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LETTER TO THE EDITOR

## Synthesis and characterization of $C_3N_4$ crystalline films on silicon

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**Abstract.** We report the successful experimental synthesis of nearly pure crystalline  $\beta$ - and  $\alpha$ - $C_3N_4$  films on a Si(100) substrate by bias-assisted hot-filament chemical vapour deposition. Scanning electron microscopy shows that the substrate surface is covered by polycrystalline  $C_3N_4$  clusters 1–2  $\mu\text{m}$  in size with a density of  $10^6$ – $10^7$   $\text{cm}^{-2}$ . Relative N/C compositions in the range 1.34–2.5 were obtained by energy-dispersive x-ray analysis. The lattice parameters  $a = 7.06$   $\text{\AA}$  and  $c = 2.72$   $\text{\AA}$  for  $\beta$ - $C_3N_4$ , and  $a = 6.48$   $\text{\AA}$  and  $c = 4.71$   $\text{\AA}$  for  $\alpha$ - $C_3N_4$  were determined both by x-ray diffraction and by transmission electron microscopy. A buffer layer of  $C_{3-x}Si_xN_y$  was found.

The initial studies of new hard materials based on the carbon nitrides were motivated by the prediction of an empirical model for the bulk modulus of tetrahedral solids [1]. In 1990, the electronic and structural properties of  $\beta$ - $C_3N_4$  with the crystal structure of  $\beta$ - $Si_3N_4$  with C substituted for Si were studied by Liu and Cohen [2] within an *ab initio* local density approximation (LDA) framework. They suggested that  $\beta$ - $C_3N_4$  could have a bulk modulus comparable to that of diamond. However, no adequate crystals had then been synthesized in the laboratory, so that almost all of its physical and chemical properties remain unknown. The synthesis of crystalline  $\beta$ - $C_3N_4$  would, therefore, not only test the effectiveness of first-principles calculations in materials science, but also provide a new step in the development of growth techniques.

Several approaches have been used to date to synthesize films of  $\beta$ - $C_3N_4$  [3–14]. Initial studies produced amorphous carbon–nitrogen films in a capacitively coupled radiofrequency (RF) plasma reactor [3] and also by RF sputtering in nitrogen [4–7]. Using sputtering deposition [8–10] and pulsed laser deposition [11], recent efforts have synthesized small fractions of crystalline  $\beta$ - $C_3N_4$  phase in amorphous C–N films. When methane and nitrogen have been used as the gas sources for microwave plasma chemical vapour deposition (MPCVD) [12], only diamond films have been obtained. Similar results have been achieved by using shock-wave compression of organic C–N–H precursors [13]. Although many attempts have been made using physical vapour deposition (PVD) and CVD methods to synthesize the desired  $C_3N_4$ , no more than 47% [14] nitrogen content was attained, and almost all of the C–N films show a featureless surface morphology. Besides the known  $\beta$ -phase, several structural prototypes for  $C_3N_4$ , such as  $\alpha$ - $C_3N_4$ , cubic and the graphite

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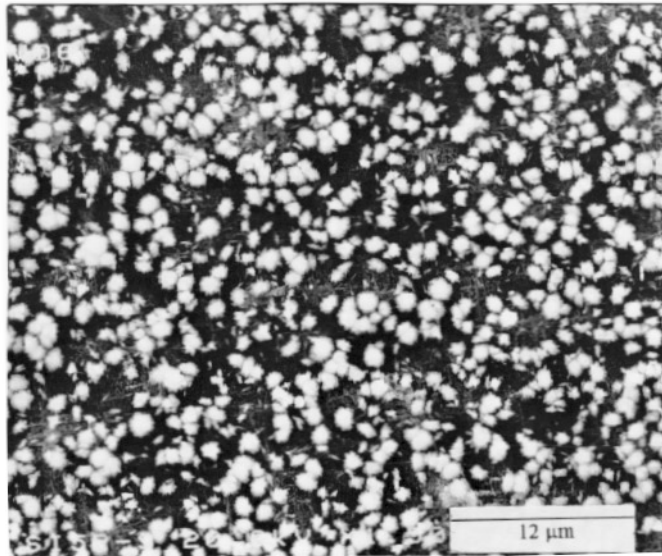
structure have been predicted by theorists. In a very recent report, Teter and Hemley [15] showed that  $\alpha$ -C<sub>3</sub>N<sub>4</sub> is lower in energy than  $\beta$ -C<sub>3</sub>N<sub>4</sub>. However, most of the work in this field so far has been focused on  $\beta$ -C<sub>3</sub>N<sub>4</sub>, other prototypes having seldom been studied experimentally.

