

Synthesis and characterization of C_3N_4 hard films

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Abstract C_3N_4 films have been synthesized on both Si and Pt substrates by microwave plasma chemical vapor deposition (MPCVD) method. X-ray spectra were calculated for single phase α - C_3N_4 and β - C_3N_4 respectively. The experimental X-ray spectra of films deposited on both Si and Pt substrates showed all the strong peaks of α - C_3N_4 and β - C_3N_4 , so the films are mixtures of α - C_3N_4 and β - C_3N_4 . The N/C atomic ratio is in the range of 1.0—2.0. X-ray photoelectron spectroscopy (XPS) analysis indicated that the binding energy of C 1s and N 1s are 286.2 eV and 399.5 eV respectively, corresponding to polarized C-N bond. Fourier transform infrared absorption (FT-IR) and Raman spectra support the existence of C-N covalent bond in the films. Nano-indentation hardness tests showed that the bulk modulus of a film deposited on Pt is up to 349 GPa.

Keywords: β - C_3N_4 , MPCVD, film deposition.

Since Liu and Cohen^[1] proposed a hypothetical new material β - C_3N_4 with a bulk modulus comparable to or greater than that of diamond, lots of researchers have tried to synthesize it in laboratory. However, little progress was achieved before 1996. Most deposited films were not good enough for further analysis, and some of them were even not continuous. A few rings of electron diffraction or a few peaks of XRD are not enough to identify a new phase. The N/C atomic ratio is also much lower than the stoichiometric value of 1.33. Data of hardness of bulk modulus have rarely been published. Someone even threw doubt upon the possibility of synthesizing β - C_3N_4 .

At the session of hard materials in '94 C-MRS (Materials Research Society of China), we proposed to perform an experiment on a system containing N, C only in order to see the tendency towards C-N phase formation. We implanted high dose of N^+ into high purity graphite to obtain C-N films and got a comparatively full X-ray spectrum in accord with the theoretical predicted crystal structure of β - C_3N_4 ^[2-4].

Significant progress has been made all over the world after 1996 and more than a hundred papers on this subject were published every year. A variety of analytical methods have been used to characterize carbon nitride films, but the results were often scattered. It is about time to carefully evaluate those data and establish some reasonable criterion to identify it. Computer simulations can be a useful tool sometimes.

In this paper, we concentrated our attention on the characterization of the films deposited on

Si and Pt substrates by MPCVD. X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDX), XPS, FT-IR, Raman spectra and nanoindentation were performed, in order to verify whether the films were composed mainly of C_3N_4 compound.

1 Experimental

Carbon nitride films were deposited on a MPCVD system as shown in fig. 1. Vacuum was provided through a combination of a turbo-molecular pump and a rotary pump. Working gases, 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. Substrate temperature was monitored by an infrared pyrometer.

