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Effect of target materials on crystalline carbon nitride film preparation by ion beam sputtering

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Abstract

In order to provide abundant chemical information, two novel bio-molecular target materials, instead of the conventional graphite target, were successfully developed to determine the possible formation mechanisms of carbon nitride during ion beam deposition. The azaadenine and adenine targets consist of carbonitro bonding, high N/C ratio as well as a six-fold carbonitro ring structure similar to that in hypothetical C₃N₄. Mass spectroscopy was used to determine the possible mechanisms of these two target materials. A lower electron beam energy at 75 eV was adopted to generate as abundant fragmental ions during the decomposition of these targets. Mass spectroscopy study on these two different targets indicates that the adenine target exhibits a more complex decomposition mechanism than the azaadenine target. However, the seven common hydrogenated carbonitro-species may suggest the same predominant mechanism during the decomposition of these two targets under the present deposition condition. The good correlation is one reason why two different targets can make almost the same quality crystalline carbon nitride films, including bonding, composition and structure. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carbon nitride has been the subject of intensive research since the theoretical work by Sung [1, 2], predicting the possibility of a covalently bound C–N compound, similar to the structure in Si₃N₄, and with unique physical and chemical properties that are comparable to those of diamond. The first-principle pseudo-potential calculation by Liu and Cohen [3] confirms that the β-C₃N₄ may exceed the hardness of diamond. In fact, more recent theoretical studies have also indicated low-compressibility carbon nitride may have a number of structures distinct from β-C₃N₄ structure [4]. To date, a variety of techniques such as laser ablation [5], DC magnetron sputtering [6], radio frequency (RF) sputtering [7], ion beam deposition [8], ion implantation [9], plasma arc deposition [10], chemical vapor deposition [11], shock wave high pressure synthesis [12], organic pyrolysis [13] and ultraviolet (UV) assisted

chemical synthesis [14] have been reported on the synthesis of the β-C₃N₄ phase but most with little success. Hence, it is essential to focus not only on the synthetic techniques but also on understanding the formation mechanisms.

The difficulty in growing carbon nitrides is primarily due to a considerable high activation energy barrier for the formation of carbon nitrides. Apparently, the activation energy barrier is too high to overcome using conventional carbon sources such as methane, graphite, etc., and nitrogen sources such as nitrogen gas, ammonia, etc., separately, in various deposition techniques mentioned above. Especially, the incorporation of nitrogen using N₂ is problematic because of its stability and bond strength ($\Delta H^0 = 945 \text{ kJ mol}^{-1}$) [15], leading to a lower nitrogen content in the common deposited films. Surface nitrogen atoms can easily be desorbed as N₂, rather than reacting to form the carbon nitride films. Alternate sources of active nitrogen species may be critical in providing the technology for carbon nitride growth.

Thus, the novel bio-molecular organics, azaadenine and adenine, were adopted as target materials for synthe-

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sizing hydrogenated carbon nitride films by ion beam deposition [16–18]. As shown in Fig. 1, azaadenine, which has a chemical formula of $C_4N_6H_4$, and adenine, which has a chemical formula of $C_5N_5H_5$, contain C–N single bonds and C=N double bonds and possess a six-fold ring structure quite similar to that in the hypothetical β - C_3N_4 phase. The similarity in the six-fold ring structure of these two targets with carbon nitride is expected to enhance nucleation and growth, and improve the crystallinity of carbon nitride. The high N/C ratio of these two targets is also anticipated to be beneficial to the formation of carbon nitride films by providing abundant carbonitro species as intermediate states to effectively reduce the high activation energy barrier for the formation of carbon nitrides.

Moreover, specific chemical information introduced by carbonitro organics may provide excellent insight on the formation mechanisms of carbon nitride. A detailed understanding of the formation mechanisms should be very important for effective synthesis of superhard carbon nitrides. It is interesting that the nearly same quality of deposited crystalline hydrogenated carbon nitride films was obtained at the condition of 1000 eV Ar ion beam sputtering, whatever azaadenine or adenine target was adopted [16–18]. In this work, the possible decomposition mechanisms of these two compounds are proposed to explore why the two different targets can deposit almost same quality of crystalline carbon nitride films, including bonding, composition and structure during ion beam deposition.

