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Crystalline carbon nitrides: thin films and bulk samples

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A new method was developed for the preparation of bulk samples of crystalline carbon nitride on exposure of an amorphous nitrogen- and carbon-containing material to high temperature and ultrahigh pressure in the presence of crystallization seeds. Amorphous carbon nitride whose composition was close to C_3N_4 was used as a starting material. Thin films of crystalline carbon nitrides prepared by the laser-electric discharge method were used as crystallization seeds.

Key words: inorganic synthesis, carbon nitrides, seed crystallization, ultrahigh pressure, thin films, laser ablation, electric discharge nitrogen plasma.

The results of *ab initio* quantum-chemical calculations provide evidence for the possible existence of a new inorganic compound, *viz.*, crystalline carbon nitride β-C_3N_4. Its structure is analogous to that of β-Si_3N_4 built from the N tetrahedra. The new compound is comparable to diamond in hardness.[1] Theoretical calculations also predicted other modifications of crystalline carbon nitride, *viz.*, α-C_3N_4, cubic, pseudocubic, and graphite-like modifications.[2—4] The structure of α-C_3N_4 is analogous to that of α-Si_3N_4 in which, unlike β-Si_3N_4, only half of the N atoms have a planar configuration, whereas the remaining N atoms have a pyramidal configuration. Cubic carbon nitride is structurally similar to willemite II, which is the Zn_2SiO_4 phase prepared at high pressure. Pseudocubic carbon nitride has a defect sphalerite structure of the α-$CdIn_2Se_4$ type. According to the results of calculations,[2—4] carbon nitride with a graphite-like structure must be thermodynamically most stable, the hardness of the cubic modification is comparable with or even slightly higher than the hardness of β-C_3N_4, and the pressure required for the direct transformation of graphite-like carbon nitride into the cubic modification is 12 GPa.

The results of experimental studies on the synthesis of crystalline β-C_3N_4 were reported in *ca.* 200 publications, including several reviews.[5—9]

The various known procedures for the synthesis of crystalline carbon nitride[9] made it possible to prepare

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mainly thin films in which small amounts of crystalline nitrogen-carbon compounds were present as inclusions in an amorphous nitrogen-carbon matrix. These inclusions proved to be[9] the theoretically predicted carbon nitrides C_3N_4 and among them its β modification.

The nitrogen content in thin films appeared to be smaller than that calculated for the C_3N_4 composition. This result was attributed to the fact that the nitrogen content in an amorphous nitrogen-carbon matrix is smaller than that in C_3N_4. It was also mentioned that films can be contaminated with carbon.[10]

Later on,[11,12] it was established that the sizes of carbon-nitride crystallites with a hexagonal structure in an amorphous nitrogen-carbon matrix are 30±10 nm. The experimental space distances are in good agreement with the theoretically calculated values for β-C_3N_4. The measured N : C molar ratio is close to that corresponding to the C_3N_4 formula.

To our knowledge, bulk samples of crystalline carbon nitride were synthesized in only a few studies. Thus, powders prepared by laser pyrolysis of a mixture of acetylene, nitrous oxide, and ammonia[13] and by the reaction of 1,3,5-trichlorotriazine ($C_6N_3Cl_3$) with lithium azide (Li_3N) in a benzene solution at 350 °C in an autoclave[14] contained crystalline carbon nitride β-C_3N_4 (according to the results of X-ray diffraction studies, photoelectron spectroscopy, and IR spectroscopy). However, the nitrogen percentage in these powders (0.41 and 0.39 at.%, respectively[13,14]) appeared to be lower than that corresponding to the C_3N_4 stoichiometry (0.57 at.%). This indicates that not only C_3N_4 but also other nitrogen-containing compounds were formed as products of the synthesis.

In the present study, we used a new approach to the synthesis of bulk samples of crystalline carbon nitride based on exposure of an amorphous nitrogen- and carbon-containing material to ultrahigh pressure and temperature in the presence of crystallization seeds. It was proposed that thin films containing crystalline carbon nitrides should be used as such crystallization seeds.[15] The latter were synthesized according to a new laser-electric discharge method, which differs from the methods used previously in that the products of laser ablation and cathode sputtering of a graphite electrode are simultaneously injected into the electric discharge nitrogen plasma.

