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CRYSTALLINE CARBON NITRIDE THIN FILMS DEPOSITED BY MICROWAVE PLASMA CHEMICAL VAPOR DEPOSITION*

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The crystalline carbon nitride thin films have been prepared on Si (100) substrates using microwave plasma chemical vapor deposition technique. The experimental X-ray diffraction pattern of the films prepared contain all the strong peaks of α-C_3N_4 and β-C_3N_4, but most of the peaks are overlapped. The films are composed of α-C_3N_4 and β-C_3N_4. The N/C atomic ratio is close to the stoichiometric value 1.33. X-ray photoelectron spectroscopic analysis indicated that the binding energies of C 1s and N 1s are 286.43eV and 399.08 eV respectively. The shifts are attributed to the polarization of C-N bond. Both observed Raman and Fourier transform infrared spectra were compared with the theoretical calculations. The results support the existence of C-N covalent bond in α- and β-C_3N_4 mixture.

Keywords: carbon nitride, microwave plasma chemical vapor deposition (MPCVD), thin film
PACC: 8115H, 6855, 7360, 6110F

I. INTRODUCTION

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, β-C_3N_4, has been predicted to have a bulk modulus of 483GPa, which is higher than that of diamond (443GPa), the hardest materials known on earth. β-C_3N_4 may possess extreme hardness, wide band gap 3.2eV, large thermal conductivity, and low friction. Exploring the synthesis and properties of such a hypothetical material is also significant to the research in the fields of condensed matter physics, materials science, and chemistry. A variety of techniques[3−12] has been employed to prepare the material, such as radio frequency and direct currency magnetron sputtering of graphite in mixed Ar-N2 plasma, microwave plasma-enhanced chemical vapor deposition, and N ion implantation in carbon. Of all the above techniques, only a few techniques have been found to be promising for forming polycrystalline carbon nitride films.

In this paper, we concentrate our attention on characterizing the films deposited on Si (100) substrates, prepared by microwave plasma chemical vapor deposition(MPCVD), analyzed by energy dispersive X-ray (EDX)analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) and Raman spectroscopy. We try to answer whether the films are composed mainly of C_3N_4 compound.

II. EXPERIMENTAL

The carbon nitride thin films were deposited on polished Si (100) in the MPCVD system.[10] 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 water load. A mixture of semiconductor grade N_2(99.999%) and CH_4(99.9%) gases in various ratio was used as source gas, typical flow rates being 100–80 sccm for N_2 and 0.5–1.0 sccm for CH_4, while the chamber pressure was maintained at about 2500 Pa. The microwave power was 500–700W and the temperature of the substrates was held at 800–950°C, as measured by an infrared pyrometer, during deposition. It may be noted that the heating of the substrates was

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achieved by the plasma itself and no separate substrate heater was provided.

Ⅲ. RESULTS AND DISCUSSION

A. Surface morphology and composition

The surface morphologies of the deposited films were investigated by a Hitachi S-4200 scanning electron microscope (SEM). Figure 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 about 1–2μm long and about 0.4μm wide.

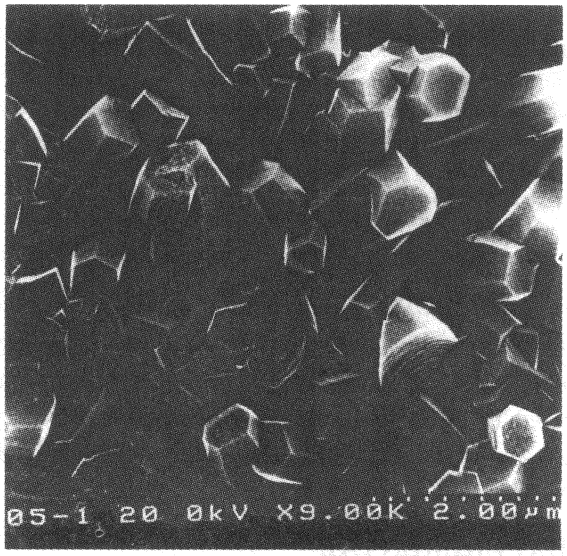


Fig.1. The surface morphology of a carbon nitride film deposited on Si substrate.