2. Experimental

The white powders of the bio-precursors were first baked at 105°C for 24 h in a flowing nitrogen atmosphere to remove moisture, and were then compacted to form a 1-inch disk target at a pressure of 1250 kg cm⁻² for ion beam deposition. The deposition conditions are: target–substrate distance 20 cm, pressure before deposition 10⁻⁶ Torr, pressure during deposition 2–4 × 10⁻⁴ Torr, Ar flow rate 1 sccm, deposition time 30–

120 min, substrate temperature 50–60°C, maximum target temperature 90°C and energy of Ar ion beam 350–1000 eV. It must be emphasized that in order to investigate the sputtering behavior of bio-molecular materials under Ar ion beam sputtering, no other activated nitrogen sources except the bio-molecular targets, and no additional substrate heating except heating from the bombardment by ion beam, were provided. The deposited films were characterized by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Fourier transform infrared (FTIR), Raman spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

To compare the sputtering behavior of bio-molecular materials under Ar ion beam sputtering with the following decomposition mechanism, mass spectroscopy was employed. A VG Biotech system Trio-2000 mass spectrometer was adopted to examine the mass spectra of these two targets. A lower electron beam energy at 75 eV was used to generate as many fragmental ions as possible during the decomposition of these targets. The target samples were bombarded in the vapor phase at right angles by an electron beam in an ionization chamber equipped with a heated inlet and a pumping system. The ionization chamber was operated at a pressure of ca 10⁻⁶–10⁻⁵ Torr, and the pressure of mass analyzer tube was evacuated to ca 10⁻⁷–10⁻⁸ Torr.

3. Results and discussion

3.1. The quality of deposited films

The results show that the atomic N/C ratio and the other film properties of the deposited films are about the same under 1000 eV Ar ion beam deposition condition, no matter what azaadenine or adenine target was used [16–18]. Briefly, the main features of the present films by these two targets are as follows: the AES and XPS analyses indicate high purity in C and N with an average atomic N/C ratio of 0.50. The infrared, Raman and XPS analyses show the presence of C–N single bonds and C=N double bonds only, without any C≡N triple bonds, which forms a good basis for further processing of the films to improve the film quality. The XRD pattern comparison for azaadenine, adenine and deposited films are depicted in Fig. 2. A high concentration nano-crystalline hydrogenated carbon nitride phase with strong preferred orientation at the d-spacing of 0.320 nm is noted in Fig. 2. It is very intriguing that the deposited films using azaadenine or adenine target exhibit the same XRD pattern, though these two target materials possess different chemical and crystal structures. This implies that the same dominant mechanism

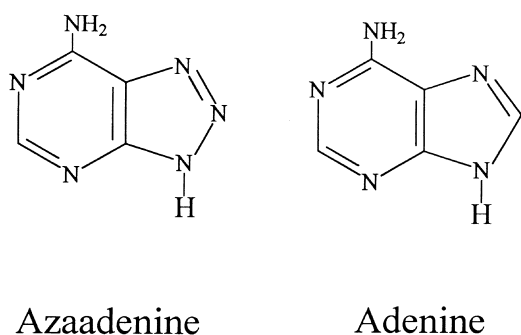


Fig. 1. Molecular structures of the azaadenine and the adenine compounds.

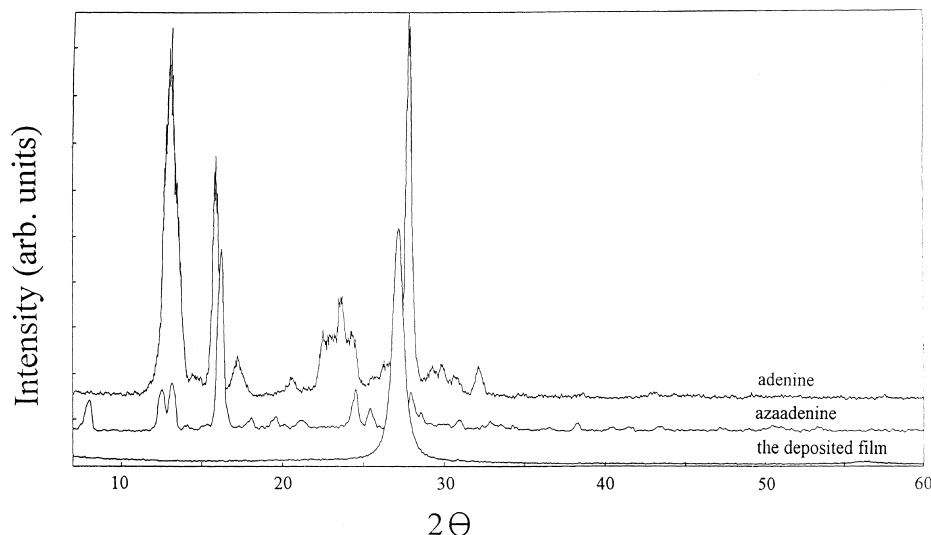


Fig. 2. The comparison of the XRD patterns of the azaadenine and adenine targets and the deposited film.

for these two targets governs the whole deposition process.

