

Functional Nanocrystalline Films of Silicon Carbonitride

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Abstract

The films of a new ternary compound, silicon carbonitride, were synthesized by means of plasma enhanced deposition (PECVD) using hexamethyldisilazane $\text{Si}_2\text{NH}(\text{CH}_3)_6$ as the precursor. Different investigation methods, namely, IR and Raman spectroscopy, XPS, ellipsometry, electron microscopy, including high-resolution methods (HRTEM, SAED) were applied to study physico-chemical properties of the films. Much attention was paid to the development of the X-ray phase analysis methods involving synchrotron radiation to determine the structure and phase composition of thin films. It was established that the silicon carbonitride films contain nanocrystals 2–5 nm in size distributed over the amorphous matrix.

INTRODUCTION

Search for new superhard and chemically inert materials is one of the main problems of modern materials science. Among possible candidates, there are carbon nitride and related compounds belonging to the ternary system Si–C–N. Silicon carbonitride films seem especially promising in this sense. These films possess important properties, for example high mechanical strength, good resistance to oxidation, high thermal conductivity, low thermal expansion and high hardness. These properties make SiCN suitable for use in oxidative and high-temperature environment. It is assumed that the unique physicochemical properties of silicon carbonitride are due to the presence of chemical bonds between the Si, C, N atoms in ternary compounds, in contrast with a mechanical mixture of phases Si_3N_4 –SiC, and due to the ability to form nanocrystalline films distinguished by improved mechanical, electrical and magnetic properties in comparison with usual materials.

Until recently, the major attention of the researchers has been paid to the problems connected with the synthesis of SiCN using gas mixtures containing inorganic compounds of nitrogen and silicon: $\text{SiCl}_4 + \text{NH}_3 + \text{C}_3\text{H}_8 + \text{H}_2$,

$\text{Si}(\text{CH}_3)_4 + \text{NH}_3 + \text{H}_2$ (Ar), $\text{SiH}_4 + \text{NH}_3$ (or N_2H_4) + $\text{CH}_4 + \text{H}_2$ (Ar) [1–9]. Since these compounds exhibit increased toxicity and are explosive, researchers are searching for new precursors in order to improve the safety of the synthesis. At present, optimal compounds for these purposes are organoelemental compounds like silazanes $\text{R}_n\text{Si}-\text{NH}-\text{SiR}_n$, because their molecules contain all the elements necessary for the synthesis of SiCN. Hexamethyldisilazane $(\text{H}_3\text{C})_3\text{Si}-\text{NH}-\text{Si}(\text{CH}_3)_3$ is one of important precursors in obtaining functional materials of the system Si–C–N from gas phase [3–5]. Various methods of film deposition may be involved: deposition from the gas phase (CVD) [1], photostimulated (laser-induced) deposition from the gas phase (LICVD) [3] and different versions of plasma-enhanced deposition (PECVD) [2, 4–7, 9].

When investigating the obtained thin layers, the major attention was paid to the studies of their chemical composition by means of Auger spectroscopy and XPS, IR and Raman spectroscopy, as well as the morphology and microstructure by means of electron microscopy.

Unfortunately, the structure and phase composition of silicon carbonitride films are studied insufficiently, perhaps because thin films of light elements have small mass (10^{-5} – 10^{-6} g).

In this case, the usual method of X-ray structural analysis does not give reliable experimental data. The use of the synchrotron radiation (SR) as the initial beam in the diffraction experiments allows overcoming these difficulties and obtaining the necessary structural data.

EXPERIMENTAL

Silicon carbonitride films were synthesized by means of the remote plasma (RPECVD) using hexamethyldisilazane as the volatile single-source precursor, and helium [4, 5]. Helium was used as an activator of the gas mixture in plasmachemical processes. Total pressure in the system was $6 \cdot 10^{-2}$ Torr, synthesis temperature was 473–1173 K. Single crystal plates of silicon and gallium arsenide, plates of optical quartz polished from both sides were used as substrates.