The chemical compositions of the deposited carbon nitride films were examined by energy dispersive X-ray (EDX) analysis. Measurement was 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 to measure the concentration of light elements down to boron (Z=5). Figure 2 is a typical EDX spectrum of the carbon nitride film deposited on Si substrate. The atomic concentrations of N, C, Si are 55%, 41%, 4% respectively, so the N/C ratio in all is close to 4/3. Measurements on different samples indicate the values of N/C in all are found to be in the range of 1.1-2.0 depending on the deposition conditions. Experiments imply that the N/C ratio is easy to be raised using our MPCVD apparatus.

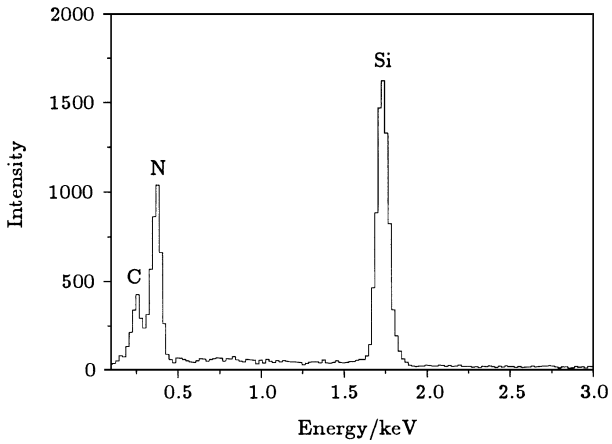


Fig.2. A typical EDX spectrum of carbon nitride film deposited on Si substrate.

B. Crystal structure

Most of the CN films reported in published papers are of multiphase, especially in those deposited on Si substrate. Si diffused into the film during deposition process. According to the electronegativity difference 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, thus the structure analysis was made more complicated. If there were a natural reference sample, just as a diamond has, then parallel experiments on natural and man-made materials would help to settle the problem. However, it is not available, hence 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.(18kW, CuK_α radiation λ=0.154056nm). Figure 3 shows the observed X-ray diffraction pattern. The experimental observation points out that we have got a complete pattern including all the strong peaks of α-C_3N_4 (100), (101), (110),(200), (201),(002), and that of β-C_3N_4, (100), (110), (200), (101), (300). Other peaks can be assigned to those of β-Si_3N_4 and the Si single crystal substrate.