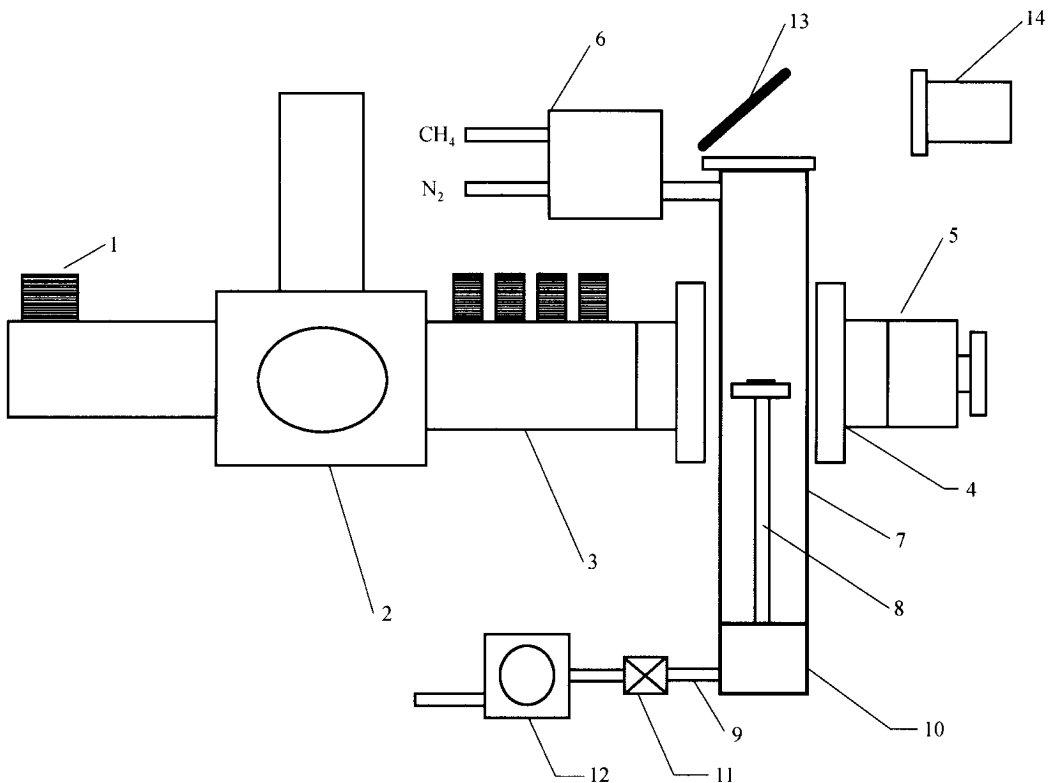


Fig. 1. An illustration of the MPCVD deposition device. 1, Microwave generator; 2, circulator and waterload; 3, four screw adapter; 4, working area of microwave; 5, movable terminator; 6, mass flow controller; 7, quartz glass tube; 8, sample holder; 9, vacuum tube; 10, turbo-molecular pump; 11, valve; 12, mechanical pump; 13, reflection mirror; 14, infrared pyrometer.

The deposition conditions were developed from typical conditions for the growth of diamond films. The substrate temperature ranged from 700 to 950°C, and the working pressure was about 2 500 Pa. The flow rates of CH_4 , N_2 were 1 sccm and 100 sccm, respectively. The growth parameters were optimized in the process to get better carbon nitride films.

Most of the samples were deposited for one and half an hours and have a thickness of a few

hundred nano-meters. The deposition rate is about 2–6 nm/min, depending on the growth conditions. It was found that substrate temperature played an important role in the growth of carbon nitride films. Lower temperature reduced the influence of the substrate, but increased the tendency to form graphite; and higher temperature was favorable to the growth of the C_3N_4 compound. Our experience conforms to the results presented by Chen^[5] and Yen^[6].

2 Results and discussion

2.1 Surface morphologies

The surface morphologies of the deposited films were investigated by a Hitachi S4200 scanning electron microscope. Fig. 2 shows a typical scanning electron microscope photograph of a carbon nitride film deposited on Si substrate for 90 min. It was found that the film consisted of hexagonal crystalline rods. These rods are about 2–3 μm long and about 0.7 μm wide.

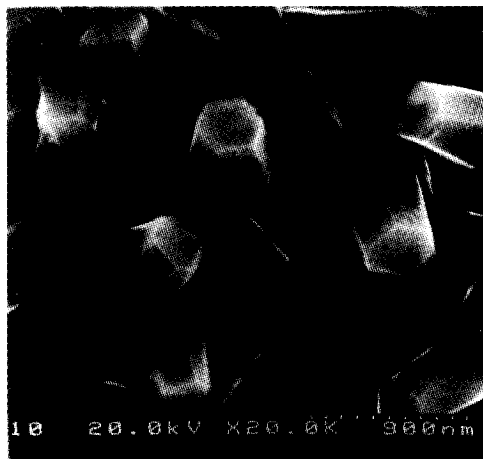


Fig. 2. The surface morphology of a C_3N_4 film deposited on Si substrate.

2.2 Crystal structure

Most of the CN films reported in published papers are composed of multiple phases, especially in those deposited on Si substrates. Si diffused into the film during deposition process. According to the electronegativity difference^[7] 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. 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 this is not available; therefore we have no alternative but to rely on computer simulations. Teter^[8] offered plentiful data which enable us to calculate the standard X-ray spectra of C_3N_4 . In this paper, we took Teter's data as standard and used the Cerius II material analysis package from Molecule Simulation Incorporation to calculate the spectra of the α - and β - C_3N_4 (figs. 3 and 4). The calculated results indicated that most of the peaks of α - C_3N_4 were overlapped with peaks of β - C_3N_4 .

X-ray diffraction experiments were performed on a Rigaku D/Max II rotating anode X-ray diffractometer. Table 1 lists the observed d-spacing of the diffraction peaks. Calculated values of α - C_3N_4 , β - C_3N_4 and data from JCPDS for Si_3N_4 and Si are also listed for comparison.

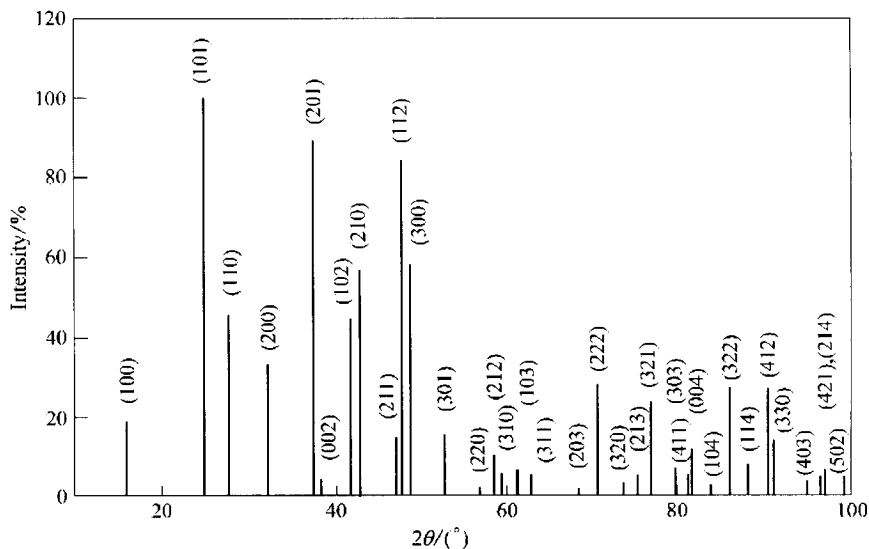


Fig. 3. The calculated full spectrum of α - C_3N_4 .