3.2. The mass spectrum analysis of azaadenine

A typical mass spectrum of azaadenine is shown in Fig. 3. There are eight major fragmental ions generated during electron beam bombardment, including a molecular ion of $C_4N_6H_4^+$ (m/z 136), and metastable ions of $C_4N_4H_4^+$ (m/z 108), $C_3N_3H_3^+$ (m/z 81), $C_3N_2H_2^+$ (m/z 66), $C_2N_2H^+$ (m/z 53), $CN_2H_3^+$ (m/z 43), C_2NH^+ (m/z 39) and CNH_2^+ (m/z 28). All of these species could act as a good intermediate state to effectively reduce the high activation energy barrier for the formation of carbon nitride. A nearly ambient deposition without substrate heating to achieve nano-crystalline hydrogenated carbon nitride films could be related to this advantage. The molecular ion peak of the azaadenine is prominent due to low electron bombardment energy.

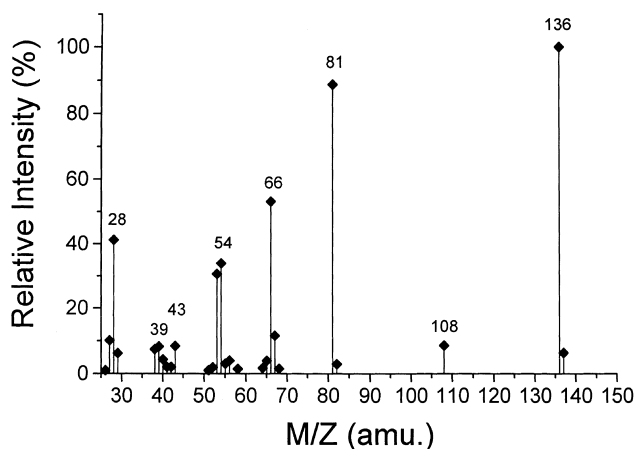


Fig. 3. Typical mass spectrum of the azaadenine target by 75 eV electron beam bombardment.

The m/z ratio of 136 from molecular ion peak confirms the molecular weight of the azaadenine compound. The peak at m/z 137 is attributed to the isotopic effect of molecular ion. The possibility of cleavage of a particular bond is related to the bond strength, the energy transitions and the stability of both charged and uncharged fragments in the fragmentation processes. Table 1 shows various carbonitro bond enthalpies [15]. The detailed delineation of possible decomposition mechanisms is proposed in Fig. 4 by considering the above factors. The most weakest location in the azaadenine chemical structure is the N–N bond with $H^0 = 163 \text{ kJ mol}^{-1}$, leading to the first cleavage in this chemical structure. Besides, the cleavage is often associated with eliminating small stable neutral molecules, such as N_2 , ammonia and hydrogen cyanide. Thus, the metastable ion $C_4N_4H_4^+$ is formed by eliminating N_2 from the azaadenine compound, and the ion $C_3N_3H_3^+$ is formed by eliminating $CNH\cdot$ from $C_4N_4H_4^+$ ion. The $C_3N_3H_3^+$ is the most strongest metastable ion peak due to a resonance-stabilized six-fold ring structure. The ions $C_3N_2H_2^+$ and $CN_2H_3^+$ are then formed by eliminating $NH\cdot$ and $C_2N\cdot$ from the $C_3N_3H_3^+$ ion, respectively. However, the routes to form $C_3N_2H_2^+$ is dominated due to a delocalization-stabilized six-membered ring structure in the above competition reaction. Similarly, the ions of $C_2N_2H^+$, C_2NH^+ and CNH_2^+ can be formed by eliminating $CH\cdot$, $NH\cdot$ and $NH\cdot$ from the corresponding preceding ions, respectively.

3.3. Comparison between the mass spectra of adenine and azaadenine

A typical mass spectrum of adenine is shown in Fig. 5. It is noted that the fragmental ions include a molecular ion of $C_5N_5H_5^+$ (m/z 135), and metastable

Table 1

The various carbonitro bond enthalpies, B (kJ mol⁻¹) [15]

Bonding types	C–N	C=N	C≡N	C–H	N–N	N=N	N≡N	N–H
B (kJ mol ⁻¹)	305	613	890	412	163	409	945	388