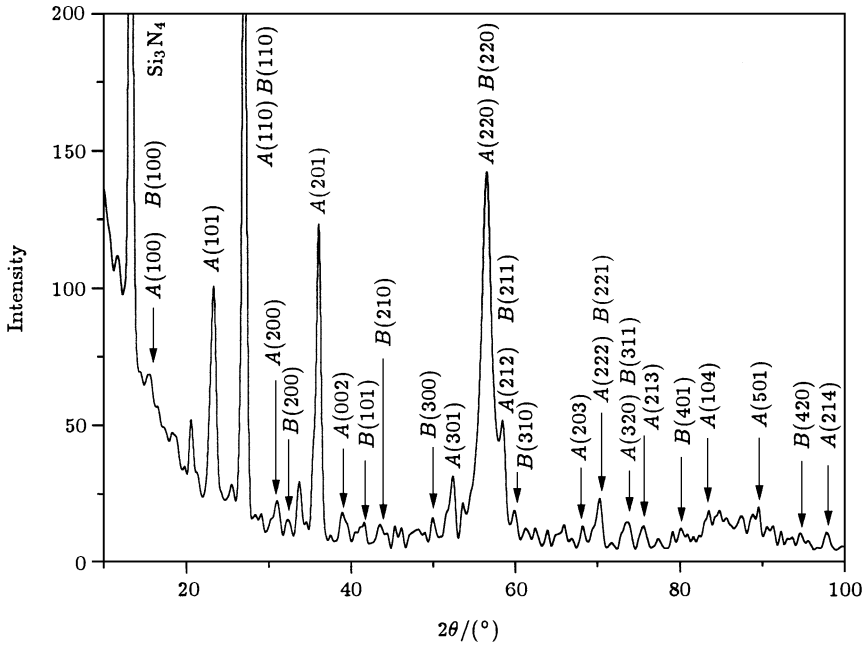


Fig.3. The XRD pattarn of carbon nitride film deposited on Si substrate. $A(hkl)$, $B(hkl)$ represent $\alpha-C_3N_4(hkl)$, $\beta-C_3N_4(hkl)$ respectively.

C. 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 (electron spectroscopy for chemical analysis). Figure 4 are the typical carbon and nitrogen 1s XPS spectra. After deconvoluting these C 1s and N 1s peaks into their components, it was found that there are two bonding states between C and N in these films. The binding energies in these two carbon nitride phases are: C1 286.43eV; N1 399.08eV; C2 287.63eV and N2 400.82eV. From a comparison of two lines of each spectrum with the binding energies in pyridine (C_5H_5N) and urotropine ($C_6H_{12}N_4$) it was concluded that in the CN films studied a two-phase system exists, one with a tetrahedral type of binding configuration and the other with an sp^2 configuration. Phase 1 is "carbon and nitrogen atoms in position resembling β-C_3N_4" and phase 2 is "areas with excess carbon."[11] The lines were assigned as follows: 399.08eV (N 1) and 286.43eV (C 1) to phase 1; 400.82eV (N 2) and 287.63eV (C 2) to phase 2. From the above results there is a significant amount of C–N bond for N and C atoms in the films, favoring the

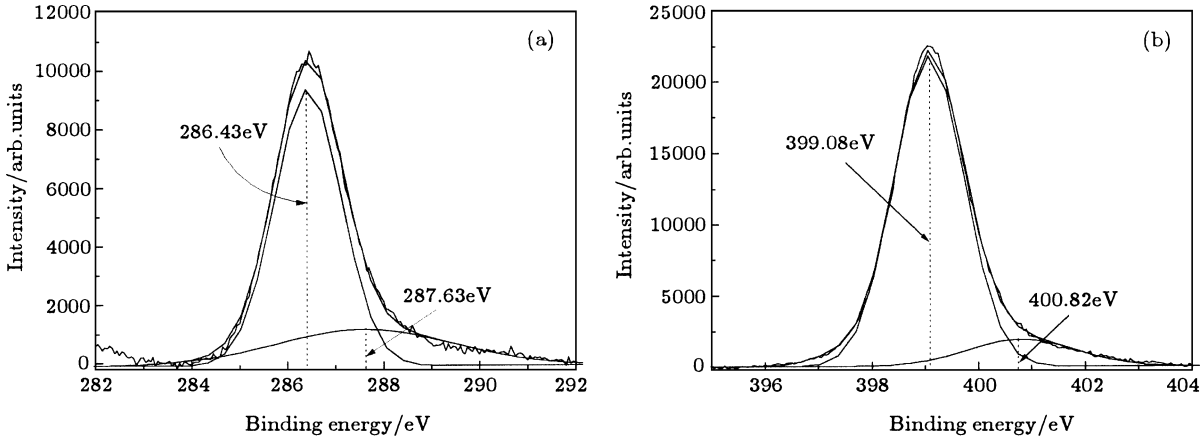


Fig.4. The typical XPS spectra of carbon nitride film deposited on Si substrate (a) C 1s region, (b) N 1s region.

formation of β-C_3N_4 phases. The [C1], [C2], [N1], and [N2] concentrations were calculated from the areas under fitted Gaussian distributions divided by their sensitive factors. The N/C ratio in phase 1 (α- and β-C_3N_4 mixture) was [N1]/[C1], which was closed to the stoichiometric value 1.33 of C_3N_4.

