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Nano-carbon nitride synthesis from a bio-molecular target for ion beam sputtering at low temperature

J.-J. Wu ^{a,*}, T.-R. Lu ^b, C.-T. Wu ^c, T.-Y. Wang ^c, L.-C. Chen ^c, K.-H. Chen ^a, C.-T. Kuo ^b,
T.-M. Chen ^d, Y.-C. Yu ^e, C.-W. Wang ^e, E.-K. Lin ^e

^a Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

^b Institute of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan

^c Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

^d Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

^e Institute of Physics, Academia Sinica, Taipei, Taiwan

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Abstract

Nano-crystalline carbon nitride has been successfully synthesized at a temperature below 100 °C from an adenine (C₅N₅H₅) target sputtered by an Ar ion beam. Because adenine possesses a ring structure similar to the hypothetical β-C₃N₄ phase, the use of this bio-molecular compound as the target is believed to reduce the energy barrier of carbon-nitride growth. The effect of Ar ion-sputtering voltage on the film growth and the effect of extra-N-atom incorporation on the carbon-nitride film growth are examined in this study. Only a carbon film is formed with an ion energy of 500 V. For the ion-beam energy above 750 V, carbon nitride films are deposited, and there is some hydrogen incorporation in the films. The N/C composition ratio in the films could reach 1:1 and is independent on the ion beam voltage. The nitrogen is bonded with carbon within the films, as determined by the IR and XPS measurements. However, the films deposited at a higher ion voltage could possess some original functional groups of adenine. A strong and broad peak at a d-spacing of 0.32 nm, comparable to the calculated d-spacing of the β-C₃N₄(110), is observed in the XRD spectra of the carbon nitride films. The TEM results indicated that the film contained nano-crystalline grains. Several d values are also in good agreement with those of adenine and the calculated values of β-C₃N₄. The C/N ratios of the films are still kept at almost 1:1 with N atoms added during deposition. The XRD spectra and IR spectra of these films are all similar to the film deposited without nitrogen source. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carbon-nitride films have been the subject of great interest in recent years due to their excellent properties predicted by theoretical calculations. Liu and Cohen [1] predicted that carbon nitride with a structure similar to β-Si₃N₄ should have a bulk modulus superior to that of diamond. Furthermore, crystalline carbon nitride could possess several other properties including a wide band gap, high thermal conductivity, high strength, high decomposition temperature and excellent resistance to corrosion and wear [2]. Carbon nitride polytypes with different stabilities like cubic-C₃N₄, α-C₃N₄ and graphite-C₃N₄ are also proposed by theoretical calculations.

[3] Various methods such as shock-wave compression [4], laser ablation [5], r.f. or d.c. magnetron sputtering [6,7], ion-beam-assisted deposition [8], ECR chemical vapor deposition [9], r.f.-plasma-assisted hot-filament chemical vapor deposition [10], and arc discharge [11] have been employed to synthesize carbon nitride. However, until now, most of these efforts have resulted in amorphous carbon-nitride films or in tiny crystals embedded in an amorphous matrix.

As a graphite target is used as a carbon source in typical sputtering carbon-nitride processing, a highly energized nitrogen source is needed to maintain the nitrogen content within the films. Unfortunately, to date, the degree of crystallinity in CN films deposited by this method is not satisfactory, and the nitrogen contents of the films are generally below 30 at.%. We attempted, therefore, to synthesize carbon nitride films

* Corresponding author. Fax: +886 2 23620200;
e-mail: jjwu@pub.iam.s.sinica.edu.tw

by using a C–N bio-molecular compound, such as azaadenine and adenine, as targets for Ar ion-beam sputtering [12–14]. Owing to the similarity in the ring structures of these C–N bio-molecular compounds and the hypothetical β -C₃N₄ phase, the use of these bio-molecular compounds as targets is believed to reduce the energy barrier of carbon nitride growth. Indeed, without any other sources of nitrogen, crystalline carbon nitride with high N/C ratios of around 0.5, as determined by Auger measurements, can be formed even at room temperature. A strong and broad peak at a d-spacing of 0.32 nm, comparable to the calculated β -C₃N₄(110), was observed in the XRD spectrum. The TEM results indicated that the film contained nano-crystalline grains. Several d values were in good agreement with the calculated values of β -C₃N₄. We have not ruled out the possibility of having a crystal structure distinct from the β -C₃N₄ phase, since some peaks were missing from our data.

