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Materials Science and Engineering B78 (2000) 11–15

MATERIALS SCIENCE & ENGINEERING B

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On the structure and composition of crystalline carbon nitride films synthesized by microwave plasma chemical vapor deposition

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Abstract

Crystalline carbon nitride thin films were prepared on Si (100) substrates by a microwave plasma chemical vapor deposition (MPCVD) method, using CH_4/N_2 as precursor gases. The surface morphologies observed by scanning electron microscopy (SEM) of the carbon nitride films deposited on Si substrate at 830°C were consisted of hexagonal crystalline rods. The effect of substrate temperature on the formation of carbon nitrides was investigated. X-ray photoelectron spectroscopy (XPS) analysis indicated that the maximum value of the N/C atomic ratio in the films deposited at a substrate temperature of 830°C was 1.20, which is close to the stoichiometric value of C_3N_4. The X-ray diffraction (XRD) pattern of the film deposited at 830°C indicates no amorphous phase in the film, which is composed of β- and α-C_3N_4 phase containing an unidentified C–N phase. Fourier transform infrared (FTIR) and Raman spectroscopy support the existence of C–N covalent bond. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbon nitride; Microwave plasma chemical vapor deposition; Thin film

1. Introduction

The quest to perfect matter with superior and remarkable properties has been in progress from Medieval era to the present. Among these materials, diamond possesses a rare combination of remarkable properties. One very important property of diamond is its high hardness which has so far not been challenged by any material, at least experimentally. According to a recent and interesting prediction by Liu and Cohen [1,2], cabon nitride films, if grown with a phase similar to that β-Si_3N_4, will have exceptional hardness comparable to or greater than that of diamond. This remarkable prediction sparked off intense theoretical and experimental activity worldwide with a view to realize experimentally this superhard material, in order to test the predictive power of the computational model of solids. Exploring the synthesis and properties of such a hypothetical material is also significant to research in the fields of condensed matter physics, material science and chemistry.

Up to now a number of experiments were performed applying different methods [3–16], such as direct current magnetron sputtering, radio frequency magnetron sputtering, laser ablation, ion beam deposition, and chemical vapor deposition or combinations thereof. It turned out to be difficult to increase the N content in the deposited film to the right stoichiometric composition of crystalline C_3N_4. In this letter, we report on CN films deposited at 830°C with high nitrogen content and C_3N_4 microstructure. These films were synthesized by microwave plasma chemical vapor deposition (MPCVD). The effect of substrate temperature on the nitrogen incorporation was investigated. Chemical bonds of these films were analyzed by means of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) and Raman spectroscopy. The crystalline structure was analyzed by X-ray diffraction (XRD) technique.

2. Experimental

The carbon nitride thin films were deposited on polished Si(100) in the microwave plasma chemical

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PII: S0921-5107(00)00505-5

vapor deposition (MPCVD) system [13]. Vacuum was created through a combination of a turbomolecular pump and a rotary pump. Working gas, CH_4 and N_2, were fed into the deposition chamber through mass flow controllers. Pressure in the chamber was controlled by adjusting a valve between the deposition chamber and the vacuum pumps. The microwave power was adjusted by a four screw adapter and monitored by measuring the back reflection power at the end of water load. A mixture of semiconductor grade N_2 (99.999%) and CH_4 (99.9%) gases in various ratio was used as source gas, typical flow rates being 100 sccm for N_2 and 1.0 sccm for CH_4, while the chamber pressure was maintained at about 2500 Pa. The microwave power was 500–700 W and the temperature of the substrates was held at 750–900°C, as measured by an infrared pyrometer, during depositions. It may be noted that the heating of the substrates was achieved by the plasma itself and no separate substrate heater was provided.

All the characterization of deposited films were carried out ex situ. The x-ray photoelectron spectroscopy (XPS) measurements were performed using unmonochromatized Mg Kα (1253.6 eV) X-ray radiation on a VG Scientific Lab 5 ESCA (electron spectroscopy for chemical analysis). The infrared spectra were obtained by Nicolet MAGNA-IR750 Fourier transform infrared spectrometer with 4cm^{-1} resolution. Laser-Raman spectroscopy was carried out on micro-Raman spectrometer (Nicolet Raman 950). A 40 mW Ar^+ laser operating at 514.5 nm was used as the light source for Raman measurement. A field emission type scanning electron microscopy (SEM) was used to observe the morphology of films. X-ray diffraction experiments were performed on a Rigaku D/Max II rotating anode X-ray diffractrometer (18 kW, Cu Kα Radiation $\lambda =$ 0.154056 nm).

