

Characterization of carbon nitride thin films deposited by microwave plasma chemical vapor deposition

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Abstract

The carbon nitride films have been prepared on Si substrates using microwave plasma chemical vapor deposition (MPCVD) technique. The experimental X-ray diffraction (XRD) spectra of films deposited on Si substrates appear to contain all of the strong peaks of α -C₃N₄ and β -C₃N₄, but there is considerable peak overlap, therefore the existence of these phases cannot, for certain, be claimed from this data. However, the N/C atomic ratio is close to the stoichiometric value 1.33. X-Ray photoelectron spectroscopy (XPS) analysis indicated that the binding energies of C 1s and N 1s are 286.43 and 399.08 eV, respectively. The shifts are attributed to the polarization of the C–N bond. Both observed Raman and Fourier transform infrared (FT-IR) spectra were compared with the theoretical calculations. The results support the existence of a C–N covalent bond in the films. © 2000 Published by Elsevier Science S.A. All rights reserved.

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

1. Introduction

A type of carbon nitride, β -C₃N₄, isomorphous to β -Si₃N₄, which may have a hardness comparable to diamond, has been suggested by Liu and Cohen [1,2]. Subsequent calculations have shown that other crystalline C₃N₄ structures should have stability comparable to or greater than β -C₃N₄ [3]. 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. A variety of techniques [4–10] has been employed to prepare carbon nitride materials, such as rf and dc magnetron sputtering of graphite in a mixed Ar–N₂ atmosphere, microwave plasma-enhanced chemical vapor deposi-

tion, N ion implantation in carbon and so on. Of all the above techniques, only a few techniques have been found to be promising for forming polycrystalline carbon nitride films, and the resulting mechanical properties are not as good as predicted. Therefore, there is some doubt as to whether this hypothetical material can be found or whether it is truly as hard as diamond.

In this paper, we concentrated our attention on characterizing the films deposited on Si substrates, prepared by microwave plasma chemical vapor deposition, and analyzed by EDX, XRD, XPS, FT-IR and Raman spectra, trying to find whether the films are composed mainly of C₃N₄ compound.

2. Experimental

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

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vapor deposition (MPCVD) system [8]. A vacuum was created through a combination of a turbomolecular 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 a water load. A mixture of semiconductor grade N_2 (99.999%) and CH_4 (99.9%) gases in various ratios was used as the source gas, typical flow rates being 100–80 cm^3/s for N_2 and 0.5–1.0 cm^3/s for CH_4 , while the chamber pressure was maintained at approximately 2500 Pa. The microwave power was 500–700 W and the temperature of the substrates was held at 800–950°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.

3. Results and discussion

3.1. Surface morphology and composition

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. It was found that the film consists of hexagonal crystalline rods. These rods are approximately 1.5–2 μm long and approximately 0.5 μm wide.

The chemical compositions of the deposited carbon

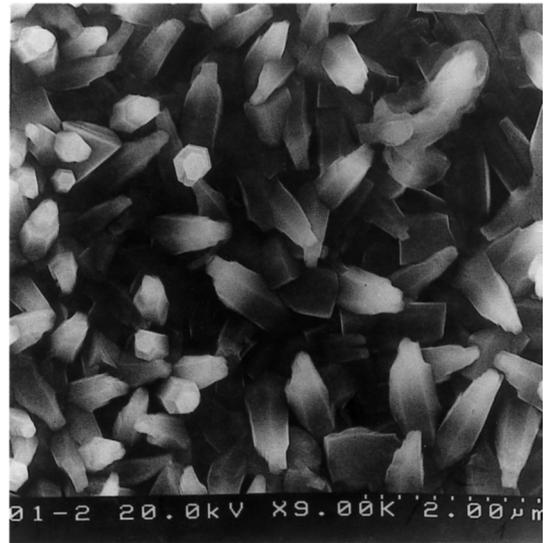


Fig. 1. The surface morphology of a carbon nitride film deposited on Si substrate.

