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Crystalline β-C_3N_4 synthesized by MPCVD

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Carbon nitride films were grown on Si and Pt substrates by microwave plasma chemical vapor deposition (MPCVD) method. Scanning electron microscope (SEM) observations show that the films deposited on Si substrates consisted of densely populated hexagonal crystalline rods. Energy dispersive X-ray (EDX) analyses show that N/C ratios of the rods were in the range of 1.0 to 2.0 depending on deposition condition. X-ray diffraction experiments show that the films consisted of crystalline phase β-C_3N_4. Comparison with films grown on Pt substrate show that the main X-ray diffraction peaks of β-C_3N_4 are existed in films deposited on both substrate. XPS study showed that carbon and nitride atoms are covalent bounded to each other. IR results show that the film is predominantly C-N bonded. Raman measurement showed characteristic peaks of β-C_3N_4 in the low wave number region. Temperature dependent growth experiments show that the amount of Si_3N_4 in the films grown on Si substrates can be significantly reduced to negligible amount by controlling the substrate temperature. © *1999 Kluwer Academic Publishers*

1. Introduction

β-C_3N_4 is a hypothetical super hard material predicated by *ab initio* calculation from first principles [1–3]. Since then, scientists all over the world tried to synthesize it in laboratory through various kinds of experimental means. After years of hard working, some progress has been made in both theoretical calculation and experimental synthesis. Theoretical studies have been made on several other forms of carbon nitrides on issues such as stability, crystal structure, hardness etc. [4–6]. Meanwhile, lots of experimental techniques have been employed to synthesize it, such as high pressure pyrolysis, ion implantation, physical vapor deposition, chemical vapor deposition, and so on [7–26]. However, the formation of crystalline β-C_3N_4 is not confirmed yet.

We have reported the formation of crystalline grains of β-C_3N_4 and planar form carbon nitride p-C_3N_4 in carbon matrix by high dose ion implantation of N^+ into pure graphite plate and carbon films [19–21]. However, the nitrogen concentration in films prepared by this method could not be increased any further. In this paper, microwave plasma chemical vapor deposition (MPCVD), an experimental method used successfully in deposition covalent hard substances such as diamond and c-BN films, was used to deposit carbon nitride films on Si and Pt substrates. The surface morphology, chemical composition, crystal structure, atomic bonding status and hardness of the samples were analyzed. Experimental results show that crystalline carbon nitrides have been synthesized in the deposited films.

2. Experimental

Carbon nitride films were deposited in a MPCVD system as illustrated in Fig. 1. Vacuum was supplied by 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 power of microwave in the chamber 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 infra-red pyrometer. It is determined by the power of microwave in the deposition chamber, the flow rates of working gases, working pressure and the position of substrate in the deposition chamber.

The deposition conditions were adapted after typical condition for the growth of diamond films. The substrate temperature ranges from 700 to 900 °C, and the working pressure is about 3000 Pa. The flow rates of CH_4 to N_2 is about 1 and 100 sccm respectively. The growth parameters are optimized in the process to get better carbon nitride films.

Most of the samples were deposited for one and half an hour and have a thickness of a few hundred of nanometers. The deposition rate is about 2–6 nm/min. depending on growth condition. Long time depositions up to several hours were also carried out for some samples. It is found that substrate temperature played an important role in the growth of carbon nitride films and

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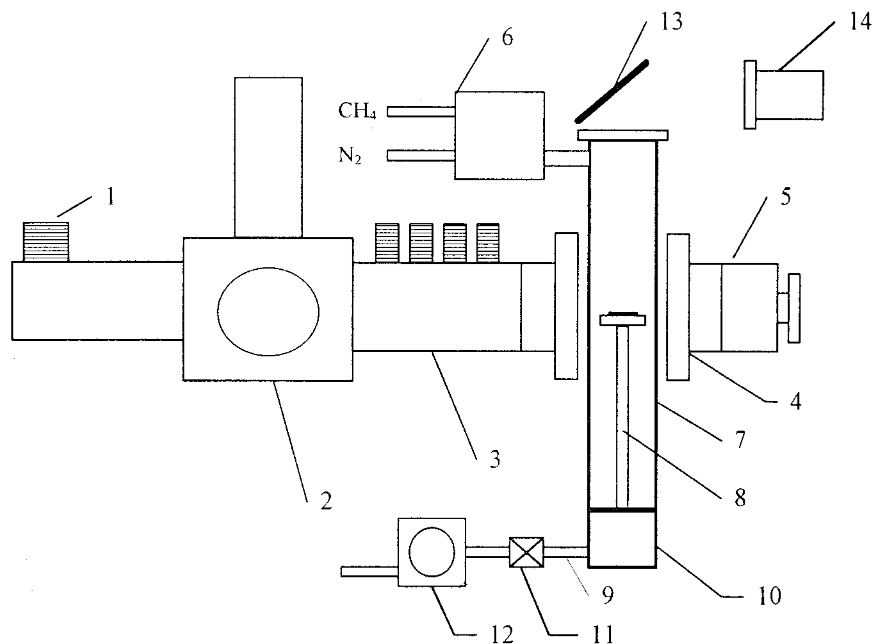

Figure 1 An illustration of the MPCVD apparatus used in the experiments. 1. Microwave generator 2. Circulator and waterload 3. Four screw adapter 4. Working area of microwave 5. Movable terminator 6. Mass flow controller 7. Quartz glass tube 8. Sample holder 9. Vacuum tube 10. Turbo molecular pump 11. Valve 12. Mechanical pump 13. Reflection mirror 14. Infrared pyrometer.

that the amount of β-Si_3N_4 can be reduced greatly in the films at low substrate temperatures.