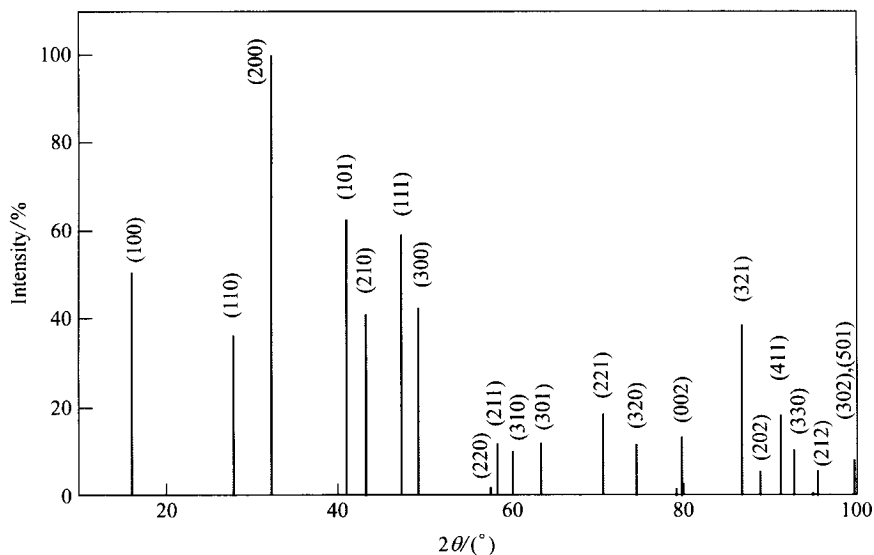


Fig. 4. The calculated full spectrum of β - C_3N_4 .

The experiment observation points out that we have got almost complete spectra including all the strong peaks of α - C_3N_4 , (101), (110), (201), (102), (210), (112) and (300), and β - C_3N_4 , (110), (200), (101), (210), (111) and (300). The (110), (102), (210), (112) and (300) peaks of α - C_3N_4 were overlapped with (110), (101), (210), (111) and (300) of β - C_3N_4 respectively. Other peaks can be assigned to β - Si_3N_4 and the Si substrates. These experiments indicate that the films deposited on Si substrates are composed of α - and β - C_3N_4 , and β - Si_3N_4 .

At the early stage of research, only a few rings of electron diffraction or a few peaks of XRD were detected which are not enough to identify an unknown new phase. Zhang^[9] got a comparative-

ly full spectrum in 1996. Fang^[10] highly evaluated and pointed out that the supporting evidence was incomplete while the strong peaks were missing.

In order to reduce the interference from substrate, we examined the samples with different thickness systematically. It is clear that Si_3N_4 was mainly located near the interface with substrate. Most of the films were about $0.5 \mu m$ thick which was much smaller than the penetration depth of the X-ray. Even though we let X-ray beams incident on the sample surface with incident angle of 2° – 3° , the influence of the substrate is still inevitable.

Table 1 The observed X-ray spectrum from a crystalline C_3N_4 film deposited on Si single crystal substrate, and the calculated spectra

No.	Observed			Calculated				β - Si_3N_4		Si single crystal	
	2θ	$d/\text{\AA}$	I/I_0	α - C_3N_4		β - C_3N_4		JCPDS1983 33-1160		5-0565	
				$a = 6.4665/\text{\AA}$ $c = 4.7097$		$a = 6.4017/\text{\AA}$ $c = 2.4041$		hkl	$d/\text{\AA}$	hkl	$d/\text{\AA}$
1	13.76	6.430	7					100	6.583		
2	23.52	3.779	5	101	3.6045			110	3.800		
3	27.36	3.257	8	110	3.2333	110	3.2009	200	3.293		
4	33.00	2.712	9			200	2.7720				
5	33.48	2.674	5					101	2.660		
6	36.24	2.477	12	201	2.4068			210	2.489		
7	38.72	2.324	6	002	2.3549			111	2.310		
8	39.72	2.267	7	102	2.1717	101	2.2057	300	2.1939		
9	43.36	2.085	9	210	2.1167	210	2.0954				
10	46.12	1.996	5	211	2.9306						
11	47.64	1.907	8	112	1.9035	111	1.9223				
12	48.72	1.867	10	300	1.8667	300	1.8480	310	1.8275		
13	54.20	1.691	8	301	1.7354						
14	57.64	1.598	6	220	1.6166	220	1.6004				
15	60.92	1.519	7	103	1.5116	310	1.5376				
16	66.80	1.399	15	400	1.4000						
17	67.80	1.381	26			400	1.3860				
18	68.60	1.367	44	203	1.3694						
19	69.28	1.355	60	401	1.3420						
20	70.08	1.342	100			221	1.3322			400	1.357
21	73.08	1.294	11			311	1.2954				
22	74.76	1.269	7			320	1.2719				

For totally eliminating the influence of the substrate, we deposited on Pt. Data are listed in table 2. We have got a spectrum with almost the same strong peaks for both α - and β - C_3N_4 . Pt has no simple nitride or carbide, so it is clear that the film is a mixture of α - and β - C_3N_4 .

