Crystalline carbon nitride films prepared by microwave plasma chemical vapour deposition

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Crystalline carbon nitride films have been synthesized on Si (100) substrates by a microwave plasma chemical vapour deposition technique, using mixture of N_2, CH_4 and H_2 as precursor. Scanning electron microscopy shows that the films consisted of hexagonal bars, tetragonal bars, rhombohedral bars, in which the bigger bar is about 20 μm long and 6 μm wide. The X-ray photoelectron spectroscopy suggests that nitrogen and carbon in the films are bonded through hybridized sp^2 and sp^3 configurations. The x-ray diffraction pattern indicates that the films are composed of α-, β-, pseudocubic and cubic C_3N_4 phase and an unidentified phase. Raman spectra also support the existence of α- and β-C_3N_4 phases. Vickers microhardness of about 41.9 GPa measured for the films. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Since the theoretical calculation about carbon nitride by Liu and Cohen [1] and others [2–5], considerable efforts have been made to realize and understand the structures and properties of the predicated metastable crystalline C_3N_4 phases (α, β, cubic, etc.). 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 being related to stability, crystal structure, hardness etc. [2, 4, 5]. Simultaneously, larger effort has been in attempts to synthesize carbon nitride films using different experimental techniques [6–13]. Unfortunately, the films obtained by these techniques were usually amorphous. So far, there have been only a few reports [6–13] confirming the synthesis of crystalline carbon nitride by X-ray diffraction (XRD) or transmission electron diffraction (TED) patterns of their resulting materials, and the resulting mechanical properties are not as good as predicated. Therefore, there is some doubt that this hypothetical material can be synthesized and whether it is truly as hard as diamond.

Stimulated by the successful application of microwave plasma chemical vapor deposition (MPCVD) to synthesized and truly have hardness like diamond. We have adopted the method [14, 15] to synthesize carbon nitride films. In this paper, crystalline carbon nitride films have been synthesized using MPCVD constructed in our lab. The surface morphology, chemical composition, crystal structure, chemical states and hardness of the samples were analyzed.

2. Experimental

The carbon nitride films were prepared using MPCVD apparatus. The microwaves are coupled with the ellipsoidal cavity via an axial antenna as illustrated in Fig. 1. The lower focal point of the ellipsoid is surrounded by a quartz bell jar defining the deposition chamber. The apparatus is equipped with a 6 kW microwave plasma
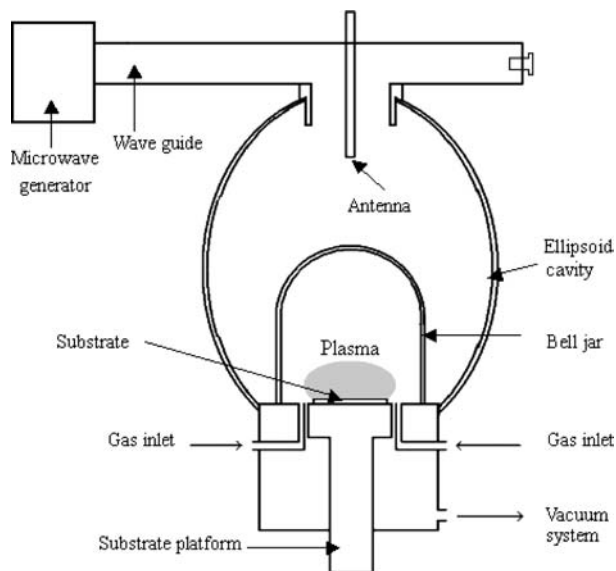
Figure 1 Schematic diagram of the ellipsoid microwave plasma reactor.