Experimental

Synthesis of thin films containing carbon nitrides. An apparatus was designed and built for the preparation of films by the laser-electric discharge method (Fig. 1). The apparatus consists of a reactor, a vacuum system, a high-voltage power-supply system, and a laser radiation source.

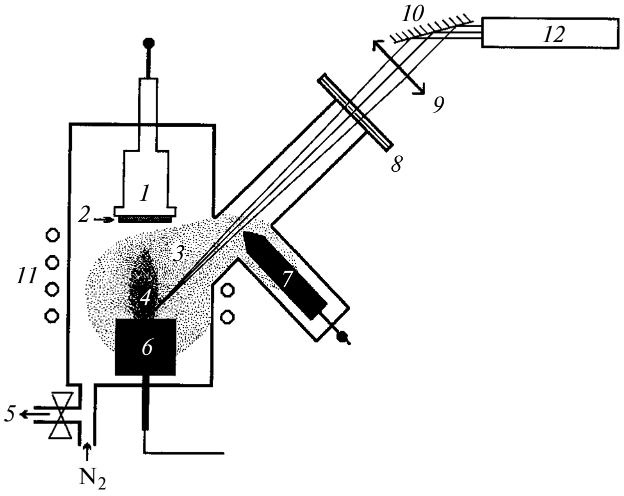

Fig. 1. Scheme of the apparatus for the preparation of crystalline carbon nitride films: *1*, holder; *2*, substrate; *3*, discharge zone; *4*, laser plume; *5*, flange for attaching a vacuum pump; *6*, cathode; *7*, anode; *8*, window; *9*, lens; *10*, mirrow; *11*, electromagnet coil; *12*, Nd : YAG laser.

The heat-resistant glass reactor has an optically transparent window for the laser radiation, ground sockets for the insertion and replacement of electrodes, a substrate, and a target made of a material, which evaporates into the discharge zone on exposure to laser radiation. A graphite electrode serving as a cathode is used as the target. The substrate is fixed in such a way that the distance from the substrate to the target can be varied and the substrate can be replaced. The substrate was made of a thin single-crystal silicon plate. The crystallographic orientation of its (100) plane should be favorable for the formation of crystalline carbon nitride β-C_3N_4.

A specially-designed system provides evacuation of the reactor up to ~10^{-3} Torr and controlled filling of the latter with gases (nitrogen, inert gas).

The electric discharge was initiated and all operations with the latter were carried out with the use of a specially-designed high-voltage power-supply system. This system enables one to apply a constant voltage (≤10 kV) to electrodes and provide the current in the discharge of ≤1 A. A solid-state Nd : YAG laser operating in the Q-switched mode was used as a source of laser radiation (energy was ≤5 mJ, wavelength was 532 nm, pulse frequency was 1 Hz).

The laser radiation was focused onto the cathode placed in such a way that the laser plume generated on its surface was introduced directly into the electric discharge plasma. The electrodes were spaced ~4 cm apart. The compounds, which were generated by the reactions of products of laser ablation and cathode sputtering of the graphite electrode (carbon atoms and clusters) with components of the gas discharge plasma (atoms, ions, and active nitrogen molecules), were deposited on the substrate. The distance between the substrate and the cathode was ~2 cm. The time of deposition of one film was ~2 h.

The films thus prepared as well as bulk samples synthesized further were studied by the following techniques: a) IR spectroscopy (Specord M-80 spectrometer, Karl Zeiss); b) secondary ion mass spectrometry (SIMS) (Cameca Ims-4f, France);

c) X-ray photoelectron spectroscopy (XPS) (Perkin—Elmer PHI-5400 spectrometer); d) Auger electron spectroscopy (JEOL JAMP-10, Japan); e) X-ray diffraction (XRD) (DRON-2, Cu-Kα radiation, Russia); f) scanning electron microscopy (SEM) (JEOL JSM-35CF, Japan); g) selected area transmission electron diffraction (STED) (JEM-2000-XII, Japan).