In this letter, we report the successful synthesis of crystalline  $\beta$ - and  $\alpha$ -C<sub>3</sub>N<sub>4</sub> films via hot-filament chemical vapour deposition (HFCVD) using a gas mixture of nitrogen and methane. The bias-assisted HFCVD technique has been described in detail elsewhere [16, 17]. In the present study, a mixture of highly purified nitrogen (99.999%) and methane (99.9%) was used as the reactive source and a carbonized tungsten filament was used to dissociate the introduced gases. Negative bias was applied to the substrate (−300 V) to increase the energy of the activated ionic species. Mirror-smooth Si(100) wafers were used as the substrates. Deposition times varied in the range 10–40 minutes. The grown films were analysed by scanning electron microscopy (SEM) (Hitachi, S-4200), energy-dispersive x-ray analysis (EDX) (an Oxford 6566 device, installed in S-4200), x-ray diffraction (XRD) (MAC Science-M18XHF) and transmission electron microscopy (TEM) (Hitachi, H-9000NA).

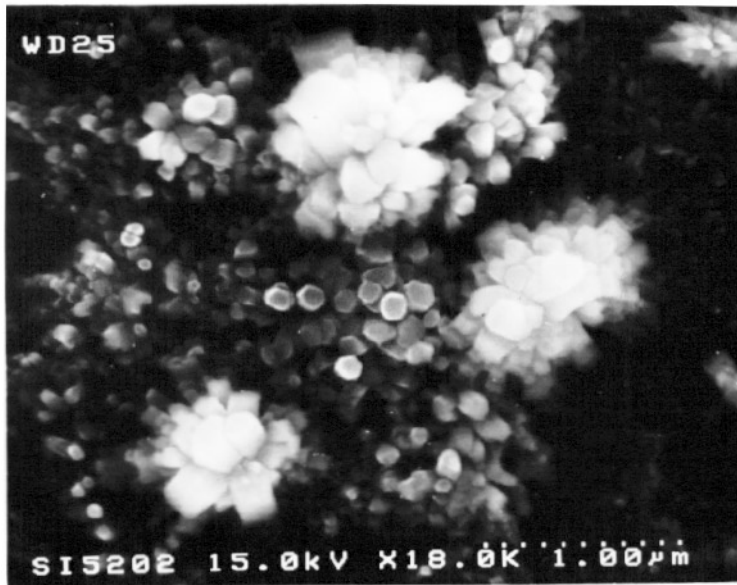
After the first five minutes of deposition, a layer of grown thin film was visible to the naked eye. After ten minutes of deposition, many small ball-shaped C–N nuclei were observed to aggregate to form clusters. Figure 1(a) shows a low-magnification SEM picture after 40 minutes of deposition. These white polycrystalline clusters 1–2  $\mu\text{m}$  in size covered the Si(100) surface with a density of  $10^6$ – $10^7$   $\text{cm}^{-2}$ . In addition, some small pin-shaped white crystals were also observed with a density lower than that of the clusters. A SEM micrograph of some clusters in the 40 minute deposition sample is shown with high magnification in figure 1(b). They are composed of many columnar crystals with hexagonal facets (20–200 nm across) radiating outwards.

EDX analysis indicates that the grown films are composed of elemental N and C. EDX measurements of different samples give relative N/C ratios in the range 1.34–2.50. No metal contaminations (such as W or Ta) are observed in the films, although Si was detected. It is believed to originate from uncovered regions of the Si substrate or from the C<sub>3-x</sub>Si<sub>x</sub>N<sub>y</sub> interfacial layer that is formed between the Si substrate and the C–N film during initial growth. These results demonstrate that the C–N films obtained are nitrogen-rich.