It is desirable to synthesize single phase film only with α - C_3N_4 or β - C_3N_4 . Since the total energy, crystal structure, composition, bulk modulus, band gap, and atomic density of the two phases are so close^[8], it is very difficult to isolate them. For practical application, we need not separate them. As in the case of carbon, it has a lot of allotropes, but people need not separate them

for practical application.

Table 2 The observed X-ray spectrum from a crystalline C_3N_4 film deposited on polycrystalline Pt substrate, and the calculated spectra

No.	Observed			Calculated				Pt Polycrystalline	
	2θ	$d/\text{\AA}$	I/I_0	$\alpha\text{-}C_3N_4$		$\beta\text{-}C_3N_4$		4 - 0862	
				$a = 6.4665/\text{\AA}$	$c = 4.7097$	$a = 6.4017/\text{\AA}$	$c = 2.4041$	hkl	$d/\text{\AA}$
				hkl	$d/\text{\AA}$	hkl	$d/\text{\AA}$	hkl	$d/\text{\AA}$
1	23.60	3.767	13	101	3.605				
2	26.04	3.419	13	110	3.233				
3	28.40	3.140	20			110	3.201		
4	29.14	3.064	40						
5	32.48	2.754	12	200	2.800	200	2.772		
6	35.76	2.509	18	201	2.407				
7	39.16	2.298	22	102	2.171	101	2.206		
8	39.88	2.259	100	210	2.117	201	2.095	111	2.265
9	46.36	1.957	2580					200	1.962
10	47.12	1.927	33	211	1.931	111	1.922		
11	48.24	1.885	26	300	1.867	300	1.848		
12	52.20	1.751	14	301	1.735				
13	55.92	1.643	13	220	1.617				
14	57.16	1.610	15			220	1.600		
15	58.04	1.588	13	212	1.574	211	1.580		
16	60.56	1.528	13	103	1.512	310	1.538		
17	64.44	1.445	14			301	1.465		
18	67.60	1.385	57					220	1.387
19	73.04	1.294	17	320	1.285	320	1.272		
20	81.40	1.181	6852					311	1.1825
21	85.84	1.131	19					222	1.1325

2.3 Concentration

It was a difficult problem to raise the N/C ratio. Up to now, only a few research groups have increased the ratio up to the stoichiometric value of 1.33.

EDX analysis was performed by an Oxford 6566 detector with an ultra-thin window on a Hitachi S-4200 SEM. The ultra-thin window allows the low energy characteristic X-rays of light elements to pass without significant loss and made it capable to measure the concentration of light elements down to Boron ($Z = 5$).

Fig. 5 is a typical EDX spectrum of the carbon nitride film deposited on Si substrate. The atomic concentrations of N, C were 42%, 31% respectively, and the N/C ratio was close to 4/3. Measurements on different samples indicated the values of N/C ratio to be in the range of 1.0—2.0 depending on the deposition conditions. Experiments imply that the N/C ratio can be easily raised using MPCVD method.

XPS is quite sensitive to the characteristics of film surface because the nonelastic scattering mean free path λ_m of the emitted photoelectron is very short. Experiments were performed on a VG

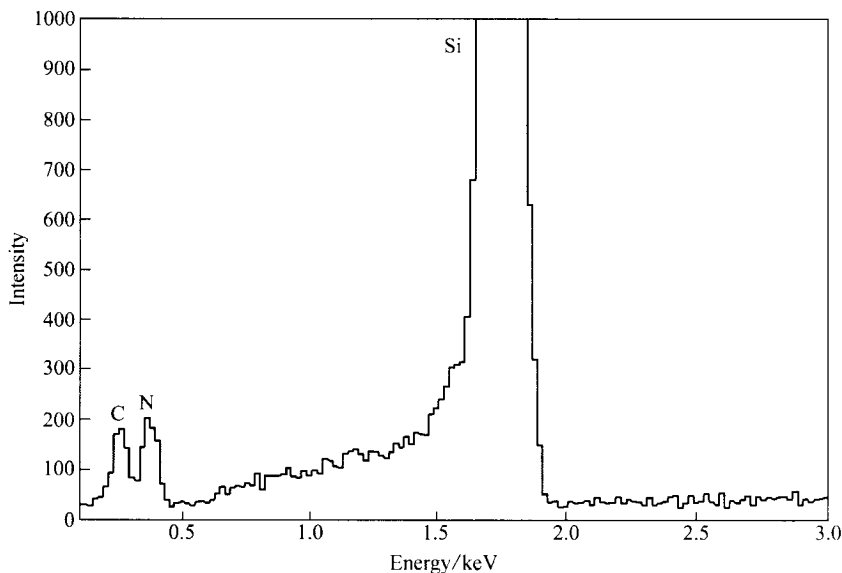


Fig. 5. A typical EDX spectrum of carbon nitride film deposited on Si substrate.