nitride films were examined by energy dispersive X-ray (EDX) analysis. Measurements were performed on a Hitachi S-4200 SEM by an Oxford 6566 detector with an ultra-thin window which allowed the low energy characteristic X-ray of the light elements to pass without significant loss and made it capable of measuring the concentration of light elements down to Boron ($Z = 5$). Fig. 2 is a typical EDX spectrum of the carbon nitride film deposited on Si substrate. The atom concentrations of N, C, and Si are 55, 41, and 4%, respectively, so the N/C ratio in each is close to 4:3. Measurements on different samples indicate the values of

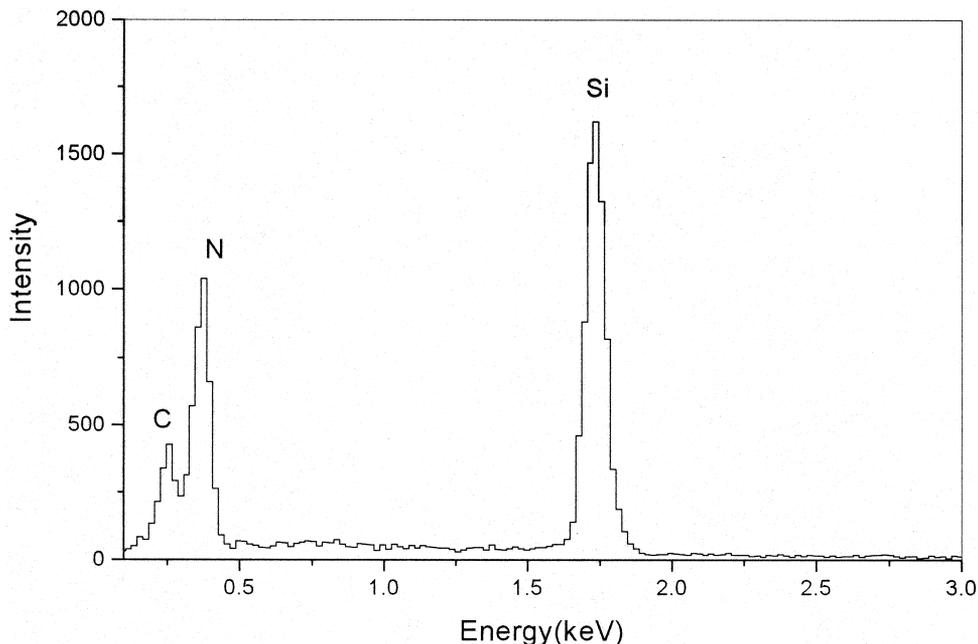


Fig. 2. A typical EDX spectrum of carbon nitride film deposited on Si substrate.

Table 1

The calculated and observed XRD spectrum from a carbon nitride film deposited on Si substrate

No.	Experimental		α -C ₃ N ₄		β -C ₃ N ₄		β -Si ₃ N ₄	
	2 θ (°)	d (nm)	(hkl)	d (nm)	(hkl)	d (nm)	(hkl)	d (nm)
1	13.34	0.6632					(100)	0.6583
2	16.68	0.5311	(100)	0.5600	(100)	0.5544		
3	20.61	0.4306						
4	23.06	0.3854	(101)	0.3605			(110)	0.3800
5	26.77	0.3327	(110)	0.3233	(110)	0.3201	(200)	0.3293
6	31.11	0.2872	(200)	0.2800	(200)	0.2772		
7	35.47	0.2528					(210)	0.2489
8	38.99	0.2308	(002)	0.2355	(101)	0.2206		
9	43.58	0.2075	(210)	0.2117	(210)	0.2095		
10	48.93	0.1860	(300)	0.1867	(300)	0.1848		
11	51.98	0.1758	(301)	0.1735				
12	56.64	0.1624	(220)	0.1617	(220)	0.1600		
13	58.96	0.1565	(310)	0.1553	(310)	0.1538		
14	62.62	0.1482	(311)	0.1475	(301)	0.1465		
15	66.04	0.1414	(400)	0.1400				
16	69.83	0.1346	(401)	0.1342				
17	73.02	0.1295	(312)	0.1297	(311)	0.1295		
18	78.04	0.1224	(410)	0.1222				
19	81.44	0.1181	(411)	0.1183				
20	84.73	0.1143	(104)	0.1152				
21	88.22	0.1107	(114)	0.1106	(202)	0.1103		
22	93.88	0.1054			(330)	0.1067		

N/C in each are found to be in the range of 1.0–2.0 depending on the deposition conditions. Experiments imply that the N/C ratio can be raised easily by using our MPCVD apparatus.