3. Results and discussion

3.1. Surface morphology

The surface morphologies of deposited films were investigated by a Hitachi S-4200 scanning electron microscope. It was found that the films consisted mainly of hexagonal crystalline rods. These rods are about 2–3 μm long and about 0.7 μm wide. They are densely populated on the surface of substrates. Fig. 2 shows a typical SEM micrograph of a carbon nitride film deposited on Si substrate for 90 minutes. We can see well edged, hexagonal shaped crystalline rods lying on the substrate.

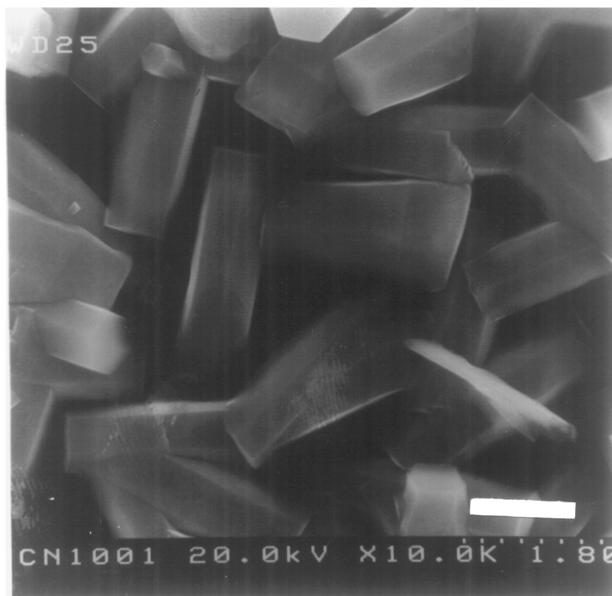

Figure 2 A typical SEM micrograph of carbon nitride films deposited on Si substrates. The white bar in the low right corner is 1 μm long. Well edged crystalline bars lying on Si substrate.

3.2. Chemical composition

The chemical compositions of the deposited CN_x films were examined by energy dispersive X-ray (EDX) analysis. Measurements were taken on crystalline rods by an Oxford 6566 detector with an ultra-thin window attached on a Hitachi S-4200 scanning electron microscope. The ultra-thin window allows the low energy characteristic X-rays of light elements to pass without significant loss, make the detector capable of measuring the concentration of light elements down to Boron ($Z = 5$). The atomic ratios of nitrogen to carbon were found to be in the range of 1.0–2.0, depending on deposition conditions. It was also found that regularly shaped hexagonal crystalline rods have an N/C ratio close to 4/3. Fig. 3 is a typical EDX spectrum of a carbon nitride film deposited on Si substrates (830 °C, 0.7 sccm CH_4, 100 sccm N_2, 19 Torr, deposited for 90 minutes). The acceleration voltage is 20 kV. The chemical concentrations of C, N and Si are evaluated by ZAF method to be 31, 42 and 27%, respectively. The N/C ratio is almost 4/3, close to the theoretical one of C_3N_4.

However, it is worth noting that the measurement of concentration of light elements in thin films is a big challenge due to their low sensitive factor, as revealed by the extremely low peaks of C and N as compared to that of Si as shown in Fig. 3. Since the size of the rods is smaller than the size of the effective region EDX experiments measure, the resulting concentration is sum of the crystal rod and the Si substrate. The existence of Si peaks in EDX spectrum is inevitable. Meanwhile,