The thickness and refractive index of the grown layers were measured using ellipsometry. IR and Raman spectroscopic studies within the range $200\text{--}4000\text{ cm}^{-1}$ were carried out to determine the character of chemical bonds in the layers. To determine the chemical composition of the layers and the character of chemical bonds in the material, X-ray photoelectron spectroscopy (XPS) was also used. Measurements were made with the Surface Science Center (SSC) instrument of the RIBER Company with the MgK_α radiation (1253.6 eV); the resolution of the analyzer was 0.5 eV. The surface of films was purified by bombarding the surface with Ar^+ ions with the energy of 3 keV falling at the sample plane at an angle of 24° . To study the microstructure of films, transmittance electron microscopy was used (HREM and SAED) with the help of the JEM2010 instrument.

X-ray diffraction measurements were carried out at the station "Anomalous scattering" of the counter-beam accelerator VEPP-3M of the International Siberian Centre of Synchrotron radiation (Institute of Nuclear Physics, SB RAS, Novosibirsk, Russia). The station is equipped with the basic monochromator Si [111] and the analyzer crystal Ge [111]. The wavelength of radiation can be varied within the

range 0.6–4.0 Å within the energy range 4–20 keV. In our experiments, the wavelength was constant (1.5405 Å). To record diffraction patterns, three methods were used:

1) θ – 2θ scanning (the geometric scheme of Bragg – Brentano) to study thin films that are ordered (textured) crystalline phases, or to study polycrystalline thick films;

2) 2θ scanning (a scheme with the grazing incident SR beam along the sample surface) to study polycrystalline thin layers;

3) Image Plate to determine diffraction reflections of both the polycrystalline and the oriented phases.

RESULTS AND DISCUSSION

The thickness of the synthesized SiCN films was 200–3000 nm, refractive index varied from 1.8 to 3.2 depending on the synthesis conditions. These films are transparent in the visible region of the spectrum (transmission coefficient is about 80 % at $\lambda = 600\text{--}700\text{ nm}$). Microhardness of the sample grown at 773 K is 2500 kg/mm². Specific resistance of the films changes from $3 \cdot 10^{10}$ to $1 \cdot 10^{14}\ \Omega\text{ cm}$.

The IR spectroscopic data

IR spectra of the films synthesized at low temperatures (523–773 K) contain a broad absorption band in the region $600\text{--}1150\text{ cm}^{-1}$ and a narrow peak at 1250 cm^{-1} (Fig. 1, a). The narrow peak corresponds to the C–N bond, while the broad band can correspond to the vibrations of the Si–C ($800\text{--}850\text{ cm}^{-1}$) and Si–N ($900\text{--}960\text{ cm}^{-1}$) bonds. The IR spectra of silicon carbonitride synthesized at higher temperature (773–1173 K) are similar to the spectrum of single-crystal $\alpha\text{-Si}_3\text{N}_4$, but a broad absorption band at $700\text{--}1100\text{ cm}^{-1}$ can also include the peak corresponding to the vibrations of the Si–C bond (see Fig. 1, b). Besides, all the IR spectra contain a narrow peak at 620 cm^{-1} that corresponds to disordered graphite-like structure. These results point to the formation of bonds between all the elements of the layer, which can be observed in a compound of the type Si–C–N.