generator operating at 2.45 GHz. The system exhibits a variety of beneficial properties such as the plasma is very intense, stable, spatially extended, in good contact with the substrate, and so on. Substrates were (100) p-type Si wafers with resistivities between 1.5 and 6 Ωcm. Before the deposition, The silicon wafer was first dipped in 20% HF solution for 5 min to remove oxides, and was then ultrasonically cleaned in acetone and methyl alcohol for 25 min, respectively, to remove contamination, followed by ultrasonically cleaning in de-ionized water before inserting into the MPCVD reactor. Prior to deposition, the surface of the substrate was cleaned in situ by Ar plasma. The deposition lasted approximately 6 hours. An independent RF heater was used to control the substrate temperature. A thermocouple placed underneath the substrate holder was used to monitor the substrate temperature. The substrate temperature was kept at $900 \pm 10°C$. Gas mixtures of CH_4 (99.995%), N_2 (99.999%) and H_2 (99.999%) were used as precursors. The CH_4, N_2 and H_2 flow rates, respectively, preset at 3, 330 and 50 sccm maintained the operation pressure of 6.5 kPa. The microwave power was kept at 4.5 kW. The growth parameters are optimized in the process to get better carbon nitride films.

Field emission scanning electron microscopic (SEM) observations were facilitated by a field emission on a JSM-6301F apparatus. X-ray photoelectron spectroscopy (XPS) measurement was conducted on a PHI-5702XPS/AES spectrometer using Mg Kα radiation of 1253.6 eV as an excitation source. X-ray diffraction (XRD) measurements were obtained on a Rigaku D/Max-IIIC X-ray diffractometer using Cu Kα_1 radiation. Raman scattering spectra measurements were performed on a Renishaw system RM 2000 micro-Raman spectrometer with Ar laser operating at 514.5 nm. The microhardness of the film was measured by MH-6-type equipment.

3. Results and discussions
3.1. Surface morphology
The surface morphologies observed with SEM of the films are shown in Fig. 2. It is clear that the film is mainly composed of perfect crystals of short and long of hexagonal bars, tetragonal bars, rhombohedral bars and irregular particles. They are densely populated on the surface of substrate and the crystals are randomly oriented on the substrate (Fig. 2a). The bigger bar is about 20 μm long and about 6 μm wide (Fig. 2b).

3.2. Chemical composition and bonding
The chemical composition of carbon nitride films was measured by both energy dispersive X-ray analysis (EDX, Oxford 6566, installed in S-4200 SEM apparatus) and XPS experiment. The average N/C atomic ratio is between 1.0 and 1.3, very close to the theoretical value of C_3N_4. It must be noted that the exact chemical composition measurement of these films is especially difficult as they are composed of non-uniformly distributed indi-
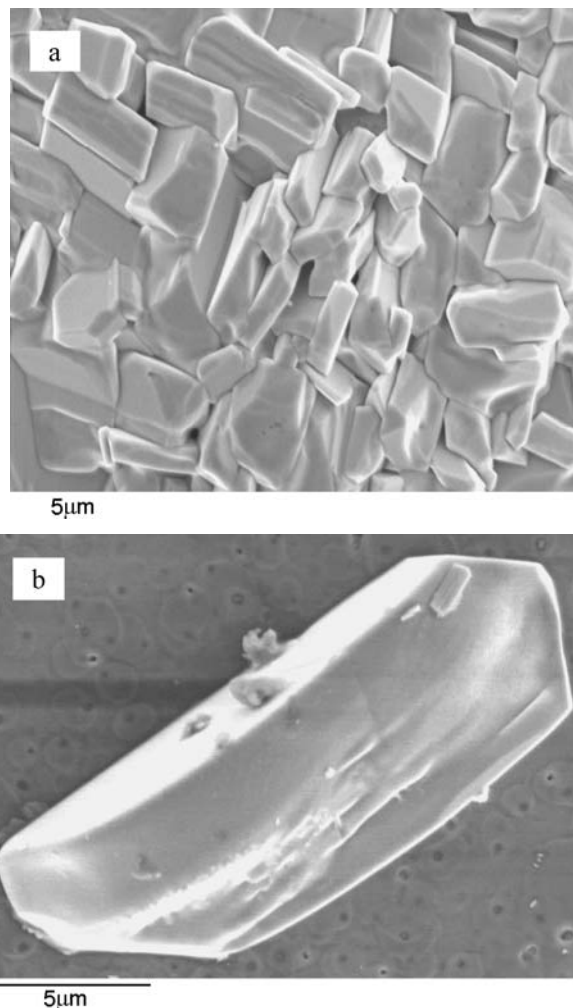

