Synthesis of crystalline carbon nitride

Klavdia P. Burdina, Nikita B. Zorov,* Oleg V. Kravchenko, Yuri Ya. Kuzyakov, Jong I. Kim and Sergei A. Kulinich

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 932 8846; e-mail: zorov@laser.chem.msu.ru

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A procedure was developed for preparing bulk carbon nitride crystals from an amorphous nitrogen- and carbon-containing material at ultrahigh pressures and temperatures in the presence of seeds of crystalline C_3N_4 films prepared by a laser–electric discharge method.

The existence of crystalline carbon nitride (β-C_3N_4) with the hardness comparable to that of diamond was predicted in 1989 by Liu and Cohen[1] on the basis of *ab initio* calculations. The experimental data concerning the synthesis of crystalline β-C_3N_4 were surveyed in refs. 2 and 3. Note that crystalline carbon nitrides were prepared as films rather than bulk samples. The nitrogen content of these films varied from 15 to 35% depending on the preparation procedure, whereas the stoichiometric nitrogen content of C_3N_4 is 57%. These low values were explained by the formation of both crystalline and amorphous carbon nitrides as a result of synthesis; the fraction of the former species was small, and they were distributed as grains in a matrix of amorphous carbon nitrides with a lower nitrogen content. The films can also be contaminated with carbon.[4]

We used films containing crystalline C_3N_4 as seeds for the crystallization of amorphous carbon nitride at high pressure and temperature. The films were prepared by a laser–electric discharge method, in which the products of both cathode sputtering and laser-induced evaporation of a graphite electrode were simultaneously introduced into a nitrogen plasma.[3] This method provided the deposition of the resulting nitrogen compounds of carbon on a single-crystal Si(100) substrate. In some experiments, a magnetic field was applied to a glow-discharge plasma.

The IR spectra of the films exhibited vibrational bands corresponding to molecules with C≡N, C=N and C–N bonds. The Auger spectra exhibited only C_{KLL} and N_{KLL} peaks; the nitrogen content of the synthesised films was found to be ~24%. As found by secondary-ion mass spectrometry, the cathode sputtering of a graphite electrode without exposure to laser radiation resulted in a halved film thickness. The X-ray diffraction patterns (DRON-2 diffractometer) exhibited only paired (100) and (200) reflections at $2\theta = 15.8$ and 32.9°; these reflections are indicative of the presence of oriented single-crystal carbon nitride compounds in the films. The application of a magnetic film resulted in the production of films with increased intensities of the reflections. A regular sequence of hexagonal crystallites oriented in parallel to the plane of the sample was observed by scanning electron microscopy. It was also found that the crystallite size of the films increased upon applying a magnetic field to the discharge. An analysis of the X-ray photoelectron spectra at 400 and 285 eV for N (1*s*) and C (1*s*) atoms, respectively, demonstrated that the film contained a compound with C–N bonds that are typical of the structure of β-C_3N_4;[5–7] according to XPS data, the nitrogen content of the films was ~20%.

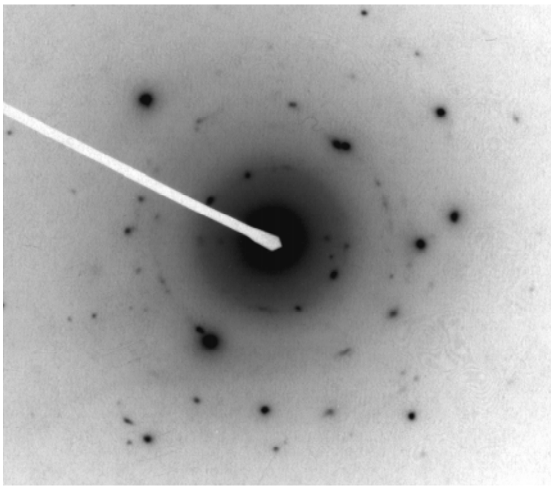

Figure 1 Electron diffraction pattern of a bulk sample prepared from amorphous carbon nitride by the thermobaric process.

Table 1 Interplanar distances (*d*) and relative intensities (in parentheses) of diffraction lines.