3. Results and discussion

3.1. Surface morphology

The surface morphologies of the deposited films were investigated by a Hitachi S-4200 Scanning electron microscopy (SEM). Fig. 1 shows a typical SEM micrograph of a carbon nitride film deposited on Si substrate at 830°C. It was found that the film consisted of hexagonal crystalline rods. These rods are about 1–2 μm long and about 0.5 μm wide.

3.2. XPS spectra

In order to understand the bonding state of the films, we performed the analysis of XPS N 1s and C 1s spectra. XPS is quite sensitive to the characteristics of the film surface because the non-elastic scattering mean free path λ_m of the emitted photoelectron is very short. In view of the fact that carbon and nitrogen do not react easily, it is very important to known the fraction of N bonded to C in the films rather than just the total nitrogen content. Since several chemical bonding states such as C–N, C=N, and C≡N may exist in the synthesized films, it is, desirable to estimate the N/C ratio in each of these phase. Marton et al. [14] have shown that XPS can be used to delineate small binding energy differences occurring in various bonding states between C and N. The N/C ratio in each phase can be calculated from the areas under fitted Gaussian distributions divided by their sensitivity factors. The fraction of either of these phases present in the films can also be calculated by simply dividing the sum of [C] and [N] concentrations corresponding to that phase by the total concentration. Thus, XPS can be an important technique to characterize carbon nitride films for their N/C ratio and the bonding states between C and N. Fig. 2 shows the typical carbon and nitrogen 1s XPS spectra of CN film deposited at 830°C. After deconvoluting these C ls and N 1s peaks into their components, it was found that there are two bonding states between C and N in these films. The binding energies in these two carbon nitride phases are: C^1 286.43 eV; N^1 399.08 eV; C^2 288.15 eV and N^2 400.82 eV. The peak at 289.9 eV is identified as originating from CO type bond. This peak is incidental and is excluded from further consideration. From a comparison of two lines of each spectrum to binding energies in pyridine (C_5H_5N) and urotropine ($C_6H_{12}N_4$) it was concluded that in the studied CN films a two-phase system exists, one with a tetrahedral type of binding configuration and one with

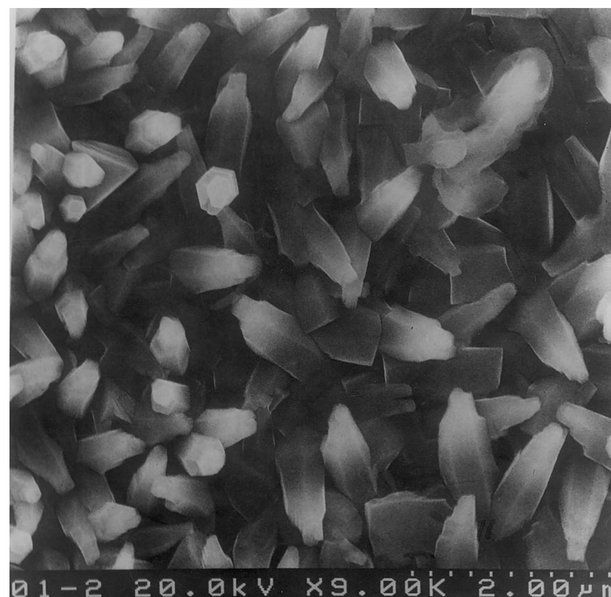

Fig. 1. Surface morphology of a carbon nitride film deposited on a Si substrate, by SEM.

