

Sputtering process of carbon nitride films by using a novel bio-molecular C–N containing target

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Abstract

In order to reduce the activation energy barrier for the formation of carbon nitride during ion beam sputtering, a novel bio-molecular target material, instead of the conventional graphite target, is successfully developed to deposit the crystalline carbon nitride films. The adenine target consists of a high N/C ratio as well as a 6-fold carbonitro-ring structure similar to that in the hypothetical C₃N₄. The mass spectrum of adenine indicates the existence of 11 main carbonitro–hydrogen containing species. Thus, the adenine target is anticipated to enhance the nucleation and growth of carbon nitride films by providing abundant carbonitro–hydrogen containing species as intermediate states. X-ray photoelectron spectrum analyses of these films indicated the presence of C and N in the films, with high nitrogen to carbon ratio at about 0.48. Both infrared and Raman spectroscopies confirm the chemical bonding between the carbon and nitrogen. X-ray and electron diffraction indicates the presence of crystalline carbon nitride in the film. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbon nitride; Bio-inorganic target; Mass spectrometry; Ion beam sputtering

1. Introduction

The design and synthesis of new materials are two of the key steps in the advancement of technology. Intense theoretical and experimental interest has been focused on the possibility of new materials with bulk modulus and hardness exceeding that of diamond. The theoretical predictions by Sung¹ and Liu and Cohen [1] of a new superhard phase β -C₃N₄ have stimulated a rapid development in carbon nitride materials witnessed today. It is also predicted that the carbon nitride can possess superior oxidation resistance, chemical inertness, wear resistance and thermal conductivity; and can be a wide band gap semiconductor material [2]. In fact, more recent theoretical studies have also indicated low-compressibility carbon nitride may have a number of structures distinct from β -C₃N₄ structure [3]. To date, several techniques such as laser ablation [4], DC magnetron sputtering [5], RF sputtering [6], ion beam deposition [7], ion implantation [8], plasma arc deposition [9], chemical

vapor deposition [10], shock wave high pressure synthesis [11], organic pyrolysis [12], and UV assisted chemical synthesis [13] have been reported on the synthesis of the β -C₃N₄ phase.

However, in considerable cases [4,9,13] only small crystallites embedded in an amorphous matrix have been observed. The crystallinity of these films is generally evidenced by the selected area electron diffraction patterns from nano- to micron-sized crystallites since the volume of the crystalline phases can be as low as less than 5% of the total volume in the deposited films [4]. An unambiguous characterization of this phase is thus difficult. The crystalline films with larger crystal sizes (several tens of microns) were reported by Chen et al. [14]; however, it is essentially a Si–C–N ternary system. Moreover, most films produced so far have nitrogen concentrations between 20 and 30 at.%, whereas incorporation of ~57 at.% of nitrogen is required to form a homogenous stoichiometric C₃N₄ film. A high atomic N/C ratio of 1.39 was reported by Diani et al. [15]. However, their results show formation of amorphous films, which contain significant fraction of C≡N bonding and are readily decomposed at about 600°C, indicating a poor thermal stability. The presence of C≡N bonding precludes an extended carbon nitride solid, since the triply bonded nitrogen breaks the continuity of the network [16].

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¹ In 1984 an unpublished patent disclosure letter was written by C.M. Sung, then at Norton Corporation's Diamond Technology Center. The history was revealed in *Diamond Depositions: Science and Technology* 5(3), March 1995.

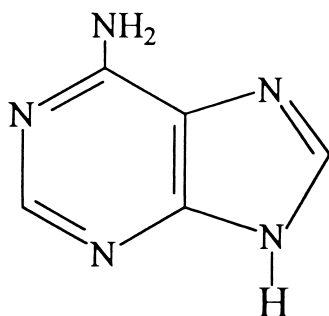


Fig. 1. Molecular structure of the adenine compounds.

Therefore, be it crystalline or amorphous, synthesis of sp^3 -bonded carbon nitrides containing substantial amounts of nitrogen remains to be a challenging issue. Various deposition techniques and high pressure synthesis to 40 GPa have not been successful thus far. Hence, it is essential to focus not only on the synthetic techniques but also on understanding the formation mechanisms.

