Phase identification of C_3N_4 in CN films prepared by rf plasma chemical vapor deposition and dc magnetron sputtering

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ABSTRACT

We prepared C_3N_4 films by rf plasma enhanced chemical vapor deposition (PCVD) and alternating C_3N_4/TiN composite films by dc magnetron sputtering. X-ray diffraction (XRD) and transmission electron diffraction (TED) revealed that the structure of the films is amorphous or polycrystalline, depending on deposition conditions and heat treatment. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy confirmed the presence of sp^3 and sp^2 hybridized C atoms bonded with N atoms in the tetrahedral and hexagonal configurations, respectively. Graphite-free C_3N_4 films were obtained by PCVD under optimal conditions. To prepare well crystallized C_3N_4 films by magnetron sputtering, we introduced negatively biased gratings in the sputtering system. CN films deposited at grating voltages (Vg) lower than 400V are amorphous. Crystallites of cubic and β-C_3N_4 were formed at increased voltages.

1. INTRODUCTION

Since Liu and Cohen [1,2] predicted that the hypothetical β-C_3N_4 may have a bulk modulus comparable to that of diamond, great effects have been made to synthesize superhard C_3N_4. CN films were prepared by a variety of methods including laser ablation [3], chemical vapor deposition (CVD) [4-6], and magnetron sputtering [7,8]. But in most cases the films obtained were carbon-rich and amorphous. A few authors obtained nano-sized β-C_3N_4 dispersed in the amorphous CN matrices.

Theoretically, there are basically seven C_3N_4 phases [2, 9, 10]. They are the two β-C_3N_4, α-C_3N_4, two c-C_3N_4, and two graphitic C_3N_4. These phases are energetically close to one another, and they are also close to diamond and graphite in energy. During deposition, these phases will grow competitively. As far as mechanical properties are concerned, a major problem is to restrain the formation of graphite and graphitic C_3N_4, which are soft phases

unwanted in making hard CN coatings.

This paper reports β-C_3N_4 films prepared by rf PCVD and dc unbalanced magnetron sputtering. The structures of the films are characterized by XRD and TED. The effects of transition layers and heat treatment are studied. Limited evidence for the presence of c-C_3N_4 in CN_x/TiN composite films prepared by magnetron sputtering is presented.

2. EXPERIMENT

In our PCVD apparatus, a cylindrical rf electrode is fitted outside a quartz tube. The rf voltage is controlled in the range of 1500-2000V and the frequency kept at 200 kHz. The substrate is placed on the grounded plate in the tube. Polished Si(111) wafers were pretreated following standard procedures. Deposition of transitional TiN or ZrN layer was performed by reactive sputtering. SiH_4 and C_2H_4 were used as working gases, respectively, for the deposition of Si_3N_4 and C_3N_4.

C_3N_4/TiN composite films were prepared using a dual-cathode closed unbalanced magnetron sputtering system, similar to that described by Li at al [8]. An NbFeB magnet is used to ensure a strong magnetic field. A soft magnet is placed at the back of each target. To increase the energy and density of the positive ions flowing to the substrate, a grating is placed 3 cm from each target. The negative grating voltage (Vg) can be adjusted between 500~600V. During deposition, the graphite and Ti targets were simultaneously sputtered. The sputtering voltages applied to the graphite and Ti targets were 560~600V and 380~420V, respectively. The pressure was kept 0.5~1.0 Pa, the flux(sccm) ratio N_2/Ar=17/33, and the substrate bias was controlled between 100~200 V. Alternating C_3N_4/TiN composite films were formed on Si(100) substrates mounted on a rotating substrate holder.