The properties of the films prepared under exposure of the carbon target in the reactor to laser radiation were compared with those synthesized without the use of laser radiation. The SIMS studies demonstrated that film deposition proceeded at an approximately twofold rate in the experiments with the use of the laser, the time of the synthesis being the same. According to the XPS data, the character of bonds formed by the C and N atoms in the films prepared with the use of laser radiation differs from that in the films prepared without exposure to laser radiation. The SEM studies showed that larger spherical particles occurred on the surfaces of the films prepared under exposure to laser radiation.

The optimum characteristics of the discharge (nitrogen pressure in the reactor was ~0.1 Torr, electrode voltage was ~2.5 kV), which provide the maximum rate of film deposition, were determined by the SIMS method.

After pre-cleaning of the substrate surface by solvents in an ultrasonic bath (15 min) followed by electric discharge cleaning (45 min), ordered particles were observed (SEM) on the film surfaces (Fig. 2). The studies of the side-views of silicon plates with deposited films also demonstrated that the above-described cleaning of the silicon plate surface gave rise to denser deposited films compared to those prepared without pre-cleaning of the substrate surface (Fig. 3).

According to the XRD data, the formation of crystalline carbon nitride films was observed only on Si(100) substrates (but not on Si(111)).

Preparation of bulk samples. Bulk samples of crystalline carbon nitrides were synthesized by thermobaric treatment of amorphous carbon nitride with the use of films prepared by the laser-electric discharge method as crystallization seeds. In the experiments on thermobaric treatment of amorphous carbon nitride, we used films synthesized by applying the magnetic field with the flux density of ~10 mT to the nitrogen plasma.

The thermobaric experiments were carried out on high-pressure apparatus in toroid chambers[16] in which amorphous carbon nitride was placed between Si(100) plates with deposited films. The films were in direct contact with amorphous carbon nitride. The thermobaric studies were carried out at 10—77 kbar and 350—1200 °C.

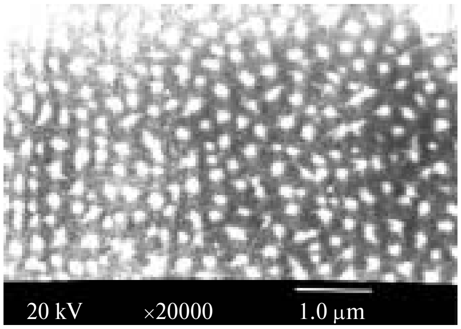

Fig. 2. The SEM image of the surface morphology of a carbon nitride film (magnification by 20000 times) after cleaning of a Si(100) substrate.

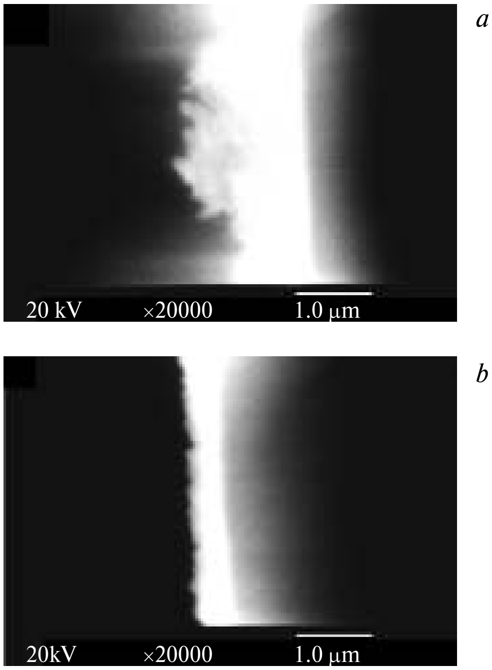

Fig. 3. Photographs of the side-views of silicon substrates with deposited films of nitrogen-carbon compounds without cleaning (*a*) and after cleaning (*b*) of the Si surface. A silicon plate is shown at the right of the photograph; the paler zone in the center of the photograph corresponds to the film synthesized.

