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Observation of crystalline C_3N_4

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We present strong experimental evidence suggesting that we have synthesized the β-C_3N_4 phase. This is a material predicted by theory to have bulk moduli comparable to diamond. Thin films containing small crystals were deposited on Si and Ge wafers by rf diode sputtering of a pure graphite target with pure N_2. The crystal structure of these phases was investigated using x-ray and electron-beam diffractometry as well as transmission electron microscopy. Our results indicate that the β-C_3N_4 particles with typical dimensions of ~ 0.5 μm are embedded in a 1-μm-thick layer of a C-N polymer. These particles are believed to crystallize preferentially on Si (100) wafers.

Recently, Liu and Cohen[1] reported a theoretical calculation which suggests that covalent C-N solids could have bulk moduli comparable to diamond and hence are good candidates for hard materials. The calculation was motivated by an empirical model[2] for the bulk moduli of tetrahedral solids which indicates that short, low ionicity bonds, such as those which form between C and N, are favorable for achieving a high bulk modulus. Using the simpler of the two known Si_3N_4 crystal structures as a prototype, Liu and Cohen performed a first-principles pseudopotential total-energy calculation to investigate the structural and electronic properties of β-C_3N_4 (C_3N_4 in the β-Si_3N_4 structure). The bulk modulus of the hypothetical compound β-C_3N_4 was found to be comparable to that of diamond. In addition the cohesive energy of β-C_3N_4 was calculated to be moderately large, indicating that it could be a metastable structure. These results suggest that the synthesis of a hard C-N solid, which could have technological applications, may be possible.

The deposition of amorphous carbon nitride thin films has been attempted by Jones and Steward[3] using plasma decomposition of nitrogen and various hydrocarbons, and by Han and Feldman[4] using rf plasma deposition. Nitrogen contents ranging from 0% to 40% in the amorphous films were achieved by these authors. However, identification of a crystalline carbon nitride material has not been reported. In 1990, we documented the synthesis of crystalline C_3N_4 material using the sputtering technique.[5] Since then there have been several reports on the positive identification of C_3N_4 crystals in the literature.[6-9] In this paper we report on our attempt to synthesize the predicted β-C_3N_4 phase by means of thin-film deposition techniques. The experimental results support the presence of the crystalline β phase on (100) oriented Si substrates.

The experimental approach involved the production of thin films containing carbon and nitrogen (C-N films) deposited on oriented single-crystal Si and Ge wafers by means of the rf diode sputtering technique at a frequency of 13.56 MHz. The target consisted of an 8-in. graphite disk situated 6 cm above the substrate. Sputtering was carried out with rf power of 300 W and pure N_2 at a pressure of 17 mTorr. The substrate temperature during sputtering was held between 400 and 600 °C. The graphite self-bias was -1700 V.

Exploratory C-N films were deposited by varying the sputtering parameters, e.g., the substrate temperature, sputtering gas, sputtering power, etc. Over twenty films

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deposited under various sputtering conditions were studied and the optimum process described above (referred to as the "standard process") was devised. We have also noticed that substrate heating reduces the deposition rate of the film but promotes crystallization. Therefore, a substrate temperature in the range of 400–600 °C was selected in our standard procedure. Depending on the substrate temperature the deposition rate ranges from 0.1 to 0.5 μm/h. The standard process was used to deposit C-N films (CN#23) on several substrates simultaneously, including (100) and (111) Si and (100) and (111) Ge wafers. The composition and thickness of the CN#23 film were studied by Rutherford backscattering spectrometry (RBS) using a 1.8-MeV $^4He^+$ beam backscattered at 105° and 165° and proton resonant scattering (PRS) using a 1.55-MeV H^+ beam. Details of the apparatus and the techniques have been published.[10] RBS and PRS results show that C-N films produced using this method have a nitrogen content ranging from 0% to 50%. Films deposited by the standard procedure, e.g., CN#23, are ~ 1 μm thick with a nominal film composition of $C_{0.6}N_{0.3}O_{0.1}$. Figure 1 shows the RBS spectrum of CN#23 on a Si substrate. RBS analysis also reveals that the film/substrate interface is abrupt with no apparent interdiffusion between the film and the substrate within the depth resolution of the technique (~ 200 Å).

Scanning electron microscopy (SEM) studies on CN#23 show that the film morphology is rather smooth. Figure 2 shows a crystalline particle of ~ 1-μm size found in CN#23 on Si (100). This type of crystalline particle is difficult to find on the film and is more frequently found in regions where the overlayer C-N film peeled off. It is therefore suggested that these particles preferentially crystallize on the crystalline Si (100) surface and are buried by an amorphous C-N film. Energy dispersive x-ray analysis (EDX) shows that the particles are composed primarily of C and N with a small amount of O. The N/C ratio of these particles is higher than the overall N/C ratio in the film. However, absolute quantitative determination of the composition of these particles is difficult due to the limitation of the electron-beam size and substrate effects. The EDX results, therefore, suggest that the particle shown in Fig. 2 is a N-rich crystalline C-N compound.