In this study, we examined the effect of Ar ion-sputtering voltage on carbon-nitride film growth at a temperature below 100 °C from an adenine target. Adenine has the chemical formula C₅N₅H₅, contains C–N single bonds and C=N double bonds and exhibits a ring structure similar to the hypothetical β -C₃N₄ phase. During sputtering of such a compound, a different energy of Ar ions interacted with the adenine target, leading to different sets of fragmental species for film growth. RBS, FTIR, XPS, SEM, XRD and TEM were employed to characterize the composition, binding, and structure of the films. Besides, a hybrid system combining the ion-beam sputtering with an atomic nitrogen source was employed to study the effect of N atom incorporation on the carbon nitride film growth.

2. Experimental

An ion-beam sputtering reactor equipped with an r.f. atomic source was employed in this study. Its schematic diagram is shown in Fig. 1a. A 3 cm Kaufman-type ion source was used to sputter the target at an incidence angle of 45°. The distance from the substrate to the target was 20 cm. An r.f. atomic nitrogen source was also at an angle of incidence of 45° to the substrate for the N atom incorporation study. The white powders of adenine (molecular structure as shown in Fig. 1b) were commercially available from Aldrich (Milwaukee, WI). Adenine powders were first baked at 105 °C for 24 h in a flowing nitrogen atmosphere to remove moisture, and were then compacted to form a 2.5 cm (1-inch) disk target at a pressure of 1250 kg cm⁻².

The base pressure of the deposition chamber was kept at 1×10^{-6} Torr before the deposition process. During deposition, the chamber pressure was about 3×10^{-4} Torr. An Ar flow rate of 1 sccm and a N₂ flow

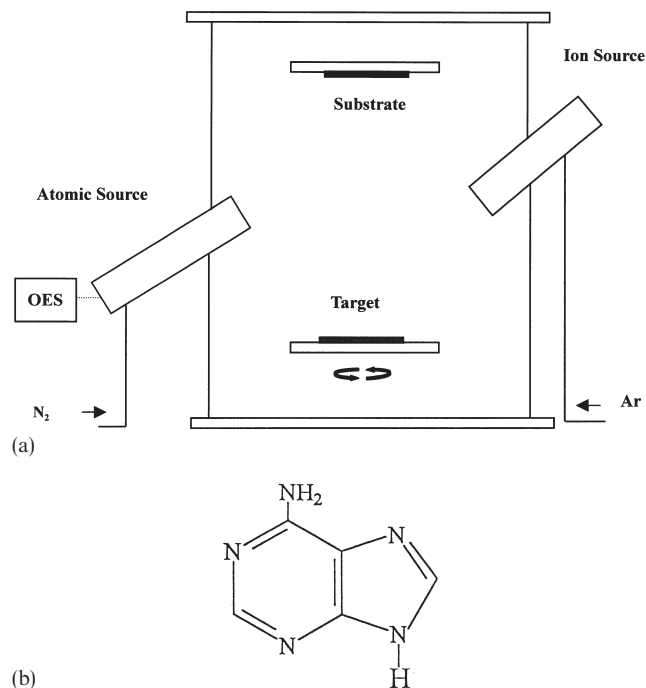


Fig. 1. (a) Schematic diagram of a hybrid system combining the ion beam sputtering with an atomic source. (b) Molecular structure of adenine.

rate of 0.4 sccm were used to maintain the Ar⁺ ion beam and the N atom source, respectively. The Ar⁺ ion beam current was held constant, and the ion beam voltage was varied from 350 to 1250 V for the study of the Ar ion sputtering voltage effect. For the study of the N atom flux effect, the ion beam voltage was held at 1000 V during the film growth. The relationship between the N atom flux and the r.f. power of the atomic source was calibrated by the N/N₂ peak-height ratio determined from optical emission spectroscopy (OES) measurements. The N atom flux increased as the r.f. power increased from 170 to 380 W at a N₂ flow rate of 0.4 sccm. Si(100), Si(111), Ag, and quartz were used as the substrates. Without external heating of the substrate, the deposition temperature measured using a thermocouple from the backside of substrate was kept below 100 °C by heating from ion-beam bombardment during deposition.

