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Carbon nitride films synthesized by NH₃-ion-beam-assisted deposition

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Abstract. Carbon nitride thin films have been prepared by NH₃-ion-beam-assisted deposition with bombardment energies of 200–800 eV at room temperature. These films have been characterized by transmission electron microscopy, Auger electron spectroscopy and x-ray photoelectron spectroscopy for chemical analysis. It was found that the structure of the films varied with the bombardment energy. In the case of 400 eV bombardment, the tiny crystallites immersed on an amorphous matrix were identified to be β -C₃N₄. X-ray photoelectron spectroscopy indicated that some carbon atoms and nitrogen atoms form unpolarized covalent bonds in these films.

1. Introduction

In recent years there has been a growing interest in the research of carbon nitride materials, since Liu and Cohen [1] predicted by means of an empirical model and *ab-initio* calculation of the bulk moduli for covalent solids that it may be possible to synthesize a covalent C–N solid, β -C₃N₄, with compressibility comparable with diamond. Very recently, using pulsed-laser ablation of graphite targets combined with intense atomic nitrogen sources, Niu *et al* [2] have produced experimentally covalent solid carbon nitride, β -C₃N₄. Previously, several approaches have been employed in attempts to prepare β -C₃N₄, including plasma decomposition of methane and nitrogen [3], pyrolytic decomposition of organic compounds that contain carbon, nitrogen and hydrogen [4], RF sputtering of a graphite target in a mixed argon–nitrogen plasma [5], DC magnetron sputtering of a graphite target in a nitrogen ambient [6] and ion-beam-assisted deposition (IBAD) [7, 8]. None of these approaches provided evidence for β -C₃N₄. However, it was noted that C–N films prepared on WC substrates by N₂ IBAD [7, 8] displayed an extremely high Knoop hardness (more than 5000 kgf mm⁻²). This result suggests that the C–N films prepared by IBAD are very promising for practical applications. In that work [8], the structure of the C–N films formed by N₂ IBAD was determined to be amorphous by transmission electron microscopy (TEM).

From the viewpoint of formation of β -C₃N₄ by IBAD, crystal growth may be promoted by bombardment of ions possessing suitable energies to enhance the mobility of surface atoms. Meanwhile it is essential that the deposited atoms possess a certain chemical activity to form the compound. Nitrogen atoms in NH₃ possess more activity than those in N₂, as nitrogen in NH₃ and N₂ are in single-bond states and triple-bond states, respectively. On the basis of these considerations, NH₃ IBAD was selected to investigate the possibility of β -C₃N₄ formation in the films. In the investigation, the emphasis was on the dependence of the film structure on the bombarding energy, since in IBAD the effect of the ion bombarding

energy on the film structure is significant [9]. In the present study, the C–N films were synthesized using NH_3 IBAD at four bombarding energies ranging from 200 to 800 eV. The formation of $\beta\text{-C}_3\text{N}_4$ was observed by electron diffraction in the synthesized samples at a bombarding energy of 400 eV. To the best of our knowledge, this is the first time that formation of $\beta\text{-C}_3\text{N}_4$ has been observed in films fabricated by IBAD.

2. Experimental details

The C–N films were prepared by a multi-purpose IBAD system [10]. Briefly, the system is equipped with two broad-beam Kaufman ion sources, a rotatable water-cooled substrate holder and a rotatable water-cooled target holder. Si(111) wafers and NaCl with freshly cleaved surfaces were used as substrates. Si(111) wafers were washed by dilute hydrofluoric acid and then ultrasonically cleaned in an acetone bath and an alcohol bath consecutively. The C–N films on Si(111) wafers were grown to a thickness of about 1 μm and were found to be adherent to the silicon substrates. The base pressure of the chamber was below 5×10^{-6} Torr. The working pressure (including ammonia partial pressure of about 9×10^{-5} Torr) was maintained below 1.4×10^{-4} Torr. Prior to actual deposition, the substrates were cleaned by NH_3 ion bombardment at 0.60 mA cm^{-2} and 1.5 keV for 20 min to remove any residual contaminants or surface oxides. A high-purity graphite target was sputtered by 3 keV Ar^+ with a beam current density of 3 mA cm^{-2} . The deposition rate of carbon was 1.0 \AA s^{-1} . The resulting films were simultaneously bombarded by NH_3 ions during synthesis. The energies of NH_3 ions were selected as 200, 400, 600 and 800 eV. At each bombarding energy, the beam current densities were adjusted to obtain the largest value of the N-to-C ratio in the films. The beam current densities were 0.15 mA cm^{-2} , 0.25 mA cm^{-2} , 0.30 mA cm^{-2} and 0.35 mA cm^{-2} , corresponding to bombarding energies of 200 eV, 400 eV, 600 eV and 800 eV, respectively.

The actual film compositions were determined by Auger electron spectroscopy (AES). The analysis of the film structure was performed by TEM observations at 200 keV energy. The electronic states of carbon atoms and nitrogen atoms in the samples were determined by x-ray photoelectron spectroscopy (XPS) (PHI model $\phi 590$).

