and Image Plate methods.

RESULTS AND DISCUSSION

As-grown silicon carbonitride samples synthesized at 573, 773 and 873 K were used for high-temperature annealing. Layer thickness was about 3000 nm, refractive index varied from 2.0 to 2.6 depending on synthesis temperature.

Thermal annealing of the films was carried out at 1123 K and low pressure (1.33 Pa) in helium for 2 h. No changes of thickness were detected during annealing; however, refractive index increased 1.5 times. At the same time, we observed the changes of other parameters recorded by different methods.

IR spectroscopic investigations

Figure 1 shows IR spectra of the films deposited at 873 K (a) and 1123 K (c) and the low-temperature film annealed at 1123 K (b).

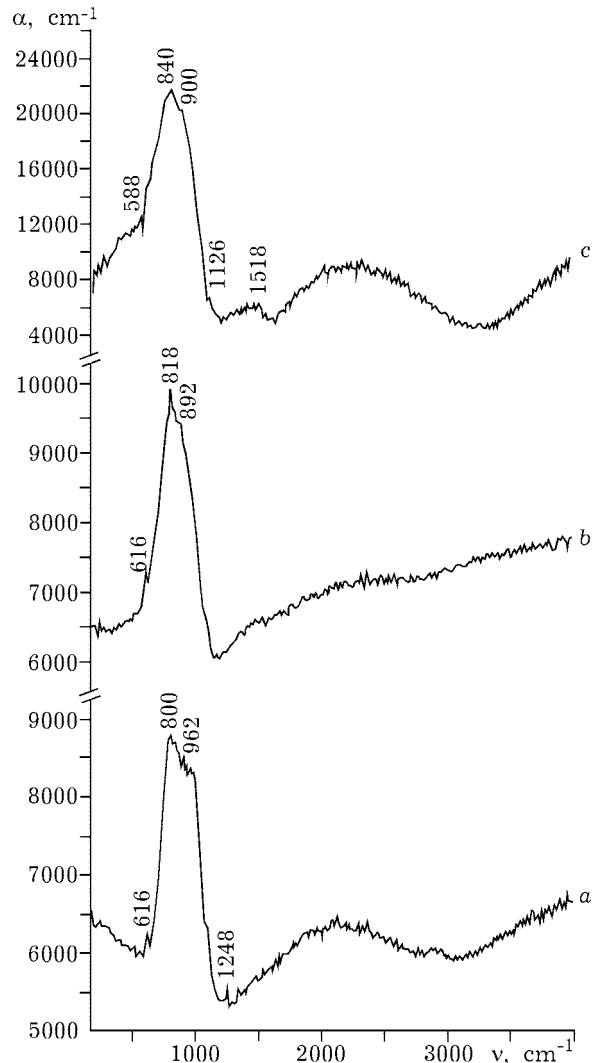


Fig. 1. IR spectra of SiCN films deposited at 873 K (a) and 1123 K (c) and annealed at 1123 K (b).

IR spectra of the films deposited at 873 K contain a broad absorption band 600–1200 cm^{-1} that can include vibrational modes of Si–C (800–850 cm^{-1}) and Si–N (900–960 cm^{-1}) bonds, a narrow peak at 620 cm^{-1} (disordering in graphite-like structures) and a narrow peak at 1250 cm^{-1} (C–N bonds) [5, 7] (see Fig. 1, a). No absorption bands corresponding to the vibrations of hydrogen-containing bonds C–H, N–H, Si–H, Si–CH₃ are observed in the spectra. It can be assumed that silicon carbonitride films synthesized under these conditions contain practically no hydrogen at the accuracy of IR spectroscopic detection limit. IR spectra of the as-grown film (see Fig. 1, c) and the film annealed at the same temperature 1123 K (see Fig. 1, b) are similar, but a peak at

TABLE 1

The ratio of the intensities I_D/I_G in SiCN films depending on the synthesis temperature

T , K	I_D/I_G
973	1.22
1023	1.29
1073	1.08
1173	0.81

1500 cm^{-1} corresponding to the vibrations of C–N or C–C bonds is exhibited in one of them. High-temperature annealing leads to the decrease of the width of the main band and shift to low frequency region and to the disappearance of the peak at 1250 cm^{-1} (see Fig. 1, b) corresponding to the vibrations of the C–N bonds.

