High purity nano-crystalline carbon nitride films prepared at ambient temperature by ion beam sputtering [☆]

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Abstract

High purity nano-crystalline carbon nitride films have been successfully deposited by ion beam sputtering. A novel bio-molecular C–N compound, 6-aminopurine, of which the characteristic features include covalent C–N bonding, high N/C ratio and a six-membered ring structure similar to that in the hypothetical C_3N_4 crystal, has been employed as the target material. The films can be deposited onto a variety of substrates, such as copper, silver, stainless steel, nickel and silicon wafer at ambient temperature. SAM examination indicates a high nitrogen-to-carbon ratio at about 0.51. XPS, IR and Raman studies reveal that the chemical bonding structures consist mainly of sp^3-hybridized carbon as well as sp^2-hybridized nitrogen and carbon. Both TEM and SAM mapping investigations indicate that the film contains a very dense and homogenous distribution of nano-crystalline grains. However, the structures of these crystals are yet to be determined since their TEM diffraction patterns only matched partially with the calculated pattern for β-C_3N_4. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The birth and development of useful technologies often hinge on the availability of new materials with appropriate physical and chemical properties. A theoretical calculation of carbon nitride (β-C_3N_4) was first reported by Liu and Cohen [1] in 1989, and it was concluded to be a new superhard compound with a bulk modulus comparable with that of diamond. More recently, first-principle calculations have indicated that a cubic C_3N_4 structure should have a bulk modulus significantly higher than that of diamond [2]. As a covalent bonded network with short bond length, carbon nitride could exhibit superior oxidation resistance, chemical inertness, wear resistance, thermal conductivity, and wide band gap property [3]. Therefore, successful synthesis of C_3N_4 would have an enormous impact not

only on the basic science but also on the technological development.

Several organic nitrogen-containing compounds have been tried in the high pressure and high temperature syntheses of carbon nitride. Because of the considerable activation energies required to break carbon–nitrogen bonds, stable carbon nitrides probably can be synthesized by a high pressure and high temperature reaction, and then quenched to ambient pressure and temperature. The pressures required to form a metastable carbon nitride have been estimated to be in the range of 50–150 GPa [4]. In fact, synthesis of carbon nitride by pyrolysis of melamine–formaldehyde resin and subsequent shock wave compression of the residues to 60 GPa has been attempted [5]. However, no tetrahedral carbon nitride could be detected in the reaction product. In a similar approach, Maya et al. obtained a carbon nitride with trigonal-coordinated carbon by pyrolysis of high nitrogen-containing organic materials such as melamine, dicyandiamide and tetracyanoethylene at 700°C and 225 MPa [6]. A molecular precursor tetracynanoethylene (TCNE), which has a molecular formula of C_6N_4, was also used for synthesizing carbon nitrides by laser

heating under pressures up to 40 GPa; the product was amorphous sp²-bonded carbon nitrides with 38 at.% nitrogen [7]. These results demonstrate that, while carbon nitrides with significant amount of nitrogen can be achieved under relatively high pressure, a pressure of 40 GPa or less is indeed insufficient to synthesize sp³-bonded carbon nitrides, consistent with some theoretical calculations. An alternative approach is to employ thin film deposition techniques with some effective kinetic control and adequate precursors to reduce the activation energy and deposition temperatures.

Over the last few years, a large number of kinetic approaches, such as laser ablation [8], d.c. magnetron sputtering [9], r.f. sputtering [10], ion beam deposition [11], ion implantation [12], plasma arc deposition [13], chemical vapor deposition [14], and UV-assisted chemical synthesis [15], have been employed. However, in many cases only small crystallites embedded in an amorphous matrix have been observed. The volume of the crystalline phases can be as low as less than 5% of the total volume in the deposited film [8]. The crystallinity of these films is generally evidenced by the selected area electron diffraction patterns from nano- to micron-sized crystallites. An unambiguous characterization of this phase is indeed quite difficult. Crystalline films with larger crystal sizes (several tens of microns) have been reported by Chen et al. [14]; however, it is essentially an Si–C–N ternary system. Moreover, most films produced so far have nitrogen concentrations lower than 30 at.%, which is much less than that required to form a homogenous stoichiometric C_3N_4 film. An atomic N/C ratio as high as 1.39 was reported by Diani et al. [16]. However, their results show the formation of an amorphous film containing a significant fraction of C=N bonding and the film was 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 [17]. Therefore, whether they are crystalline or amorphous, the synthesis of sp³-bonded carbon nitrides containing substantial amounts of nitrogen remains a challenging issue via kinetic control approaches.