2. Strategy for the synthesis of carbon nitrides

One of the main reasons for the extreme difficulty in synthesizing superhard carbon nitrides may be due to a considerable high activation energy barrier for the formation of carbon nitrides. Apparently, the activation energy barrier is too high to overcome by using the conventional carbon sources such as methane, graphite, etc. and nitrogen source such as nitrogen gas, ammonia, etc. separately, in various deposition techniques mentioned above. Especially, in the case of using N_2 as nitrogen source, because of the extremely high bond dissociation energy, 945 KJ/mol, of N_2 , it provides little possibility of activated nitrogen atoms

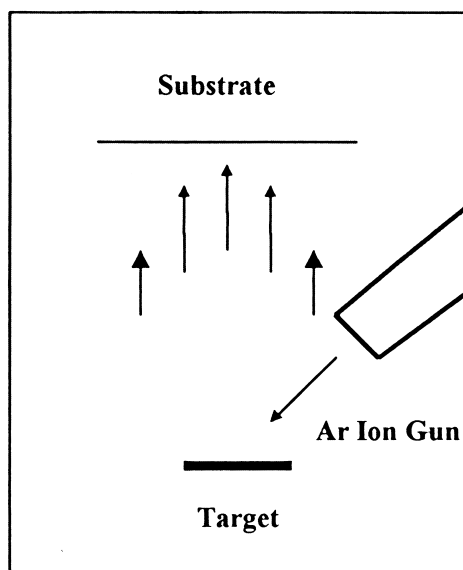


Fig. 2. Schematic diagram for ion beam deposition system.

for incorporation with carbon leading to a lower nitrogen content in the common deposited films.

Hence, the use of appropriately designed molecular or solid-state precursors and low enough synthesis temperatures to insure kinetic control of reaction products appears to be a promising direction for future efforts. In fact, an early effort on preparation of a novel target with bonding and structure similar to that of β - C_3N_4 had been developed by us [13]. However, this method involves a very high possibility of explosive free radical reaction.

Therefore, a novel bio-molecular organic, 6-aminopurine (vitamin B4), is first proposed to be developed for synthesizing carbon nitride films since one of its advantages being easy preparation into target applications without any explosive danger. Other bio-molecular organic (such as azzadenine) has also been adopted and the effects of using different target materials will be discussed in a separate paper. As shown in Fig. 1, adenine (hereafter, short for 6-aminopurine), which has a chemical formula of $C_5N_5H_5$, contains C–N single bonds and C=N double bonds and possesses a 6-fold ring structure quite similar to that in the hypothetical β - C_3N_4 phase. The 6-fold ring structure similar to that in the hypothetical β - C_3N_4 phase of adenine is expected to enhance the nucleation and growth and improve the crystallinity of carbon nitride. The high N/C ratio of adenine 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. Besides, specific chemical information introduced by carbonitro-organic may provide excellent probes on the formation mechanisms of carbon nitride. A detailed understanding of the formation mechanisms is very important for effective synthesis of superhard carbon nitrides. Moreover, an interconnection between bio-organic derived from the metabolism of creatures and superhard materials is also interesting from both science and engineering application point of view. To our knowledge, this is the first attempt to adopt bio-molecular compounds for carbon nitride synthesis.

An optimum integration between carbon nitride precursors and synthetic techniques is emphatic to the future development on this superhard material. The choice of synthetic technique should accommodate the precursor's properties such as low melting temperature and electrical insulation. The ion beam sputtering technique provides a good energy controllability and flexibility of target shape and morphology.

3. Experiment

The bio-molecular organic of adenine was developed as the target material to deposit carbon nitride films on Si wafers or metal substrates by an ion beam sputtering system. Adenine powder is commercially available by Aldrich Co.. Target preparation procedure of adenine started with baking

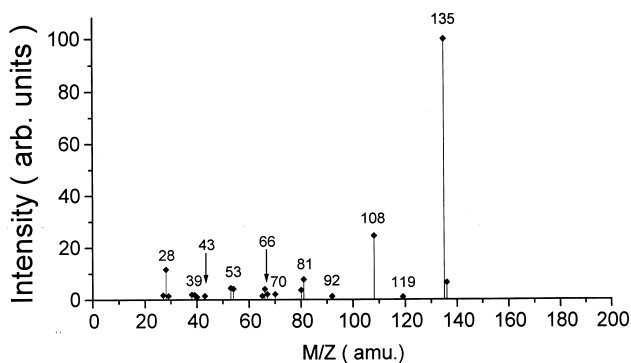


Fig. 3. Typical mass spectrum of the adenine target by 75 eV electron beam bombardment.

