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LETTER TO THE EDITOR

Observations of Laue pattern and stability of β - C_3N_4 grains

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Abstract. Carbon nitride films have been prepared by ion beam assisted deposition with high N-ion fluxes up to the order of 1 mA cm^{-2} . Both Auger electron spectroscopy and Rutherford backscattering spectroscopy measurements show that an average nitrogen concentration of up to 45 at.% has been incorporated into the films. The nitrogen concentration in some local areas reaches as high as 59 at.% examined by energy-dispersive x-ray analysis. In such a high nitrogen content area, Laue spots of the predicted β - C_3N_4 structure have been observed for the first time by transmission electron microscopy. Under continuous electron irradiation, β - C_3N_4 grains refine to dimensions of $< 0.1\text{--}0.4 \mu\text{m}$ in diameter.

Recently, considerable effort has been directed towards the synthesis of the covalent solid carbon nitride β - C_3N_4 . This effort was initiated following a theoretical prediction by Liu and Cohen [1] that β - C_3N_4 would have excellent properties, such as a hardness comparable to or greater than that of the hardest known material, diamond. Further attention stems from the fact that six electron diffraction rings of the predicted β - C_3N_4 phase have been observed in the C–N thin film prepared by pulsed laser ablation [2]. In addition, the potential applications of this new material will be extensive, for example, Si is lattice-matched to β - C_3N_4 [3], which can promote a layer by layer growth of β - C_3N_4 on Si.

So far various approaches of material synthesis have been used in attempts to prepare β - C_3N_4 , such as pulsed laser ablation of graphite targets combined with an atomic nitrogen beam [2], N- [4, 5] or NH_3 - [6] ion beam assisted deposition (IBAD), electron cyclotron resonance plasma assisted vapour deposition [7], rf diode sputtering [8], N-ion implantation into carbon [9] and dc magnetron sputtering [3], etc. None of these efforts have succeeded in synthesizing carbon nitride films with the stoichiometry of β - C_3N_4 . In most of the films the concentration ratio C/N is about 0.7 or below. Based on x-ray photoelectron spectroscopy (XPS) analysis for binding states of carbon and nitrogen atoms, Marton *et al* found that their carbon nitride films, deposited by three different methods, were composed of two phases that have sp^3 and sp^2 bonded structures, respectively [4]. As far as the growth of crystalline β - C_3N_4 is concerned, the direct evidence reported is rare. Most films were found to be amorphous except that a few reports show the existence of crystalline β - C_3N_4 by presenting several electron diffraction rings from the tiny β - C_3N_4 grains embedded in the matrix of the films [2, 6, 8]. In the literature [2, 6] the grain size of β - C_3N_4 crystallites was $< 10 \text{ nm}$. In [8], the β - C_3N_4 crystallites were reported to have typical dimensions of $\approx 0.5 \mu\text{m}$ and occupy less than 5% of the film volume.

Herein, we present experimental evidence of crystalline β - C_3N_4 formation with Laue patterns of the β - C_3N_4 phase obtained in the carbon nitride films by transmission electron

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microscopy (TEM). The carbon nitride films were synthesized by the IBAD system described previously in [6] with N-ion bombardment. In order to increase the N-to-C concentration ratio, exploratory C-N films were deposited by varying the ion bombardment energy in the range 0.1–1 keV and using four kinds of beam current densities, i.e., 0.1, 0.5, 1.0, 2.5 mA cm⁻². It is worth mentioning that the current density used here is very high, while that in the previous IBAD synthesis was only of the order of 1 μA cm⁻² [4–6]. A high-purity graphite target was sputtered by 3 keV Ar⁺ and the deposition rate of carbon was 1.0 Å s⁻¹. Empirical data of the used ion source give the N⁺/N₂⁺ ratio in the beam current to be about 1:1.1. Thus, the arrival ratio of C/N, which is evaluated from the deposition rate of carbon and the bombarding nitrogen beam current, ranged from 1.8 to 0.07. Clean Si(111) wafers and NaCl with freshly cleaved surfaces were used as substrates for composition and structure analysis, respectively. The substrate temperature measured during deposition was below 250 °C. The film thicknesses were made to be about 0.1 μm for TEM analysis and more than 1 μm for other measurements. Prior to actual deposition, the substrates were cleaned by Ar ion bombardment at 0.6 mA cm⁻² and 1.1 keV for 20 min to remove any residual contaminants or surface oxides. The substrate self-bias voltage was -200 V.