The grown crystals are hexagonal in cross section with the top (0001) facet revealed. In order to determine the actual structural parameters, XRD was used to analyse the grown films. Figure 2 gives the XRD result of the Si(100) substrate before deposition. The only diffraction peak observed is associated with Si(400) at  $2\theta = 69.05^\circ$ . Figure 2(b) shows the XRD spectrum of the same sample as that viewed by SEM in figure 1. No amorphous phases are visible in the spectrum. The main diffraction peaks do not correspond to those of Si<sub>3</sub>N<sub>4</sub>, 3C-diamond, graphite and SiC and so on. A further Raman examination also excludes the existence of diamond, graphite and SiC, because no Raman peaks are present in the range 400–1800  $\text{cm}^{-1}$  [18, 19]. C<sub>3</sub>N<sub>4</sub> structures appear to be the only remaining possibilities. If the theoretical lattice constants of  $a = 6.44$  Å [2] or 6.40 Å [20] and  $c = 2.47$  Å [2] or 2.40 Å [20], are expanded by 10% to  $a = 7.06$  Å and  $c = 2.72$  Å, then most of the XRD peaks coincide well with calculations based on the  $\beta$ -C<sub>3</sub>N<sub>4</sub> structure. A detailed analysis shows that this increase may be associated with the presence of a Si–C–N phase at the interface. This is because XRD cannot be localized to a monocrystal and results in an average value of the lattice constant over a larger area. Notably, the present  $c/a$  ratio of 0.385 is close to the earlier theoretical predictions  $c/a = 0.383$  [2] and 0.375 [20]. In figure 2(b) the full width at half maximum (FWHM) of the Si substrate (400) peak is enlarged compared with that prior to deposition shown in figure 2(a). This means that some peaks of  $\beta$ -C<sub>3</sub>N<sub>4</sub> occur in this region, such as (311), (320), (002), (400), (321) and



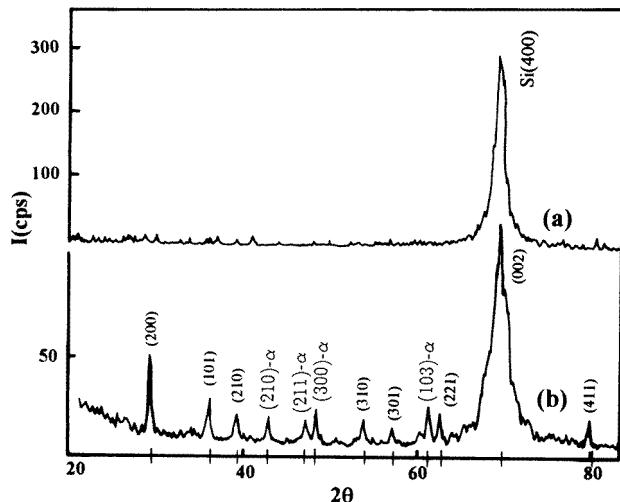
(a)



(b)

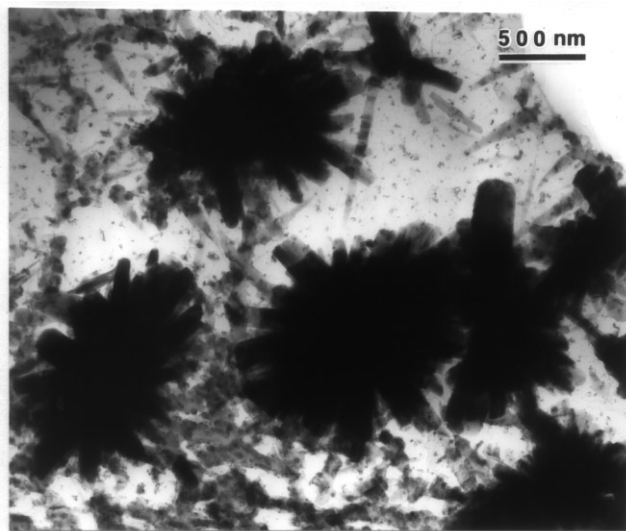
**Figure 1.** SEM micrographs of the crystalline C–N films grown for 40 minutes on silicon by hot-filament chemical vapour deposition: (a) surface morphology and (b) some polycrystalline clusters.

(002). In addition, some peaks present at  $d$  spacings of 2.11, 1.93, 1.88 and 1.52 Å can be indexed as (210), (211), (300) and (103) for  $\alpha$ -C<sub>3</sub>N<sub>4</sub>, respectively. The lattice constants of  $\alpha$ -C<sub>3</sub>N<sub>4</sub> based on our XRD results are  $a = 6.48$  Å and  $c = 4.71$  Å, which are in very good agreement with the theoretical predictions  $a = 6.4665$  Å and  $c = 4.7097$  Å given recently



**Figure 2.** XRD spectra of the substrate and the grown C–N film: (a) the Si(100) substrate before deposition and (b) the sample viewed by SEM in figure 1, where the theoretical results of  $\beta$ - $C_3N_4$  [2] and  $\alpha$ - $C_3N_4$  [15] are also given for comparison.