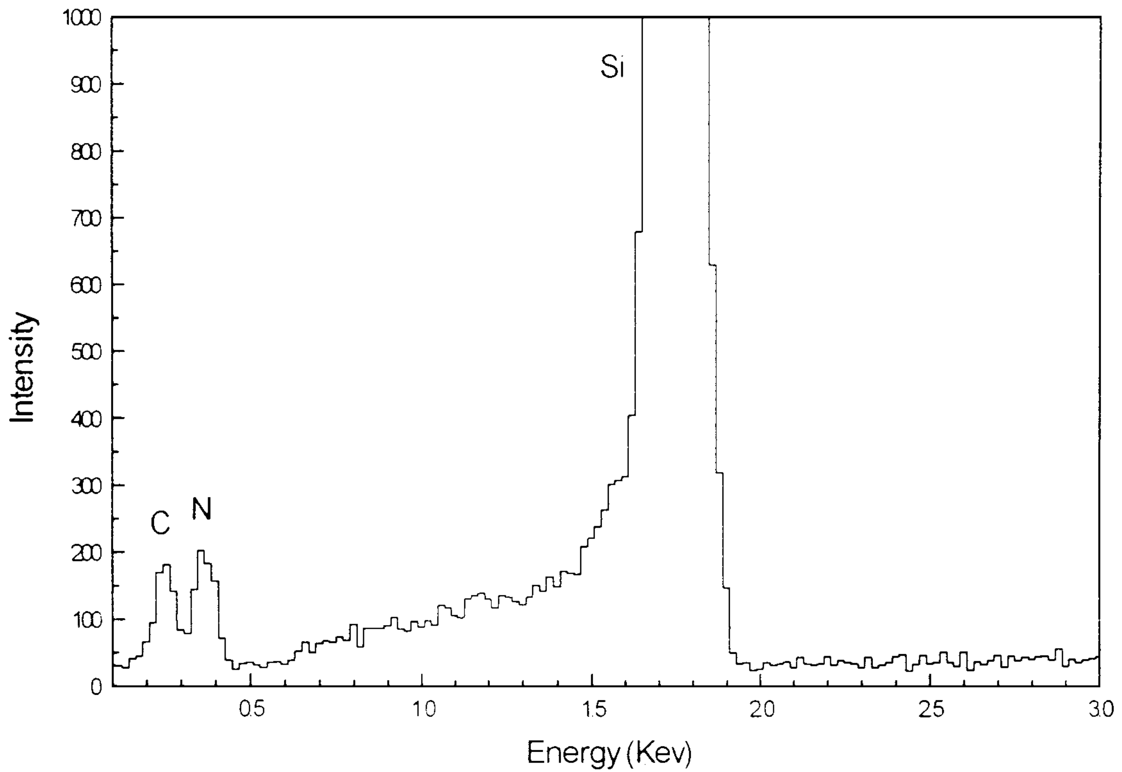

Figure 3 A typical EDX spectrum of carbon nitride films deposited on Si substrates. The acceleration voltage of electron beam is 20 kV.

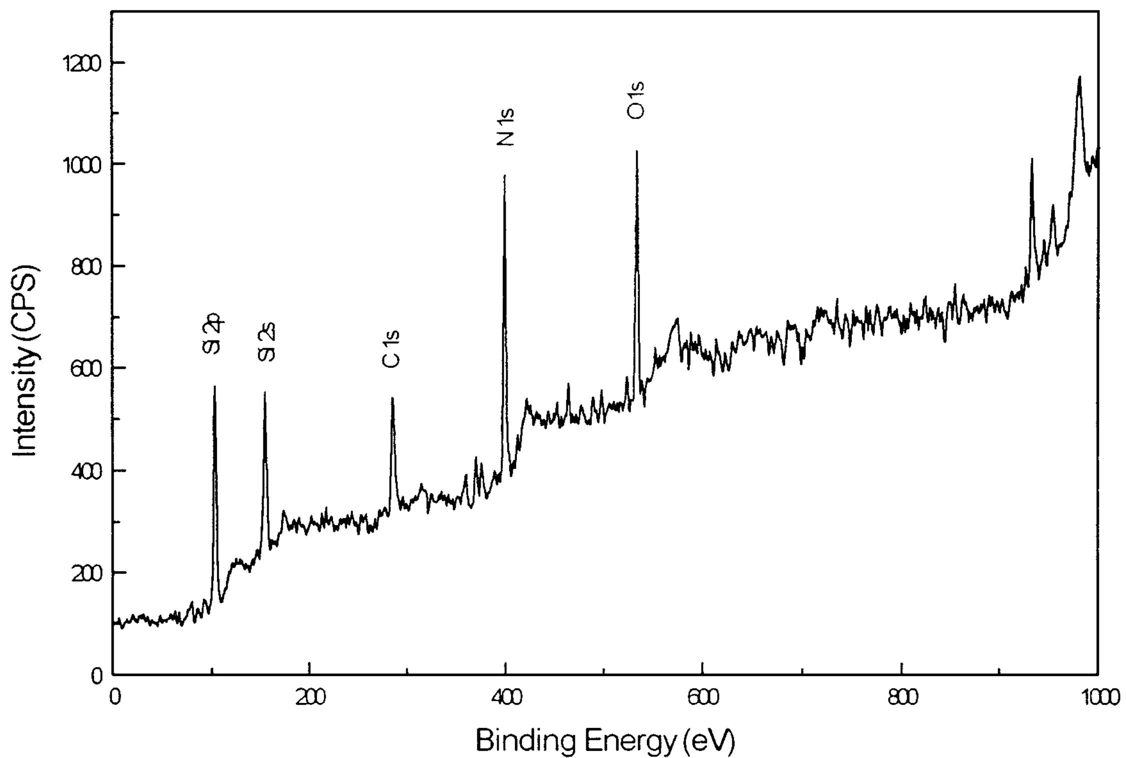

Figure 4 An overall XPS spectrum of carbon nitride films deposited on Si substrates.

the measured concentration varies from rod to rod, indicating that concentration differs among them. The significance of concentration measurement should best be confirmed by other techniques.