The composition depth profiles of the C-N films were analysed by Rutherford backscattering spectrometry (RBS) and Auger electron spectrometry (AES). Both RBS and AES results showed that the C-N films may have a nitrogen content ranging from 10 to 45 at.%. AES results indicated that the C-N films consisted of only C and N and their concentrations were almost constant through the film thickness beneath a surface layer of 2.5 nm. In the surface layer, the oxygen content decreased rapidly to zero from approximately 7 at.% at the very surface. It was found that the maximum average percentage of nitrogen, 45 at.%, was obtained in the samples (noted as 1#) deposited by 200 eV N-ion bombardment with a beam current density of 2.5 mA cm⁻². The samples 1# were also characterized by XPS. The XPS data show that the films are composed of two chemical binding states of sp³ and sp² for C 1s^{1/2}, which have energies of 285.5 eV and around 284.5 eV, respectively. These data are consistent with the results in [4].

TEM investigations of the structure of the C-N films were performed using a JEM-200 CX microscope, mostly at an operating voltage of 200 kV. Energy-dispersive x-ray analyses (EDX) of micro-beams (50 nm in diameter) were also carried out to examine the local composition of the film corresponding to the selected area. One of three kinds of diffraction pattern may be observed, mainly depending on the nitrogen concentrations of the samples. For samples with a nitrogen concentration lower than 35 at.%, an amorphous pattern with at least a halo will occur. The feature of the amorphous pattern is similar to that reported in [6]. As the sample increases in nitrogen content, a different pattern with several rings might appear. Remarkably, in the samples 1#, we obtained Laue spots.

Figure 1(a) shows an example of the Laue patterns from samples 1# obtained by using selected area diffraction (SAD). Figure 1(b) gives the reciprocal lattice section relevant to figure 1(a) to illustrate the diffraction spots. The spots are indexed to the reflections for the β-C₃N₄ structure as shown in figure 1(b). The diffraction patterns match with the [1213] orientation patterns in the hexagonal β-C₃N₄ structure within experimental error of 4%. Assuming a hexagonal structure, the lattice parameters of the observed crystalline phase were determined as $a = 6.32$ Å and $c = 2.42$ Å. The predicted values are $a = 6.41$ Å and $c = 2.40$ Å [10]. The angle between the reciprocal lattice vectors 200 and 011 in figure 1(b) was measured to be 81°, while the theoretical angle between reflecting planes (200) and (011) in this β-C₃N₄ structure is 78.5°. We have excluded the possibility of reflections from other possible structures, such as diamond, graphite and NaCl.

We found that the Laue diffraction spots were unstable during TEM observation. Regular

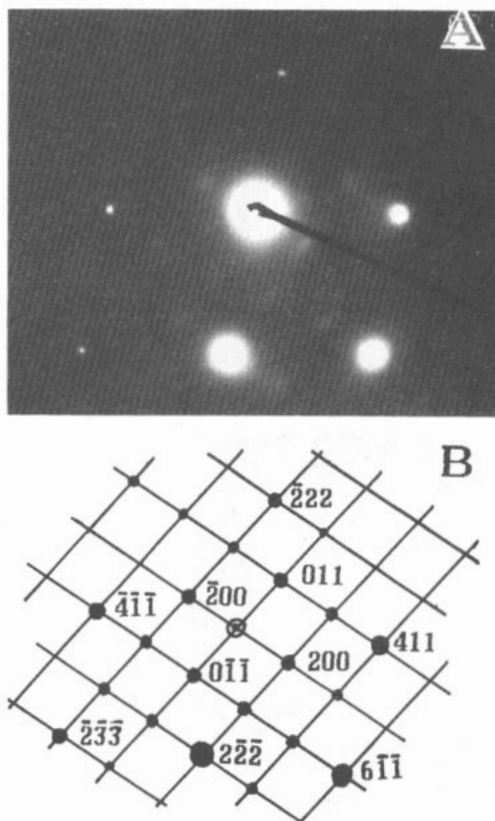


Figure 1. (a) Laue pattern of a sample 1# under SAD TEM. (b) Reciprocal lattice section relevant to (a).