Quantitative composition analyses of the films were performed by Rutherford backscattering spectroscopy (RBS). A high-energy ⁴He ion beam of 3.5 MeV was employed to increase the sensitivity of the N and C elements [15,16]. The beam current was typically held between 5 and 25 nA during measurements. The scattering angle was fixed at 165°. The non-RBS cross-sections of ⁴He ion from C and N [15,16] were linked to the RUMP2 program for the RBS data analysis. The IR spectra were obtained on a Bomem MB series Fourier-transform infra-red (FTIR) spectrometer to analyze the chemical bonding of the carbon nitride films in the

reflection mode. A Perkin Elmer (Palo Alto, CA) Phi 1600 ESCA system was used to study the chemical bonding state of the films. A $\text{MgK}\alpha$ radiation of 1253.6 eV was used as the X-ray source with a linewidth of 0.7 eV. The analysis area for XPS measurement was 800 μm in diameter and with a pass energy for chemical-state analysis of 11.75 eV. The film thickness was measured from a SEM cross-section of the deposited sample. TEM studies were carried out with a 2010 JEOL electron microscope.

3. Results and discussion

The compositions of a series of films deposited by Ar^+ ion sputtering of an adenine target at various voltages were determined by RBS. A typical RBS spectrum is shown in Fig. 2. C and N were present, and the compositions of the films were homogeneous throughout the films. Due to the limitations of RBS measurements, the hydrogen content within the film was not detectable. Quantitative analyses of RBS data for the N/C composition ratios at four different ion-sputtering voltages are listed in Table 1. As shown in Table 1, only a carbon film was formed with an ion-sputtering energy of 500 V. The carbon-nitride film with N/C ratios of around 1:1 was deposited at an ion-sputtering energy of 750 V. However, as the ion-sputtering energy increased further from 750 to 1250 V, the N/C ratios were also kept at around 1:1. It appears that the composition of the films is not a strong function of the ion-sputtering voltage above 750 V.

The dependence of growth rate on ion-sputtering voltage is also shown in Table 1. At a constant Ar^+ ion current, the growth rate increased with increasing ion-sputtering voltage. With almost the same N/C composition ratio, the growth rate of carbon nitride film increased by a factor of four as the ion-sputtering voltage was increased from 750 to 1250 V.

The phase present in the carbon nitride films was evaluated by FTIR spectroscopy. IR transmittance spectra of the carbon nitride films deposited at various ion beam voltage are shown in Fig. 3. For comparison,

Table 1

Composition and growth rate of the films for some selective growth conditions

Ar ion beam voltage (V)	r.f. power of atomic source (W)	Composition C:N	Growth rate ($\mu\text{m h}^{-1}$)
500	0	100:0	0.27
750	0	48:52	0.28
1000	0	53:47	0.51
1250	0	47:53	1.12
1000	170	53:47	0.38
1000	230	48:52	0.35
1000	350	52:48	0.39

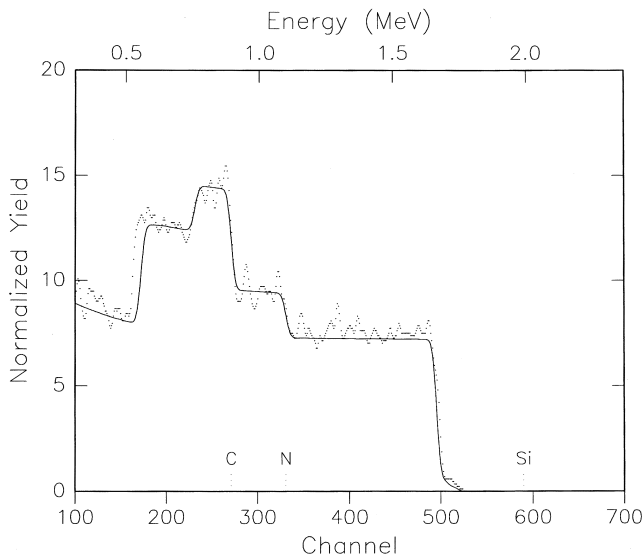


Fig. 2. Typical RBS spectrum of the film deposited in this study.