The chemical composition of carbon nitride films were also measured by XPS experiment. XPS can give more accurate results of light elements in surface layer. It was performed on a VG scientific Lab 5 ESCA (electron spectrometer for chemical analysis). X-rays was produced by Al targets on this equipment. Fig. 4 shows an overall spectrum of a carbon nitride film grown on silicon substrate (800 °C, 1.0 sccm CH_4, 100 sccm N_2, 90 minutes). Integrated intensity of the XPS peaks obtained by detailed scan showed that the atomic

concentration of the C, N, O and Si is 20.8, 26.3, 12.2 and 40.7%, respectively. Since XPS measurements are surface sensitive and surface adsorbed oxygen played an important role, the measured data showed a large amount of oxygen. The large amount of Si is due to the uncovered surface of substrate (about one third as revealed in SEM observation on this sample). The Atomic ratio of N to C is about 1.33, close to the theoretical value of C_3N_4.

From the above concentration measurements, it is clear that the atomic ratio of N/C in films deposited by MPCVD meet with the theoretical value of β-C_3N_4.

3.3. Crystal structures

X-ray diffraction experiments were performed on a Rigaku D/Max II rotating anode X-ray diffractometer (12 kW, CuK_α Radiation). Lots of Bragg's peaks were found on the spectra. Therefore, the deposited films are crystalline. Fig. 5 shows a typical X-ray diffraction spectrum of a carbon nitride film. Table I lists the d-spacing of all the diffraction peaks in the spectrum. Theoretically calculated values of β-C_3N_4 and β-Si_3N_4 are listed in the table. We can see that most of the low index, high intensity peaks of β-C_3N_4, such as (110), (200), (101), (210), (111) and (300), show up

TABLE I The X-ray diffraction results of Fig. 5. The experimental d-spacing are listed along with the theoretical predicated ones of β-C_3N_4 and β-Si_3N_4. CuK_α radiation are used in the experiments

	Experimental			β-C_3N_4			β-Si_3N_4		
No.	2θ	d (Å)	I	(hkl)	d (Å)	I	(hkl)	d (Å)	I
1	12.80	6.910	474				(100)	6.580	34
2	20.64	4.300	54						
3	22.84	3.890	91				(110)	3.800	35
4	26.48	3.363	912						
5	27.88	3.197	126	(110)	3.201	36	(200)	3.293	100
6	28.60	3.118	238						
7	31.84	2.808	96	(200)	2.772	100			
8	35.44	2.531	368						
9	38.60	2.330	56				(111)	2.310	9
10	40.40	2.231	26	(101)	2.206	63			
11	42.28	2.136	97	(210)	2.095	41			
12	46.68	1.944	62	(111)	1.922	59			
13	47.72	1.904	87				(220)	1.900	8
14	49.40	1.843	53	(300)	1.848	42	(310)	1.830	12
15	51.68	1.767	33				(301)	1.750	37
16	53.16	1.721	29						
17	56.68	1.623	37	(220)	1.600	2.			
18	60.04	1.540	35	(310)	1.538	10			
19	60.72	1.524	38				(320)	1.511	15
20	64.08	1.452	41	(301)	1.465	12	(002)	1.454	15
21	69.68	1.348	37				(321)	1.341	39
22	71.00	1.326	31	(221)	1.332	18			
23	73.04	1.294	19	(320)	1.272	12	(411)	1.288	18
24	80.68	1.190	21	(002)	1.202	13			
25	94.40	1.050	31	(212)	1.043	6			

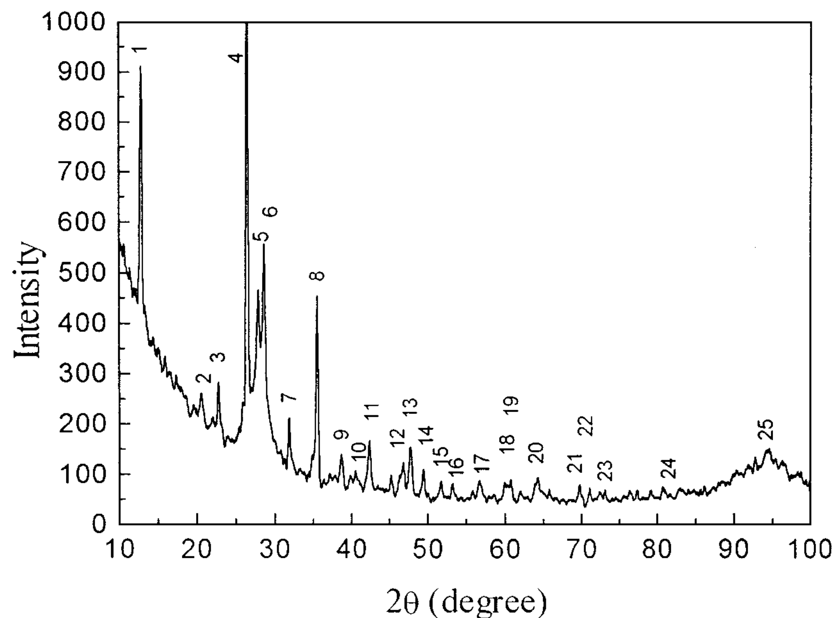

Figure 5 A typical X-ray diffraction spectrum of carbon nitride films deposited on Si substrates.

in the spectrum. Therefore, carbon nitride film consists of β-C_3N_4 and β-Si_3N_4 and unknown phases. Due to the high X-ray scattering factor of Si, the relative small peaks of β-Si_3N_4 show that the amount of β-Si_3N_4 in the film is much smaller than that of carbon nitride.

