

Preparation and Characterization of β - C_3N_4 in Presence of Seed Carbon Nitride Films Deposited by Laser-Electric Discharge Method

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A procedure was developed for preparing bulk carbon nitride crystals from a polymeric α - $C_3N_{4.2}$ at high pressure and temperature in the presence of seeds of crystalline carbon nitride films prepared by a high voltage discharge plasma combined with pulsed laser ablation of graphite target. The samples were evaluated by x-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy, Auger electron spectroscopy (AES), secondary-ion mass spectrometry (SIMS), scanning electron microscopy (SEM) and x-ray diffraction (XRD). Notably, XPS studies of the film composition before and after thermobaric treatments demonstrate that the nitrogen composition in α - $C_3N_{4.2}$ material initially containing more than 58% nitrogen decreases during the annealing process and reaches a common, stable composition of ~45%. The thermobaric experiments were performed at 10-77 kbar and 350-1200 °C.

Keywords : Thermal annealing, Crystalline carbon nitride, XPS, XRD

1. INTRODUCTION

The existence of crystalline carbon nitride 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, including laser and vapor deposition[2-4]; dc/rf magnetron sputtering[5,6]; and ion-beam assisted deposition[7,8], 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]. It was proposed that bulk composition of the films is

conditioned by presence in them of diverse compounds of carbon with nitrogen, including β - C_3N_4 .

The main purpose of the present study was a production of crystalline C_3N_4 in the conditions of high-temperature and high-pressure treatment of amorphous $C_3N_{4.2}$ using films, containing crystalline C_3N_4 as seed crystals.

2. EXPERIMENTAL

We used films containing crystalline C_3N_4 as seeds for the crystallization of amorphous carbon nitride at high-pressure and high-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 discharge plasma[3]. The second harmonic of Nd:YAG laser irradiation with fluence 15 J/cm² was used. This method provided the deposition of the resulting nitrogen compounds of carbon on a basement of Si(100) substrate, placed at

distance of 20mm over the cathode. In some experiments on plasma of glow discharge a magnetic field was imposed, that was created by electromagnet with flux density $\sim 10\text{mT}$.

In the thermobaric preparation of bulk samples of crystalline carbon nitride, we used an amorphous product with the formula $\text{C}_3\text{N}_{4.2}$, which was obtained by the thermal decomposition of mercury thiocyanate at 180°C in an inert atmosphere[9]. 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[3]. Amorphous carbon nitride was sandwiched between Si(100) wafers with the deposited films, which were in direct contact with amorphous carbon nitride powder. The thermobaric experiments were performed at 10-77 kbar and $350\text{-}1200^\circ\text{C}$.

3. RESULTS AND DISCUSSION

The IR spectra of the films exhibited vibration bands corresponding to molecules with $\text{C}\equiv\text{N}$ (band II), $\text{C}=\text{N}$ (band I) and $\text{C}-\text{N}$ (band I) bonds as shown in Fig. 1. The Auger spectra exhibited only C_{KLL} and N_{KLL} peaks (see Fig. 2); the nitrogen content of the synthesized films was found to be $\sim 26\%$. As found by SIMS, the cathode sputtering of a graphite electrode without exposure to laser radiation resulted in a halved film thickness as shown in Fig. 3[10]. The XRD patterns 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 field resulted in the production of films with increased intensities of the reflections[11]. A regular sequence of hexagonal crystallites oriented in parallel to the plane of the sample was observed by SEM. It was also found that the

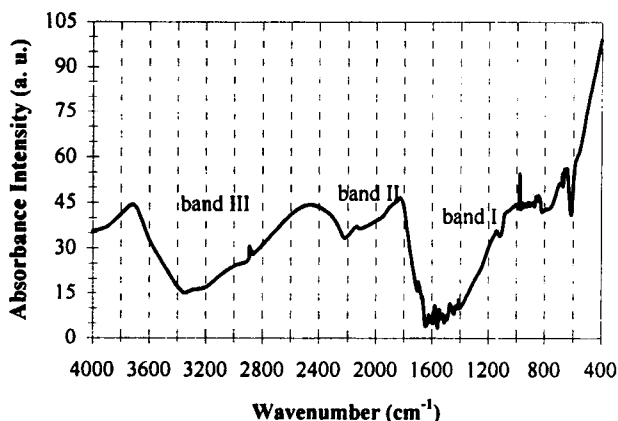


Fig. 1. IR spectra of carbon nitride films.