Raman spectroscopy

Due to structural sensitivity, Raman spectroscopy is widely used to analyze carbon and related materials. Observation of changes of the position, width and intensity ratios of the bands during annealing can give some information concerning the evolution of the film structure.

Raman spectrum of low-temperature films ($<773\text{ K}$) of silicon carbonitride is continuous, without characteristic peaks, which is likely to be the consequence of the presence of broken bonds and the distortion of the lattice symmetry, which is typical for the amorphous state. Raman spectra of high-temperature films ($>773\text{ K}$) contain a broad band in the region $1200\text{--}1600\text{ cm}^{-1}$ and a weak peak at 980 cm^{-1} . This makes them similar to the spectra of the amorphous carbon, boron carbonitride, carbon nitride, i.e. materials containing carbon, with two broad bands centered in the Raman spectra near 1370 and 1540 cm^{-1} (D and G bands of the disordered sp^2 carbon) [5].

We analyzed the Raman spectra of silicon carbonitride films grown by RPECVD using hexamethyldisilazane in the high-temperature region $973\text{--}1123\text{ K}$ and annealed at 1123 K . For the analysis, the spectra were approximated by a sum of two Gaussian curves (peaks D and G) and their integral intensity was calculated. The obtained band intensity ratios

I_D/I_G of the samples synthesized at high temperatures for 1 h are shown in Table 1. Temperature increase up to 1173 K leads to decreasing the intensity and width of the D band in the Raman spectra of silicon carbonitride film. It should be noted that the nature of this defect has not been investigated yet. It is assumed that the band D is responsible for the distortion of the crystal symmetry. The intensity of the band D decreases when the synthesis time is increased ($I_D/I_G = 1.80$ at $t = 3\text{ h}$) and at high-temperature annealing of the SiCN layers.

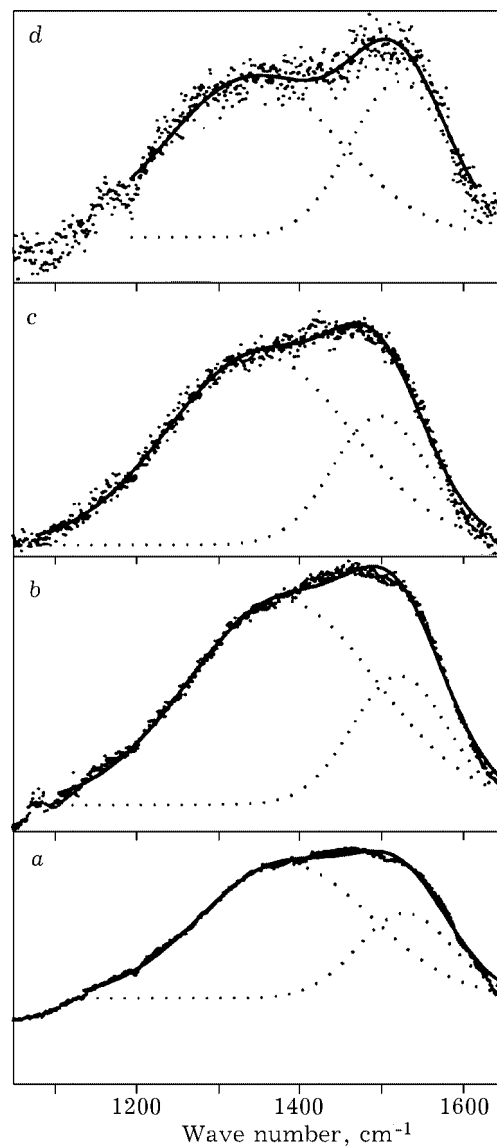


Fig. 2. The evolution of the Raman spectra of the SiCN film during heating to 293 K (a), 703 K (b), 1143 K (c) and 1273 K (d).

