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Materials

Carbon Nitride Films Deposited on Pt Substrates by Microwave Plasma Chemical Vapor Deposition

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Abstract: Carbon nitride thin films have been synthesized on polycrystalline Pt substrates using microwave plasma chemical vapor deposition (MPCVD) technique. The N/C atomic ratio is close to the stoichiometric value 1.33 of C_3N_4. The experimental X-ray diffraction spectra contain all the strong peaks of α-C_3N_4 and β-C_3N_4. The films are a mixture of α-C_3N_4 and β-C_3N_4. The observed Raman and FT-IR spectra support the existence of C–N covalent bond in carbon nitride compound. The bulk modulus detected by Nano II nanoindentor is up to 349 GPa.

Key words: carbon nitride; MPCVD; thin film deposition

A type of carbon nitride,isomorphic to β-Si_3N_4,has been suggested by Liu and Cohen [1–2]. From *ab initio* calculations based on an empirical model for the hardness of the light covalent materials, a particular phase of carbon nitride, β-C_3N_4,has been predicted to have a bulk modulus of 483 GPa, which is higher than that of diamond (443 GPa), the hardest known materials on earth. β-C_3N_4 may possess extreme hardness, wide band gap(3.2 eV), large thermal conductivity, and low friction factor. These properties make the material attractive in a wide range of application. 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 [3–8] have been employed to prepare the material, such as RF and DC magnetron sputtering of graphite in a mixed Ar-N_2 plasma, microwave plasma-enhanced chemical vapor deposition, N ion implantation in carbon. Of all the above techniques, only a few techniques have been found promising for forming polycrystalline carbon nitride films.

This paper reports on the deposition of CN_x thin films on polycrystalline Pt substrates with x up to 1.33 by microwave plasma chemical vapor deposition from the precursor systems N_2/CH_4. Pt substrates are selected due to the factor that Pt has no simple compound with C and N, so the interpretation of the compositional and structural data is easy and clear.

1 Experimental

The carbon nitride films were deposited on polycrystalline Pt substrates in the microwave plasma chemical vapor deposition (MPCVD) system [8]. A mixture of semiconductor grade N_2 (99.999%) and CH_4 (99.9%) gases in various ratio was used as source gas. The typical flow rates were 100–80 sccm for N_2 and 0.5–1.0 sccm for CH_4. The chamber pressure was maintained at about 2.5 kPa. The microwave power was 500–700 W and the temperature of the substrates was held at 800–950 ℃, 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. The typical experimental conditions are listed in **table 1**.

Table 1 Typical deposition conditions for microwave plasma CVD

[N_2] flow rate / sccm	80–100
[CH_4] flow rate / sccm	0.5–1.0
Microwave power / W	500–700
Total pressure / kPa	2.5
Substrate temperature / ℃	800–950

2 Results and Discussion

2.1 Surface morphology and composition

The carbon nitride films obtained by microwave plasma CVD techniques were characterized by scanning electron microscopy (SEM, Hitachi S-4200), energy dispersive X-ray analysis (EDX, Oxford-6566, installed in the S-4200 apparatus). **Figure 1** gives typical surface morphology of the film observed by SEM. The film was composed of high-density small grains.

The chemical composition of the carbon nitride films

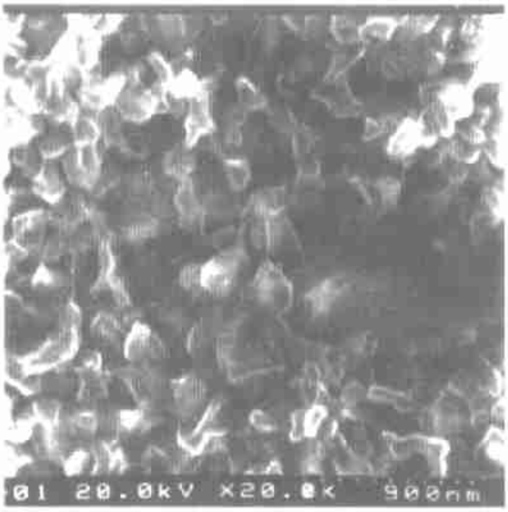

Figure 1 Surface morphology of a carbon nitride film deposited on a Pt substrate, by SEM.