2. Lessons from carbonitro precursors

Another important point to be stressed is the possibility of using different carbon and nitrogen sources in film deposition techniques. In most of the literature, methane, graphite, nitrogen gas and ammonia have been conventionally used as the source materials of carbon and nitrogen. In the case of using N_2, of which the bond dissociation energy is extremely high (945 kJ mol^{-1}), there is little activated nitrogen atoms available for incorporation with carbon, leading to a lower nitrogen content in the deposited films. Molecular precursors

such as $C_3N_3F_2N(Si(CH_3)_3)_2$ and $C_3N_3Cl_2(Si(CH_3)_3)_2$ have been used alternatively in chemical vapor deposition at 450–500°C [18,19]. Only sp²-bonded carbon nitrides were obtained. Recent studies have achieved an amorphous hydrogenated carbon nitride with a higher N/C ratio of up to 0.64 by using N–C compounded organic precursors such as trimethylamine and methylamine via PECVD [20,21]. Hence, the use of appropriate molecular or solid-state precursors and low enough synthesis temperatures to ensure kinetic control of reaction products appears to be a promising direction for future efforts.

We believed that the main challenge here is to develop adequate carbonitro precursors combined with due kinetic control approaches. Any precursor with a high atomic N/C ratio and possessing a ring structure similar to that in the hypothetical β-C_3N_4 will be a good starting precursor for crystalline carbon nitride synthesis. The possibility of providing abundant carbonitro species in the process is also crucial for enhancing the nucleation and growth. Therefore, in this work, a bio-molecular organic, 6-aminopurine (vitamin B4), is proposed for synthesizing carbon nitride films. Other organic compounds, such as azzadenine, have also been adopted and the effects of using different target materials will be published in a separate paper. In fact, a previous effort on the preparation of a novel target with bonding and structure similar to that of α-C_3N_4 has been reported by Lu et al. [15]. However, this method involves a very high possibility of an explosive free radical reaction.

As shown in Fig. 1, 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 sixfold ring structure quite similar to that in the hypothetical β-C_3N_4 phase. The sixfold ring structure is expected to be a main factor to enhance the nucleation and growth and to improve the crystallinity of carbon nitride. The high N/C ratio of 6-aminopurine is also anticipated to be beneficial for the formation of carbon nitride films. Furthermore, dissociation of 6-aminopurine can provide abundant carbonitro species as intermediate states to effectively reduce the high activation energy barrier for the formation of carbon nitrides. An optimum integration between carbon nitride precursors and synthetic techniques is emphatic to be the main issue in developing this superhard material. The choice of the synthetic
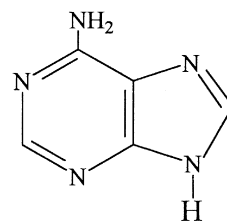

Fig. 1. The molecular structure of the 6-aminopurine compound.

technique should accommodate this precursor's properties such as low melting temperature and electrical insulation. In the present work, we use the ion beam sputtering technique. This technique also provides a good energy controllability and flexibility for the shape and morphology of the target.

Optimization and control of the ion beam deposition process require an improved knowledge of ion beam interaction with organic targets and the evolution and dynamics of the ion beam induced plasma plume. The use of carbonitro-organic targets, instead of conventional separated carbon and nitrogen sources, does provide more abundant chemical information to probe on the formation mechanisms of carbon nitride during ion beam sputtering [22]. A detailed understanding of the formation mechanisms is very important for effective synthesis of superhard carbon nitrides. Moreover, a transformation between organic materials derived from the metabolism of creatures and superhard materials is also intriguing from both scientific and engineering application points of view. To our knowledge, this is the first attempt to adopt bio-molecular compounds for carbon nitride synthesis.

3. Experiments

The ion beam sputtering system consists of a 1 in 6-aminopurine target and a 3 cm Kaufman-type ion source with Ar ion energies of 350–1250 eV [22]. The ion beam was at an incidence of 45° to the target and the target-to-substrate distance was 20 cm. The base pressure of the apparatus was 10^{-6} Torr and typical deposition pressure was $(2–4) \times 10^{-4}$ Torr at an Ar flow rate of 1 sccm. Except for heating from ion beam bombardment, no additional heating source was used. Therefore, the deposition temperatures were close to ambient temperature (50–60°C), as measured by a thermocouple from the backside of the substrate. It must be emphasized that, except for the carbonitro target material, no other activated nitrogen sources were provided during ion beam sputtering. The white powder of the 6-aminopurine was first baked at 105°C for 24 h in a flowing nitrogen atmosphere to remove moisture, and was then compacted to form a 1 in disk target at a pressure of 1250 kgf cm^{-2}. For examining the substrate effect, different substrates including (111) Si wafer, (100) B-doped Si wafer, AISI-304 stainless steel, Cu, Ag, Co, and Ni were compared under the same deposition conditions.