3.2. Crystal structure

Most of the CN films reported in published papers

are composed of multiphases, especially in those deposited on Si substrate. Si diffused into the film during the deposition process. According to the electronegativity difference between C, N and Si, phases should be formed in accordance with the following sequence SiN, SiC, and CN. The X-ray diffraction peaks of different phases were overlapped which made the structure analysis more complicated. If there is a natural reference

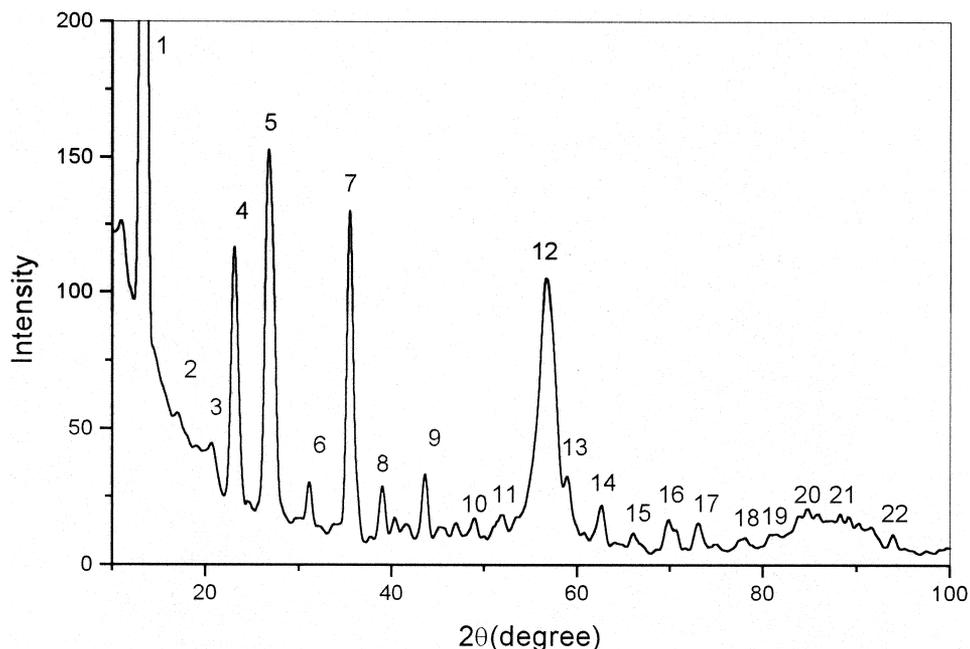


Fig. 3. AN XRD spectrum of carbon nitride film deposited on Si substrate.

Table 2
The XPS results of a carbon nitride film deposited on Si substrate

Peaks		Peak area	Center (eV)	Width (eV)	Height
C 1s	[C ¹]	16 591	286.43	1.40	9458
	[C ²]	5730	287.63	3.68	1242
N 1s	[N ¹]	36 857	399.08	1.32	21 780
	[N ²]	4839	400.82	2.01	1921

sample, as in the case of diamond, parallel experiments on natural and man-made materials will help to settle the problem. However, this is not available, so we have no alternative but to rely on computer simulations.

X-Ray diffraction experiments were performed on a Rigaku D/Max II rotating anode X-ray diffractometer. Fig. 3 showed a typical XRD spectrum of carbon nitride film deposited on Si substrate. Table 1 listed the observed d-spacing of the diffraction peaks, calculated values of α -C₃N₄ and β -C₃N₄. The experiment appears to contain all of the strong peaks of α -C₃N₄ (100), (101), (110), (200), (201), (002), (102), and that of β -C₃N₄, (100), (110), (200), (101), (210), (300), but there is considerable peak overlap with SiC, SiN and Si(CN), therefore, the existence of these phases cannot, for certain, be claimed from this data. Other forms of evidence are needed to make the conclusion more solid.