Since Si can react with both C and N to form compound, complicating the phase identification process, Pt plates have been used as substrate for deposition carbon nitride films. Results show that most of the low index, high intensity peaks of β-C_3N_4 are also presented in X-ray diffraction spectrum of carbon nitride films deposited on Pt. Meanwhile, EDX analysis shows that N/C atomic ratio in the films also close to 4/3. Details on carbon nitride films deposited on Pt substrate will be given in an upcoming paper.

3.4. Chemical bonding

Detailed XPS scans were used to analysis the C, N and Si peaks to study their chemical shift. Fig. 6 shows the detailed shapes of the C ls, N ls and Si 2p peaks. These peaks are de-convoluted by Gaussian peaks. Table II list the results of deconvolution of the peaks, including the area, center, height and width of the Gaussian peaks. The atomic composition of the peaks are also calculated according to the area and sensitive factor and listed in it. Although there are disagreements on the shift of the XPS peaks as reported in literature, the peaks may be assigned tentatively as follow. The C ls peaks at 286.2 and 288.9 correspond to two difference states of C-N bonds [26], respectively. The N ls peaks at 399.5 and 402.1 correspond to N-C and N-O bonds [27], respectively. And the Si 2p peaks at 103.69 and 101.24 may be assigned to Si-O and Si-N bonds, respectively. From the above results, there is a significant amount of N-C and C-N bonds for N and C atoms in the films, favoring the formation of β-C_3N_4 phases.

FT-IR spectrum are also made to study the vibration mode of the samples. Fig. 7 shows a typical IR spectrum of a carbon nitride films. It was characterized by a very high double peak at 853 and 888 cm^{-1}. There are also some sharp peaks at low wave number and a big bump from 850 to 1200 cm^{-1}. In order to identify the peaks, standard spectrum of Si_3N_4 are used for comparison [28]. The feather of IR spectrum of Si_3N_4 is characterized by a wide absorption band between 850 and 1200 cm^{-1}, together with some peaks at low wave number region. The big bump and some peaks at low wave number are indexed to Si_3N_4.

TABLE III List of experimental peaks from Fig. 7, together with standard IR spectrum of Si_3N_4 and theoretically calculated peaks of β-C_3N_4 and α-C_3N_4

Experimental peaks (cm^{-1})	Standard IR peaks (cm^{-1}) Si_3N_4	Calculated IR spectrum (cm^{-1}) β-C_3N_4	Calculated IR spectrum (cm^{-1}) α-C_3N_4
409			
432	433		
461			
494	490		
510			
573	570		
610			
686	680		
739			
853			
888		891	
1033	1033		
1100		1285	1051/1065
1457		1814	1678
2340	2300		1968
			2061
2362		2227	
2850			2224

The strong double peaks is in the range of C-N bond. The IR peaks of β-C_3N_4 and α-C_3N_4 are also calculated by Cerius II material analysis package from Molecule Simulation Incorporation (MSI) to identify the peaks of C_3N_4. All the results are summarized in Table III. The Strong double peak can be assigned to be β-C_3N_4.

Fourier Transform Raman spectroscope was used to study the chemical bond and the crystal symmetry in the films. It is done on a FT-Raman JY U-1000 spectroscope. Fig. 8 shows a typical result of Raman spectroscopy of a carbon nitride film on silicon. The strong peak at 520 cm^{-1} is due to silicon substrate. There are two characteristic peaks located at 251 and 302 cm^{-1}, respectively. Yan and Chou [25] argued that since the crystal structure of β-C_3N_4 is modeled after β-Si_3N_4, its Raman spectrum should resemble that of β-Si_3N_4. From the data of atomic mass and elastic modules of the two substances, they obtained an estimated Raman spectrum of β-C_3N_4. The two experimentally observed Raman peaks are close to the characteristic lines of the estimated spectrum of β-C_3N_4.

The above IR/Raman results show strong evidence to support the formation of β-C_3N_4.