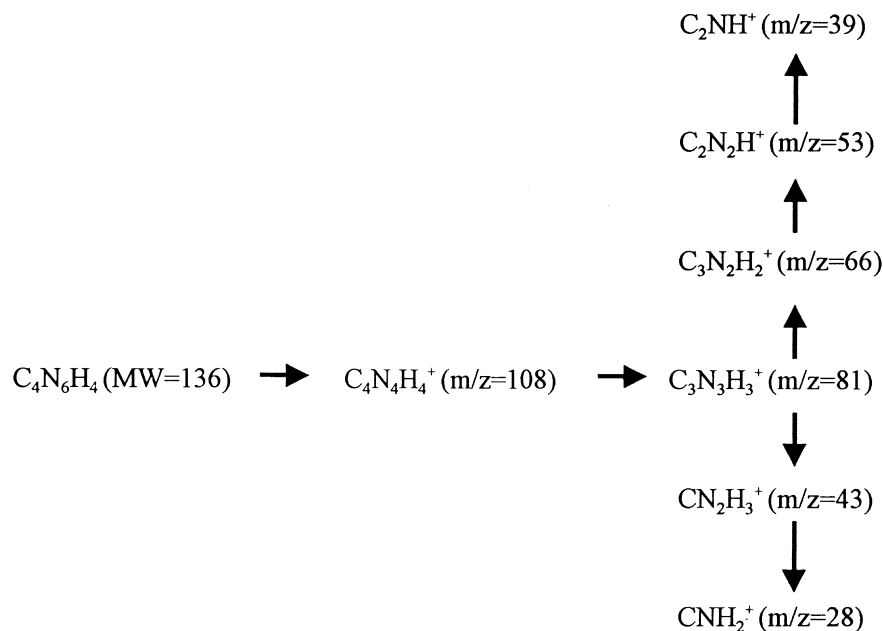


Fig. 4. The decomposition mechanisms of the azaadenine by 75 eV electron beam bombardment.

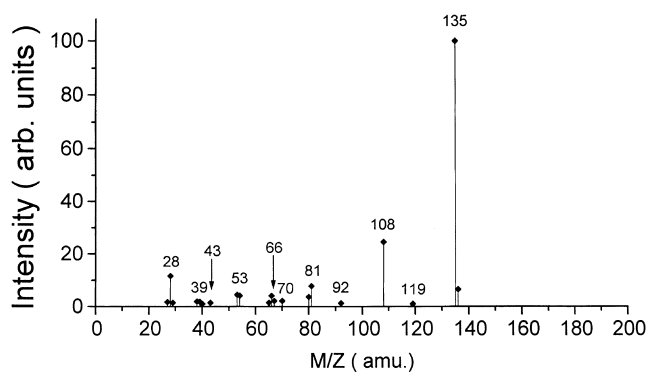


Fig. 5. Typical mass spectrum of the adenine target by 75 eV electron beam bombardment.

ions of $\text{C}_5\text{N}_4\text{H}_3^+$ (m/z 119), $\text{C}_4\text{N}_4\text{H}_4^+$ (m/z 108), $\text{C}_4\text{N}_3\text{H}_2^+$ (m/z 92), $\text{C}_3\text{N}_3\text{H}_3^+$ (m/z 81), $\text{C}_2\text{N}_3\text{H}_4^+$ (m/z 70), $\text{C}_3\text{N}_2\text{H}_2^+$ (m/z 66), $\text{C}_2\text{N}_2\text{H}^+$ (m/z 53), CN_2H_3^+ (m/z 43), C_2NH^+ (m/z 39) and CNH_2^+ (m/z 28). The m/z ratio of 135 from molecular ion peak confirms the molecular weight of the adenine compound. The peak at m/z 136 is attributed to the isotopic effect of molecular ion. The similar stoichiometric carbonitro-species, such as C_2N_2^+ , CN^+ , C_2N^+ and C_3N_2^+ are also observed in reactive RF magnetron sputtering of graphite in pure nitrogen [19,20]. However, there are several significant abundance of the unreacted species, such as C^+ , C_2^+ ,

C_3^+ , N^+ , N_2^+ and N_3^+ existing in their system. The detailed delineation of possible decomposition mechanism is proposed in Fig. 6. It exhibits that the adenine compound has a more complex decomposition mechanism than the azaadenine compound. It is attributed to more competition reactions due to insignificant reaction enthalpy difference in the decomposition of the adenine. Similar to the case of azaadenine, both the stable and metastable ions in Fig. 6 can be obtained by eliminating some small stable neutral molecules from the corresponding preceding ions, respectively. These three metastable ions including $\text{C}_5\text{N}_4\text{H}_3^+$, $\text{C}_4\text{N}_3\text{H}_2^+$ and $\text{C}_2\text{N}_3\text{H}_4^+$ of the side routes can make the difference in decomposition mechanisms between the azaadenine and the adenine. The difference could be rationalized by the existence of weak N=N bond in the azaadenine chemical structure. However, this weak point in chemical structure of azaadenine becomes an advantage to achieve a higher average film growth rate ca $1.10 \mu\text{m h}^{-1}$ than $0.51 \mu\text{m h}^{-1}$ using the adenine target. Moreover, the seven common major fragmental ions observed both in the decomposition mechanisms of azaadenine and adenine suggest the same predominating mechanisms governing the formation of carbon nitride films under 1000 eV Ar ion beam deposition condition. A higher energy bombardment to the target could tend to generate more smaller specific fragmental ions. The hydrogenated