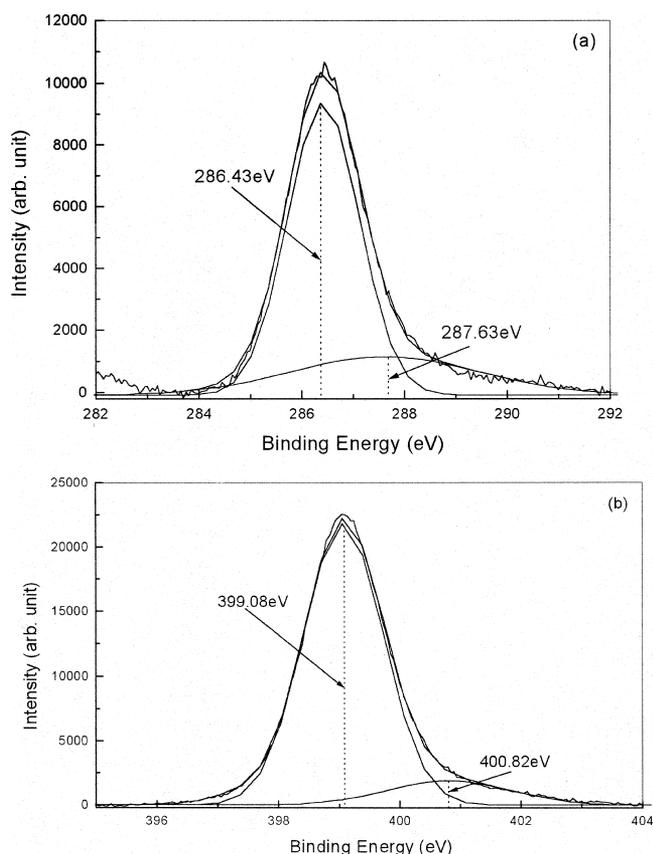


Fig. 4. The typical XPS spectra of carbon nitride film deposited on Si substrate: (a) C 1s region; AND (b) N 1s region.

Table 3
Observed and calculated Raman frequencies in α - and β -C₃N₄

Calculated Raman spectrum (cm ⁻¹) [10]		Observed peaks (cm ⁻¹) α - and β -C ₃ N ₄
α -C ₃ N ₄	β -C ₃ N ₄	
	206	
219		
	266	
289		
	300	306
	327	
330		
369		
403		
426		
438		436
459		
482		
509		
516		
548		
559		
	645	623
658		669
672		678
735		
	885	
955		944
	1047	981
	1237	
	1327	
	1343	
	1497	

3.3. XPS 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. Experiments were performed on a VG Scientific Lab 5 ESCA. Fig. 4 shows the typical carbon and nitrogen 1s XPS spectra. Two Gaussians are necessary to fit the profile. The fitted results are listed in Table 2, including the area, center, height and width of the Gaussian peaks. From a comparison of binding energies with those of pyridine (C₅H₅N) and urotropine (C₆H₁₂N₄) 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 an sp² configuration. Phase 1 is 'carbon and nitrogen atoms in position resembling β -C₃N₄', and phase 2 is 'areas with excess carbon' [9]. The lines were assigned as follows: 399.08 eV (N¹) and 286.43 eV (C¹) to phase 1; 400.82 eV (N²) and 287.63 eV (C²) to phase 2. The [C¹], [C²], [N¹], and [N²] concentrations were calculated from the areas under fitted Gaussian distributions divided by their sensitive factors. It was found that the average composition $\{([N^1] + [N^2])/([C^1] + [C^2])\}$ was approximately 1.01, and the N/C ratio in phase 1 ($[N^1]/[C^1]$) was