TABLE II Detailed analysis of XPS peaks of a carbon nitride films deposited on Si substrate. For each deconvoluted peaks, the area, center, width and height are listed together with the calculated composition and tentative assignment of bonding status

Peaks	Peak area	Center (eV)	Width (eV)	Height	Peak composition	Element composition	Bond
C 1s	1033	286.17	2.29	360	16.9%	20.8%	C-N
	233	288.87	3.15	59	3.9%		C-N
N 1s	2764	399.46	2.04	1083	24.3%	26.2%	N-C
	219	402.14	2.63	66	1.9%		N-O
Si 2p	1789	103.69	2.18	655	35.2%	40.8%	Si-O
	288	101.24	1.89	122	5.6%		Si-N

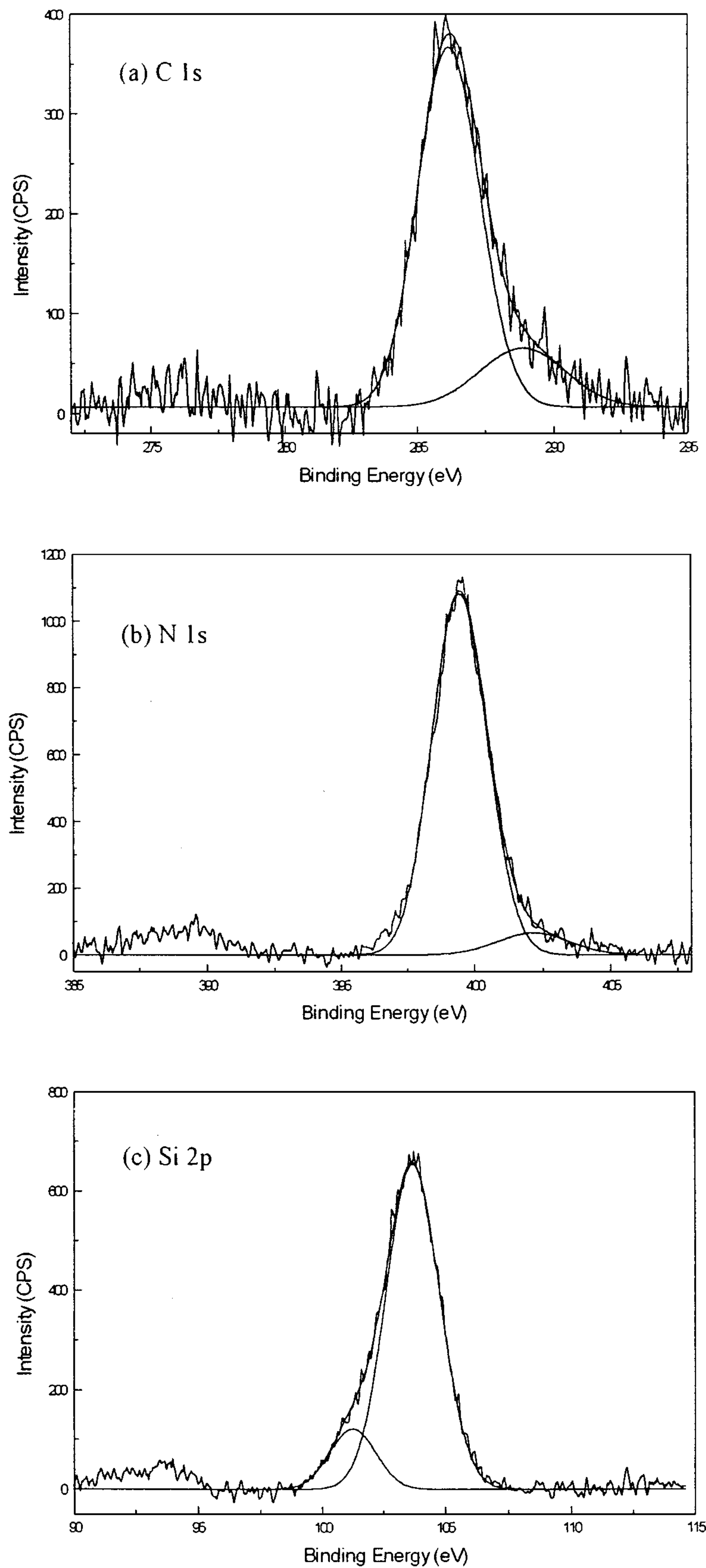

Figure 6 Detailed scans of the C 1s, N 1s and Si 2p XPS peaks.

3.5. Growth conditions

Comparing the film deposited for different time at the same condition, it is clear that samples grown for a long time have a relative small amount of β-Si_3N_4 as compared with the carbon nitride phases. We can infer that β-Si_3N_4 grows more easily near the substrate surface at the first stage of growth. As the film becomes thick, its growth rate decrease and more carbon nitrides are deposited. Therefore, in carbon nitride films on Si substrate, β-Si_3N_4 is mainly located near substrate and carbon nitrides are mainly located near the outer surface of the film.