the powder at 105°C for 24 h in a flowing nitrogen atmosphere to remove moisture, and then compacting the powder to form a one-inch disk target with a pressure at 1250 kg/cm². A schematic ion beam sputtering system is shown in Fig. 2. To investigate the substrate effect, various substrates including (111) Si wafer, (100) B-doped Si wafer, AISI-304 stainless steel, Cu, Ag, Co, and Ni have been experimented. Typical deposition conditions are listed as follows: target to substrate distance at 20 cm, Kaufman-type ion beam source under an incidence of 45° to the target, pressure before deposition at 10⁻⁶ Torr, pressure during deposition at about 2~4 × 10⁻⁴ Torr, Ar flow rate at 1 sccm, deposition time around 30~120 min, substrate temperature at 50~60°C, and energy of Ar ion beam between 350 to 1000 eV. It must be emphasized that to investigate the behavior of bio-molecular target under Ar ion beam sputtering, no other activated nitrogen sources except the bio-molecular targets and no separate substrate heating except heating from the bombardment by ion beam were provided.

The infrared (IR) spectra were obtained on a Nicolet Protégé 460 Fourier transform infrared (FTIR) spectrometer to analyze the chemical bonding structures of the films. The chemical state of the films was determined by X-ray photoelectron spectroscopy (XPS) using a VG Microtech MT-500 ESCA system. Mg K α radiation of 1253.6 eV was used as the source with a linewidth of 0.7 eV. The typical analyzer pass energy was 20 eV. Curve-fitting software (ESCA-Tools) provided by Surface Interface was used to analyze the XPS data. The experimental uncertainty in the determination of the binding energy is about 0.4 eV. An in situ calibration in XPS is made by using Ag substrate. Depth profiling with XPS and Auger electron spectroscopy (AES) were performed by Ar ion bombardment of the sample. A Perkin-Elmer scanning Auger nanoprobe system (SAN 760) was used for the AES study. It should be noted that the X-ray probe size for XPS study is inherently larger than the individual crystal size. In contrast, the AES system is capable of acquiring the depth profile data from area as small as 5000 nm, thus allowing us to investigate the variations in composition from crystal to crystal in the same film. A Renishaw system 2000 micro-Raman spectrometer was

used to record the Raman spectra. A 25 mW He-Ne laser operating at 632 nm was used as an excitation source. The line shift was calibrated by comparing the spectrum with that of natural diamond and Si. with a 5 μ m exit slit, the spectral resolution was better than 1 cm⁻¹. A VG Biotech system Trio-2000 mass spectrometers was used to investigate the mass spectrum of adenine. The X-ray diffraction (XRD) patterns of samples were obtained from a automatic X-ray diffractometer (Mac Science MXP3, Japan) using a graphite-monochromatized Cu K α radiation and equipped with a Ni filter. Transmission electron microscope (TEM) investigations of the film were performed on a Hitachi H-7100 microscope. The TEM specimens were prepared for microscopic analysis by directly scraping the film onto Cu grids or grinding the deposited film, suspending the particles in methyl alcohol and then depositing the suspension onto the grid.

4. Results and discussions

4.1. Effects of substrate and target materials during ion beam deposition

One advantage of this system is that an uniform and dense crystalline carbon nitride films over a four-inch wafer could be obtained at the substrate temperatures close to ambient temperature (50~60°C). During deposition process with the argon ion beam energy at 1000 eV, the target holder was at a temperature below 90°C, which is much lower than the melting temperatures of 360°C for adenine target, as measured by a thermocouple from the backside of the target holder. Comparing the results from seven different substrates there is no significant difference in the atomic N/C ratio and the bonding structure of the deposited films prepared at low deposition temperature.