4. Results and discussion

4.1. Atomic N/C ratio of the films

Fig. 2 shows a typical Auger spectrum for the films deposited on an Ag substrate at the Ar ion energy of
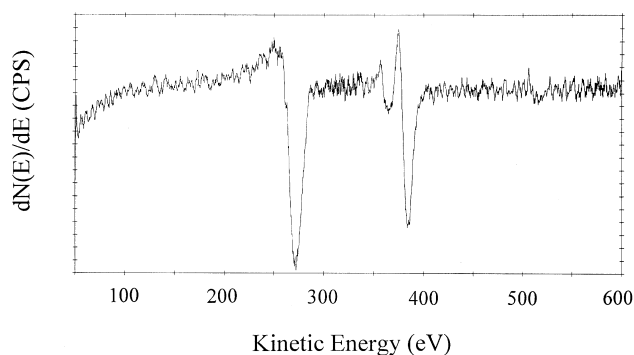

Fig. 2. Typical Auger spectrum of the carbon nitride films.

1000 eV. Using a cross-section specimen and probing near the Ag substrate can effectively reduce charging of sample. There are no peaks for oxygen or other impurities, the only two significant peaks being at 272 and 380 eV, which correspond to C and N, respectively, indicating a high purity carbon nitride film. Scanning Auger electron mapping revealed that the N and C distributions on the film surface were quite uniform. From Auger analyses, the atomic N/C ratio is about 0.51, which is close to the stoichiometric composition C_2N. The N/C ratio derived from XPS analyses is 0.48, also in good agreement with the Auger result. A similar N/C ratio was reported by Lieber's group [8], but their films were deposited by laser ablation with an additional nitrogen atom source. The fact that C_2N can be obtained by two entirely different processes implies that C_2N may be a metastable phase with relatively high stability in the C–N phase diagram.

It is noted that the N/C ratio of the films is much less than that of the 6-aminopurine target (N/C = 1), indicating that the Ar ion beam sputtering process must involve some decomposition of the target materials. Further, without any extra source of nitrogen, a 6-aminopurine target alone can lead to the formation of carbon nitride films by generating plentiful carbonitro species as intermediate states. Although there are some losses in N during sputtering, the N content in the resultant films is still remarkably high, as compared with most of the literature data.

Another advantage of this process is that a uniform and dense crystalline carbon nitride films over a 4 in wafer could be obtained at substrate temperatures close to ambient (50–60°C). At argon ion beam energy of 1000 eV, the highest target temperature was 90°C, still much lower than the melting temperature of 360°C for 6-aminopurine material. Therefore, the deposition process is essentially a sputtering process with insignificant contribution from vaporization. For seven different substrates, there were no significant differences in the atomic N/C ratio and the crystal structure of the films. This may be due to low deposition temperature at which any reaction between the substrate and the deposited film is

suppressed. Detailed investigation on the effects of argon ion beam energy is beyond the scope of this manuscript and will be published elsewhere.