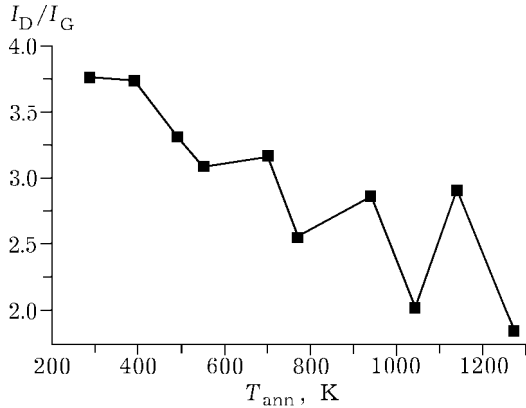


Fig. 3. Changes of the I_D/I_G ratio with the annealing temperature.

The evolution of the structure of SiCN film synthesized at 873 K was investigated during thermal annealing also by *in situ* Raman spectroscopy in the region of 600–2000 cm^{-1} in a special thermal module of the Raman spectrometer Triplemate, Spex. Annealing was carried out at temperature changed from 293 to 1273 K with a step of 100 K; annealing time was 10–15 min for each temperature. The evolution of the Raman spectra and the ratios I_D/I_G calculated from these spectra, accompanying the increase of annealing temperature, are shown in Figs. 2 and 3. One can see that the trend of decreasing the intensity of I_D band is conserved with increasing annealing temperature, though numerical values are somewhat different due to the changes of experimental conditions.

The annealing causes the decrease of the amorphous constituent and the increase of the graphite-like mode G, which is likely to be due to the growth of nanocrystals present in as-grown film.

Electron-microscopic studies

The microstructure of the SiCN film synthesized at 773 K was investigated by means of the high-resolution transmitting electron

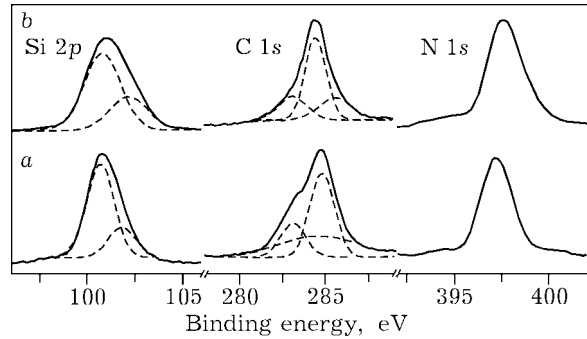


Fig. 4. N 1s, C 1s and Si 2p XPS spectra of SiCN film grown at 773 K (a) and annealed at 1123 K (b).

microscopy (HREM). Electron patterns of the local region (SAED) consists of the halo and weak diffraction rings pointing to the presence of the amorphous and crystalline constituents in the film. HREM image of the cross section of the sample shows the presence of nanocrystals with a size < 2 nm distributed over the film volume.

XPS studies

XPS was used to detect the elemental composition of the silicon carbonitride films before and after annealing. Relative concentrations of the main elements and the Auger parameter (difference in energy between the Auger electrons and photoelectrons) are shown in Table 2. Attention should be paid to the presence of oxygen impurity in films; its concentration is less than 10 %. The concentration of the main elements remained practically unchanged during the annealing, but Auger parameter increased substantially. It should be noted that this parameter is very sensitive to the changes of chemical bond. For the investigated sample, it was intermediate between $\alpha\text{-Si}_3\text{N}_4$ (1714.1), $\alpha\text{-SiC}$ (1714.1) and $\alpha\text{-Si}$ (1716.1).