No.	d_{exp}/Å	No.	d_{exp}/Å	No.	d_{exp}/Å
1	5.6 (1)	14	1.862 (1)	27	1.460 (1)
2	5.39 (2)	15	1.850 (4)	28	1.405 (4)
3	3.67 (2)	16	1.827 (2)	29	1.387 (1)[a]
4	3.48 (5)[a]	17	1.796 (20)	30	1.345 (8)
5	3.427 (2)	18	1.742 (1)	31	1.337 (4)
6	3.23 (2)	19	1.702 (3)[a]	32	1.320 (5)[a]
7	2.788 (4)	20	1.697 (3)[a]	33	1.312 (1)
8	2.696 (2)	21	1.642 (2)	34	1.287 (5)
9	2.356 (2)	22	1.605 (1)	35	1.238 (3)
10	2.30 (5)	23	1.576 (1)	36	1.191 (2)
11	2.171 (3)	24	1.548 (7)	37	1.186 (5)
12	2.044 (4)	25	1.540 (3)	38	1.179 (1)
13	1.913 (1)	26	1.503 (7)	39	1.167 (6)[a]

[a] Data, inconsistent with theoretically calculated for α- and β-C_3N_4.

In the thermobaric preparation of bulk samples of crystalline carbon nitride, we used an amorphous product with the formula $C_3N_{4.2}$, which was obtained by the thermal decomposition of mercury thiocyanate at 180 °C in an inert atmosphere.[8] The composition and structure of the amorphous carbon nitride were determined by chemical analysis and IR spectroscopy.

The thermobaric experiments were performed in high-pressure toroid chambers.[9] Amorphous carbon nitride was sandwiched between Si(100) wafers with the deposited films, which were in direct contact with amorphous carbon nitride. The thermobaric experiments were performed at 10–77 kbar and 350–1200 °C.

The crystallization of amorphous carbon nitride was not observed with the use of silicon wafers without the above films applied to their surface. Bulk samples of crystalline carbon nitride were prepared with the use of wafers with the films. A pressure of 70 kbar, a temperature of 550 °C, and an exposure time of 2 h are optimum conditions for the transformation of amorphous carbon nitride into the crystalline product. According to X-ray diffraction and XPS data, a further increase in the temperature resulted in the graphitization of samples. At lower temperatures and shorter exposures to high pressure, the amorphous material remained unchanged.

The size of the prepared bulk samples was about 30 mm^3. According to the XPS data, the nitrogen content of these samples was approximately 40 at.%.

The bulk samples were characterised by electron diffraction. Figure 1 demonstrates an electron diffraction pattern, which is evidence for the presence of a crystalline phase in a bulk sample.

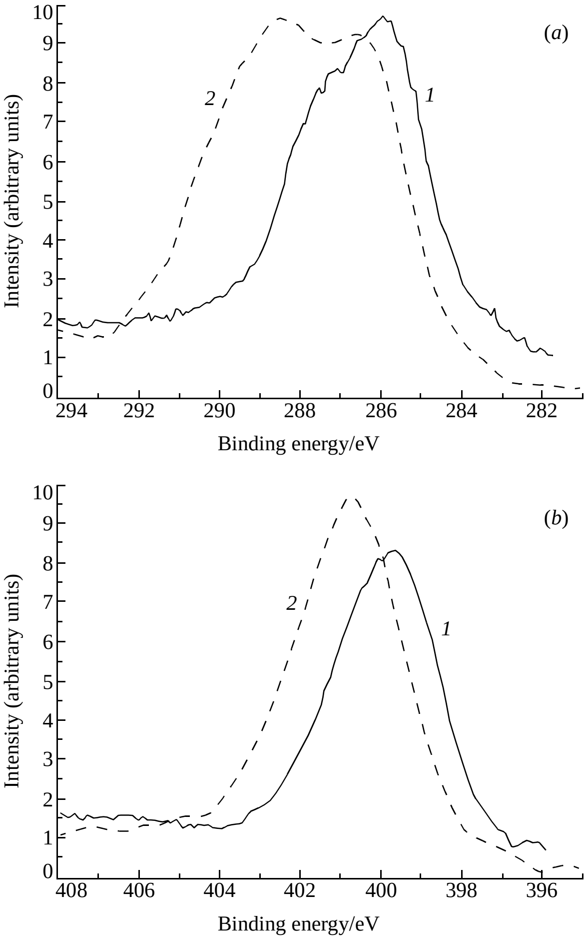

Figure 2 XPS spectra of (*a*) carbon and (*b*) nitrogen for crystalline and amorphous carbon nitride; (*1*) crystal and (*2*) amorphous phase.