Scientific Lab 5 ESCA. Fig. 6 showed a typical carbon and nitrogen 1s XPS spectra. Two Gaussians are necessary to fit the peaks. The data are listed in table 3.

Table 3 The XPS data of a carbon nitride film deposited on Si substrate

Peaks	Peak area	Center/eV	Width/eV	Height
C 1s	1033	286.2	2.3	360
	233	288.9	3.2	59
N 1s	2764	399.5	2.0	1083
	219	402.1	2.6	66

A lot of XPS spectra were published in literature, but results were rather scattered and the assignment of the peaks was different. Someone directly compared the spectrum with the spectrum of diamond, but Marton^[11] argued that it was not appropriate. Diamond, the tetrahedral allotrope of carbon, has about the same binding energy as other pure carbon forms and hydrogenated carbons^[12,13]. The binding energy of the 1s electrons is quite insensitive to the coordination as long as the bonds are not polarized. Marton pointed out that in the tetrahedrally bonded nitrogen-containing compound urotropine ($C_6H_{12}N_4$), the C 1s binding energy is 286.9 eV^[14]; and N 1s is 399.4 eV^[15]. The shifts are due to the higher degree of polarization of the C-N bonds in urotropine. The above binding energy values are close to the data listed in table 3.

The electro-negativities of C and N are 2.5 and 3.07 respectively. There is charge transfer from C to N atom while forming C^+-N^- bond. For carbon atom, reduced outer-shell electron charge weakened its screening effect on the nuclear charge, causing an increase in the mutual attraction between nuclear charge and 1s electron, and bringing about an increase in the binding energy of 1s electron. For the nitrogen atom, it is the reverse. Polarization may give rise to a much larger chemical shift. Diani^[7] has made a map on binding energy shifts referring to Si-Si or C-C binding energies as a function of electro-negativity differences and found a linear relation for SiO,

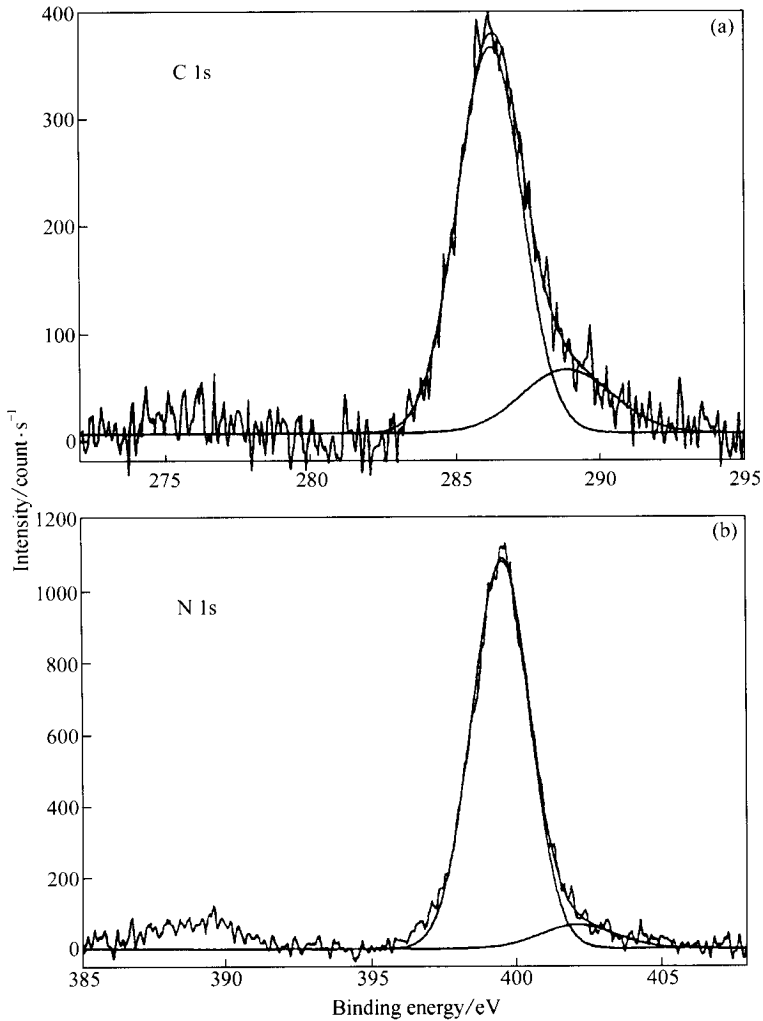


Fig. 6. The typical XPS spectra of carbon nitride film deposited on Si substrate. (a) C 1s region; (b) N 1s region.