3. RESULTS AND DISCUSSION

3.1. CN films prepared by PCVD

Fig. 1 shows the XRD spectra of a PCVD CN_x/Si_3N_4/Si specimen at different stages of preparation. For the Si_3N_4/Si specimen, we see three peaks at 2θ=26.8°, 58.9°, and 94.9°, attributed to the diffraction of β-Si_3N_4 (200), (221), and (322), respectively. These peaks are not seen after deposition of the CN film. Only a contour around 28° is left and it is attributed to a modification of the above diffraction by the freshly grown CN film. After annealing at 800 °C in vacuum for 2h, the specimen shows three new peaks at 28.4°, 58.7°, and 94.9°, attributed to β-C_3N_4(110), (211), and (330), respectively. The strong peak at 28.4° suggests a preferred growth of β-C_3N_4(110). No diffraction due to graphite, which has a large mismatch with Si_3N_4, is seen in the spectra. Based on the XRD spectra, the lattice constant of β-C_3N_4 were calculated as a=0.628 nm and c=2.34 nm, in good agreement with reported results of a=0.63 nm and
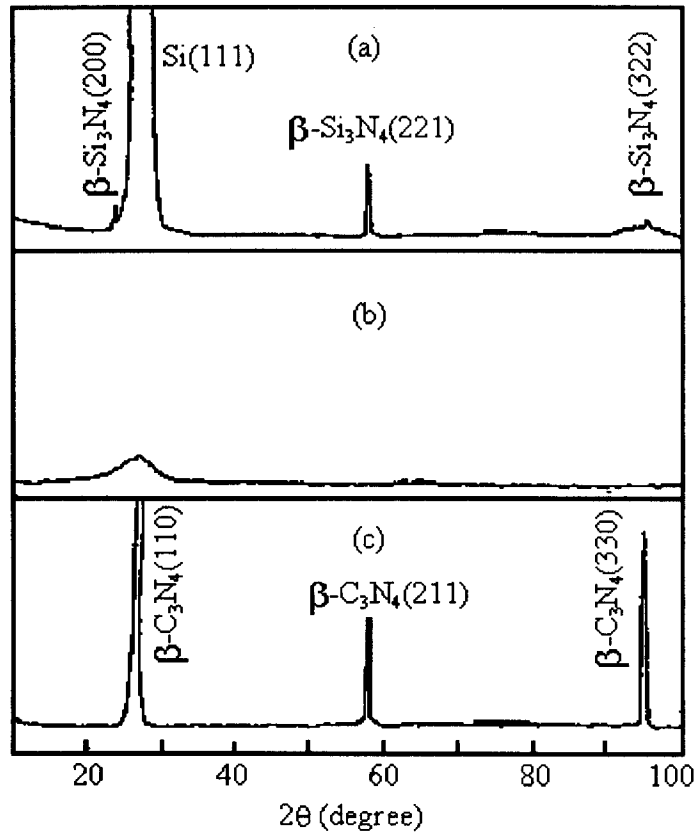
c=0.238 nm by Yu et al [12].

Fig. 1 The XRD spectra for (a) Si_3N_4/Si, (b) C_3N_4/Si_3N_4/Si, and (c) C_3N_4/Si_3N_4/Si after annealed at 800 °C in vacuum for 2 hours.

Table 1   d-spacings of C_3N_4 deposited on Si_3N_4/TiN/Si (designated Sample A) and Si_3N_4/ZrN/Si (Sample B) by PCVD.

hkl	d (nm, calc.)	Sample A	Sample B	hkl	d (nm, calc.)	Sample A	Sample B
110	0.3213	0.348	0.325	320	0.1277	0.127	0.127
200	0.2783	0.256		321	0.1133		0.113
101	0.2259	0.221		500	0.1106	0.111	
111	0.1953		0.195	330	0.1071	0.085~0.100	
211	0.1598	0.157	0.157	611	0.080	0.079, 0.075	
221	0.1345	0.135					

Free CN films were obtained by putting CN_x/Si_3N_4/Si in the corrosive solution of HF:HNO_3=2:1. TED observation revealed that CN films deposited on Si_3N_4/Si are amorphous. But for annealed specimens, distinct Laue spots were observed, verifying an amorphous to crystalline phase transition of the CN films during annealing. CN films deposited on Si_3N_4/TiN(ZrN)/Si are polycrystalline. Crystal parameters calculated from the TED photos are

summarized in Table 1. The CN films deposited on both Si_3N_4/TiN/Si and Si_3N_4/ZrN/Si are structurally close to the hypothetical β-C_3N_4; the CN_x/Si_3N_4/ZrN/Si seems closer to it. Laue spots were also observed for as-grown C_3N_4/ZrN/Si, suggesting that large C_3N_4 crystallites can be formed when an intermediate ZrN layer is used.