Amorphous carbon nitride of composition $C_3N_{4.2}$ was synthesized by thermal decomposition of mercury thiocyanate at 180 °C under inert gas.[17] The composition and structure of the amorphous carbon nitride were determined by elemental analysis and IR spectroscopy.[17]

In the experiments with the use of silicon plates without deposited nitrogen-carbon films, crystallization of amorphous carbon nitride did not occur. Bulk samples of crystalline carbon nitrides were prepared with the use of plates with deposited films prepared by the laser-electric discharge method. The optimum conditions of the transformation of amorphous carbon nitride into a crystalline product were as follows: the pressure was 70 kbar, the temperature was 550 °C, the time of exposure was 2 h. An increase in the temperature led to graphitization of samples. At lower temperature as well as at smaller times of exposure to high pressure, no noticeable conversion of an amorphous product was observed.

Crystalline samples with a size of ~30 mm^3 prepared from amorphous carbon nitride were withdrawn from the container and separated from the silicon plates. The samples possessed abrasive properties, *e.g.*, made marks on glass.

Results and Discussion

Characterization of films. *IR spectroscopy.* The IR spectra of films have three broad bands at 1050—1650, 1750—2400, and 2550—3650 cm^{-1} with maxima at 1620, 2310, and 3280 cm^{-1}, respectively, and a low-intensity band at 600 cm^{-1}. Based on analysis of the vibration frequencies (see, for example, Refs. 9, 12, and 18), it can be stated that bands at 1050—1650 cm^{-1} belong to C≡N, C=C, and C—N stretching vibrations, bands at 1750—2400 cm^{-1} are attributed to C≡N stretching vibrations, and bands at 2550—3650 cm^{-1} belong to C—H, N—H, and O—H stretching vibrations and vibrations of the NH_2 group. The band at 600 cm^{-1} was not assigned. Analysis of the IR spectra led to the conclusion that the films thus synthesized contained compounds with the nitrogen—carbon bonds.

The bands associated with the C—H, N—H, O—H, and NH_2 stretching vibrations are attributable to the fact that the films contained compounds generated either due to the oxygen and hydrogen impurities in nitrogen (used for the synthesis of carbon nitride films) or to atmospheric moisture and oxygen (in the preparation of the samples and IR spectroscopic studies).

Auger spectroscopy. The Auger spectra of films have only C_{KLL} and N_{KLL} peaks (Fig. 4). The nitrogen content in the films, which was calculated from the intensity ratio of these peaks taking into account the sensitivity factors, was ~24 at.%.

X-ray diffraction. The X-ray diffraction patterns show the (100) reflection at 2θ = 68.9° caused by the single-crystal silicon substrate and two reflections at 2θ = 15.8 and 32.9°. We assigned these reflections to microcrystals of carbon nitrides oriented along the (*h*00) direction. The space distances calculated from 2θ = 15.8 and 32.9° (*d* = 5.61 and 2.72 Å, respectively) are in good agreement with the theoretical space distances in crystalline C_3N_4.[19,20]

X-ray photoelectron spectroscopy. Studies of the films by the XPS method at 400 eV for the N(1s) atom and at 285 eV for the C(1s) atom demonstrated that the films contained a compound with the C—N bonds characteristic[21—23] of the β-C_3N_4 structure, the fraction of this compound being substantial. The nitrogen content in the films determined by XPS was ~20 at.%.

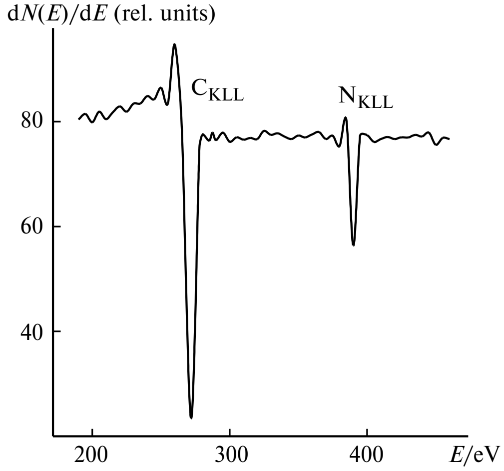

Fig. 4. Auger spectrum of nitrogen-carbon films.