SiN, SiC, CN. We extended the map to fig. 7. For $C^+ - N^-$, with the electronegativity difference $3.07 - 2.50 = +0.57$ the observed binding energy of the major peak of C 1s is 286.2 eV; and for $N^- - C^+$, with $2.50 - 3.07 = -0.57$ difference, the binding energy of N 1s is 399.5 eV. The data are well located on the straight line, thus providing a strong evidence for the presence of $C^+ - N^-$ bond in α - and β - C_3N_4 mixture. Here the electronegativity rule may be served as a criterion to guide the assignment of the XPS peaks.

For the minor peak of C 1s, the binding energy is 288.9 eV which may be attributed to SiC or CO due to the inevitable diffusing of Si and surface oxygen contamination. The minor peak of N 1s with binding energy 402.1 eV may refer to N-O or N-N^[11]. We do not discuss this minor part any further in this paper.

From the detailed analysis of C 1s, N 1s peaks (table 3), with sensitivity factors 0.205, 0.38 for C, N respectively, simple calculation can be made to estimate the concentration of N and

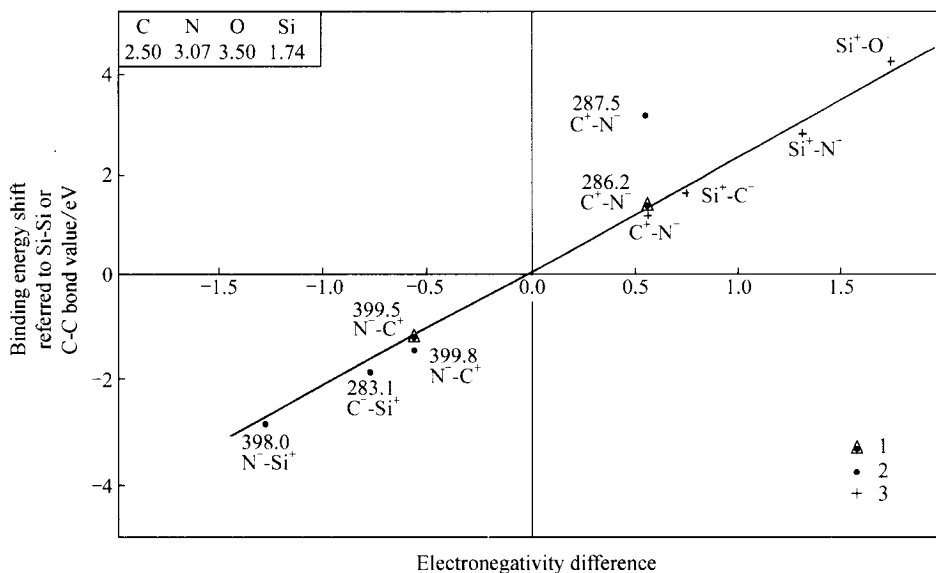


Fig. 7. Experimental binding energy shifts referring to Si-Si, C-C and N-N binding energies as a function of electronegativity differences involved in the different bonds. The electronegativities of the relevant elements are given in the inset.

C. The overall N/C ratio is found to be 1.27, and the N/C ratio in α - and β - C_3N_4 mixture is 1.44. In phases containing C and N, the fractional concentration of α - and β - C_3N_4 is estimated to be 87.8%. We concluded the film was mainly composed of α - and β - C_3N_4 mixture, and the N/C atomic ratio was close to the stoichiometric value 1.33.

Here we need to distinguish three concentration concepts, overall N/C atomic ratio, N/C ratio in α - and β - C_3N_4 and the fractional concentration of sp^3 . These concepts are different but closely related. Marton's^[11] experiment data show a tendency for the sp^3 component to increase as the overall nitrogen content increases. We attribute super-hardness to sp^3 , so the work underway in our laboratory is to further increase the fractional concentration of sp^3 .

2.4 The vibration mode of C_3N_4 .

It is well known that diamond has a sharp Raman peak at 1332 cm^{-1} , and graphite has two broad G, D band centered at 1575 cm^{-1} and 1360 cm^{-1} respectively^[16]. The peaks can be used as fingerprint to identify the existence of diamond and graphite. But for C_3N_4 , the assignment of Raman peaks is just tentative, and no universally accepted spectrum is available.

It should be noted that the comparisons directly with diamond at the early stage of the research were not reasonable, because the structures of C_3N_4 and diamond are quite different. Since the β - C_3N_4 was proposed to adopt the crystal structure of β - Si_3N_4 ^[1], the Raman spectrum of β - C_3N_4 would be analogous to β - Si_3N_4 .

Wada^[17] employed a group theory to calculate possible IR and Raman active modes of Si_3N_4 and experimentally verified the theoretical calculations. Wixom^[18] suggested an approach to estimate the Raman peaks for β - C_3N_4 by correlating the stretching frequency for the C-N bond to that of Si-N bond through Hook's law:

$$\frac{\nu_{\text{CN}}}{\nu_{\text{SiN}}} = \sqrt{\frac{B_{\text{CN}} d_{\text{CN}} \mu_{\text{SiN}}}{B_{\text{SiN}} d_{\text{SiN}} \mu_{\text{CN}}}}, \quad (1)$$

where B , d , μ are the bulk modulus, bond length and reduced mass respectively. Yen^[6] found a scale factor of 1.43 by numerical substitution into eq. (1) and have calculated the analogous peaks for β -C₃N₄ (table 4).