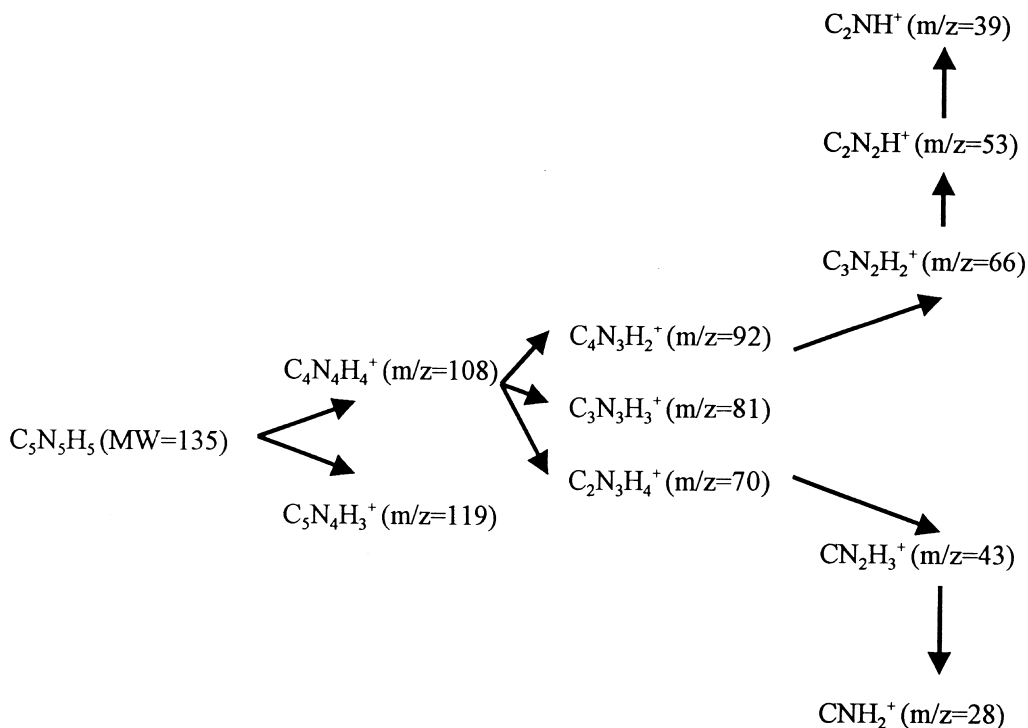


Fig. 6. The decomposition mechanisms of the adenine by 75 eV electron beam bombardment.

carbon nitride films with higher atomic N/C ratio could be achieved by controlling the above specific high nitrogen content species in due bombardment beam energy. The nitrogen content of deposited films suggests the real predominating species could be the C_2NH^+ ion under 1000 eV Ar ion beam sputtering conditions. The existence of the resonance structure, $^+C=N-C-H \leftrightarrow C-N=C^+-H$, can be beneficial to the stabilization of the C_2NH^+ species. The detailed studies on the effect of different ion beam energies and on the mechanism by in situ secondary ion mass spectroscopy and optical emission spectroscopy are underway.

4. Conclusions

In addition to possessing six-fold carbonitro-ring structure similar to that in the hypothetical C_3N_4 , novel bio-molecular targets, azaadenine and adenine, with carbonitro bonding and high N/C ratios beforehand, were successfully developed to deposit crystalline carbon nitride films and to explore the mechanisms of the formation of carbon nitride in an ion beam deposition system. It suggests that the novel targets may enhance nucleation and improve the crystallinity of carbon nitride films by providing abundant carbonitro-hydrogen-containing species as intermediate states so as to effectively reduce the high activation energy barrier for the formation of carbon nitrides. Moreover, the specific chemical information introduced by carbonitro organics

may provide excellent insight into finding the formation mechanisms of carbon nitride. The seven common hydrogenated carbonitro species may suggest the same predominant mechanisms during the decomposition of these two targets under the present deposition conditions. The good correlation is the reason why two different targets can make almost the same quality crystalline carbon nitride films, including bonding, composition and structure.

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