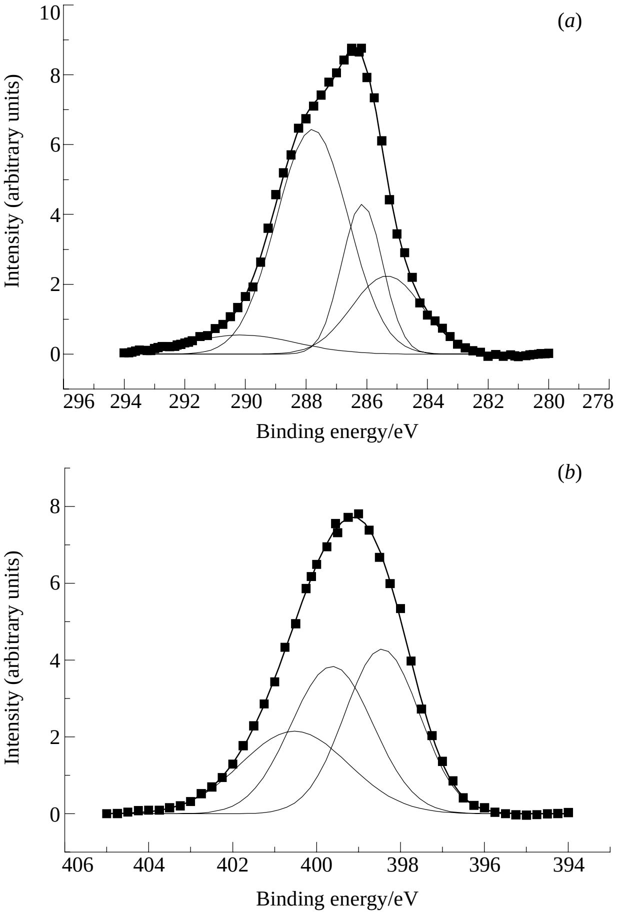

Figure 3 Deconvoluted XPS C 1*s* (*a*) and N 1s (*b*) spectra of a crystalline carbon nitride bulk sample.

It was found by *ab initio* calculations that, in principle, several modifications of crystalline carbon nitride can occur, namely, α-, β-, cubic, pseudocubic, and graphite-like C_3N_4.[1,10] The majority of interplanar distances calculated from X-ray diffraction data (Table 1) on the assumption that the structure of the test substance corresponds to C_3N_4 are consistent with the theoretically calculated interplanar distances[10,11] for crystalline α- and β-C_3N_4 phases.

We detected no reflections that correspond to cubic and pseudocubic C_3N_4 phases. Thus, we concluded that carbon nitride phases with cubic $Zn_2(SiO_2)_4$-type and pseudocubic $CdIn_2Se_4$-type structures[11] were absent from the products prepared in our experiments.

The most intense reflection of a graphite-like phase coincides with the intense reflection of the α-C_3N_4 phase, and the intensities of the other reflections of the graphite-like phase are too low to indicate the presence of this phase in our samples.

Note that the X-ray diffraction patterns exhibit several unidentified reflections (marked in Table 1); we believe that they can be attributed to an unknown phase of carbon nitride.

We found by XPS that the electronic states of nitrogen and carbon atoms in the bulk samples are different from those in an amorphous sample. This is evidently due to the crystallization of amorphous carbon nitride (Figure 2).

The XPS spectrum of carbon for a crystalline bulk sample can be most adequately represented as a sum of four Gaussian components [Figure 3(*a*)], which were assigned according to published data.[5–7] The predominant component with a maximum at 287.8 eV was attributed to C–N bonds typical of the β-C_3N_4 structure; less intense components with maxima at 286.2 and 285.3 eV, to C=N bonds; and a very weak component with a maximum at 290.1 eV, to carbon–oxygen bonds. The spectrum of nitrogen can be represented as a sum of three Gaussian components [Figure 3(*b*)]: the predominant component with a maximum at 398.4 eV, which was attributed to C–N bonds typical of the β-C_3N_4 structure, and two less intense components. One of them with a maximum at 399.6 eV was attributed to either non-polarised C–N bonds or C–N bonds typical of the structure of pyridine, and the other with a maximum at 400.5 eV can be attributed to C=N bonds.

Thus, we can conclude that the bulk samples contained a crystalline phase of β-C_3N_4.

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