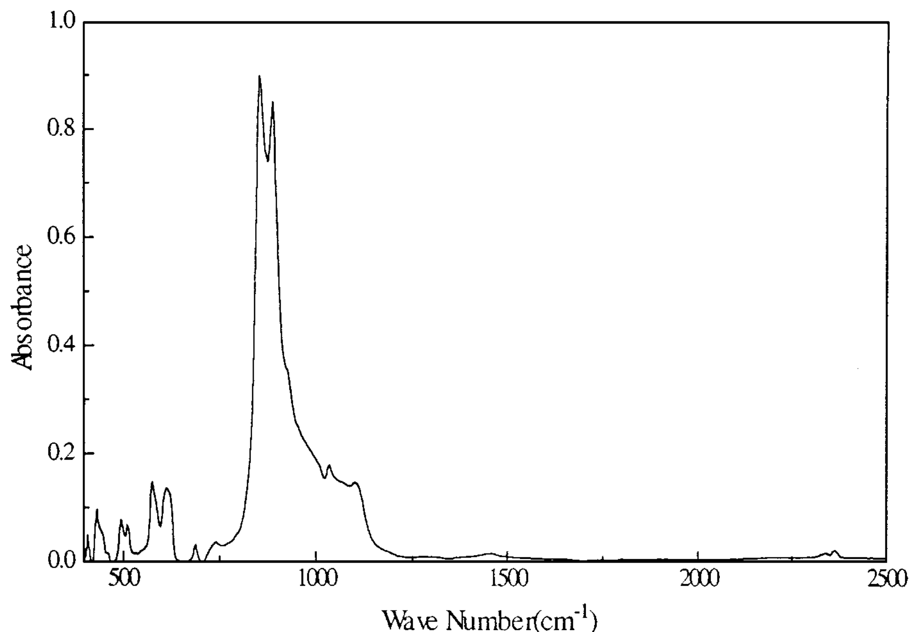

Figure 7 A typical IR spectrum of carbon nitride films deposited on Si substrates.

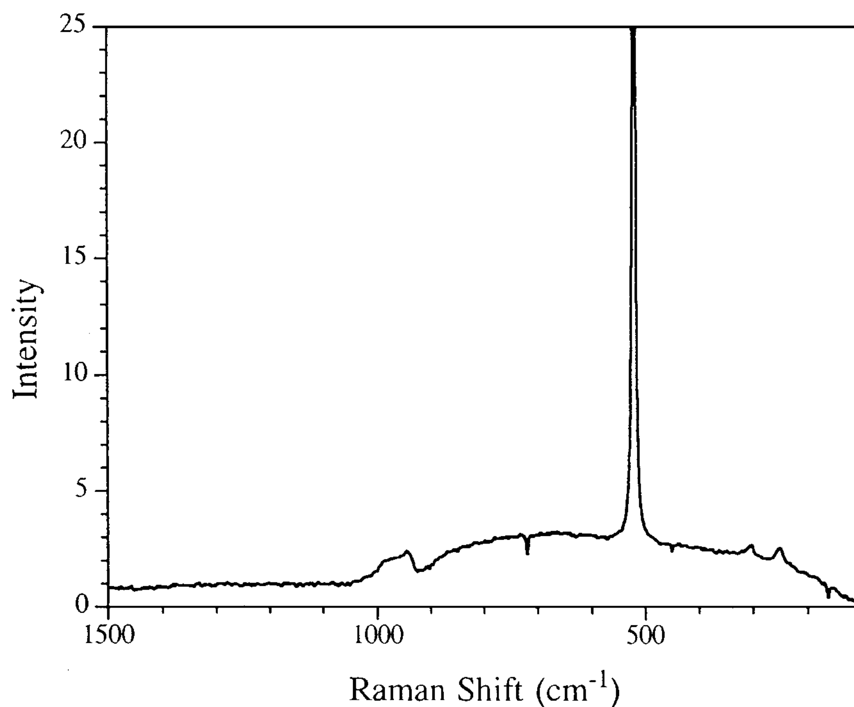

Figure 8 A typical Raman spectrum of carbon nitride films deposited on Si substrates.

In order to optimize the growth condition and obtain better films, carbon nitride films are grown at various conditions. Fig. 9 shows a series of samples grown at three substrate temperatures: 805, 830 and 870 °C. The peaks of β-Si_3N_4 grown very rapidly as the substrate temperature increases. Table IV list all the main X-ray diffraction peaks with intensity. It is found that substrate temperature is an important parameter affecting the quality of the films: higher substrate temperature corresponding to larger amount of β-Si_3N_4. Films grown at substrate temperatures as low as 805 °C have remarkably low X-ray diffraction peaks of β-Si_3N_4.

Therefore, the amounts of β-Si_3N_4 can be significantly reduced under suitable growth conditions.

3.6. Film hardness

In order to test the mechanical properties of the deposited films, hardness tests were performed on a Nano indentor (Nano II). Indentations were done on eight randomly selected points on each sample to reduce the fluctuation of the results. Film hardness are calculated according to loading curve of a carbon nitride film. The calculated hardness of a carbon nitride film on Si substrate is 23.9 GPa. It is close to that of common hard substances, such as TiN, TiC, Al_2O_3, etc. Due to the feature of the films as revealed by Fig. 1, the films are as thick as the crystalline rods (about 0.7 μm), and are not homogeneous on micro-scale. Hardness test will be affected by substrate effect and the choice of the site for

TABLE IV X-ray diffraction results of carbon nitride films deposited at different substrate temperatures