Figure 2 SEM micrographs of the crystalline C_3N_4 film deposited on Si (100) substrate. Images (a) and (b) are obtained for different regions of the film with different magnifications.
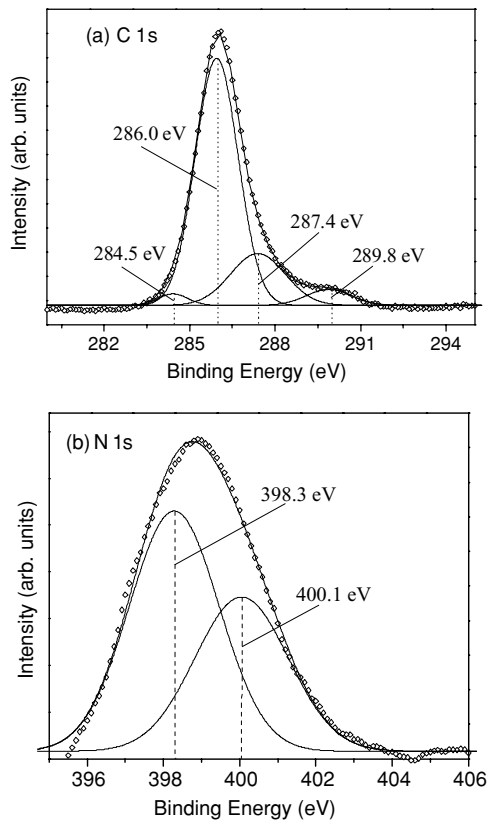
Figure 3 Detailed scans of the C 1s and N 1s XPS peaks.

vidual crystals of small size. The sizes of both EDX and XPS probe beams are larger than the crystals; moreover, the films obtained are composed of one phase not yet identified.

XPS measurements have been made in order to obtain further information about the chemical bonds. For all our examples, no C–Si bonding (282.8 eV in C 1s) [15] or N–Si bonding (397.5 eV in N 1s) [15] was detected. Typical C1s and N 1s XPS spectra are deconvoluted and shown in Fig. 3a and b for the carbon nitride film. The C 1s photoelectron peak could be resolved into four peaks. The main peak is detected at 286.0 eV and attributed to sp^2 type C=N bond. The minor peak at 287.4 eV and corresponds to sp^3 type C–N bond. The small peak of 289.8 eV is assigned to C–O bonds formed at the surface upon air exposure prior to analysis, and another very small peak of 284.5 eV, which is attributed to carbon bonded to carbon and is considered to represent adventitious carbon. These assignments are in agreement with those reported in literature [16]. Three different peaks are supposed to be possible for the nitrogen in CN-films [16], but Fig. 3b shows two peaks. The main peak is at 398.3 eV and is attributed to N–C (N–sp^3 C) bonding. The minor peak at 400.1 eV corresponds to N = C (N–sp^2 C) bonding. The deconvolution of the N 1s spectra confirms the presence of two different C–N bonding states, consistent with the result obtained for the C 1s spectra.
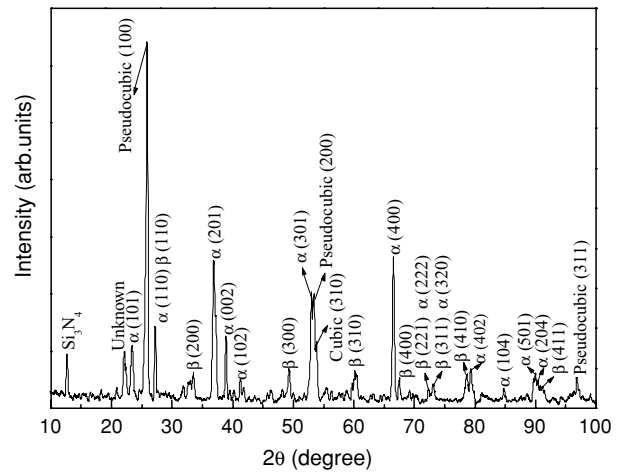