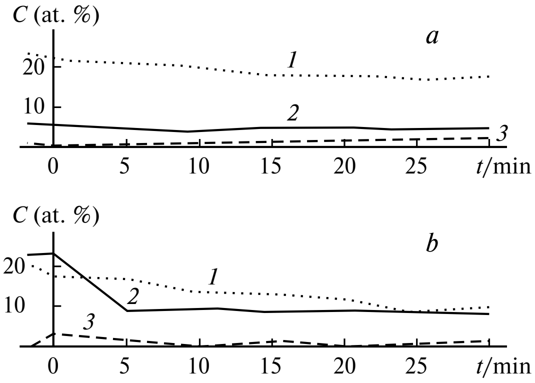

Fig. 5. Distribution of nitrogen (*1*), oxygen (*2*), and silicon (*3*) over thickness (according to XPS) of films prepared by the laser-electric discharge method (*a*) and using electric discharge without exposure to laser radiation (*b*).

The distribution of the N, O (unbound), and Si atoms with film thickness was studied by XPS using surface etching with an argon-ion gun. It was demonstrated (Fig. 5, *a*) that the N content (~20 at.%) in the films prepared by the laser-electric discharge method remained virtually unchanged with film thickness when the time of etching was <90 min. The O (unbound) atoms were also uniformly distributed over the film thickness, and the O content was ~4 at.%, which was consistent with the data published in the literature.[24]

In the films prepared with the use of only discharge (Fig. 5, *b*), the nitrogen content varied with thickness from 17 to 10 at.%. The oxygen content in the film was much higher (~10 at.%), and the oxygen content on the surface was higher than 20 at.%. The study of the surface layers of the films showed that the bands belonging to N(1s) and C(1s) in the photoelectron spectra of these layers are unsymmetrically broadened due to the presence of the C—O and N—O bonds. The oxygen-containing layer was readily removed by surface etching with an argon-ion beam.

Secondary ion mass spectrometry. The study of the distribution of the C and N atoms with film thickness by the SIMS method (Fig. 6) demonstrated that the use of cathode sputtering of a graphite electrode without exposure to laser radiation led to a reduction in the film thickness by approximately half. The character of nitrogen distribution with thickness in the films synthesized by the laser-electric discharge method and with the use of only discharge without exposure to laser radiation is consistent with that determined by XPS.

Scanning electron microscopy. The films, which were prepared by applying the magnetic field with the flux

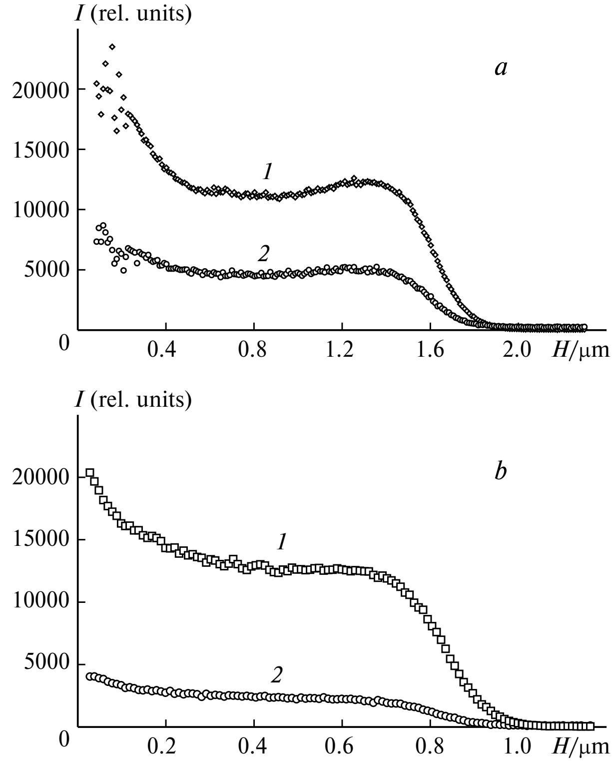

Fig. 6. Results of SIMS studies of the distribution of carbon (*1*) and nitrogen (*2*) over thickness of films prepared by the laser-electric discharge method (*a*) and using electric discharge without exposure to laser radiation(*b*); *H* is the film thickness.

density of ~10 mT to the discharge, contained agglomerates of larger crystallites (Fig. 7).