	805 °C		830 °C		870 °C		β-Si_3N_4			β-C_3N_4		
No.	d (Å)	I	d (Å)	I	d (Å)	I	(hkl)	I	d (Å)	(hkl)	d (Å)	I
1	6.430	51	6.632	74	6.544	353	(100)	34	6.580			
2	4.619	50	4.609	20	4.544	23						
3	4.111	55	4.133	41	4.211	20						
4	3.811	30	3.824	45	3.792	109	(110)	35	3.800			
5	3.257	100	3.290	158	3.280	983	(200)	100	3.293	(110)	3.20	36
6	3.081	95	3.118	50	3.140	50						
7	3.007	280	3.039	135	3.064	172						
8	2.712	104	2.738	45	2.703	3268				(200)	2.77	100
9	2.477	183	2.490	121	2.482	386						
					2.393	37						
10	2.319	60	2.333	37	2.361	35	(111)	9	2.310			
11	2.267	77	2.287	46	2.298	69				(101)	2.21	63
12	2.089	113	2.096	58	2.105	69				(210)	2.095	41
13	1.966	37	1.978	38	1.991	28						
14	1.907	70	1.916	43	1.919	85	(220)	8	1.900	(111)	1.922	59
15	1.867	123	1.876	72	1.886	76						
16	1.806	20	1.821	17	1.821	56	(310)	12	1.830	(300)	1.848	42
17	1.691	112	1.699	19	1.710	45	(301)	37	1.750			
18	1.598	47	1.605	41	1.604	39				(220)	1.600	2
19	1.519	57	1.527	32	1.508	26	(320)	15	1.511	(310)	1.538	10
20	1.468	26	1.512	27	1.478	87				(301)	1.465	12

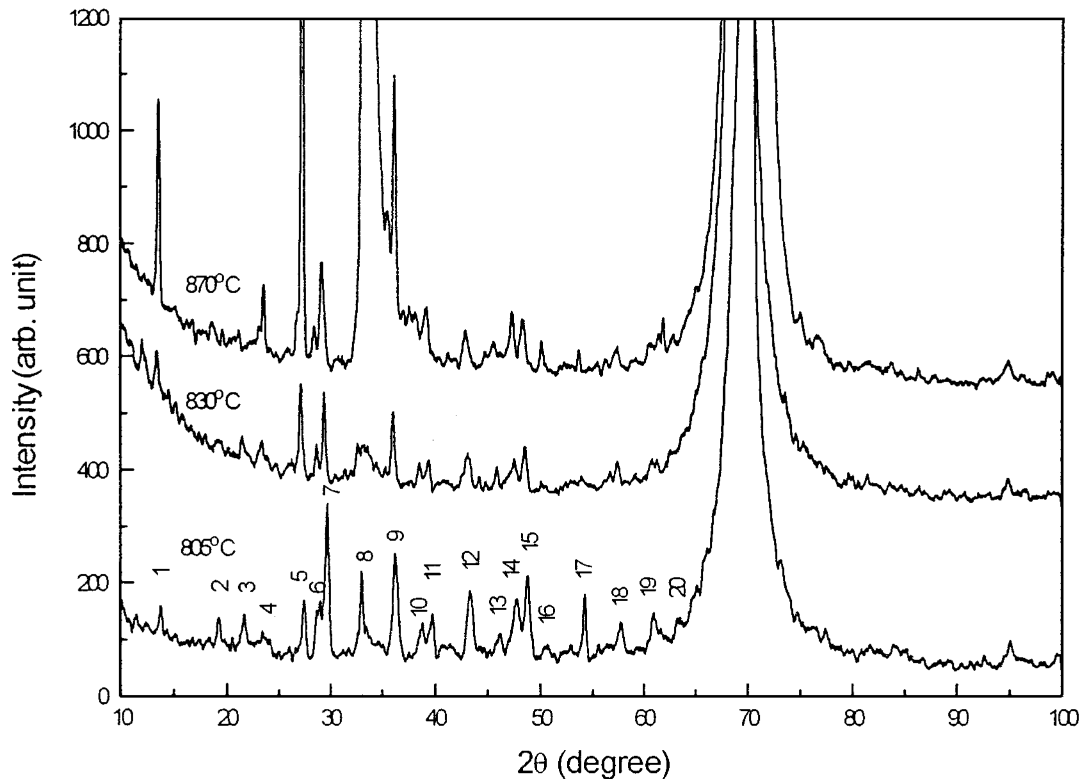

Figure 9 X-ray diffraction spectrum of a series of carbon nitride films deposited at different substrate temperatures on Si substrates.

indentation. The real hardness of a rod may be much higher.

4. Conclusions

From the above experimental results, we can see that crystalline carbon nitride films were successfully deposited on silicon substrate. Hexagonal shaped crystalline rods are formed on silicon substrates. Enough nitrogen concentration has been incorporated into these crystalline rods to form C_3N_4. X-ray diffraction and Raman spectroscopy experiments support strongly the formation of β-C_3N_4. β-Si_3N_4 were also found near the substrate. Its amount can be significantly reduced by optimized growth condition. High hardness of 23.9 GPa was found in the deposited films.

Acknowledgements

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