crystallite size of the films increased upon applying a magnetic field to the discharge. An analysis of the x-ray

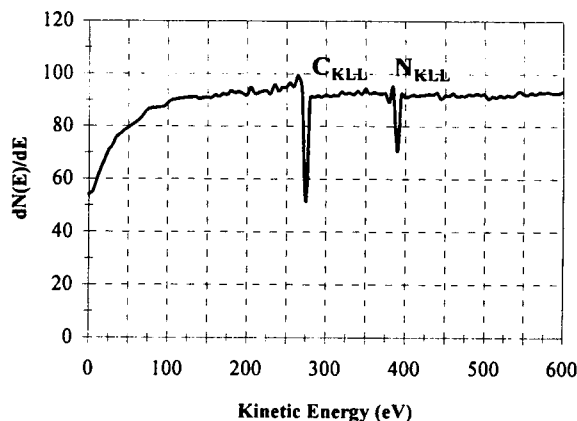


Fig. 2. Auger spectra of carbon nitride film.

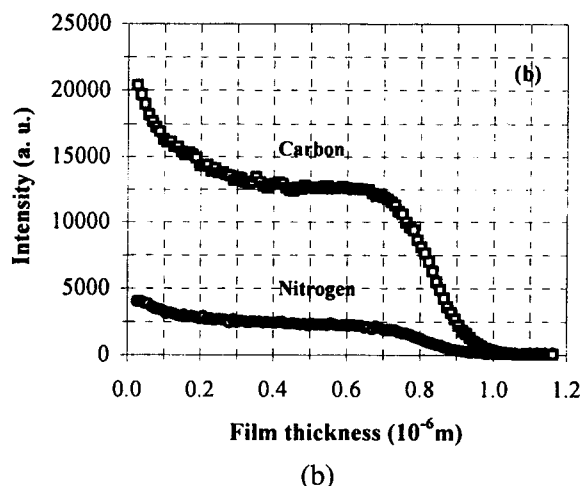
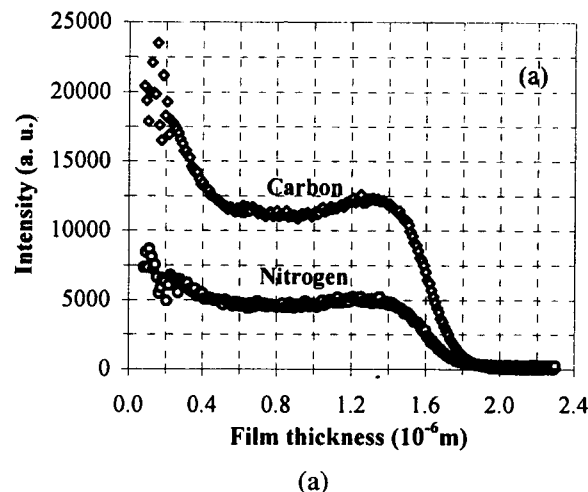


Fig. 3. Results of SIMS depth profiling for carbon nitride films. (a) with, and (b) without exposure to laser radiation.

photoelectron spectra at 400 and 285 eV for N(1s) and C(1s) 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 $\sim 20\%$.

The thermobaric experiments were performed in high-pressure toroid chambers[3]. Amorphous carbon nitride was sandwiched between Si(100) wafers with the deposited magnetic films, which in direct contact with amorphous $C_3N_{4.2}$. 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. The 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 2 h are optimum conditions for the transformation of amorphous carbon nitride into the crystalline product. According to XRD and XPS data, a further increase in the temperature resulted in the graphitization of samples. At lower temperature and shorter exposures to high pressure, the amorphous material remained unchanged. The size of the prepared bulk samples was about 30 mm². According to the XPS data, the nitrogen content of these samples was approximately 45 %.