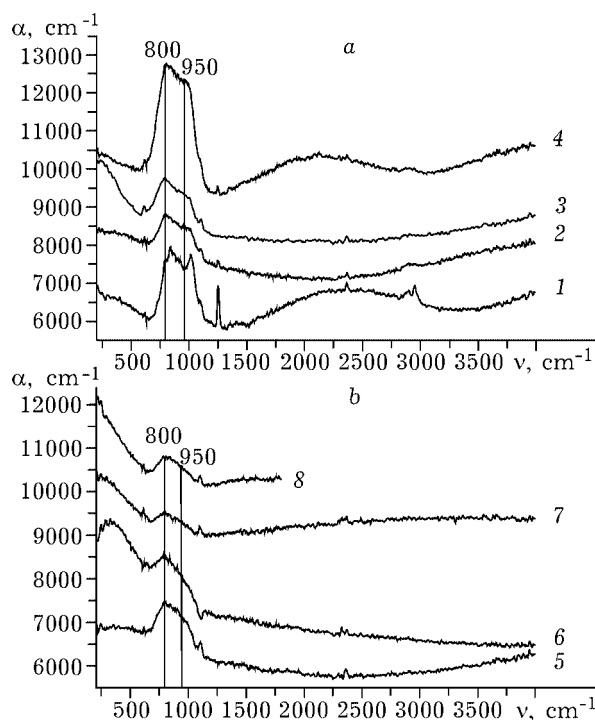


Fig. 1. IR spectra of the silicon carbonitride films synthesized at temperature, K: 523 (1), 623 (2), 773 (3), 873 (4), 923 (5), 973 (6), 1023 (7), and 1073 (8).

Raman spectral data

The Raman spectra of low-temperature films 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. The Raman spectra of high-temperature films contain a broad band in the region 1200–1600 cm^{-1} . This feature makes these spectra similar to the spectra of amorphous carbon, boron carbonitride, carbon nitride, i.e. materials containing carbon and exhibiting two broad bands centred near 1360 and 1540 cm^{-1} (D and G bands of the disordered sp^2 carbon).

Chemical composition of the films

The determination of the chemical composition of the SiCN films was carried out by means of XPS with calculations of the Auger parameter. Relative concentrations of the main elements in films obtained at different temperatures are shown in Table 1.

XPS analysis showed that the films were contaminated with oxygen at a level below

TABLE 1

Relative concentrations of elements in the SiCN films

T, K	O	N	C	Si	Auger parameter
523	0.09	0.12	0.53	0.26	1714.2
773	0.08	0.13	0.50	0.29	1714.6
1123	0.04	0.12	0.56	0.28	1715.4

10 %. The concentrations of the major elements change only weakly with the growth of the synthesis temperature; however, Auger parameter increases monotonously. This fact is likely to be explained by the increase of $-\text{Si}-\text{Si}-$ cluster content of the films synthesized at high temperature (Auger parameter for $\alpha\text{-Si}$ is 1716.1 [8]). It is in good correlation with the data of ellipsometry according to which the refractive index of the film also increases up to 3.2 at 1123 K (for $\alpha\text{-Si}$, $n = 3.56$).

The analysis of chemical bonds by means of XPS

The analysis of N 1s, C 1s and Si 2p XPS peaks of silicon carbonitride films was carried out depending on the growth temperature. High-temperature silicon nitride and thermal silicon oxide were used as reference compounds. The purification of the film surface by Ar^+ ions was not carried out in this case, in order to avoid preferential spraying of nitrogen. The centres bond energies of the mentioned XPS peaks are shown in Table 2.

In [3, 9], chemical binding of silicon atoms with carbon and nitrogen atoms is described by Si–C bonds with the energy 100.7 eV and Si–N bonds with the energy 101.7 eV. In [3], a review of the XPS data for silicon nitride, silicon carbide and Si–C–N powder is presented. The range of bond energies reported by

TABLE 2

Centred bond energies Si 2p, C 1s and N 1s of the X-ray photoelectron spectral peaks of SiCN films, eV

T, K	Si 2p	C 1s	N 1s
523	101.1	284.1	397.5
773	100.8	284.8	397.0
1123	101.3	284.3	397.7

these authors is 101.3–102.9 eV for Si–C, 101.8–102.1 eV for Si–N and 101.6–103.3 eV for Si–C–N powder. Analyzing these data one can conclude that the formation of silicon bonds with nitrogen and carbon atoms occurs in the silicon carbonitride films. Comparing bond energies of C 1s in graphite 284.5 eV and silicon carbide 238.8 eV with the values listed in Table 2 we assume that in this case carbon forms C–Si and/or C–C bonds. XPS spectrum of the N 1s, similarly to the previous spectra, contains more than one Gaussian peak with points to the complicated structure of the bond between the substituted atoms of silicon, carbon and nitrogen [8].