3. Results and discussion

The AES depth profile of the elemental composition showed only carbon and nitrogen beneath a surface layer of 30 \AA . In the surface layer, the oxygen content decreased rapidly to zero from about 7 at.% at the very surface. The largest N-to-C atomic ratios of the C–N films obtained at the four energies were 0.25 (200 eV), 0.35 (400 eV), 0.27 (600 eV) and 0.22 (800 eV). The actual values of N-to-C arrival ratios were estimated as 0.25, 0.42, 0.48 and 0.54, respectively. It is worthwhile to mention that the films contain hydrogen which is not detected by AES.

TEM diffraction patterns and densitometer traces for the deposited C–N films at three bombarding energies are shown in figure 1. Since the results at 600 eV are very similar to those at 800 eV, they are not shown here. The densitometer traces reflect the electron diffraction intensity which varies as a function of the interplanar spacings in the films. The diffraction patterns in figures 1(a) and 1(b) were taken using two exposure times, so as to show clearly the characteristics of the diffraction patterns. In this figure, three points should be noted. First, figures 1(a) and 1(c) indicated that the typical amorphous halo

Table 1. Interplanar spacings evaluated from figure 1(b).

$(hk \cdot l)$	$\beta\text{-C}_3\text{N}_4$ d^a (Å)	Observed d (Å)	Difference (%)
10.0	5.50	5.10 (peak e)	7.3
10.1	2.20	2.23 (peak d)	1.4
20.1	1.81	1.83 (peak c)	1.1
32.0	1.27	1.29 (peak b)	1.6

^a Theoretical values [2].

rings are apparent. For the samples at 200 eV, there is only a halo in the diffraction pattern, which corresponds to peak a in the densitometer trace and appears at an interatomic spacing of around 1.44 Å. The value is close to the sum of atomic radii of carbon and nitrogen. The diffraction angle parameter $s = (2\pi \sin \theta)/\lambda$ for the halo was determined as $s = 4.38 \text{ \AA}^{-1}$. For the C-N films subjected to 800 eV bombardment, there are two haloes (peaks f and g) in the diffraction pattern. The diffraction angle parameters were $s_1 = 4.38 \text{ \AA}^{-1}$ (strong) and $s_2 = 1.28 \text{ \AA}^{-1}$ (weak). The strong but diffuse diffraction ring corresponds to an interatomic distance of 1.44 Å. Second, there are four weak rings (peak b-e) appearing in the diffraction pattern of the films formed at 400 eV bombardment. The weak rings combined with the respective densitometer traces which are not so sharp show a poor crystallinity of the tiny grains in the films. The interplanar spacings to which these rings correspond are listed in table 1. Among these interplanar spacings, 2.23, 1.83 and 1.29 Å are very close to the theoretical values for a $\beta\text{-C}_3\text{N}_4$ structure and can be well indexed as the (101), (201) and (320) reflections, respectively, from $\beta\text{-C}_3\text{N}_4$. As to the diffraction peak e, we have excluded the possibility of reflection from other possible structures, such as diamond, graphite and NaCl. The reason for the larger shift from the theoretical values of (100) interplanar spacing of $\beta\text{-C}_3\text{N}_4$ structure might be the overlap with the halo ($s = 1.28 \text{ \AA}^{-1}$) from the amorphous matrix whose peak position corresponds to an interplanar spacing of 4.9 Å. Third, the diffraction patterns were obtained by selected area diffraction (SAD). For the samples at 200, 600 and 800 eV, all the SAD patterns were always the same as those shown in figures 1(a) and 1(c). The situation is different for the sample at 400 eV. Two kinds of SAD pattern were observed. One was that shown in figure 1(b), and the other was similar to that in figure 1(c).

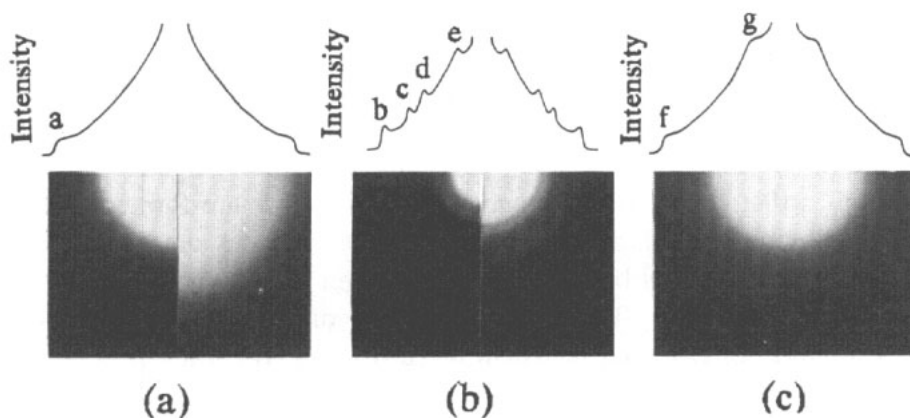


Figure 1. Electron diffraction patterns and densitometer traces of the NH_3 IBAD C-N films at (a) 200 eV, (b) 400 eV and (c) 800 eV.