The crystallinity and binding structure of bulk samples were characterized by XRD and XPS, respectively. Fig.4 demonstrates an x-ray diffraction pattern, which is evidence for the presence of a crystalline phase in a 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 [1,12]. The majority of interplanar distances calculated from XRD 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[12] for crystalline, α - and β - C_3N_4 phases. We detected no reflections that correspond to cubic and pseudocubic C_3N_4 phases. Thus,

Table 1. Interplanar distance (d_{exp}) and relative intensities (in parentheses) of diffraction peaks.

No.	d_{exp}	No.	d_{exp}
1	5.580(1.0)	18	1.607(0.2)
2	5.385(1.5)	19	1.600(1.0)
3	3.680(0.5)	20	1.576(6.0)
4	3.485(1.5)	21	1.540(1.0)
5	3.427(60) ^a	22	1.503(0.5)
6	2.290(0.5)	23	1.460(5.0)
7	2.788(0.3)	24	1.405(0.3)
8	2.696(1.0)	25	1.387(2.0) ^a
9	2.455(6.0)	26	1.337(2.0)
10	2.171(1.5)	27	1.320(0.5) ^a
11	2.044(0.7) ^a	28	1.312(0.4)
12	1.913(4.0)	29	1.287(100)
13	1.862(0.2)	30	1.238(2.0)
14	1.850(0.5)	31	1.191(1.8)
15	1.827(2.0)	32	1.183(5.0)
16	1.796(2.0) ^a	33	1.138(1.0) ^a
17	1.702(0.2) ^a	34	1.109(0.5)

^aData, inconsistent with theoretically calculated for β - C_3N_4 .

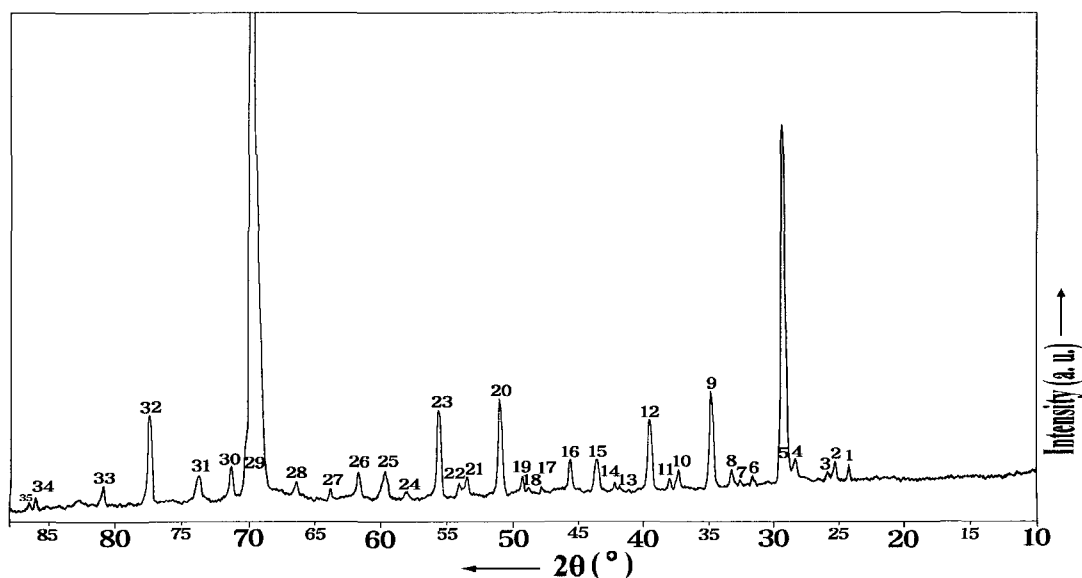
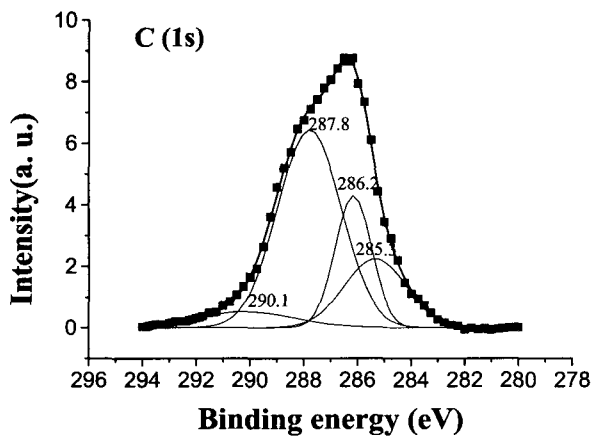