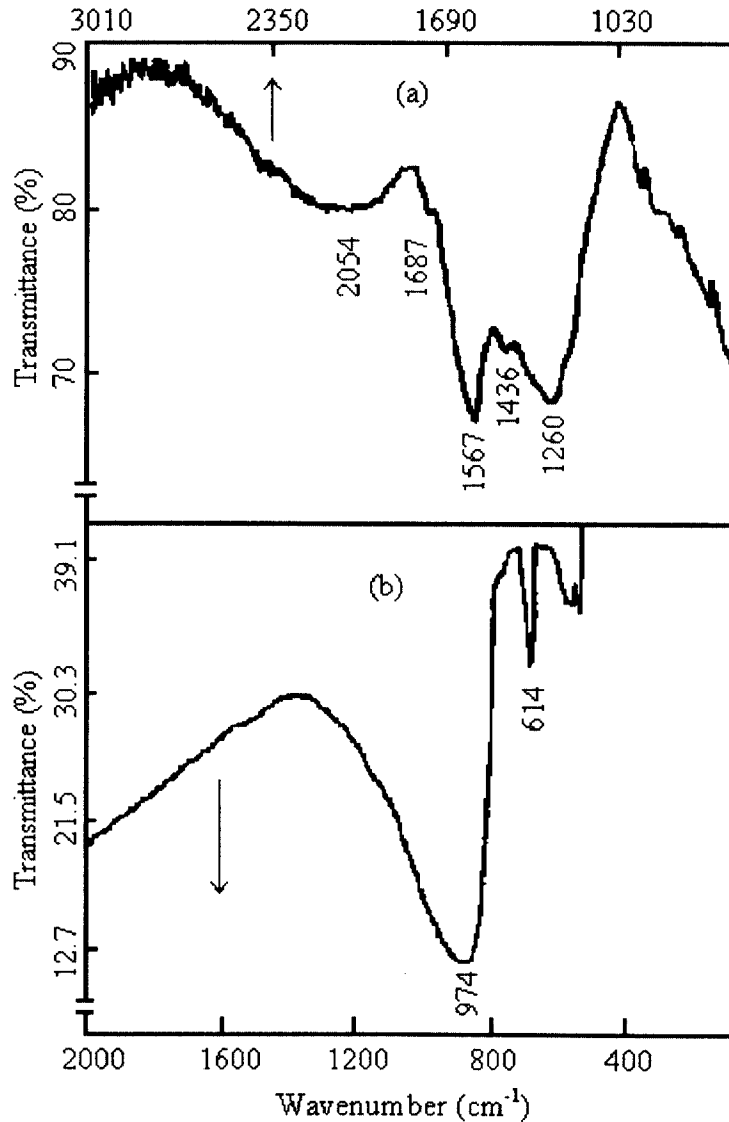**Fig. 2** FTIR spectra of (a) CN_x/Si(111) and (b) C_3N_4/Si_3N_4/ZrN/Si.

To study the chemical bonding of the C and N atoms, we measured the XPS and FTIR spectra of the PCVD C_3N_4 films. XPS demonstrated both C and N atoms have two groups of binding energies. One is the 286.2-287.1 eV for C atoms and 398.0-398.7 eV for N atoms. The other is 284.6-284.8 eV for C and 400.3-400.9 eV for N atoms. The binding energy values were found to be greatly influenced by the N_2 flux. The results indicate that both sp³ and sp² hybridization exist in the CN films. In either β- or c-C_3N_4 compound, each C atom is sp³ hybridized and σ-bonded with four N atoms in a tetrahedral configuration. In graphitic C_3N_4, however, each C atom is sp² hybridized and σ-bonded with three N atoms, forming a hexagonal

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configuration; and between the interplanar C and N atoms, π-bonds (C=N bonds) are formed. The XPS results suggest the existence of β- and graphitic C_3N_4 in the PCVD CN films. The N contents of the films were evaluated from the XPS spectra to be between 12-53.7 at %.