D. The vibration mode

For diamond and related materials, diamond has sharp Raman peak at 1332 cm^{-1}, and graphite has two broad G, D bands centered at 1575 cm^{-1} and 1360 cm^{-1} respectively. These results were tested and verified repeatedly, 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 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[12] argued that since 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.

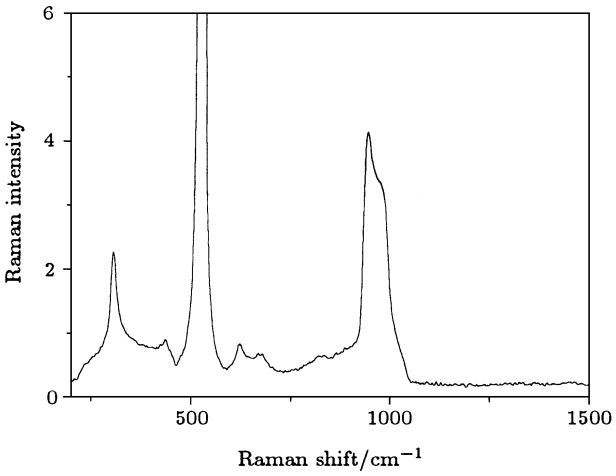


Fig.5. The Raman spectrum of carbon nitride film deposited on Si substrate.

Experiments were performed on a FT-Raman JY U-1000 spectroscope. Figure 5 is the Raman spectrum detected from a film deposited on Si substrate. The Raman spectrum showed no signs of the G, D band which are the fingerprint of graphite. The observed Raman shifts 306, 623, 981cm^{-1} are close to the calculated data for β-C_3N_4 300, 645, 1047cm^{-1}; observed peaks 436, 669, 678, 944cm^{-1} are close to the calculated data for α-C_3N_4 438, 658, 672, 955cm^{-1}. The strong peak at 520cm^{-1} is due to silicon substrate. The experimental results support the existence C–N bond in α- and β-C_3N_4 mixture.

For FT-IR analysis, we rely on a computer simulation using the Cerius II materials analysis package from Molecule Simulation Incorporation (MSI) to identify the peaks of C_3N_4. Experimental results are shown in Fig.6. Observed peaks at 852, 886cm^{-1} are close to the calculated β-C_3N_4 IR active mode 891cm^{-1}; and observed peaks at 1012, 1031, 1075cm^{-1} are close to the calculated α-C_3N_4 IR active mode 1051, 1065cm^{-1}. Other weak peaks may be attributed to Si_3N_4 or other compounds. The results also support the formation of C–N bond in α- and β-C_3N_4 mixture.

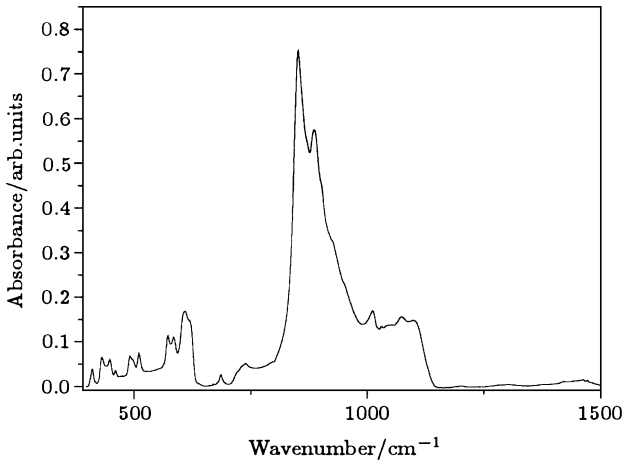


Fig.6. The FT-IR spectrum of carbon nitride film deposited on Si substrate.

IV. CONCLUSIONS

Carbon nitride films have been prepared on Si substrates using MPCVD technique. The major part of the film is composed of α- and β-C_3N_4. The N/C atomic ratio is close to the stoichiometric value of C_3N_4 . XPS, FT-IR and Raman spectra support the existence of C–N covalent bond in α- and β-C_3N_4 .

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