deposited on Pt substrates were examined by energy dispersive X-ray (EDX) analysis. The ultra-thin window on the detector 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 acceleration voltage is 20 kV during measurements and the N/C ratio is evaluated by ZAF (Atomic number, Absorption and Fluorescence factors correction) method.EDX analysis (with instrumental error smaller than 5%) indicated that the chemical composition ratio of N/C was 1.00–1.40 in different areas of the films, close to the stoichiometic value of 1.33 of C_3N_4. **Figure 2** shows

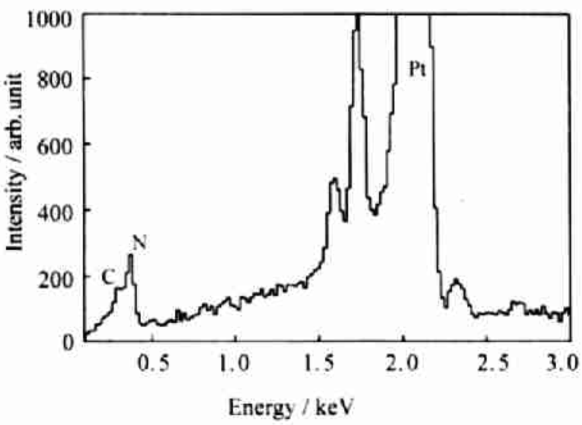

Figure 2 Typitål EDX spectrum of carbon nitride films

a typical EDX spectra of carbon nitride films deposited on Pt substrates. Since the thickness of the films is smaller than the size of the effective region of EDX experiments measure, the resulting concentration is the sum of the film and substrate. Strong Pt peaks are also show up in the spectrum.

2:2 Crystal structure

X-ray diffraction (XRD) was used to determine the structure of the carbon nitride films deposited on polycrystalline Pt substrates. **Appendix 1** gives the typical XRD result of the film. The d-spacing of most peaks in this spectrum coincides well with the calculated spectra of β-C_3N_4 and α-C_3N_4. The low index, high intensity peaks of β-C_3N_4 and α-C_3N_4 all show up in this spectrum, including (100), (110), (200), (101), (210), (111), (300), (220), (310), (400), (221), (320) peaks of α-C_3N_4 and the (100), (101), (110), (200), (002), (102), (210), (211), (300), (301), (212), (103), (311), (203), (222), (320), (321), (410) peaks of β-C_3N_4. It can be seen that both β-C_3N_4 and α-C_3N_4 existed in the films. Since the structure and property of these two substances are close, clearly distinguish them is not necessary.

2.3 Raman and FT-IR Spectroscopy study

Besides the X-ray diffraction study, the samples were also analyzed by Raman spectroscopy, **Figure 3** shows a typical Raman spectrum of the carbon nitride film on Pt substrate, there are two characteristic peaks in 1 284 cm^{-1} and 1 605 cm^{-1}.

FT-IR spectrum was used to study the vibration mode of the carbon nitride films. **Figure 4** shows a typical IR spectrum of carbon nitride films. There are some peaks in 667 cm^{-1},849 cm^{-1},887 cm^{-1}, 1 099 cm^{-1}.