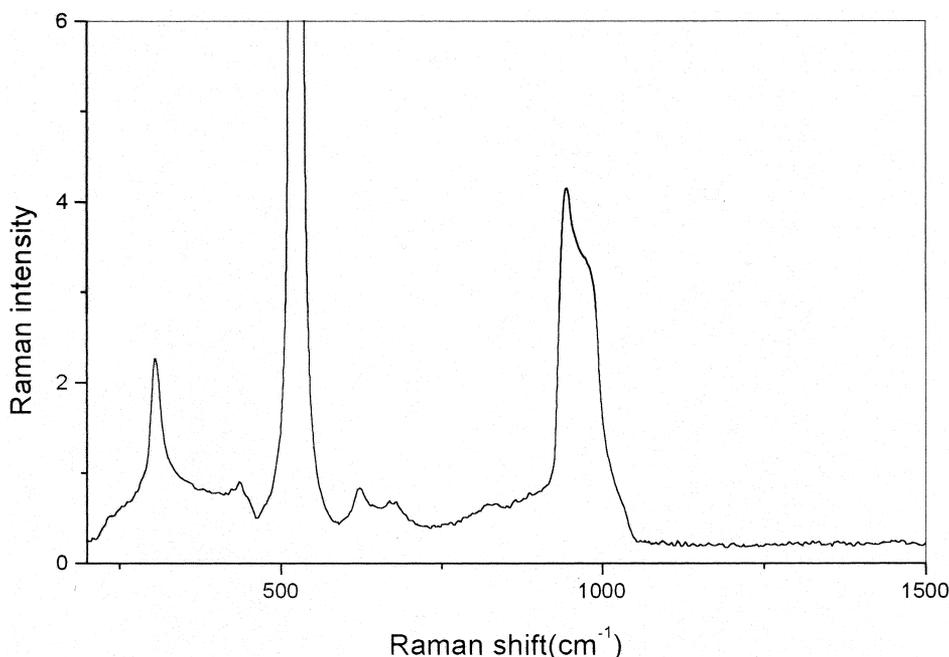


Fig. 5. The Raman spectrum of carbon nitride film deposited on Si substrate.

1.20, close to the C_3N_4 stoichiometric value of 1.33. The fractional concentration of phase 1, $([N^1] + [C^1])/([N^1] + [C^1] + [N^2] + [C^2])$, was approximately 81.4%. From the above results there is a significant amount of C–N bonds for N and C atoms in the films, favoring the formation of β - C_3N_4 phases.

3.4. The vibration mode

For diamond and related materials, diamond has a sharp Raman peak at 1332 cm^{-1} , and graphite has two broad G, D bands centered at 1575 and 1360 cm^{-1} , respectively. These results were tested and verified by repeating, 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 the 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 [10] 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 .

Experiments were performed on a FT-Raman JY U-1000 spectroscope. Fig. 5 is the Raman spectrum detected from a film deposited on Si substrate. Table 3 lists the observed and calculated Raman frequencies in α - and β - C_3N_4 compounds. The Raman spectrum showed no signs of the G, D bands which are the fingerprint of graphite. The observed Raman shifts 306, 623, and 981 cm^{-1} are close to the calculated data for

Table 4

The observed and calculated FT-IR spectra of a carbon nitride film deposited on Si substrate

Observed peaks (cm^{-1})	Calculated IR spectrum (cm^{-1})		Standard IR peaks (cm^{-1}) Si_3N_4
	α - C_3N_4	β - C_3N_4	
412			
432			433
449			
461			
492			490
511			
572			570
585			
609			
686			680
739			
852			
886		891	
1012			
1031	1051		1033
1075	1065		

β - C_3N_4 300, 645, and 1047 cm^{-1} ; observed 436, 669, 678, and 944 cm^{-1} are close to the calculated data for α - C_3N_4 438, 658, 672, and 955 cm^{-1} . The strong peak at 520 cm^{-1} is due to silicon substrate. The experimental results support the existence C–N bonds in the α - and β - C_3N_4 mixture.

For FT-IR analysis, we rely on a computer simulation using the Cerius II material analysis package from Molecule Simulation Incorporation (MSI) to identify the peaks of C_3N_4 . Fig. 6 shows the FT-IR spectrum of