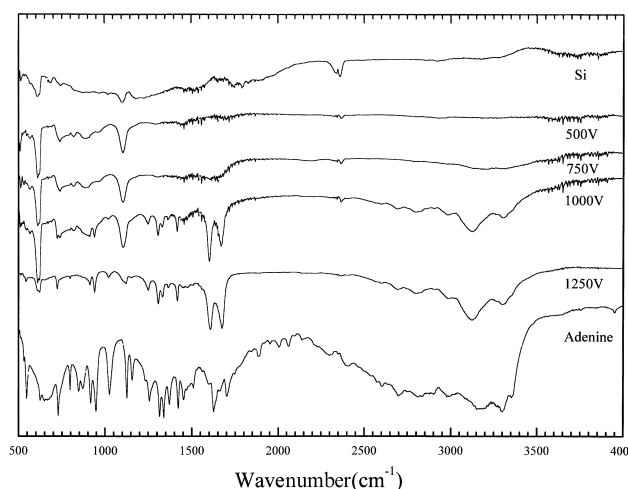


Fig. 3. IR spectra of Si substrate, adenine and the films deposited at various Ar ion beam voltages.

the spectra of the Si substrate and adenine are also shown in Fig. 3. The peaks corresponding to the CH_n group in the regions $1400\text{--}1450\text{ cm}^{-1}$ and $2800\text{--}3000\text{ cm}^{-1}$ as well as N–H bonding at around $3000\text{--}3500\text{ cm}^{-1}$ were observable in the spectra of the films deposited at an ion-beam energy above 750 V, suggesting that there was some hydrogen incorporation in the films. There was no significant peak in the vicinity of 2200 cm^{-1} , assigned as $\text{C}\equiv\text{N}$, for any of the films deposited at various ion-beam voltages. A broad absorption at around 1650 cm^{-1} was observed in the films deposited above 750 V. For the films deposited at 1000 and 1250 V, a peak at around 1250 cm^{-1} was observed. These two peaks can be assigned as the $\text{C}=\text{N}$ and $\text{C}-\text{N}$ stretching modes, respectively [17]. The suppression of the formation of $\text{C}\equiv\text{N}$ bonding suggested that the molecule cracking with this processing was not serious, and the film still possessed the bonding character of the