A series of the x-ray photoelectron spectra of C $1s_{1/2}$ electrons and of N $1s_{1/2}$ electrons from the films formed by 200, 400 and 800 eV bombardment are shown in figures 2(a) and 2(b), respectively. As a comparison, the peak positions of the bonding energy for diamond (285.8 eV) [7], nitrogen (399.0 eV) [7] and graphite (284.0 eV) are indicated by arrows in figure 2. Here the peak position of graphite was actually determined using the same condition as that of our C-N films. We noted that the standard peak position of graphite reported in [7] was also at 284.0 eV, and thus comparison between the two groups of XPS data was feasible. Figure 2(a) reveals that the C $1s_{1/2}$ peak position of these films has various chemical shifts compared with graphite. For the films obtained by 200 and 800 eV bombardment, the peak positions are around 284.5 eV, which is very close to that of diamond-like carbon films obtained in the previous work [8]. In contrast, the main peak position in the films obtained by 400 eV bombardment is located at 284.8 eV, and more importantly an obvious hump can be seen near the peak position of diamond. On the other hand, figure 2(b) indicates that the N $1s_{1/2}$ peak positions also vary to some extent with the bombarding energy. In the case of 200 and 800 eV bombardment, the peak positions are at about 398.2 eV, which are slightly lower than that of nitrogen itself, 399.0 eV. In the case of 400 eV bombardment, the peak position of 398.9 eV is close to that of nitrogen.

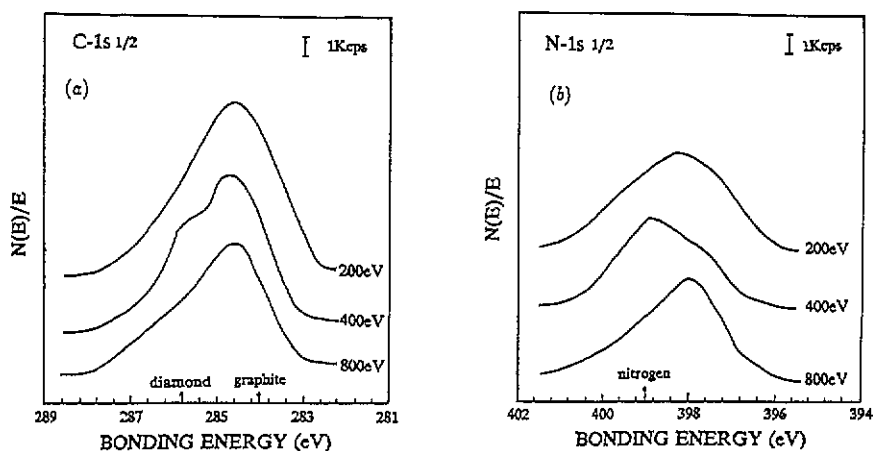


Figure 2. X-ray photoelectron spectra of (a) C $1s_{1/2}$ electrons and (b) N $1s_{1/2}$ electrons from NH_3 IBAD films at 200, 400 and 800 eV. The peak positions of bonding energies for diamond, graphite and nitrogen are indicated by arrows.

For the films obtained by 400 eV bombardment, the emergence of a hump in the C $1s$ spectra implies that charge transfer occurs and sp^3 bonds are formed. Also the N $1s$ signal displays an obvious unpolarized character. Thus, our XPS data indicate that unpolarized covalent bonds between carbon atoms and nitrogen atoms form in the C-N films obtained by 400 eV bombardment. This chemical nature of the C-N films is consistent with the predicted property of $\beta\text{-C}_3\text{N}_4$, in which there is no charge transfer between C and N [1].

Although the average N concentration (about 30 at.%) of the C-N films determined by AES is less than the expected value of N concentration for an ideal $\beta\text{-C}_3\text{N}_4$ solid, the formation of $\beta\text{-C}_3\text{N}_4$ crystallites was observed by SAD TEM in the case of 400 eV bombardment. This phenomenon could be explained by the composition fluctuations which often occur in films irradiated by high-energy ions [11].

Understanding why it is possible to form β -C₃N₄ by NH₃ IBAD, while under the same experimental conditions the formation of β -C₃N₄ was not observed in the case of N₂ IBAD [7, 8], may be clarified if we consider the difference between the chemical activities of nitrogen in the two ions. On the other hand the presence of H in the films could facilitate the formation of C sp³ bonds associated with β -C₃N₄, according to a mechanism proposed for diamond film fabrication by CH₄ IBAD [12].

4. Conclusions

β -C₃N₄ crystallites were observed in C-N films synthesized by NH₃ IBAD at a bombarding energy of 400 eV. In the films the tiny β -C₃N₄ crystallites were immersed in an amorphous matrix. Our XPS data indicated that some of the carbon atoms and nitrogen atoms in the films formed unpolarized covalent bonds. In the case of 200, 600 and 800 eV bombardment, the structures of these films were of a typical amorphous nature.

Acknowledgments

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