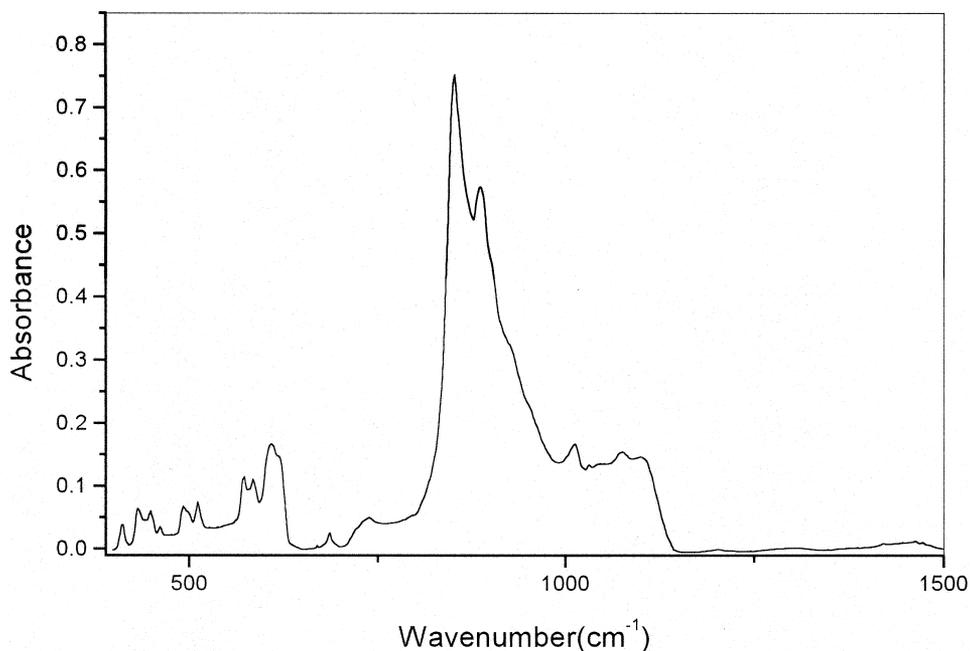


Fig. 6. The FT-IR spectrum of carbon nitride film deposited on Si substrate.a:

carbon nitride film prepared on Si substrate. Calculated and experimental results are shown in Table 4. Observed peaks at 852, and 886 cm^{-1} are close to the calculated $\beta\text{-C}_3\text{N}_4$ IR active mode 891 cm^{-1} ; observed peaks at 1012, 1031, and 1075 cm^{-1} are close to the calculated $\alpha\text{-C}_3\text{N}_4$ IR active mode 1051, and 1065 cm^{-1} . In our IR spectrum, no C=N or C \equiv N bonds were found at approximately 1600 and 2200 cm^{-1} . Other weak peaks may attribute to Si_3N_4 or other compounds. The results also support the formation of C–N bonds in the α - and $\beta\text{-C}_3\text{N}_4$ mixture.

4. Conclusions

Carbon nitride films have been prepared on Si substrates using microwave plasma chemical vapor deposition technique. The N/C atomic ratio is close to the stoichiometric value of C_3N_4 . There is some XRD evidence to suggest the presence of α - and $\beta\text{-C}_3\text{N}_4$; however, this has to be treated with some caution, due to the considerable overlaps in the peaks, and the fact that several authors have referred to the possibility of other peaks [such as SiC, SiN and Si(CN)] causing the XRD data to be difficult to interpret. However, we do point out that the XPS, FT-IR and Raman data do support the existence of the C–N covalent bond in the α - and $\beta\text{-C}_3\text{N}_4$, so there is circumstantial evidence for

the existence of these phases. These kinds of polycrystalline films may find many applications in the future as alternatives (for example) to polycrystalline diamond.

Acknowledgements

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References

- [1] M.L. Cohen, Phys. Rev. B 32 (1985) 7988.
- [2] A.Y. Liu, M.L. Cohen, Science 245 (1989) 841.
- [3] D.M. Teter, R.J. Hemley, Science 271 (1996) 53.
- [4] L.C. Chen, C.Y. Yang, D.M. Bhusari et al., Diamond Relat. Mater. 5 (1996) 514.
- [5] D.J. Johnson, Y. Chen, Y. He, R.H. Pring, Diamond Relat. Mater. 6 (1997) 1799.
- [6] L.C. Chen, C.K. Chen, S.L. Wei et al., Appl. Phys. Lett. 72 (1998) 2463.
- [7] D.X. Shi, X.F. Zhang, L. Yuan et al., Appl. Surf. Sci. 148 (1999) 50.
- [8] Y.S. Gu, Y.P. Zhang, Z.J. Duan et al., J. Mater. Sci. 34 (1999) 3117.
- [9] D. Matton, K.J. Boyd, A.H. Al-Bayati, S.S. Todorov, J.W. Rabalais, Phys. Rev. Lett. 73 (1994) 118.
- [10] T.Y. Yen, C.P. Chou, Appl. Phys. Lett. 67 (1995) 2801.