4.2. Bonding states of C–N

For FTIR examination, the deposited films were scraped off the substrate, ground into powders, mixed with KBr powders and compacted to form a disk. Typical FTIR spectrum is depicted in Fig. 3. There are insignificant changes of the spectra with ion beam energy varied from 350 to 1000 eV. Peaks at 1388 and 1640 cm^{-1} correspond to C–N single and C=N double
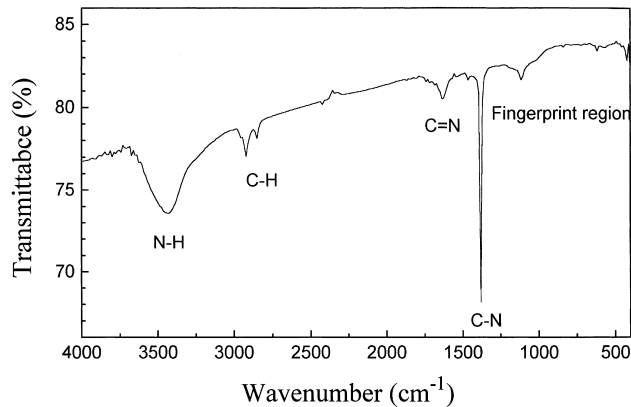
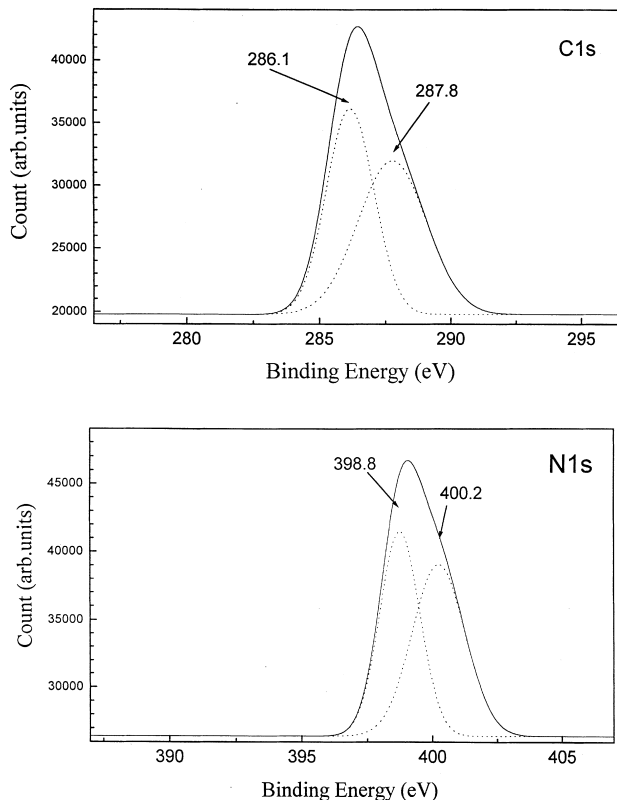Fig. 3. Typical FTIR spectrum of the carbon nitride films.

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

stretching bonds, respectively [23]. Peaks at 3448 and 2853–2955 cm^{-1} are attributed to the N–H and C–H bonds, respectively. 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 a C≡N triple stretching bond can be found in Fig. 3. This indicates that the films exhibit a good bonding character, because the existence of a C≡N bond can break the continuity of the network structure in the films.

Raman spectra are sensitive to changes in the translation symmetry of materials, and so are useful for the study of disorder and crystalline formation. There is a shift in the D (1360 cm^{-1}) and G (1575 cm^{-1}) band positions to lower wavenumbers in the deposited carbon nitride films [22]. The D peak position shifts to 1339 cm^{-1} and the G peak position to 1518 cm^{-1}. A slight shift in Raman peaks to a lower wavenumber side is in agreement with the results reported by Bousetta et al. [24]. This shift of G peak could indicate the presence of bond-angle disorder. Similarly, the shift of the D peak indicates that the as-deposited films may contain more fourfold coordinated sp^3 bonds, as well as more disorder.

X-ray photoelectron spectroscopy (XPS) has been used to determine both the stoichiometry and the bonding of the carbon nitride films. However, a major problem in the search for β-C$_3$N$_4$ is the chemical characterization of the deposited films owing to the absence of an adequate reference sample. The attributions of the obtained core level binding energies to values already known in the literature are, in some cases, questionable. In the present work, the XPS signal from the Ag substrate was used for in situ calibration. Fig. 4 shows the deconvoluted XPS C 1s and N 1s peaks for the deposited films. The contribution at 286.1 eV is assigned to sp^2 trigonal CN bonding and the peak at 287.8 eV is attributed to sp^3 tetrahedral CN bonding. The N 1s peak shows two main contributions. The first contribution at 398.8 eV corresponds to sp^3 CN bonding, while the second one at 400.2 eV is due to sp^2 CN bonding. A slight shift to higher binding energies in XPS peaks is in agreement with some literature results [20,25–28]. Furthermore, these attributions are similar to the fine structures of differential AES shown in Fig. 2. All these bonding characterizations once again indicate the existence of chemical bonding between C and N in the films.