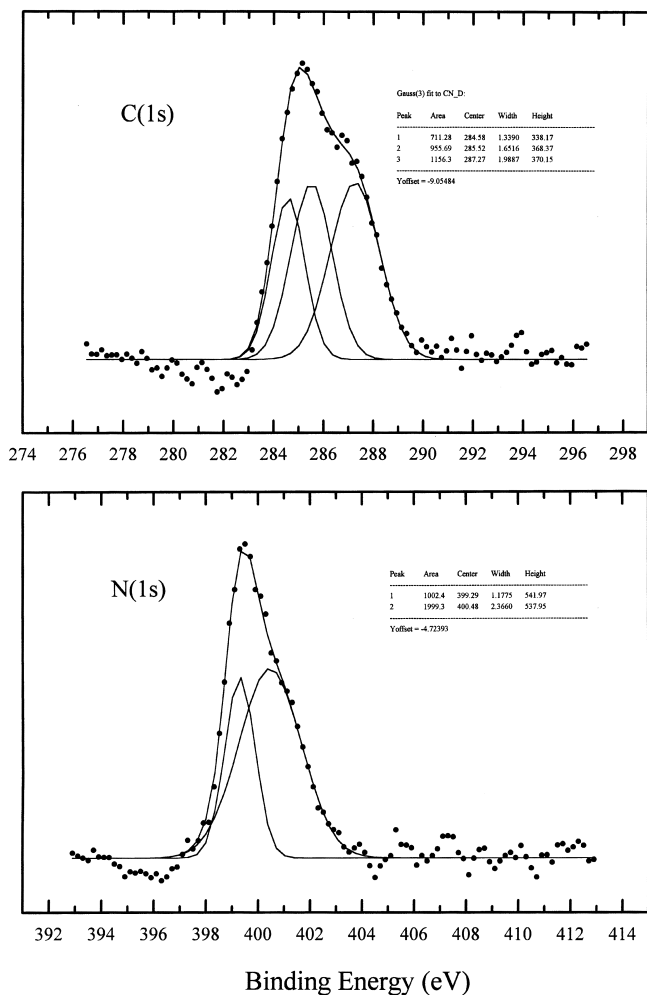


Fig. 4. Typical XPS spectra of C(1s) and N(1s) in this study.

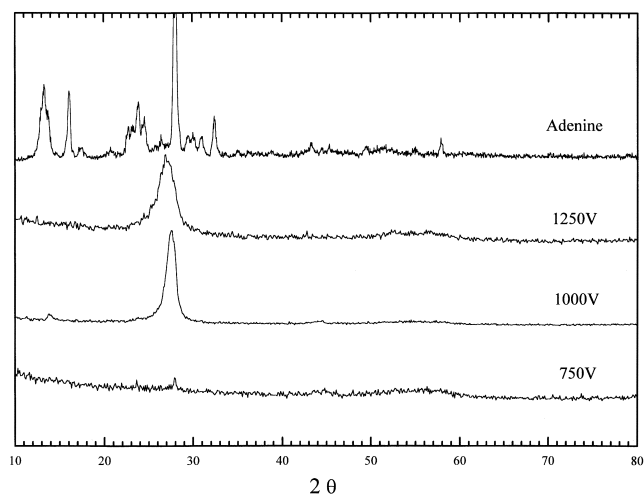


Fig. 5. XRD spectra of the films deposited at various Ar ion voltage.

adenine target, namely, C=N and C–N. As shown in Fig. 3, no significant C–N, C=N and C≡N peaks were present in the film deposited at an energy of 500 V. The absence of nitrogen incorporation was consistent with

Table 2

Comparison of the d spacings of the carbon film determined experimentally from TED with adenine and the calculated β -C₃N₄

TED measured		Calculated β -C ₃ N ₄ pattern		Adenine		
d (Å)	Intensity	d (Å)	hkl	Intensity	d (Å)	Intensity
		5.5	100	m	5.58	60
3.1	m	3.17	110	m	3.19	100
2.76	s	2.75	200	s	2.77	40
2.2	s	2.25	101	s		
		2.08	210	s	2.09	20
		1.95	111	m		
1.76	m	1.83	300	m	1.84	10
		1.59	211	w	1.60	20
1.53	w	1.52	310	w		
		1.47	301	w		
1.32	w	1.33	221	w		
		1.26	320	w		
		1.23	002	w		
		1.12	321	m		
		1.08	411	w		

RBS results. It was not clear why only carbon film was formed at an ion voltage of 500 V. In the fingerprint region below 1200 cm⁻¹, attributable to the contribution from the multi-functional group interaction, the films deposited at 1250 and 1000 V were more complex than those deposited at 750 and 500 V. Moreover, some features were similar to that of adenine, indicating that the films deposited at high voltages could possess some original functional groups of adenine. From the differences in IR spectra and a significant increase in the growth rates from 750 to 1250 V, it was speculated that the films formed at high voltages could involve the target evaporation process by high-energy Ar-ion heating.