Hence, the employment of the laser-electric discharge method made it possible to prepare films containing compounds with the C—N bonds on a crystalline (100) silicon substrate. Among the compounds thus prepared, crystalline carbon nitride β-C_3N_4 was obtained.

Characterization of bulk samples. *Scanning electron microscopy.* The SEM studies revealed the presence of agglomerates at the interface between a bulk sample and a silicon plate with a deposited film. These agglomerates are fragments of hexagonal networks oriented parallel to the surface of the sample.

X-ray diffraction. The reflections with the space distances *d* = 3.136 and 1.358 Å observed in the powder X-ray diffraction patterns were assigned to Si and the reflections with *d* = 3.348 Å were attributed to graphite. We assume that graphite was formed due to partial decomposition of amorphous carbon nitride upon its thermobaric treatment. The presence of silicon in bulk samples is, apparently, associated with the use of single-crystal silicon plates with deposited C_3N_4 films (as seeds) in the thermobaric synthesis. All other reflections in the X-ray patterns were assigned to different modifications of the crystalline carbon nitride. The reflections with *d* = 5.6 and 2.696 Å (2θ = 15.7 and 33.0°, respectively) are consistent with the reflections recorded in the X-ray spectrum of the films used as crystallization seeds.

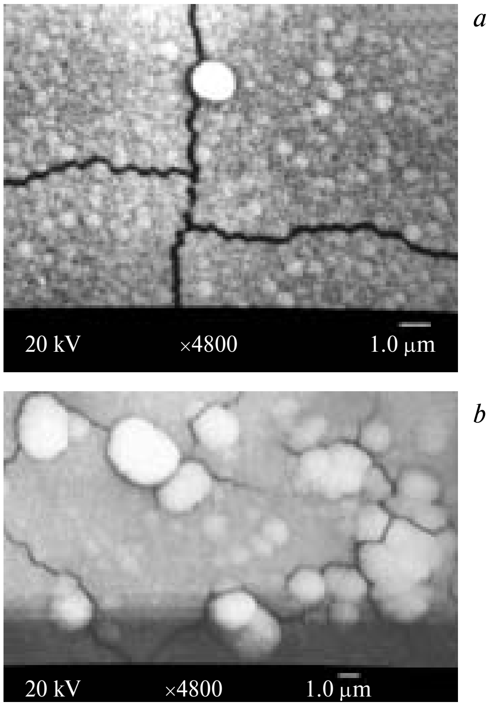

Fig. 7. Influence of the magnetic field on the surface of films prepared without application (*a*) and with application of the magnetic field to the zone of electric discharge in the reactor (*b*).

Table 1 gives the experimental space distances (d_{exp}), space distances calculated (d_{calc}) from our experimental data, and theoretical values (d_{theor}) calculated earlier.[19,20]

The total set of space distances (d_{exp}) could not be assigned to the single crystal modification of carbon nitride (TREOR program).[25] Indexing was carried out under the assumption that the sample contained different hexagonal modifications of C_3N_4. A comparison of d_{exp} with the space distances theoretically calculated[19,20] for the hexagonal α- and β-C_3N_4 phases allowed us to assign most of d_{exp} to these phases. The measured X-ray patterns contained no reflections corresponding to the cubic or pseudocubic C_3N_4 phases. We failed to unambiguously confirm the presence of a graphite-like modification of C_3N_4 in the samples under examination because the most intense reflection (2θ = 26.5°) of the graphite-like phase[19] coincides with the (002) reflection of graphite and the intensities of other reflections of this phase are low. Apparently, a series of non-assigned observed reflections (d_{exp} = 3.48, 3.427, 3.348, 3.136, 2.30, 1.796, 1.702, 1.697, 1.405, 1.387, 1.358, 1.320, and 1.312 Å) are attributable to the presence of other unknown phases of carbon nitride in the sample. Judging from the relative intensities of reflections, these unknown phases (phase) were present in substantial amounts.