4.3. Crystal structure and morphology of the films

The crystallinity and the volume fraction of the crystalline phases in the films were high enough to be detected by X-ray diffraction (XRD). A typical XRD pattern for the film taken at low incident angle is shown in Fig. 5. The inter-plane spacing (*d*) for the strongest
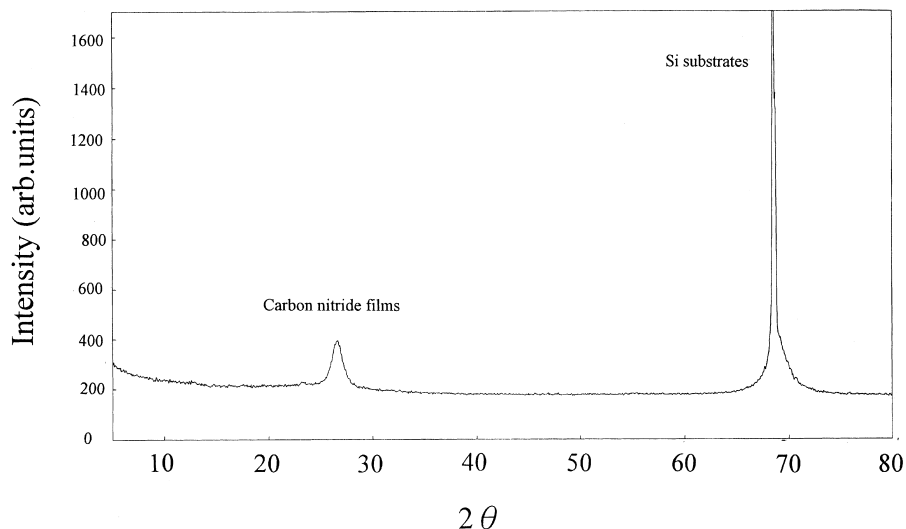
Fig. 5. Typical XRD pattern taken at a low incident angle of the films on silicon substrate.

diffraction peak at $2\theta = 24.78°$ is 0.324 nm, which corresponds to the theoretical value at 0.320 nm spacing of the (110) plane in the β-C_3N_4 structure [29]. Another diffraction peak in Fig. 5 is from the silicon substrate. No diamond or graphite peaks can be observed. It is noted that the 0.324 nm peak is quite broad, presumably because of very small crystal sizes in the films. The atomic force microscopy image of the films revealed that the original surface morphology of the stainless steel substrate is still visible even after covered by a layer of the carbon nitride film (Fig. 6). Both bright field and dark field TEM images (Fig. 7) suggested dense and uniformly distributed nano-sized crystallites in the film. The reason for a small grain size in the present films may be due to a low deposition temperature (50–60°C), at which nucleation instead of grain growth process is predominant.
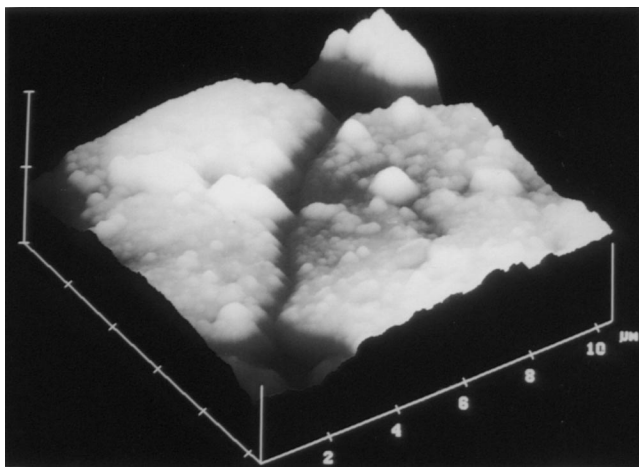
More diffraction rings can be observed in TEM

Fig. 6. Atomic force microscopy image of the film on a stainless steel substrate (*X*-axis, 2.000 µm per division; *Y*-axis, 1.200 µm per division).

diffraction pattern as shown in Fig. 8. The *d* spacings determined from TEM diffraction rings are 0.310, 0.276, 0.220, 0.176, 0.153 and 0.132 nm, respectively. These can be compared with the theoretical values of the β-C_3N_4 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 [29]. The '(110) diffraction' is also the most intense one among all TEM diffraction rings, in consistent with the XRD investigation. However, we do not claim the presence of crystalline β-C_3N_4 phase because the (110) diffraction is not the strongest peak in theory and there is little evidence of any strongly preferred orientation in the film. Although the measured *d* spacings and the theoretical ones are in close proximity, we may have a new structure yet to be determined.