Table 4 Observed and calculated Raman frequencies in α - and β -Si₃N₄, and α - and β -C₃N₄ (cm⁻¹)

α -Si ₃ N ₄	β -Si ₃ N ₄	α -C ₃ N ₄	β -C ₃ N ₄	β -C ₃ N ₄	α - and β -C ₃ N ₄ mixture
observed ^[17]		calculated ^[6]		observed ^[6]	observed, this work
I	II	III ^{a)}	IV ^{a)}	V	VI
	144		206		
153		219			251
	186		166	266	
				280	
202		289			
	210		300		302
	229		327		
231		330		330	
258		369			
282		403			
298		426			
306		438			
321		459			
337		482			
356		509			
361		516			
383		548			
391		559			
				611	
	451		645		
460		658			
470		672			
514		735			
	619		885		946
668		955			984
	732		1047		
				1110	
	685		1237		
	928		1327		
	939		1343		
	1047		1497		

a) Column III = Column I \times 1.43; Column IV = Column II \times 1.43.

Experiments were performed on a FT-Raman JY U-1000 spectroscope. Fig. 8 is the Raman

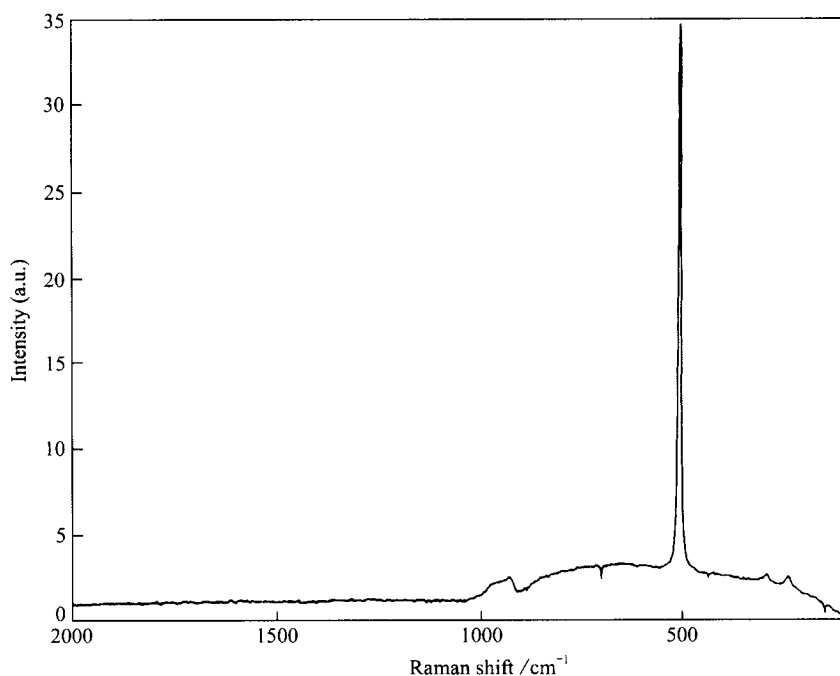


Fig. 8. The Raman spectrum detected from a C_3N_4 film deposited on Si substrate.

spectrum detected from a film deposited on a Si substrate. The Raman spectrum showed no signs of the G, D band which are the fingerprint of graphite. The observed Raman shifts $251, 302\text{ cm}^{-1}$ are close to the calculated data for $\alpha\text{-}C_3N_4(289\text{ cm}^{-1})$ and $\beta\text{-}C_3N_4(266, 300\text{ cm}^{-1})$; observed peaks at $946, 984\text{ cm}^{-1}$ are close to the calculated data for $\alpha\text{-}C_3N_4(955\text{ cm}^{-1})$ and $\beta\text{-}C_3N_4(885, 1\ 047\text{ cm}^{-1})$. The experimental results support the existence C-N bond in α - and $\beta\text{-}C_3N_4$ mixture. It is interesting to mention here that the peaks both in Raman and IR spectra always occur in a pair. It is probable that $251, 946\text{ cm}^{-1}$ may be attributed to $\alpha\text{-}C_3N_4$; and $302, 984\text{ cm}^{-1}$ to $\beta\text{-}C_3N_4$.

For FT-IR analysis, we rely on a computer simulation using the Cerius II material analysis package. Calculated and experimental results are shown in table 5 and fig. 9. Observed peaks at $853, 888\text{ cm}^{-1}$ are close to the calculated $\beta\text{-}C_3N_4$ IR active mode at 891 cm^{-1} ; observed peaks at $1\ 033, 1\ 100\text{ cm}^{-1}$ are close to the calculated $\beta\text{-}C_3N_4$ IR active mode at $1\ 051$ and $1\ 065\text{ cm}^{-1}$. Other weak peaks may be attributed to Si_3N_4 or others unknown phases. The above results also support the formation of C-N bond in α - and $\beta\text{-}C_3N_4$ mixture.