The FTIR spectra of the PCVD CN films are illustrated in Fig. 2. For the CN film deposited on Si, we observe a peak at 1260 cm^{-1} due to the stretch vibration of C-N bonds, the 1436 cm^{-1} peak due to amorphous sp^3 C-C bonds, the absorption due to graphite at 1576 cm^{-1}, and a peak at 1687 cm^{-1} due to the vibration of C=N bonds present in graphitic C_3N_4. For the CN film prepared using a transitional Si_3N_4/TiN(ZrN) layer (Fig. 2b), we see only a broad and strong absorption around 974 cm^{-1} due to C-N bonds, in addition to the lattice vibration of Si at 614 cm^{-1}. Since no evidence for the existence of graphite is detected, it is suggested that its growth is suppressed by the transition layers.

3.2. CN films prepared by dc magnetron sputtering

Fig. 3 shows the XRD spectra typical of CN_x/TiN/Si specimens prepared by dc magnetron sputtering at various grating voltages. For the specimen deposited at Vg=400V, we observe two peaks around 35.9° and 67.0°, attributed to the diffraction of TiC(111) and Ti_2N(311) planes, respectively. The short and broad shapes of the peaks indicate that the grains of TiC and Ti_2N are very small. No peak caused by the diffraction of C_3N_4 is observed, suggesting that the CN coating is amorphous. For the specimen deposited at Vg=450V, one sees four peaks. The two peaks at 36.2 and 60.2° are attributed to Ti_2N(200) and (002). It is interesting that, with so much N_2 in the system, a Ti-rich Ti_2N has been formed. We attribute this to an inadequate ionization of N_2. The two adjacent peaks at 69.1° and 70.0° are assigned to the (400) plane of the Si(100) substrate and to β-C_3N_4(221), respectively. For the specimen prepared at Vg=550V (Fig. 3c), a strong peak at 36.7° originated from TiN(111) is observed. The four peaks located at 42.7°, 58.6°, 70.2°, and 72.4°, are attributed to β-C_3N_4(210), (211), (221), and (311). The three peaks at 23.4° (d=0.3798 nm), 64.5° (0.1443), and 69.5° (0.1351) cannot be attributed to diffraction of β- or α-C_3N_4 [6, 11, 13]. We tentatively attributed them to c-C_3N_4(110), (321), and (400). The strong diffraction intensities of β-C_3N_4 (221) and c-C_3N_4 (400) suggest texture growth of both crystallographic planes over the substrate. Although the sequence of diffraction intensities differ slightly from theoretical predictions [11], the above results provided limited evidence for the existence of c-C_3N_4. And we believe an increase of Vg help crystallization of the C_3N_4 phases.
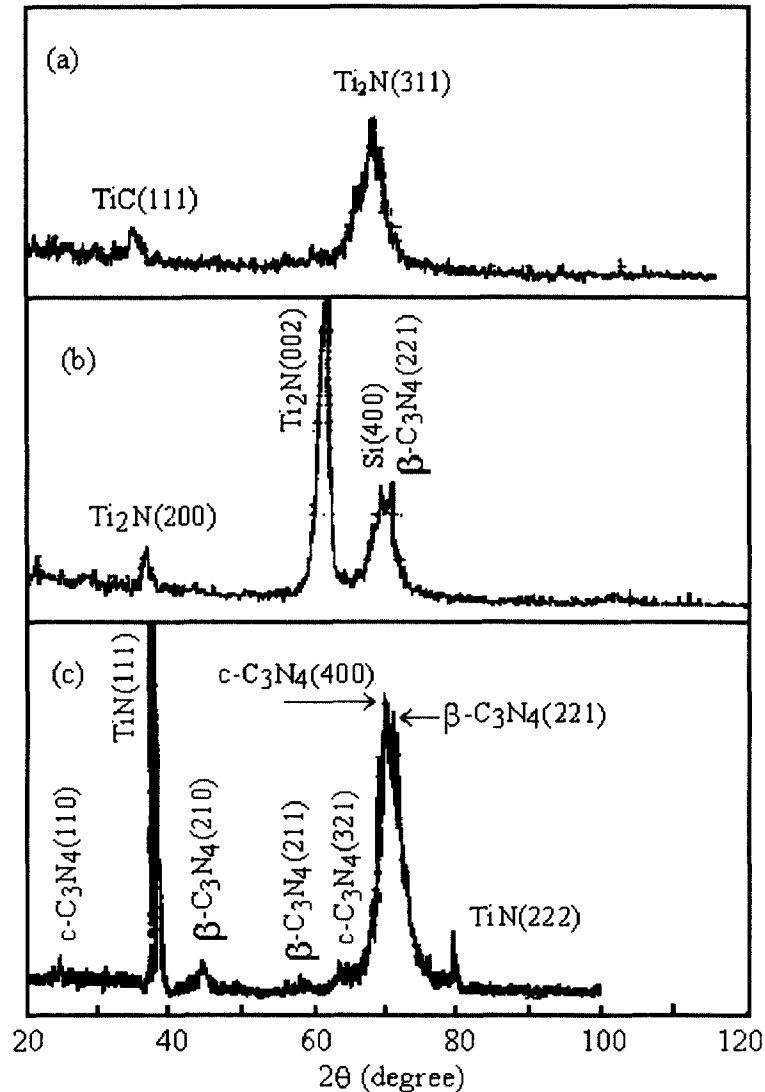
Fig. 3 XRD spectra of the alternating CN_x/TiN composite films prepared at (a) Vg=400 V, (b) Vg=450 V, and (c) Vg=550 V.