Electron-microscopic studies

The microstructure of SiCN films grown on GaAs (100) was investigated with the help of the high-resolution transmittance electron microscopy (HREM). The films synthesized at low temperatures (below 600 K) exhibit a diffuse halo in the selective area electron diffraction (SAED), while the HREM image is a typical appearance of the amorphous material. The electron diffraction patterns of the local region of the film obtained at high temperature consists of halo and weak diffraction rings pointing to the presence of the amorphous and crystalline constituents of the film (Fig. 2). HREM image points to the presence of nanocrystals with a size of <3 nm distributed over the amorphous matrix.

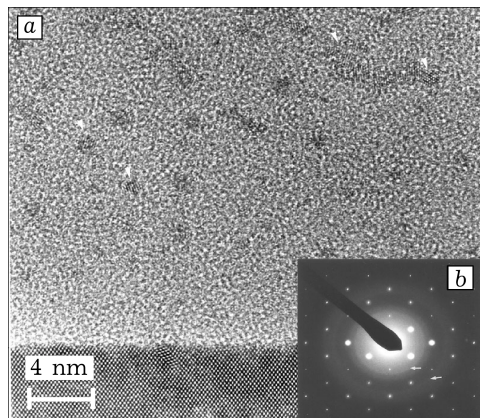


Fig. 2. The microstructure of SiCN film grown at 773 K: a – HREM image of the cross section; b – microelectron diffraction pattern of the local region.

X-ray phase analysis: θ – 2θ scanning

In order to study the structure and phase composition of thin SiCN films, the procedures of registering and recording the diffraction spectra are developed. As a rule, the diffraction spectra obtained by θ – 2θ scanning have only a few reflections; they are often of high intensity and narrow profile (0.05 – 0.1°) because of the formation of texture in thin films. In order to increase the number of reflections, diffraction spectra were multiple-recorded at different angles of the sample turnover with respect to the initial SR beam; the obtained diffraction patterns were summed. It was determined that the SiCN films synthesized within the whole temperature range 473–1173 K consist of nanocrystals with the composition close to that of the bulk phase α -Si₃N₄ [10]. Besides the reflections of the α -Si₃N₄ phase, the diffraction patterns contain unknown reflections in the region of small diffraction angles; they are marked with the «?» sign. These reflections do not correspond to the positions of the reflections of the known phases of silicon carbide, silicon nitride and graphite.

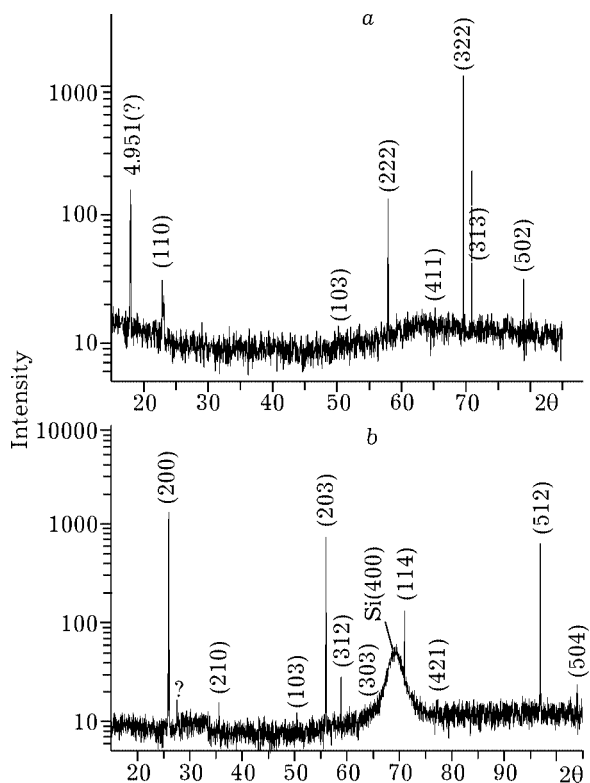


Fig. 3. Diffraction spectra of the SiCN films grown at 523 (a) and 1073 K (b). $\lambda = 1.5405$ Å.