In order to reveal chemical bonds present in both as-grown and annealed samples of SiCN, we analyzed the XPS spectra of N 1s, C 1s and Si 2p shown in Fig. 4. The spectra of

TABLE 2

Relative concentration of elements in deposited and annealed SiCN films

Film	Si	N	C	O	Auger parameter
Deposited at 773 K	0.29	0.13	0.50	0.08	1714.6
Deposited at 1123 K	0.28	0.12	0.50	0.10	1715.1

C 1s and Si 2p were approximated by Gaussian curves. From the spectra of Si 2p, binding energies of 100.7 eV was obtained for the as-grown film, and 100.8 eV for the annealed one (Si-C bonds [5, 7, 8]) and 101.8 eV for the as-grown film, 102.2 eV for the annealed one (Si-N bonds [5, 7, 8]). For the C 1s spectra, binding energies of 283.1, 284.7 and 285.8 eV were obtained for the as-grown film; 283.1, 284.5 and 285.7 for the annealed film, corresponding to the energies of the bonds Si-C, C-C and $C(sp^3)$ -N [7-8]. The N 1s peak was approximated by one curve; its bond energy is 397.1 eV, corresponding to the Si-N bond. Analyzing the data obtained, one can assume that the formation of the bonds of silicon with nitrogen and silicon atoms occurs in silicon carbonitride films. The annealing of films results in the decrease of the intensity ratio I_{Si-C}/I_{Si-N} 1.3 times; the ratio of the intensities $I_{Si-C}/I_{C(sp^3)-N}$ increases twice. The annealed samples are close to silicon nitride in their composition but they are likely to have the inclusions of Si-Si broken bonds, which increases Auger parameter and the refractive index of films.

X-ray structural investigations

The studies of the structure and phase composition of as-grown and annealed films was carried out by XRD using synchrotron radiation. Typical Θ - 2Θ diffraction patterns of silicon carbonitride films synthesized at 523 and 1023 K and the film annealed at 1123 K are shown in Fig. 5. These diffraction patterns contain reflections that can be assigned to the pseudo α - Si_3N_4 phase [8]. Besides the reflections of the α - Si_3N_4 phase, the diffraction patterns contain unknown reflections in the region of small diffraction angles; they are marked with "?" in Fig. 5; they do not correspond to the known phases of silicon carbide, silicon nitride and graphite.

Interplanar distances d_{hkl} calculated from the diffraction patterns of the investigated sample, together with the d_{hkl} of the standard phase α - Si_3N_4 , are shown in Table 3. One can see that the films SiCN and α - Si_3N_4 have somewhat similar structures, though carbon is present in the films at a high level. Carbon