Further characterization by TED showed that the CN films deposited at Vg=400V were amorphous. With electron beams directly incident upon the grains, however, faint Laue spots were observed. This reveals that a small number of C_3N_4 grains are dispersed in the amorphous CN matrix. TED photos for the CN films prepared at Vg=450V and 550 V are shown in Fig. 4. Up to nine rings is observed for the CN film prepared at Vg=450 V, revealing the polycrystalline nature of the specimen. d-spacings and relative intensities of the peaks evaluated from the diffraction rings are presented in Table 2. The d-values are in accordance with both the theoretical values for β-C_3N_4 and experimental results by other authors [11, 12]. They are also consistent with the XRD results since β-C_3N_4(221), the plane with maximum intensity on the TED micrograph, has also appeared on the XRD spectrum for the same sample.
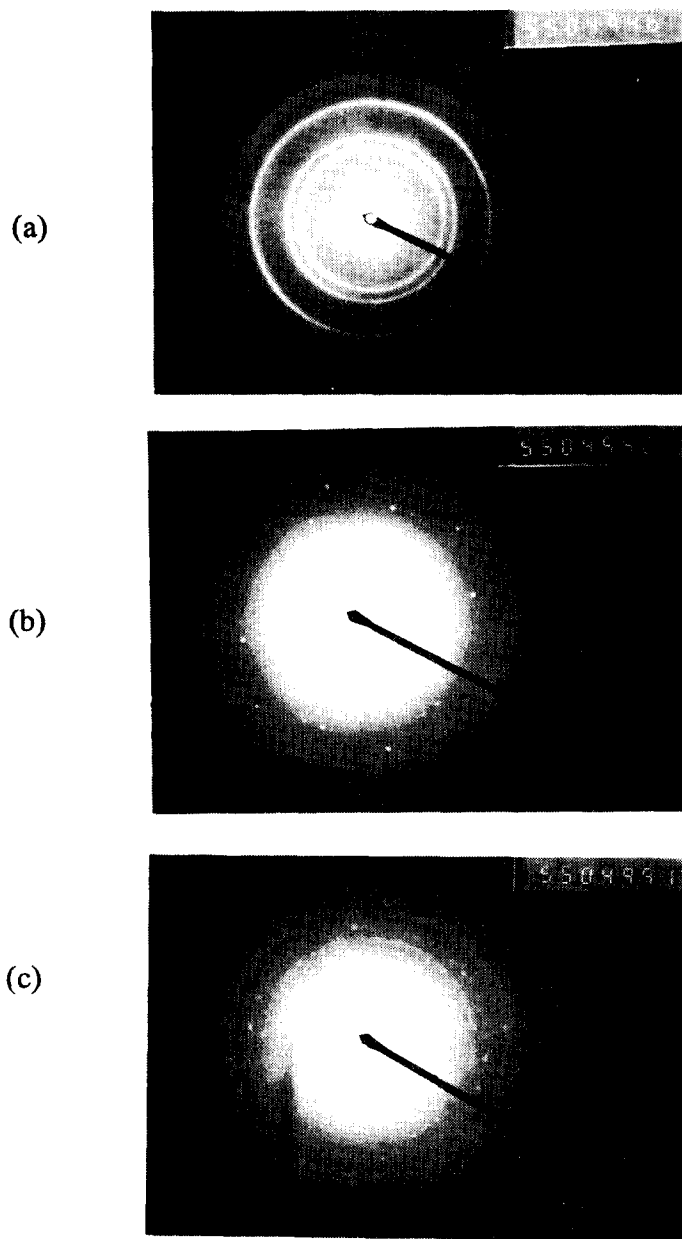
Fig. 4 Typical TED photos of CN films prepared at (a) Vg=450V, (b) Vg=550 V (Laue pattern), and (c) Vg=550 V (Superimposition of the Laue pattern on the polycrystalline diffraction pattern).