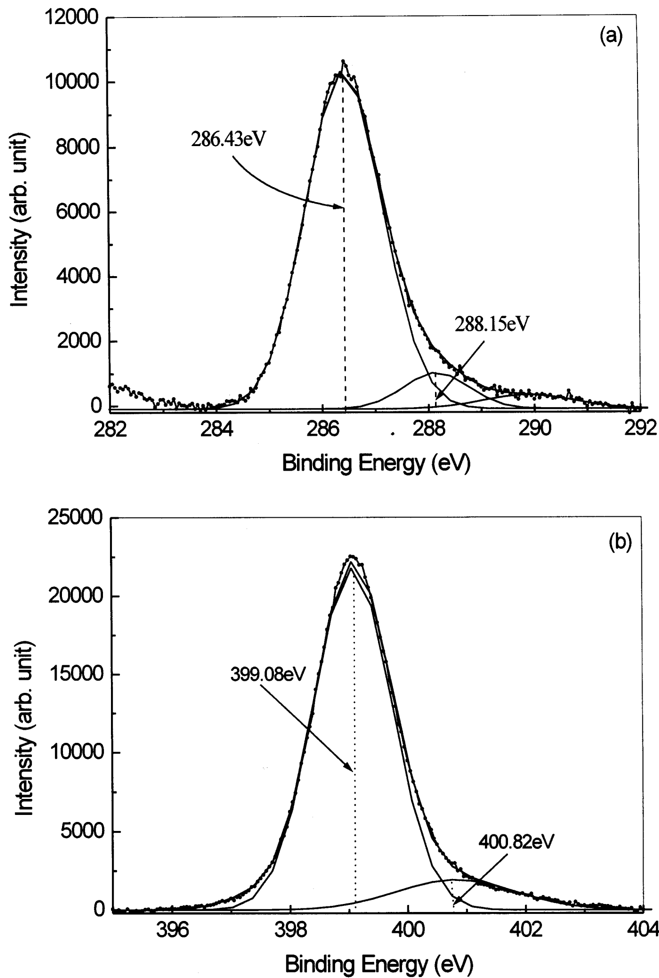

Fig. 2. The typical XPS spectra of carbon nitride film deposited on Si substrate: (a) C 1s region; (b) N 1s region.

a sp^2 configuration. Phase 1 is 'carbon and nitrogen atoms in position resembling β-C_3N_4' and phase 2 is 'areas with excess carbon' [14,15]. The lines were assigned as follows: 399.08 eV (N^1) and 286.43 eV (C^1) to phase 1; 400.82 eV (N^2) and 288.15 eV (C^2) to phase 2. From the above results there is a significant amount of C–N bond for N and C atoms in the films, favoring the formation β-C_3N_4 phases. The [C^1], [C^2], [N^1], and [N^2] concentrations were calculated from the areas under fitted Gaussian distributions divided by their sensitive factors. The N/C ratio in phase 1 (α- and β-C_3N_4 mixture) was [N^1]/[C^1], which was closed to the stoichiometric value 1.33 of C_3N_4.

The effect of substrate temperature on the nitrogen incorporation was investigated by XPS spectra. The results are listed in Table 1, including N ls, C ls binding energy in different states, the average N/C atomic ratios, and [N^1]/[C^1] ratios. The binding energy in these two carbon nitride phases are: C^1 286.36–286.49 eV, C^2 287.56–288.16 eV, N^1 398.64 eV, N^2 399.67–400.82 eV. The average N/C atomic ratios and N/C in phase 1 are

Table 1
C ls, N ls binding energy and N/C atomic ratios of CN films deposited at different substrate temperature

Samples	SiO_6	SiO_1	SiO_2	SiO_5
substrate temperature (°C)	790	810	830	890
C^1/eV	286.41	286.49	286.43	286.36
C^2/eV	287.56	288.16	288.15	287.83
N^1/eV	398.64	398.97	399.08	398.88
N^2/eV	399.99	399.67	400.82	400.11
average N/C ratio	0.56	0.70	1.01	0.99
N/C ratio in C_3N_4 phase	0.61	0.65	1.20	1.04

illustrated in Fig. 3. It was found that N/C atomic ratios were increased as substrate temperature increased below 830°C, and decreased a little above 830°C.

3.3. Crystal structure

Most of the CN films reported in published papers are composed of multiphase, especially in those deposited on Si substrate. Si diffused into the film during deposition process. According to the electronegativity difference between C, N and Si, Phases should be formed in accordance with the following sequence SiN, SiC, CN. The X-ray diffraction peaks of different phases were overlapped which made the structure analysis more complicated. On the other hand, due to the low mass number of C and N, the intensity of observed XRD spectra from carbon nitride films was very weak owing to the greater penetration depth of X-rays and the low scattering efficiencies of both C and N. If there is a natural reference sample just as a diamond has, parallel experiments on natural and man-made materials will help to settle the problem. However as this is