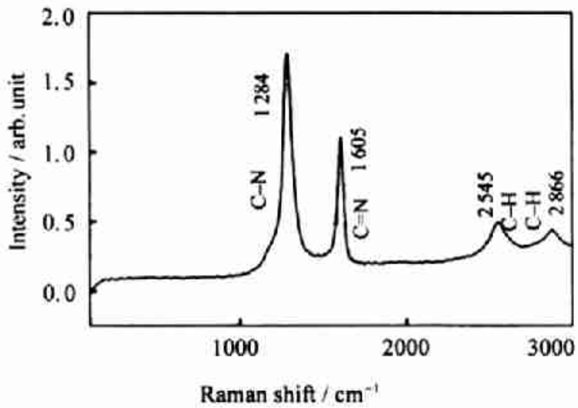

Figure 3 A Roman spectrum of carbon nitride films deposited on Pt substrate

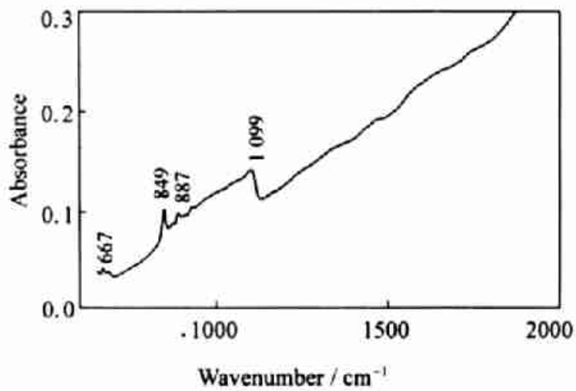

Figure 4 An IR spectrum of carbon nitride films deposited on Pt substrate

2.4 Mechanical property

The bulk modulus tests were performed on a Nano II nanoindenter. Intentions were done on eight randomly selected points on each sample to reduce the fluctuation of the results. The bulk modulus was calculated according to the loading curve of a carbon nitride film. The best bulk elastic modulus of carbon nitride was obtained in the film deposited on Pt substrate. The highest calculated bulk elastic modulus is 349 GPa, not far from the theoretical one (425 GPa).

3 Conclusions

From the above experimental results, crystalline carbon nitride films were successfully prepared using microwave plasma chemical vapor deposition technique. Nitrogen concentration is enough to form C_3N_4. The major part of the film is composed of α-C_3N_4 and β-C_3N_4. Raman and FT-IR spectra support the existence of C–N covalent bond in carbon nitride compound. The bulk modulus is up to 349 GPa.

Acknowledgement

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Appendix 1 X-ray diffration result of a carbon nitride film deposited on Pt substrate

No.	Experimental		α-C_3N_4		β-C_3N_4		Pt
	d / nm	Intensity	(*hkl*)	*d* / nm	(*hkl*)	*d* / nm	(*hkl*)
1	0.590 6	w	(100)	0.560 0	(100)	0.554 4	—
2	0.355 6	w	(101)	0.360 5	—	—	—
3	0.326 4	w	(110)	0.323 3	—	—	—
4	0.317 8	w	—	—	(110)	0.320 1	—
5	0.310 4	w	*	*	*	*	—
6	0.285 9	w	(200)	0.282 2	—	—	—
7	0.275 3	m	—	—	(200)	0.277 2	—
8	0.235 6	s	(002)	0.235 5	—	—	—
9	0.224 5	m	—	—	(101)	0.220 6	—
10	0.215 5	m	(102)	0.217 1	—	—	—
11	0.209 2	w	(210)	0.211 7	(210)	0.209 5	—
12	0.204 4	m	*	*	*	*	—
13	0.201 4	vs	—	—	—	—	(220)
14	0.193 3	s	(211)	0.193 1	(111)	0.192 2	—
15	0.183 8	w	(300)	0.186 7	(300)	0.184 8	—
16	0.176 1	w	(301)	0.173 5	—	—	—
17	0.158 3	w	(212)	0.157 4	(220)	0.160 0	—
18	0.152 9	vw	(103)	0.151 2	(310)	0.153 8	—
19	0.149 5	vw	(311)	0.147 5	—	—	—
20	0.137 6	s	(203)	0.136 9	(400)	0.138 6	—
21	0.132 8	w	(222)	0.133 3	(221)	0.133 2	—
22	0.128 0	vw	(320)	0.128 5	(320)	0.127 2	—
23	0.124 9	vw	(321)	0.123 9	—	—	—
24	0.122 6	w	(410)	0.122 2	—	—	—

Note: In Intensity, vw, w, m, s, vs represent very weak, weak, medium, strong, very strong, respectively; *, unidentified peaks.