TABLE 3

Interplanar distances for the SiCN films and α -Si₃N₄ [10]

SiCN		α -Si ₃ N ₄ [10]	
523 K	1023 K		$\{hkl\}$
	5.7119	–	
4.9511		–	–
3.8885		3.887	110
	3.1345	–	–
	1.9434	1.9370	220
	1.8450	1.8640	310
1.8158		1.806	103
	1.6612	1.680	400
1.5913	1.5828	1.5960	222
	1.5475	1.5402	320
1.4287		1.4180	411
1.3496	1.3522	1.3510	322
1.3280	1.3321	1.321	313
1.2116		1.2130	502
	1.0739	1.0758	520
	1.0443	1.0403	602
	0.9925	1.0048	522

The comparison of interplanar distances shows that d_{hkl} of the hexagonal lattice of silicon carbonitride and the α -Si₃N₄ phase [10] are close to each other within the limits of the experimental error (Table 3). There are some differences in the diffraction patterns obtained from thin films, compared to the standard α -Si₃N₄ structure, namely:

- 1) the intensity of $\{hkl\}$ reflections differs from the intensity of the corresponding reflections of the α -Si₃N₄ phase;
- 2) the spectra of SiCN contain unknown additional reflections in the region of small diffraction angles. These results allow us to conclude that SiCN films have a structure similar to that of α -Si₃N₄. It is usually referred to as pseudo α -Si₃N₄ phase [6, 7].

SiCN nanocrystals contain carbon atoms that have insignificant effect on the lattice parameters because atomic radii of carbon and silicon are close to each other. Carbon atoms may substitute silicon atoms in the lattice without changing valence because Si and C atoms both belong to the IV group of the Periodic Table.

X-ray phase analysis: 2 θ scanning

The formation of the polycrystals of α -Si₃N₄ phase was detected by this procedure. The size of crystals was estimated from the broadening of the diffraction peak, by using the known Debye – Scherrer equation. Mean size of nanocrystals was 2 to 9 nm depending on growth temperature.

Image Plate

This method of registering the reflected SR beam allows obtaining more complete diffraction picture. Some number of high-intensity point reflections was detected with the help of this method. The presence of these reflections points to the possibility of the formation of oriented crystals in the film. The mentioned phenomenon is typical for high-temperature SiCN films.

CONCLUSIONS

The films of the new ternary compounds, silicon carbonitride, were synthesized by RPECVD using volatile non-traditional organoelemental compounds. These films are transparent in the visible region of the spectrum; they possess high resistance and micro-hardness. On the basis of the results of X-ray photoelectron investigations, it can be concluded that silicon atoms of the silicon carbonitride are mainly bound with nitrogen and carbon atoms. It is stated that the new material contains nanocrystals distributed over the amorphous matrix of the film. The nanocrystalline component is the pseudo α -Si₃N₄ phase that may contain carbon atoms; their presence has insignificant effect on the changes of lattice parameters of the α -Si₃N₄ phase due to close atomic radii of carbon and silicon. Carbon atoms may substitute silicon atoms in the lattice points of α -Si₃N₄ without any valence changes because Si and C atoms belong to one group. The size of these nanocrystallites increases from 2–3 to 7–9 nm with increasing synthesis temperature.

New functional materials based on silicon carbonitride are considered as promising pro-

protective coatings because of their unique physicochemical and tribological properties.

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