To investigate the behavior of bio-molecular target under Ar ion beam sputtering and the following decomposition mechanism, mass spectrum analysis was employed. A lower electron beam energy at 75 eV was adopted to generating as abundant fragmental ions as possible during the decomposition of adenine target. A typical mass spectrum of adenine is shown in Fig. 3. The fragmental ions including a molecular ion C₅N₅H₅⁺ (*m/z* 135) and metastable ions C₅N₄H₃⁺ (*m/z* 119), C₄N₄H₄⁺ (*m/z* 108), C₄N₃H₂⁺ (*m/z* 92), C₃N₃H₃⁺ (*m/z* 81), C₂N₃H₄⁺ (*m/z* 70), C₃N₂H₂⁺ (*m/z* 66), C₂N₂H⁺ (*m/z* 53), CN₂H₃⁺ (*m/z* 43), C₂NH⁺ (*m/z* 39), and CNH₂⁺ (*m/z* 28) are generated during electron bombardment. The signal at *m/z* 136 is attributed to the isotopic effect of molecular ion. It is likely the adenine target is beneficial by providing abundant carbonitro-hydrogen containing species as intermediate states, consequently reducing the high activation energy barrier effectively for the formation of carbon nitrides via Ar ion beam deposition techniques. The detailed studies on the effect of different ion beam energy and on the

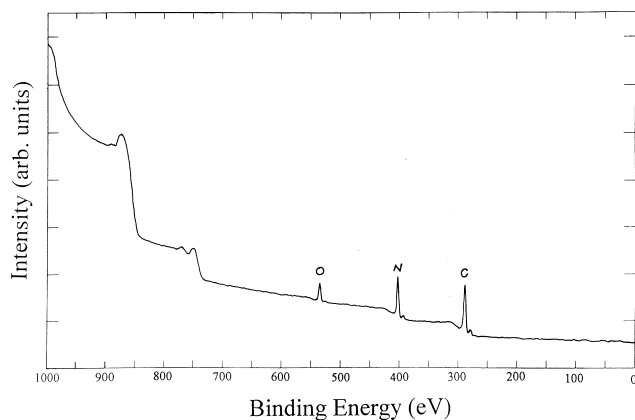


Fig. 4. Typical XPS spectra of the carbon nitride films.

mechanism by in situ secondary ion mass spectrum and optical emission spectroscopy analyses are also underway.

4.2. Atomic N/C ratio of the films

A typical wide-scan XPS spectrum of the film deposited on AISI-304 stainless steel at 1000 eV Ar ion beam bombardment is shown in Fig. 4., which indicates the presence of C, N and O in the film. The oxygen peak at 534 eV, however, disappeared after sputtering with Ar ions, indicating that oxygen is present mostly on the surface. The peaks at 288 and 402 eV can be assigned as C and N, respectively, with a slight shift to high binding energies due to the charging effect [17]. The average atomic ratio of nitrogen to carbon (N/C) is 0.48 after sensitivity factor correction, which is in good agreement with the result of 0.51 from AES analysis. Scanning Auger mapping reveals that the N and C distributions on the film surface are quite uniform. From the results of XPS and Auger electron analyses (AES), the film composition is close to C_2N (i.e. the average atomic N/C ratio is 0.50). The same N/C ratio was reported by Lieber's group [15], but their films were deposited by laser ablation with additional nitrogen atom source. This implies C_2N may be a relative stable metastable

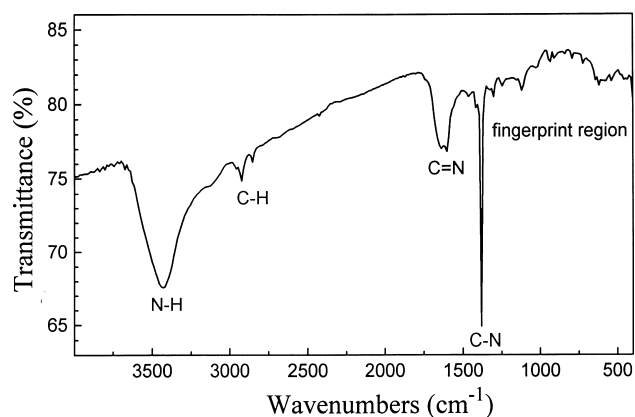


Fig. 5. Typical FTIR spectrum of the carbon nitride films.

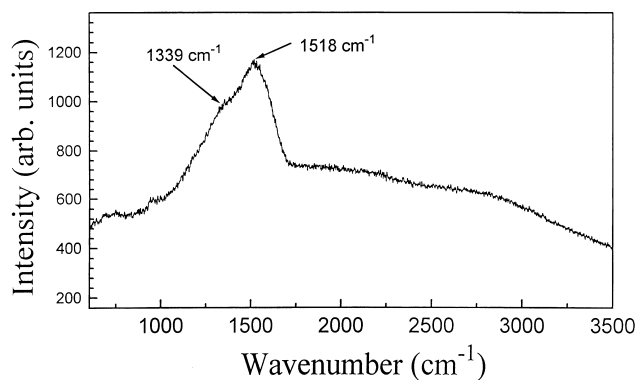


Fig. 6. Typical Raman spectrum of the carbon nitride films

phase in C–N phase diagram because it can be achieved by two thoroughly different processes.