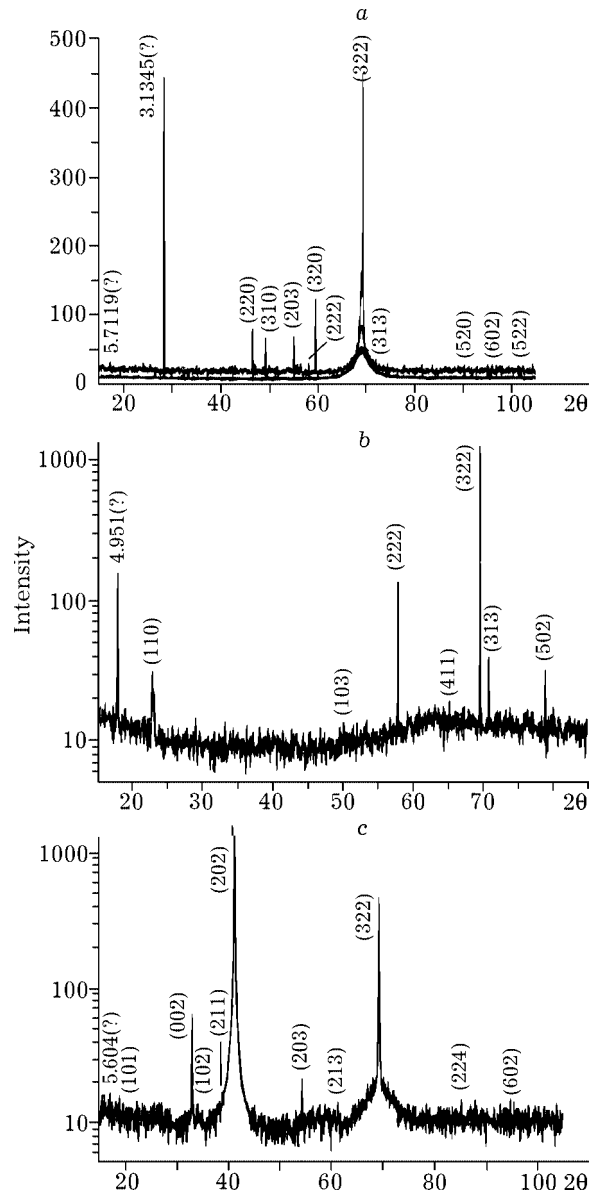


Fig. 5. X-ray diffraction patterns of SiCN films deposited at 523 (a) and 1023 K (b) and annealed at 1123 K (c).

atoms very likely substitute isovalent silicon atoms in the points of the α - Si_3N_4 lattice without changes in lattice parameters, due to the similarity of their atomic radii.

High-temperature annealing of the samples results in substantial increase of the intensity of the corresponding reflections in the diffraction patterns and in the appearance of some additional peaks.

Thus, the reflections (002), (102), (211), (203) corresponding to low-indexed planes of the α - Si_3N_4 phase are exhibited only in the case of the annealed samples.

TABLE 3

Interplanar distances d_{hkl} in SiCN films: synthesized at 523 and 1023 K, and annealed at 1123 K; as well as in α -Si₃N₄ films [8]

SiCN			α -Si ₃ N ₄ [8]	
523 K	1023 K	1123 K		{hkl}
	5.7119	5.604	–	–
4.9511			–	–
3.8885			3.887	110
	3.1345		–	
		2.712	2.823	002
		2.6382	2.599	102
		2.316	2.32	211
		2.189	2.158	202
	1.9434		1.9370	220
	1.8450		1.8640	310
1.8158			1.806	103
	1.6612	1.688	1.680	400
1.5913	1.5828		1.5960	222
	1.5475		1.5402	320
		1.5109	1.507	213
1.4287			1.4180	411
1.3496	1.3522	1.356	1.3510	322
1.3280	1.3321		1.321	313
1.2116			1.2130	502
		1.1374	1.1382	224
	1.0739		1.0758	520
	1.0443		1.0403	602
	0.9925		1.0048	522

Using the scheme of recording with the grazing incident beam of synchrotron radiation along the sample surface (2Θ scanning) we obtained diffraction patterns on the basis of which we carried out the estimations of the size of microcrystals in silicon carbonitride films before and after annealing, using the known Debye – Scherrer equation. The size of nanocrystals in the synthesized SiCN films was 2–3 nm, which agreed well with the data of electron microscopy. The size of microcrystals increases up to 100 nm during annealing.

The use of the Image Plate method allowed us to determine the presence of point defects with high intensity, which points to the possibility of the formation of oriented crystals during high-temperature annealing.

CONCLUSIONS

Thin films of the new ternary material, silicon carbonitride, were synthesized by

RPECVD using the organometallic compounds, hexamethyldisilazane. As a result of the physicochemical investigations using ellipsometry, IR and Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffractometry using synchrotron radiation, and high-resolution transmittance microscopy (HREM and SAED), it was established that chemical bonds between silicon, nitrogen and carbon atoms are formed. The phase composition of the grown silicon carbonitride films corresponds to the pseudo α -Si₃N₄ phase in which the substitution of silicon atoms by the isovalent carbon atoms is possible in the points lattice. As-grown films contain nanocrystals 2–3 nm in size distributed in the amorphous matrix. High-temperature annealing leads to decreasing the amorphous character of the film and forming the oriented microcrystals with the size of up to 100 nm.

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