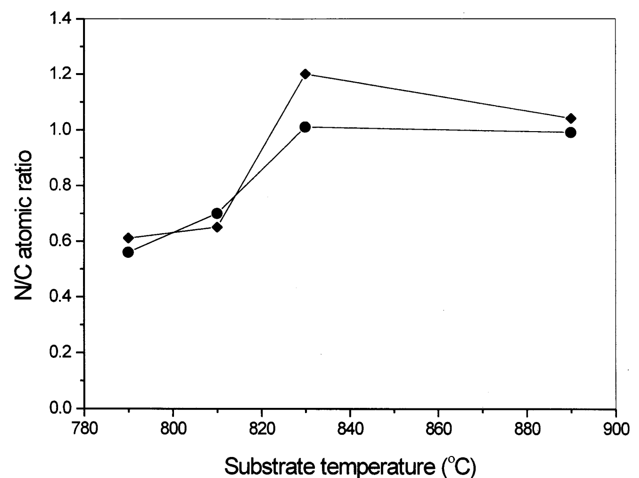

Fig. 3. The N/C atomic ratios of carbon nitride films deposited at different substrate temperature ◆,● represent ([N^1]/[C^1]), and average N/C atomic ratio respectively.

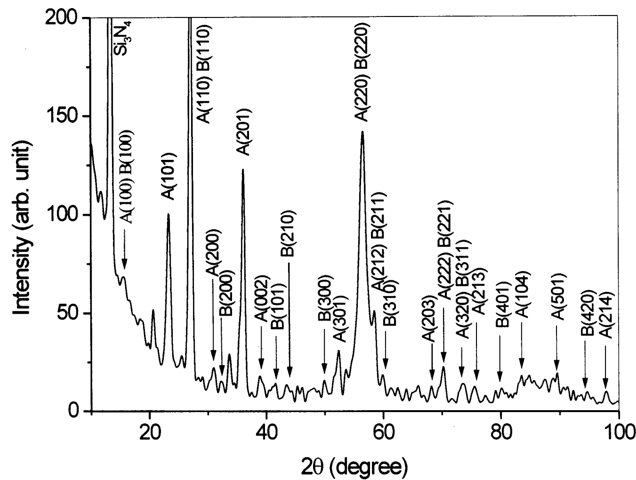

Fig. 4. The observed XRD spectrum of a carbon nitride film deposited on Si substrate, A(*hkl*), B(*hkl*) represented α-C_3N_4(*hkl*), β-C_3N_4(*hkl*) respectively.

not available, we have no alternative but to rely on computer simulations.

Recently, Zhang et al.[11] have presented XRD spectra of crystalline CNx films produced by hot filament CVD technique. The d values measured from the XRD data show that their data can be matched with that of β-C_3N_4 apart from some unknown reflections. In fact, some of their unknown reflections match that of α-C_3N_4. Fig. 4 showed the observed X-ray diffraction spectrum. The experimental observation points out complete spectra including all the strong peaks of α-C_3N_4 (100), (101), (110), (200), (201), (002), and that of β-C_3N_4, (100), (110), (200), (101), (300). Other peaks can be assigned to β-Si_3N_4 and the Si single crystal substrate.

3.4. The vibration mode

Raman spectroscopy is an important tool for studying the nature of chemical bonding in materials. For diamond and related materials, diamond has sharp Raman peak at 1332 cm^{-1}, and graphite has two broad G, D band centered at 1575 and 1360 cm^{-1} respectively. These results were tested and verified repeatedly, and received general recognition. But for C_3N_4, the assignments were just tentative, and not universally accepted.

There is one point of view that is worth paying attention to. It was considered that at early stage of the research, the comparisons directly with diamond were not reasonable because the structure of C_3N_4 and diamond are quite different. Yen and Chou [16] argued that since the β-C_3N_4 was proposed to adopt the structure of β-Si_3N_4, the Raman spectra of β-C_3N_4 would be analogous to β-Si_3N_4. A scaling factor of 1.43

Table 2
The observed Raman peaks from Fig. 5 and the calculated peaks of α- and β-C_3N_4

Observed peaks (cm^{-1})				Calculated Raman spectra (cm^{-1})	
No.	SiO_1	SiO_2	SiO_5	α-C_3N_4	β-C_3N_4
1	251	251	251		266
2	305	305	306		300
3	436	436	436	438	
4	623	623	623		645
5	676	671	677		672
6	823	827	825		885
7	943	943	943	955	
8	982	982	982		1048

was calculated through Hooke's law. Raman active modes for α-C_3N_4 and β-C_3N_4 were calculated and experimentally observed in crystalline carbon nitride films are given in Table 2.

Fig. 5 is the Raman spectra detected from carbon nitride films deposited on Si substrates. The Raman spectra showed no signs of the G, D band which are the fingerprints of graphite. The observed Raman shifts 306, 623, 981 cm^{-1} are close to the calculated data for β-C_3N_4 300, 645, 1047 cm^{-1}; observed 436, 669, 678, 944 cm^{-1} are close to the calculated data for α-C_3N_4 438, 658, 672, 955 cm^{-1}. The strong peak at 520 cm^{-1} is due to silicon substrate. The experimental results support the existence of C–N bond in α- and β-C_3N_4 mixture.