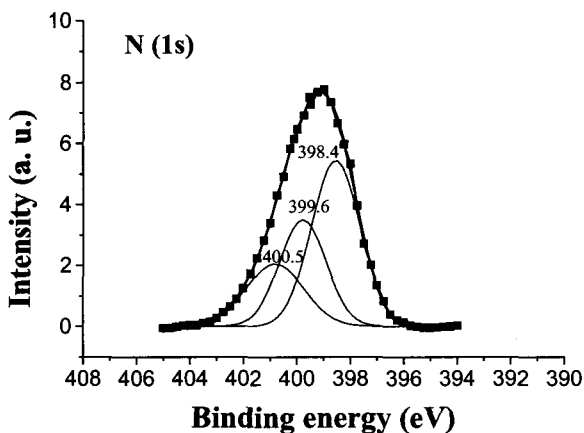
Fig. 4. X-ray diffraction pattern of bulk sample.

we concluded that carbon nitride phases with cubic $Zn_2(SiO_2)_4$ -type and pseudocubic $CdIn_2Se_4$ -type structure[3] 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 phases, 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 XRD 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.



(a)



(b)

Fig. 5. Deconvoluted XPS C1s (a) and N1s (b) spectra of a crystalline carbon nitride bulk sample.

The XPS spectrum of carbon for a crystalline bulk sample can be most adequately represented as a sum of four Gaussian components as shown in Fig. 5(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 maximum 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 (see Table 2). The spectrum of nitrogen can be represented as a sum of three Gaussian components as shown in Fig. 5(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, 400.5 eV can be attributed to C=N bonds (see Table 3).

Table 2. XPS C1s peak position (in eV) for the bulk samples (Literature values are also listed for comparison).

Experiment results(eV)	Results in literatures		
	Peak position(eV)	Binding type	Refs
285.3	285.1	C-C	[13]
	285.8	DLC	[8]
286.2	286.6	C-N(β - C_3N_4)	[14]
	286.8	C-N(β - C_3N_4)	[13]
287.8	288.1	C=N	[14]
290.1	289.0	C-O	[13]
	289.6	O-C=N	[14]

Table 3. XPS N1s peak position (in eV) for the bulk samples (Literature values are also listed for comparison).

Experiment results(eV)	Results in literatures		
	Peak Position(eV)	Binding type	Refs
398.4	398.6	C-N(β - C_3N_4)	[15]
	398.9	C-N(β - C_3N_4)	[8]
399.6	400.2	C=N	[16]
400.5	400.8	C=N	[14]

4. CONCLUSION

Thus, we can conclude that the bulk samples contained a crystalline phase of β - C_3N_4 by XRD and XPS data. The pressure of 70 kbar, a temperature of 550 °C, and an exposure time 2 h are optimum conditions for the transformation of amorphous carbon nitride into the crystalline product. The crystallization of amorphous carbon nitride was not observed with the use of silicon wafers without the deposited carbon nitride films applied to their surface. In view of the experience and existing synthesis techniques, it is effective to synthesize large sized (maximum size of 30 mm²) crystals of super hard materials such as diamond under the conditions of high pressure and high temperature. The high pressure and high temperature process with 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, is very important for us to obtain carbon nitride crystals whose size is large enough to determine their composition, structure and properties.

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