Table 1. Results of powder X-ray diffraction analysis of bulk samples

Reflection	d_{exp}/Å	I/I_0	β-C_3N_4		α-C_3N_4		β-C_3N_4 [19,20]		α-C_3N_4 [19,20]	
			d_{calc}/Å	*hkl*	d_{calc}/Å	*hkl*	d_{theor}/Å	I/I_0	d_{theor}/Å	I/I_0
1	5.6	7.5	—	—	5.40	100	—	—	5.600	18.95
2	5.39	10	5.54	100	—	—	5.544	50.87	—	—
3	3.67	12.5	—	—	3.60	101	—	—	3.604	100
4	3.230	24	3.20	110	3.23	110	3.201	36.36	3.233	45.53
5	2.788*	5	2.77	200	—	—	2.772	100	—	—
6	2.696	10	—	—	2.70	200	—	—	2.800	33.37
7	2.356*	5	—	—	2.40	201	—	—	2.407	87.93
8	2.171	7.5	2.20	101	2.17	102	2.206	62.34	2.171	44.45
9	2.044*	12.5	2.09	210	2.10	210	2.095	40.84	2.117	55.69
10	1.913	22.5	1.92	111	1.90	112	1.922	56.40	1.904	14.45
11	1.862	7.5	—	—	1.86	300	—	—	1.867	79.77
12	1.850	15	1.85	300	—	—	1.848	40.01	1.735	54.57
13	1.576*	12.5	1.58	211	1.57	212	1.580	11.34	1.574	9.82
14	1.503	5	—	—	1.54	103	—	—	1.512	6.51
15	1.460	35	1.46	301	1.47	311	1.465	11.90	1.475	5.31
16	1.345	5	—	—	1.34	401	—	—	1.342	1.81
17	1.337	20	1.33	221	1.33	222	1.332	17.13	1.333	2.22
18	1.287	80	1.28	320	1.27	213	1.272	10.91	1.261	4.77
19	1.238	30	—	—	1.24	321	—	—	1.239	22.19
20	1.191	5	1.20	002	1.20	303	1.202	12.39	1.201	6.59

* Broad lines in the spectrum are indicated.

The parameters *a* and *c* calculated from our experimental data are 6.412 and 2.391 Å, respectively, (c/a = 0.373) for the β-C_3N_4 phase and 6.237 and 4.671 Å, respectively, (c/a = 0.728) for the α-C_3N_4 phase. The error of the determination of the unit cell parameters was 0.003 Å. The results of experimental X-ray diffraction studies of C_3N_4 crystal phases have been also published in the literature earlier. However, these studies were carried out only for films of C—N-containing materials including small amounts of C_3N_4 crystal phases and the results reported by different authors were substantially different. For example, the unit cell parameters of the β-C_3N_4 phase calculated from these experimental data vary in the ranges a = 6.24—6.44 Å and c = 2.357—2.48 Å.[26—34]

It should be noted that the unit cell parameters of the α- and β-C_3N_4 phases determined by us for bulk samples are in agreement with the theoretically calculated values.[19,20]

Based on the powder X-ray diffraction patterns, it can be stated that amorphous carbon nitride in our thermobaric experiments crystallized as the α- and β-C_3N_4 phases and also as one or several unknown crystal modifications of carbon nitride.

Electron diffraction study. The selected-area transmission electron diffraction pattern of a carbon nitride bulk sample is shown in Fig. 8. The space distances *d* for the sample under study were calculated from the electron wavelength λ and the instrument constant *L* by the formula $d = \lambda L/x$, where *x* is the distance from the center of the electron diffraction pattern to the spots forming the electron diffraction ring. The rings were revealed and the corresponding space distances were calculated: 3.19, 2.80, 2.04, 1.96, and 1.27 Å. For comparison, let us list the most similar space distances theoretically calculated[19,20] for C_3N_4: 3.20 (β), 2.77 (β), 2.09 (β), 1.93 (α), and 1.27 (β). Apparently, the selected area of the bulk sample contained primarily the β phase of crystalline C_3N_4.