The high-resolution XPS scan of the C(1s) and N(1s) peaks was measured to examine the chemical bonding state of the carbon-nitride films. For the carbon-nitride films deposited in this study, the C(1s) and N(1s) could be adequately fitted by three and two peaks, respectively. Typical XPS spectra of the C(1s) and N(1s) are shown in Fig. 4. According to the tentative assignment by Marton et al. [18], the carbon-binding energies, as shown in Fig. 4, revealed a pure carbon network, C(1s)=N, and C(1s)–N bonding structures at 284.6, 285.5, and 287.2 eV, respectively. For the N(1s) peak, the 399.2 and 400.5-eV binding energies were related to the N(1s)–C and the N(1s)=C, respectively. The XPS measurements were consistent with the IR measurements, in that both showed that the nitrogen within the films was bonded with carbon.

The XRD spectra of adenine and the carbon nitride films deposited at an ion-sputtering voltage of 750, 1000 and 1250 V are shown in Fig. 5. In comparison with adenine in which several peaks were observed, only a broad peak at a d-spacing of 0.32 nm was observed in the XRD spectra of the films. The structure of the film

was also studied by transmission electron microscopy (TEM) [13]. The TEM results indicated that the film contained nano-crystalline grains. Several diffraction rings were observed in the TED pattern. The corresponding lattice spacings of the TED pattern are given in Table 2. For comparison, the d-spacings of the theoretical β -C₃N₄ [1] and adenine are also listed. A proximity of the peak is observed. The most intense ring of the film exhibited a d-spacing of 0.32 nm, which was also confirmed by XRD to be the most intense. Note that this d-spacing is similar to that calculated for β -C₃N₄ (110). The other d-spacings were all comparable with those of β -C₃N₄. However, we do not rule out the possibility of having a crystal structure distinct from the β -C₃N₄ phase since one of its strongest peaks, the (101) direction, is missing from our data. As can be seen in Table 2, some of the d-spacings of the film were also in good agreement with those of adenine except the d-spacing of 0.22 nm. According to the d-spacing calculated from the TED pattern and IR analysis, another possibility was that some nano-crystals embedded in the films were still the target material, adenine.

In order to enhance the N incorporation in the films, an atomic nitrogen source was further employed during processing. The films were deposited at an ion-beam voltage of 1000 V with various r.f. powers of atomic source. From OES measurements, the N atom flux was found to increase significantly as the r.f. power was increased from 170 to 380 W. The compositions of the films determined by RBS are shown in Table 1. Although the N atom flux increased as the r.f. power was increased from 170 to 380 W, the C/N ratios of the films were still kept at around 1:1. The growth rates at different r.f. powers of atomic source are also shown in Table 1. At an Ar⁺ ion voltage of 1000 V, the growth rate was reduced with the addition of N atom source. The growth rates were not sensitive to the N atom flux, however. The XRD spectra and the FTIR spectra of the films deposited in the hybride system were similar to those of the film deposited without a nitrogen source. It was speculated that the reduction in growth rates by adding N atoms could be due to N atoms reacting with the carbon-nitride films to form C₂N₂ molecules during deposition of the films [19].

It is intriguing to note that the C/N ratios of the films were kept at around 1:1 despite the chemical sputtering during films deposition. It is likely that there are not just one meta-stable carbon nitride stoichiometry and structure. Among the accessible compositions and structures, CN phase might exhibit high kinetic stability.

4. Conclusion

Nano-crystalline carbon nitride has been successfully synthesized at a temperature below 100 °C from an adenine target sputtered by an Ar ion beam. Only a

carbon film is formed with an ion energy of 500 V. For the ion-beam energy above 750 V, carbon-nitride films are deposited, and there is some hydrogen incorporation in the films. The N/C composition ratio in the films can reach 1:1, and this has been found to be independent of the ion beam voltage. IR and XPS measurements indicate that the nitrogen is bonded with carbon in the films. However, the films that deposit at a higher ion voltage could possess some original functional groups of adenine. A strong and broad peak at a d-spacing of 0.32 nm, comparable to the calculated β -C₃N₄(110), is observed in the XRD spectra of the carbon nitride films. The TEM results indicate that the film contained nano-crystalline grains. Several d values are also in good agreement with those of adenine and the calculated values of β -C₃N₄. The C/N ratios of the films are still kept at 1:1 with various levels of N atom flux added during deposition. The XRD and IR spectra of these films are all similar to those of the film deposited without a nitrogen source.

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