It is noted that the N/C ratio of the films is much less than that of the adenine target (N/C = 1). This implies that the Ar ion beam sputtering process can involve some decomposition of target materials, in which the loss of N is more than that of C. A similar trend is observed in MS spectrum. Thus, it confirms that, without any extra source of N, adenine target alone can lead to the formation of carbon nitride films by generating plentiful carbonitro–hydrogen containing species during Ar ion beam bombardment. While some loss of N dose occur during sputtering, the N content in the resultant film is still remarkably high, compared to most data reported in the literature.

4.3. Bonding states of C–N

The deposited films were scratched out from the substrate, ground into powder, mixed with KBr powder and compacted to form a disk for FTIR characterization. The typical FTIR spectrum is depicted in Fig. 5. Main absorption peaks at 3436, 2926, 1639 and 1387 cm^{-1} correspond to NH stretching vibration, CH stretching vibration, C=N stretching vibration and C–N stretching vibration, respectively [18]. The signals below 1300 cm^{-1} , fingerprint region, are contributions from multi-functional group interaction. Therefore, it is hard to resolve these signals into vibrations of specific functional group. No significant peak around 2190 cm^{-1} , corresponding to C≡N stretching bond, can be found in Fig. 5. This indicates that the films have a good bonding character since the existence of C≡N bond can break the continuity of the network in the structure of the films.

To cross check bonding state of these carbon nitride films, Raman was also used. A typical Raman spectrum is shown in Fig. 6. Two weak peaks at 1339 and 1518 cm^{-1} corresponding to D (1360 cm^{-1}) and G (1575 cm^{-1}) band absorptions of amorphous carbon are observed. A slight shift in Raman peak to the lower frequency side is probably due to the incorporation of nitrogen in the present films, which is in agreement with the results reported by Bousetta et al. [19].

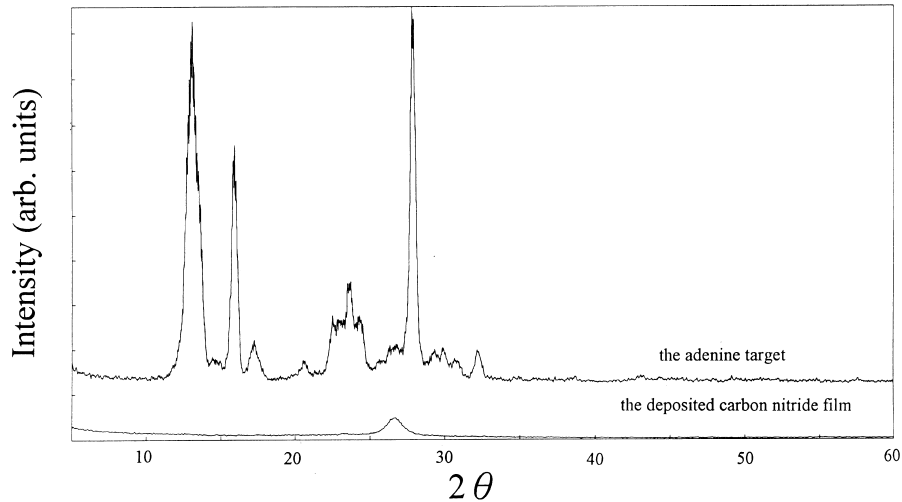


Fig. 7. The comparison on XRD pattern between the adenine target and deposited film.

All these results once again indicate the existence of chemical bonding with no significant physical bonding between C and N.