5. Conclusions

A bio-molecular carbonitro organic, 6-aminopurine, was used as the target to deposit crystalline carbon nitride films on seven different substrates at 50–60°C. With no extra nitrogen source, a 6-aminopurine target alone can produce crystalline carbon nitrides by the ion beam sputtering technique. The resultant films contained high nitrogen content with an average N/C ratio at about 0.5. The chemical bonding structure consisted of sp^3 hybridization of the carbon and sp^2 hybridization of the nitrogen and carbon. Furthermore, dense and uniformly distributed nano-sized crystalline carbon nitride films can be achieved. While the diffraction peak positions are in close proximity with some theoretical values for the β-C_3N_4 phase, the crystal structure of our film is yet to be determined. In perspective, this novel target material combined with additional
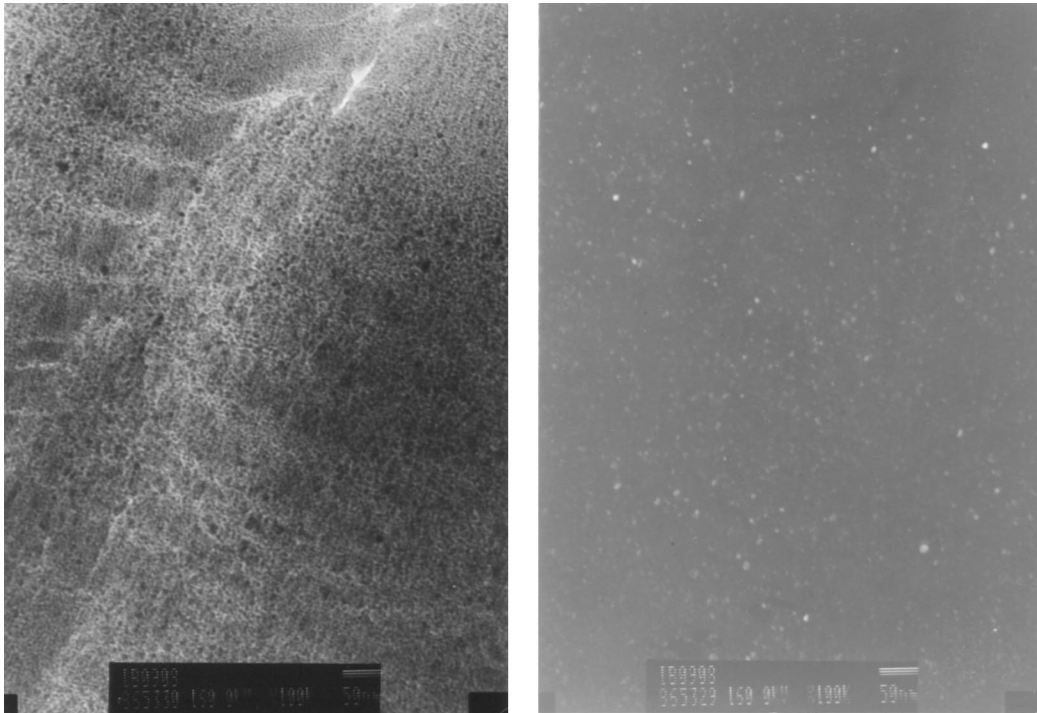
Fig. 7. TEM bright field and dark field images of deposited carbon nitride films.
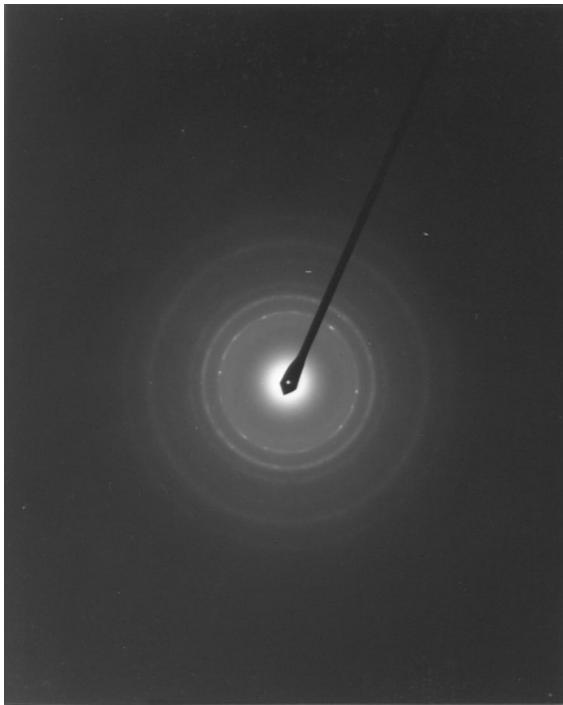

Fig. 8. Electron diffraction pattern of the carbon nitride films.

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activated nitrogen source is expected to further increase the nitrogen content as well as the degree of crystallinity of the carbon nitride films.

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