Figure 4 The XRD pattern of the film deposited on Si (100) substrate.

3.3. Microstructure
A typical XRD spectrum is shown in Fig. 4. The results from the XRD data of Fig. 4 are compared with the calculated C_3N_4 data [17] as summarized in Table I. There are no graphite or diamond diffraction peaks in our XRD pattern. The experimental observation points out that we obtained a complete pattern, including all the strong peaks of α-C_3N_4 (101), (110), (201), (102), and β-C_3N_4 (110), (200), (101) and (300). The result also shows three peaks of pseudocubic C_3N_4 (p-C_3N_4), one peak of cubic C_3N_4, one peak of β-Si_3N_4 and an unidentified phase with a lattice spacing of 4.002 Å. On the basis of energetics it is reasonable to assume that both α- and β-C_3N_4 may be coexisting in the deposited film. Since the total energy, crystal structure, bulk modulus, and atomic density of the two phases are so close [2], the non-equilibrium processes as used in our experiments are likely to lead to the simultaneous presence of both of these phases. The formation mechanism of p-C_3N_4 and cubic C_3N_4 is unclear. As for p-C_3N_4, this may be caused by different temperature at varying positions of plasma sphere. Around the center, the temperature is high which would be likely to produce α- or β-C_3N_4 crystal grains. In the other area of plasma sphere, slightly lower temperature than center may cause the formation of p-C_3N_4 with less cohesive energy than α- or β-C_3N_4.

3.4. Raman study
Raman spectroscopy is a useful tool for studying crystalline quality because of its sensitivity to slight variations in the lattice symmetry. Therefore, it is desirable to use Raman spectroscopy to characterize carbon nitride phases in all carbon-nitrogen films. Up to now, most of the Raman spectra reported for synthesized carbon nitride films showed two main peaks, similar to that for amorphous carbon films, the so-called D (disorder) and G (graphite) bands approximately at 1375 and 1580 cm^{-1}, respectively. Chen et $al.$ [15] had reported that there were 28 and 11 Raman active bands for α- and β-C_3N_4, respec-

TABLE I Comparison of the experimental results from Fig. 4 with the calculated results

| Experimental d (Å) | Calculated | | | | | | | |
| | β-C$_3$N$_4$ | | α-C$_3$N$_4$ | | p-C$_3$N$_4$ | | cubic-C$_3$N$_4$ | |
	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl	d (Å)	hkl
6.914[a]								
4.002[b]								
3.765			3.604	101				
3.420					3.423	100		
3.258	3.201	110	3.233	110				
2.656	2.772	200						
2.426			2.407	201				
2.306			2.355	002				
2.180			2.171	102				
1.840	1.848	300						
1.723			1.735	301				
1.710					1.712	200		
1.698							1.707	310
1.544	1.538	310	1.553	310				
1.402			1.400	400				
1.385	1.386	400						
1.298	1.332	221	1.333	222				
1.286	1.295	311	1.285	320				
1.216	1.210	410	1.222	410				
1.206	1.202	002	1.203	402				
1.141			1.152	104				
1.091			1.090	501				
1.088			1.085	204				
1.085	1.081	411	1.085	412				
1.029					1.032	311		

[a] β-Si$_3$N$_4$ peak.
[b] Unidentified peak.