For FT-IR analysis, we rely on a computer simulation using the Cerius II materials analysis package from Molecule Simulation Incorporation (MSI) to identify the peaks of C_3N_4 Experimental results are shown in Fig. 6 and Table 3. Observed peaks at 852, 886 cm^{-1} are close to the calculated β-C_3N_4 IR active mode 891 cm^{-1}; observed peaks at 1012, 1031, 1075 cm^{-1} are close to the calculated α-C_3N_4 IR active mode 1051,

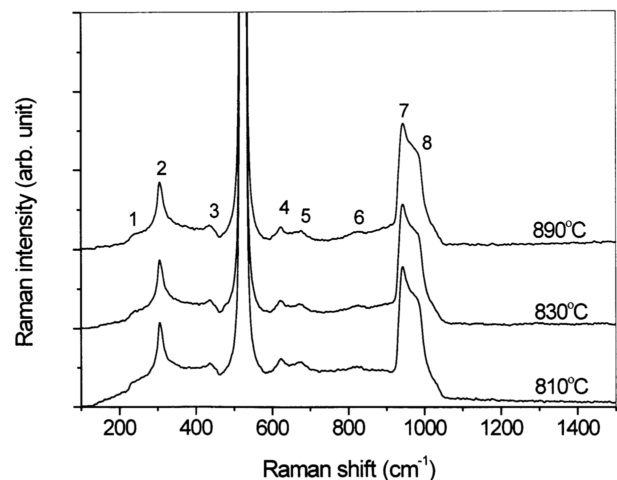

Fig. 5. The Raman spectra of carbon nitride films deposited at different substrate temperature.

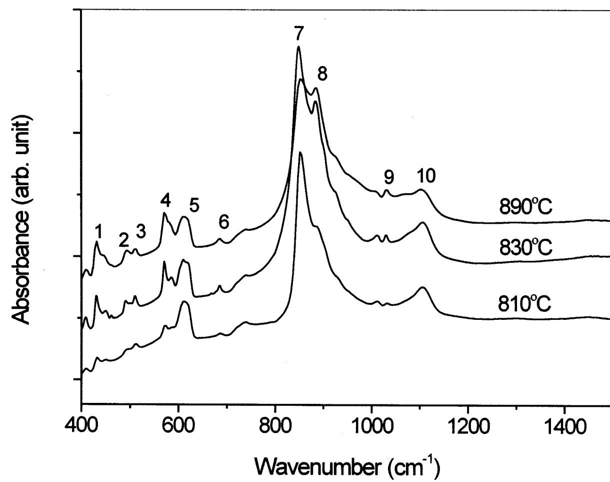

Fig. 6. The FTIR spectra of carbon nitride films deposited at different substrate temperature.

Table 3
List of observed IR peaks from Fig. 6, together with calculated peaks of Si_3N_4, α- and β-C_3N_4

Peaks	Observed (cm^{-1})			Calculated (cm^{-1})		
	SiO_1	SiO_2	SiO_5	α-C_3N_4	β-C_3N_4	Si_3N_4
1	432	430	432	–	–	433
2	494	492	494	–	–	490
3	513	511	509	–	–	–
4	575	571	571	–	–	570
5	613	611	613	–	–	–
6	687	685	687	–	–	680
7	852	850	852	–	–	–
8	887	883	887	–	891	–
9	1034	1030	1034	1051/1065	–	1033
10	1107	1107	1103	–	1285	–

1065 cm^{-1}. In our IR spectrum, no C=N or C≡N bonds were found at about 1600 cm^{-1} and 2200 cm^{-1}. Other weak peaks may be attributed to Si_3N_4 or other compounds. The results also support the formation of C–N bond in α- and β-C_3N_4 mixture.

4. Conclusions

Crystalline carbon nitride films have been synthesized on Si(100) substrate by microwave plasma chemical vapor deposition method. The effect of substrate temperature on the structure and composition of carbon nitride films was analyzed by XPS, XRD, FTIR and Raman spectroscopy. It was found that appropriate substrate temperature was important for synthesizing C_3N_4 compounds.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China, Grant No. 19674009, and Beijing Laboratory of Vacuum Physics, Chinese Academy of Sciences.

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