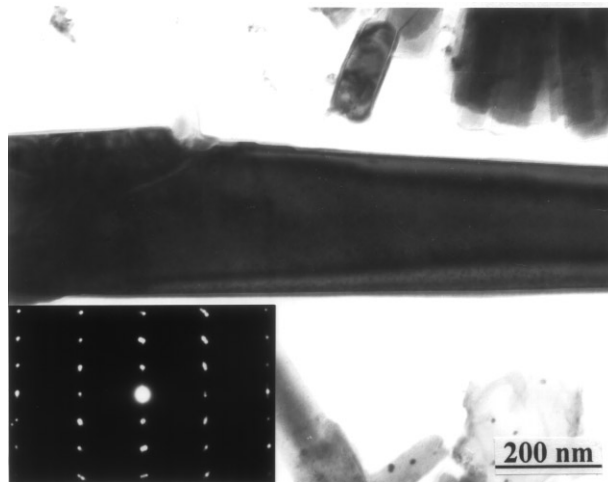
by Teter and Hemley [15]. In the present sample, most of the  $\beta$ -phase  $C_3N_4$  appears to be the longer columnar crystals grown on a Si–C–N buffer layer, whereas  $\alpha$ -phase  $C_3N_4$  is some smaller grains covering the substrate directly. This should explain why the experimental lattice constants for  $\alpha$ - $C_3N_4$  are closer to the first-principles calculations than are those for  $\beta$ - $C_3N_4$ , because the latter grew on a mixed phase buffer layer.



**Figure 3.** A TEM bright-field micrograph of several polycrystalline clusters.

A further TEM observation was used to characterize the crystal structure of the C–N film studied by SEM and XRD. A plane-view TEM specimen was prepared by grinding

and polishing to about 30  $\mu\text{m}$  thickness and then ion milling with one ion gun along the substrate side until perforation occurred. The TEM was operated at 300 kV. Figure 3 is a bright-field micrograph of some clusters which display a morphology similar to that shown by SEM in figure 1(b). The corresponding selected-area electron diffraction (SAED) pattern of one cluster, not shown here, exhibits many spots and discontinuous rings, indicating a polycrystalline structure. Figure 4 shows a bright-field micrograph of a pin-shaped crystal grown along the substrate surface and its SAED pattern. This pattern confirms that this crystal has a hexagonal structure. TEM results, therefore, provide strong evidence for a  $\text{C}_3\text{N}_4$  phase with hexagonal structure.



**Figure 4.** A TEM bright-field image of a pin-shaped crystal and its SAED pattern.

During the growth of  $\beta\text{-C}_3\text{N}_4$ , the hybrid  $\text{sp}^3$  atomic carbon bonds must be maintained by nitrogenous or other species, but certainly not carbonaceous ones, since each C atom has to bond tetrahedrally with four N atoms in the  $\beta\text{-C}_3\text{N}_4$  structure. If C catenated C, the structure of  $\beta\text{-C}_3\text{N}_4$  would be destroyed and diamond or graphite phases would be formed. Therefore, nitrogenous active species must have enough energy to break the formed C–C  $\text{sp}^3$  or  $\text{sp}^2$  bonds. In consideration of the lower migration rate of active species on the growing surface of a strongly covalent solid, abundant active carbonaceous and nitrogenous precursors must be maintained above the growing surface. So, a relatively low pressure ( $\leq 0.1$  Torr) will be needed in order to maintain enough precursors. In addition, the high-density precursors must have enough active energy. All of these facts suggest that the surface chemical reactions during the growth of  $\beta\text{-C}_3\text{N}_4$  are more complex than those during that of diamond [21, 22].

In conclusion, nearly pure crystalline  $\text{C}_3\text{N}_4$  has been synthesized by hot-filament chemical vapour deposition using a mixture of nitrogen and methane on silicon. SEM, XRD, EDX, TEM and Raman spectroscopy were used to characterize the structure of the grown films. Our results demonstrate the successful synthesis of high-quality C–N films in the  $\beta\text{-C}_3\text{N}_4$  structure with lattice constants  $a = 7.06 \text{ \AA}$  and  $c = 2.72 \text{ \AA}$ , and in the  $\alpha\text{-C}_3\text{N}_4$  structure with  $a = 6.48 \text{ \AA}$  and  $c = 4.71 \text{ \AA}$ , which supports the earlier theoretical prediction [2, 15]. Given the success of the bias-HFCVD method, we surmise that the intense covalent C–N crystalline phase may be more difficult to synthesize in a high-vacuum environment such as that during RF sputtering [4–7] or pulsed laser deposition [11]. From

these considerations, we believe that the surface chemical reactions in the present system are more complex than those in diamond formation.

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