Laue patterns like those in figure 1(a) were obtained only when the SAD operation was performed very quickly. Under electron irradiation of 200 kV, many spots will gradually evolve towards diffraction rings within several minutes. Figures 2(a) and (b) demonstrate this process. The diffraction pattern in figure 2(a) was taken from another sample 1# after electron irradiation for about eight minutes, in which the first three minutes were used to get a clear Laue pattern projected on the viewing screen. It is seen in figure 2(a) that continuous or discontinuous rings have developed and all the diffraction rings coincide with the β - C_3N_4 spots. After an additional five minutes of electron irradiation, the pattern had become almost complete diffraction rings superimposed with a few spots, as recorded in figure 2(b). Such a diffraction pattern remained steady, even though electron irradiation proceeded for more than thirty minutes. The time taken for the transformation from spots to rings was estimated to be 15 min. Such a transformation process has been repeated under 100 kV TEM observation. In the latter case, the transformation was obviously slower (about 0.5 h) than that in the case of 200 kV TEM. Figure 2(c) is a dark-field image that was obtained by using a section of the $\{210\}$ β - C_3N_4 diffraction ring shown in figure 2(b). This image was taken on the edge of the sample hold on the Cu grid. Most of the β - C_3N_4 crystallites shown in the dark image are smaller than $0.1 \mu\text{m}$ in diameter. An exceptionally big grain with dimension of about $0.4 \mu\text{m}$ (near the middle of the figure) remains.

There are thirteen diffraction rings reproducibly observed in the films. The interplanar

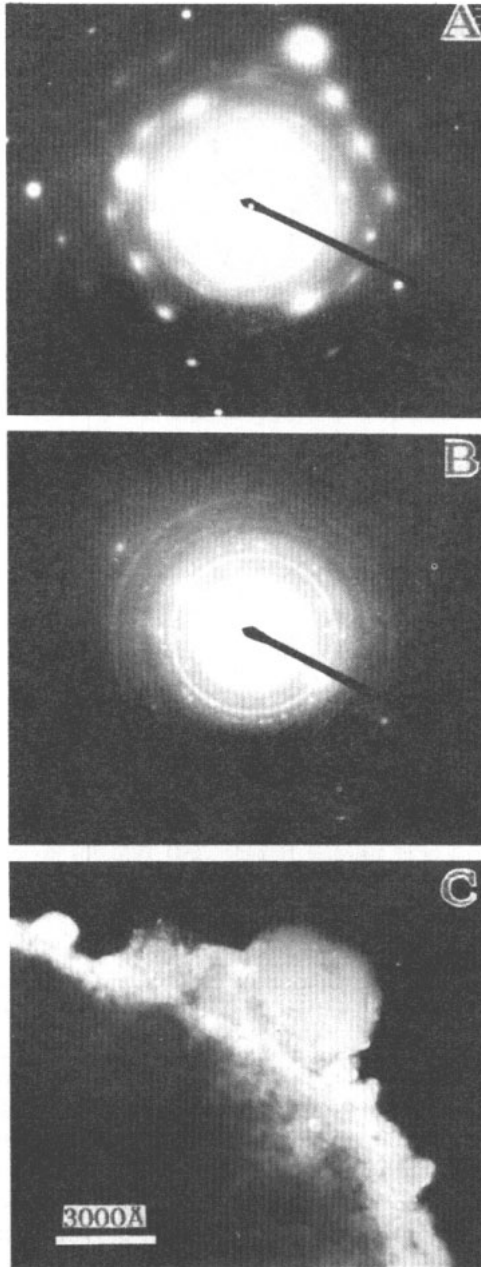


Figure 2. Evolution of electron diffraction patterns illustrating the refinement of β - C_3N_4 grains under continuous irradiation. (a) Eight minutes irradiation. (b) Stable pattern after 13 min irradiation. (c) TEM dark-field image using $\{210\}$ β - C_3N_4 diffraction of the sample.