TABLE II Comparison of the measured Raman shift (cm^{-1}) from Fig. 5 and the calculated α- and β-C$_3$N$_4$ Raman shifts

| Measured Raman shift | Calculated Raman shift | | Measured Raman shift | Calculated Raman shift | |
	β-C$_3$N$_4$	α-C$_3$N$_4$		β-C$_3$N$_4$	α-C$_3$N$_4$
203	206		665	645	662
227		220(s)			677
249	266(s)		741		740
285		291			773
290	300(s)		821		819(s)
336	327(s)	333			865
350			886	885	
367		372(s)			960
383		406	997		995
		429		1047	1098
		441	1160		1221
460		462		1237	1250
495		485	1290	1327	1316
		513(s)	1352	1343	1369
		520(s)			1404
		552		1497	1486
567		563			
586					

tively, which were calculated from the Raman spectrum of crystalline α- and β-Si$_3$N$_4$. These calculated Raman frequencies in the range of 150–1500 cm^{-1} are listed in Table II. However, our Raman spectrum, in the range of 150–1500 cm^{-1}, is entirely different from all those re-

ported. A series of sharp peaks was observed (see Fig. 5). Nineteen of them match well with the calculated Raman peaks for α- and β-C$_3$N$_4$ as listed in Table II. Since there are many as nineteen peaks matching well with the calculated frequencies, which were directly deduced from
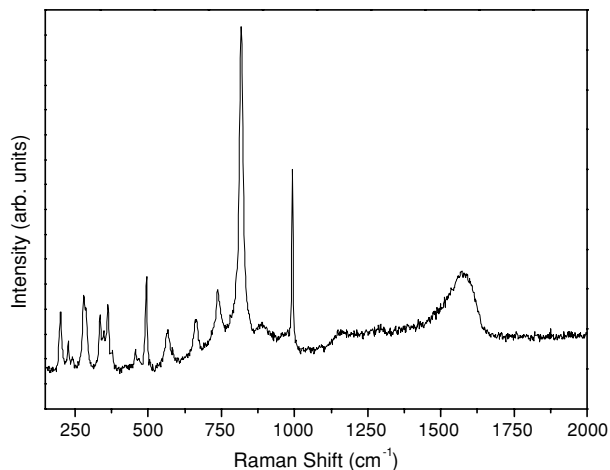
Figure 5 Raman spectrum of the carbon nitride film deposited on Si (100) substrates.

the α- and β-Si_3N_4 material, our Raman spectrum provides unambiguous evidence that the structure of the film is similar to that of α- and β-Si_3N_4, suggesting that the deposited film is containing the α- and β-C_3N_4 phases. Fig. 5 also shows two broad bands at 1384 and 1580 cm^{-1} (D and G bands).

3.5. Film hardness

In order to investigate the mechanical properties of the deposited films, the Vickers microhardness were performed on MH-6-type equipment. Indentations were done on eight randomly selected points on each sample to reduce the fluctuation of the results. We measured the hardness of the same film observed by SEM, using a pure polycrystalline MPCVD diamond film as a reference. The Vickers microhardness value of the carbon nitride film is 41.9 GPa, which is lower than that for the diamond film (70.5 GPa). Due to the carbon nitride film is not compaction and homogeneity on micro-scale (Fig. 2), the hardness test will be affected by the choice of the site for indentation. The real hardness of a crystal grain may be much higher.

4. Conclusions

In conclusion, crystalline carbon nitride films have been synthesized on Si (100) substrate by MPCVD method. The SEM shows that the morphology of the films con-

sists of perfect crystals of hexagonal bars, tetragonal bars, rhombohedral bars and irregular particles. Enough nitrogen concentration has been incorporated into these crystalline bars to form C_3N_4. C–N single and C=N double bonds were observed by XPS. The XRD results indicate that the films are composed of α-, β-, p- and cubic-C_3N_4, and an unidentified phase. Raman measurements showed that α- and β-C_3N_4 bands, D band and G band coexisted in the films. High hardness of 41.9 GPa was found in the deposited films.

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