2.5 Bulk modulus and hardness

Hardness is an important aspect on synthesizing C_3N_4 because it is its superhardness that brings about an outburst of enthusiasm on synthesizing it. But we regret that little data were published. Tests were carried on a Nano II nano-indenter. The bulk modulus was measured on a film deposited on Pt substrate. The film thickness, and maximum load were $0.6\ \mu\text{m}$, 3.86 mN respectively. 6 iterations of a power law fit function were performed to determine the best correlation of the slope. The bulk modulus was up to 349 GPa . It is about 80% of the diamond's and close to that of c-BN. This film is really a new member of the hard material family, but not as hard as dia-

mond, because:

(i) Except the major part α - and β - C_3N_4 , the film is also composed of other phases, and sp^2 bonding may reduce the hardness of films considerably.

(ii) Imperfections in crystal are unavoidable for a film quickly deposited within 1—2 h at 1 073 K. Until now, some properties of man-made diamond are still lower than those of natural one.

After a decade of painstaking efforts all over the world, great progress has been achieved, but the situation mentioned above seems rather complicated, and there is still a long way to reach the end of this task. A film of high quality and reliable data on crystal structure, concentration, properties of the bond and hardness are crucial while making a convincing conclusion.

Table 5 The observed and calculated FT-IR spectra of a carbon nitride film deposited on Si substrate (cm^{-1})

Observed	Calculated		
	α - C_3N_4	β - C_3N_4	Si_3N_4
409			
432			433
461			
494			490
510			
573			570
610			
686			680
739			
853			
888		891	
1 033	1 051		1 033
1 100	1 065		
		1 285	
1 457	1 678	1 814	
2 340	1 968		
	2 061		
2362	2 224	2 227	2 300
2850			

3 Conclusions

Films of good quality have been synthesized on Si, Pt substrate using a MPCVD apparatus. The major part of the film is composed of α - and β - C_3N_4 . Other phases and impurities need to be removed. The overall N/C atomic ratio is in the range over 1.0—2.0. The fractional concentration of sp^3 is 87.8%. The binding energy of C 1s and N 1s are 286.2 eV and 399.5 eV respectively. The shifts are attributed to the polarization of the C-N bond. FT-IR and Raman spectra support the existence of C-N covalent bond in α - and β - C_3N_4 . The bulk modulus is up to 349 GPa. Detailed discussions were offered on issues in attempting to establish a criterion for characterizing carbon nitride films.

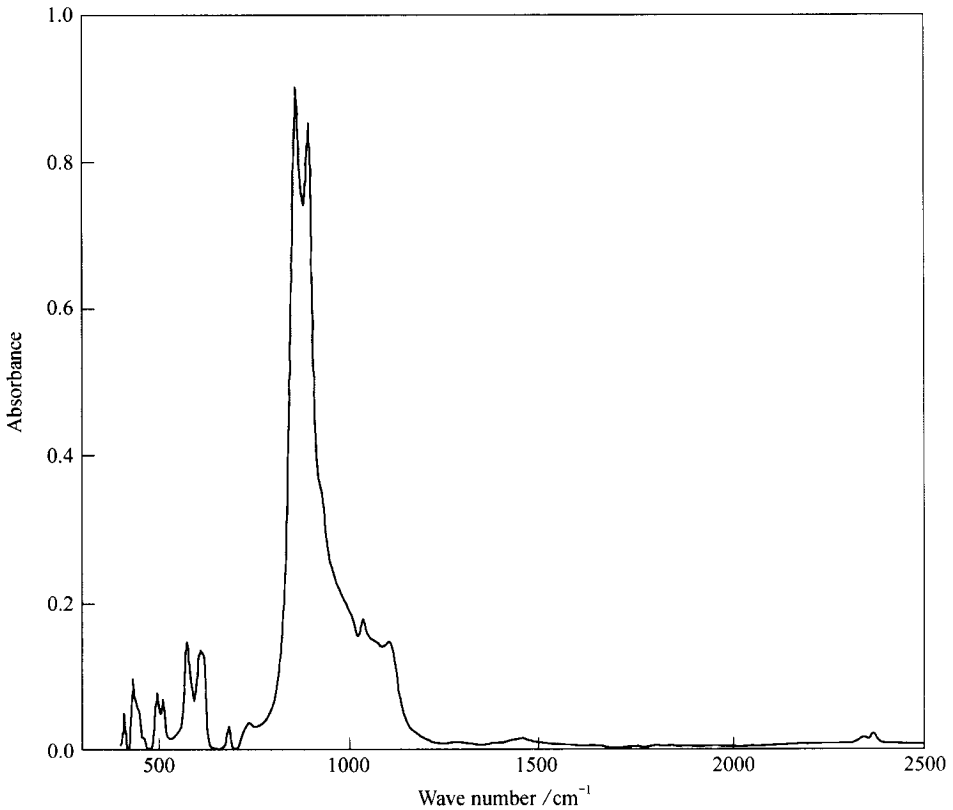


Fig. 9. The FT-IR spectrum of a C_3N_4 film deposited on Si substrate.

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