spacings to which these rings correspond are listed in table 1. Data in the table again provide evidence for the presence of the β - C_3N_4 structure in the films synthesized by IBAD. All the detected diffraction peaks, within experimental error, can be consistently

indexed as the corresponding reflections of the β - C_3N_4 phase. On the other hand, although two reflections of the predicted β - C_3N_4 (i.e. (310) and (301)) are not detected, there is a reasonable explanation. This might be due to the overlap of the two weak peaks with the halo from the amorphous matrix of the films. The diffraction peak position of the halo corresponds to an interplanar spacing of 1.44 Å [6]. The peak positions of (310) and (301) are rather close to the halo.

Table 1. Comparison of the interplanar spacing (d) data from experiments with theoretical values based on β - C_3N_4 lattice constants [10]. s, m, and w represent strong, medium, and weak diffraction intensities.

TEM		Calculated β - C_3N_4 pattern	
d (Å)	Intensity	d (Å)	hkl
3.12	s	3.205	110
2.74	m	2.776	200
2.42	m	2.404	001
2.20	s	2.206	101
2.08	s	2.098	210
1.93	m	1.923	111
1.81	w	1.850	300
1.58	w	1.581	211
		1.540	310
		1.466	301
1.32	w	1.333	221
1.24	m	1.274	320
1.11	m	1.125	321
1.08	w	1.082	411
0.80	w	0.798	611

The above diffraction data indicate clearly that the crystalline β - C_3N_4 has been formed and the dimension of the stable grains under electron irradiation is of the order of < 0.1 – 0.4 μm . We also measured the composition of the film corresponding to the area where Laue patterns were observed by means of EDX. The results give the nitrogen concentration in this area to be about 59 at.%. The high concentration of the nitrogen may account for the formation of crystalline β - C_3N_4 . On the other hand, the N bombardment with intense flux during the film preparation could have resulted in high local temperature in the specimens. It is known that hot implantation is favourable for the formation of sp^3 bonds [9] and can thus promote the growth of β - C_3N_4 .

The phenomenon of the Laue spots transferring to rings implies that the grains were refined under electron irradiation. It seems by the following considerations that there may be two reasons for the grain refinement incited by electron irradiation. Firstly, the displacement threshold energy for the β - C_3N_4 crystal is abnormally small, so that the energetic electrons can induce atom displacement from the β - C_3N_4 lattice. Under 100 kV electron irradiation, the maximum kinetic energies of the primary knock-on atoms for N and C were evaluated to be 15 eV and 18 eV, respectively. Both of the two values are lower than the displacement thresholds (>20 eV) for N and C atoms in normal carbides or nitrides [11]. If the displacement thresholds in the carbon nitrides are smaller than 15 eV, radiation damage will occur and lead to the grain refinement. Secondly, the β - C_3N_4 grains in the films contain many defects, like vacancy clusters or small voids, formed during deposition. Atoms around the defects may be moved to relax under the electron irradiation, and thus make the large grains collapse into the fine crystallites. We noted that here the situation is in

some ways similar to the previous TEM observations on aragonite grains of μm size [12], in which the Laue spots of the aragonite grain were gradually transformed into diffraction rings under electron irradiation.

In summary, we have performed RBS, AES, XPS, EDX and TEM measurements on the C-N films synthesized by IBAD with a high flux of N ions. It is found that the average nitrogen content of the films can be up to 45 at.%, while the nitrogen concentration in some local areas reached as high as 59 at.%. Both Laue spots and a set of thirteen diffraction rings from the theoretically predicted $\beta\text{-C}_3\text{N}_4$ phase have been obtained by electron diffraction. $\beta\text{-C}_3\text{N}_4$ grain refinement under energetic electron irradiation has been observed. Stable $\beta\text{-C}_3\text{N}_4$ grains after electron irradiation are measured to be $< 0.1\text{--}0.4 \mu\text{m}$ in diameter.

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