Table 2   d-spacings and relative intensities evaluated from the TED photo of
the C_3N_4 film deposited at Vg=450V.

d(nm, exp.)	0.2188	0.1850	0.1313	0.1124	0.1071	0.0925	0.0848	0.0831	0.0761
hkl	101	300	221	112	411	511	412	521	441
d(nm, ref. 12)	0.218	0.182	0.156		0.106				
d(nm, calc.)	0.2256	0.1859	0.1348	0.1125	0.1092	0.0920	0.0853	0.0833	0.0759
Relative int.	90	70	100	40	40	10	10	20	15

Table 3   d-values and relative intensities of the Laue spots for the C_3N_4 film
deposited by dc magnetron sputtering at Vg=550V.

d(nm, exp.)	0.3840	0.2224	0.2087	0.1469	0.1300	0.1146	0.0857	0.0764
hkl	110	211	210	301	311	332	602	543
d(nm, calc.)	0.3816	0.2203	0.2095	0.1465	0.1295	0.1151	0.0853	0.0763
Relative int.	weak	strong	medium	weak	strong	medium	weak	weak
C_3N_4 phase	Cubic	Cubic	β	β	β	Cubic	Cubic	Cubic

Figures 4b and 4c show the Laue pattern of a C_3N_4 film prepared at Vg=550 V and the superimposition of the Laue pattern and its polycrystalline diffraction rings, respectively. From the Laue spots eight d-values were obtained (Table 3). Five of them are attributed to c-C_3N_4(110), (211), (332), (602), and (543) planes. The d-spacing of 0.2087 nm is not attributed to c-C_3N_4, since it differs much from the theoretical prediction. The rest two d-values, if they were the results of the c-C_3N_4 diffraction, should be attributed to its (320) and (322) planes. According to the diffraction rules for cubic crystals, however, diffraction due to these planes should extinct. Noticing the accordance of the above three d-spacings with those of three β-C_3N_4 planes, we attribute them to the diffraction of β-C_3N_4. Thus the sample measured contains both cubic and β-C_3N_4 phases. Referring to the XRD intensities, we see that c-C_3N_4 predominates the specimen. We also calculated d-values from Fig. 4c and obtained similar results. Calculations based on the TED data give a=0.5380 nm for c-C_3N_4 and a_0=0.6444 nm and c_0=0.2421 nm for β-C_3N_4. Compared with predictions of Teter and Hamley [10], our results have deviations of -0.33%~0.93% for c-C_3N_4 and -0.97~1.6% for β-C_3N_4. Note the strong TiN(111) peak present in Fig. 4c, it is suggested that crystallization of c-C_3N_4 is favored and enhanced by the cubic TiN seed layer.

4. CONCLUSION

(1) Polycrystalline β-C_3N_4 films were prepared by rf PCVD. Laue patterns were observed for the C_3N_4/Si_3N_4/ZrN/Si and annealed C_3N_4/Si_3N_4/Si samples. Intermediate TiN and ZrN layers enhance the growth of C_3N_4 films over Si_3N_4. Growth of graphite is effectively

suppressed by use of TiN, ZrN, and Si_3N_4 layers.

(2) Alternating C_3N_4/TiN composite films were prepared by dc unbalanced magnetron sputtering. The structure of the CN films is influenced by the grating voltage. C_3N_4 crystallites were formed at Vg>450 V. Limited evidence was found for the existence of c-C_3N_4 phase in the C_3N_4 films.

ACKNOWLEDGMENT

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