4.4. Crystal structure and morphology of the films

A comparison of the XRD pattern between the adenine target and the deposited film is shown in Fig. 7. There is a drastic change in crystal structure from the adenine target to the deposited film. The only one interplane spacing (d) for the strongest diffraction peak at $2\theta = 24.78^\circ$ of the depos-

ited film is 0.3243 nm, which is quite close to 0.3200 nm spacing of the (110) plane in the theoretical β - C_3N_4 structure [20]. The crystallinity and the volume fraction of the crystalline phases in the films are high enough to be detected by X-ray diffraction. It is also noted that the (110) peak is very broad, suggesting fine-sized crystallites. The TEM bright field and dark field images in Fig. 8 do indeed show dense and uniformly distributed nano-sized crystallites. Part of the reasons for a small grain size in the present films may be due to a low deposition temperature

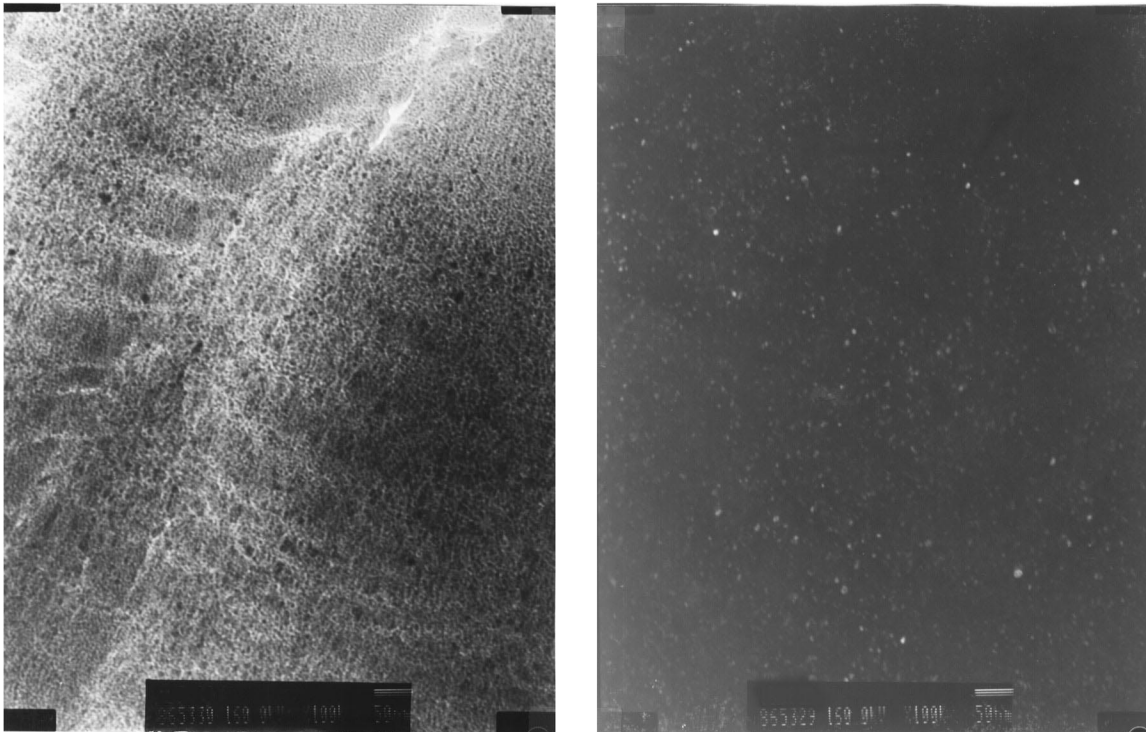


Fig. 8. Typical TEM bright field and dark field images of the carbon nitride film.

(50–60°C), where the nucleation process, not the grain growth process is predominant.

In addition to the (110) peak, more diffraction rings can be observed in TEM. The *d*-spacings resolved from each TEM diffraction ring are 0.310, 0.276, 0.220, 0.176, 0.153 and 0.132 nm, respectively, which can be compared to spacings of the theoretical β -C₃N₄ structure: 0.317 nm for (110), 0.275 nm for (200), 0.225 nm for (101), 0.183 nm for (300), 0.152 nm for (310) and 0.133 nm for (221), respectively [20].

5. Conclusions

A novel bio-molecular adenine target with covalently bonded carbon and nitrogen atoms is successfully developed to deposit the crystalline carbon nitride films. X-ray photoelectron spectrum analyses of these films indicate the presence of C and N in the films, with high nitrogen to carbon ratio at about 0.5. Both infrared and Raman spectra confirm the chemical bonding between the carbon and nitrogen. X-ray and electron diffraction indicates the presence of crystalline carbon nitride in the film. It has been suggested that this novel target may enhance the 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.

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