X-ray photoelectron spectroscopy. The XPS studies demonstrated that the electronic states of the N and C atoms in the samples prepared by thermobaric treatment

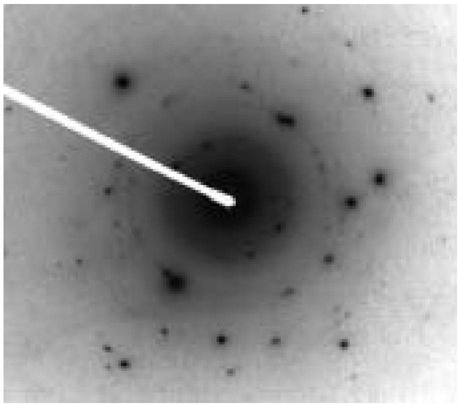

Fig. 8. Electron diffraction pattern of a bulk sample prepared by thermobaric treatment of amorphous carbon nitride.

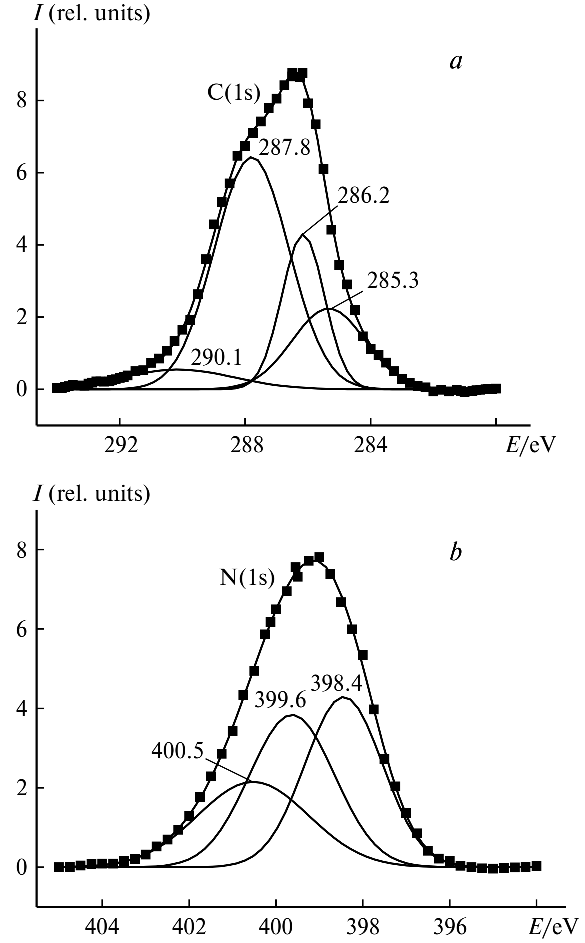

Fig. 9. Fitting of Gaussian components to the carbon (*a*) and nitrogen (*b*) photoelectron spectra of crystalline carbon nitride (after etching for 1 min).

of amorphous carbon nitride with the use of films containing crystalline C_3N_4 as seeds differ from the electronic states of these elements in an amorphous sample. Apparently, this fact is attributable to crystallization of the amorphous carbon nitride.

Below are given the assignments of the bands, which were made by the fitting of Gaussian components to the carbon and nitrogen photoelectron spectra (Fig. 9) based on the data published in the literature.[21–23,35,36]

Spectrum	Bond energy/eV	Bond
C(1s)	287.8	C—N in β-C_3N_4
	286.2, 285.3	C=N
	290.1	C=O
N(1s)	398.4	C—N in β-C_3N_4
	399.6	C—N (nonpolarized) or C—N (Py)
	400.5	C=N

Hence, the photoelectron spectra demonstrated that the resulting product contained compounds characterized by the presence of the carbon—nitrogen bonds (β-C_3N_4 structure). On the surface of carbon nitride bulk samples synthesized by thermobaric treatment, a large portion of the C and N atoms are bound to the O atoms. Thus, the X-ray photoelectron spectra of carbon and nitrogen have components in the regions of 289—290 and 401—402 eV, respectively. After surface etching with an argon-ion beam for 1 min, the fraction of these components was substantially reduced. It can be assumed that a rather thin oxygen-containing layer was formed in the course of treatment of the sample in air.

To summarize, the present study was the first where the laser-electric discharge method was proposed and used for the synthesis of crystalline carbon nitride films and a new method was developed and employed for the preparation of bulk samples of crystalline carbon nitrides. The latter method is based on exposure of the amorphous carbon nitride to ultrahigh pressure and temperature with the use of films synthesized by the laser-electric discharge method as crystallization seeds.

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