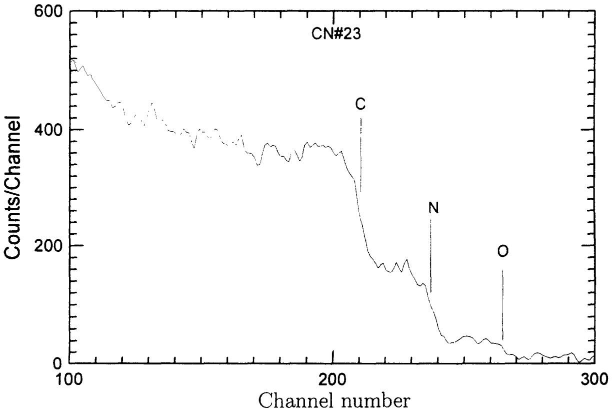

FIG. 1. RBS spectrum of the CN#23 film on Si. The detector is oriented at 105° with respect to the 1.8-MeV He ion beam. The maximum He backscattering energies for C, N, and O are marked.

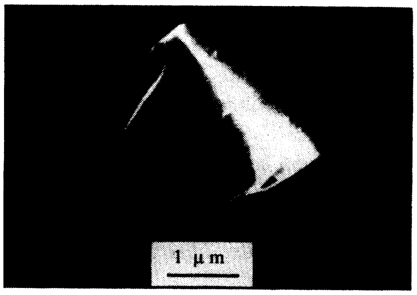

FIG. 2. SEM micrograph of crystalline particles in the CN#23/Si (100) sample. The composition of these particles is also measured by EDX to be more N-rich than the C-N film.

x-ray-diffraction (XRD) measurements were carried out in a Siemens D500 x-ray diffractometer using a Cu anode. In order to increase the diffraction volume, a glancing incident angle of 1° was employed. XRD results in this glancing incident geometry on all of our films do not show any diffraction peak. This can be explained by the small atomic scattering factors of C and N in the particles; the relatively small amount of crystalline material present in the films, and the possibility that the crystalline particles may be textured with respect to the substrate Si so that the Bragg diffraction condition is not satisfied under a fixed incident angle. XRD analyses of the CN#23 film using the (θ-2θ) Bragg geometry show many broad and sharp diffraction peaks. The broad peaks are believed to be from the amorphous graphitic phase in the film. Since the film is C-rich in composition, the presence of amorphous carbon phases is expected. Some of the strong diffraction peaks from the XRD spectrum of CN#23 do match the calculated β-C_3N_4 pattern. However, a similar diffraction pattern has also been observed for amorphous C or Si thin films on the (100) Si substrate.[11] These strong sharp peaks, therefore, can be attributed to substrate-related diffraction. We believe that they are forbidden reflections for a perfect Si crystal, e.g., the (200) and (320) reflections, but become allowed due to stress induced by the presence of an overlayer on the substrate. Moreover, the strongest diffraction peak of the β-C_3N_4 phase, namely, the (200) peak, is very close to the (200) peak of Si. Phase identification of the C_3N_4 crystal using XRD is therefore difficult unless a rather thick uniform layer of the material can be produced.

Transmission electron microscopy (TEM) investigations of the C-N films were performed using a Philips 301 microscope at an operating voltage of 100 kV. The specimens were prepared by first mechanically grinding the samples into 3-mm disks. The disks were then mounted face down on a clear mica plate. The film surface was protected with wax. The specimen was backpolished from the substrate side in etching solution until a small hole was formed. A TEM dark field (DF) image of a plan-view specimen from CN#23 on Si (100) and its corresponding transmission electron-diffraction (TED) pattern are shown in Figs. 3(a) and 3(b), respectively. A section of both the {101} and {210} β-C_3N_4 diffraction rings was used for the dark field image shown in Fig. 3(a). The crystalline particles which we believe to be β-C_3N_4 grains shown in the DF image in Fig. 3(a) are ~0.5 μm in diameter and are observed on the edge of the hole in the specimen attached to the Si substrate. This is consistent with the SEM observation. These grains, which are distributed near the film/substrate interface embedded in the C-N polymeric matrix, are estimated to occupy less than 5% of the film volume.

The ring pattern in Fig. 3(b) indicates that the grains in Fig. 3(a) are polycrystalline. Since the β-C_3N_4 grains are attached to the single-crystal Si substrate, the ring pattern in Fig. 3(b) overlaps with the {220} Si diffraction spot pattern. The lattice spacings are measured directly from the TED pattern and are tabulated in Table I. All the diffraction rings, with the exception of only a few rings with weak intensities, match with the theoretical β-C_3N_4 pattern. However, the lattice spacings as observed from TED are consistently smaller by a few percent than the calculated values for the theoretically predicted β-C_3N_4. Using the strong (110) and (101) rings in the TED data, and assuming a hexagonal structure, we calculated the lattice parameter of our observed crystalline phase to be $a = 6.3$ Å and $c = 2.38$ Å. While these values are ~2% lower than the results from the total-energy calculations ($a = 6.43$ Å and $c = 2.46$ Å), the experimental and theoretical c/a ratios are in good agreement. One possible reason for the slight reduction in the lattice parameters is that the crystals in our film may not have the perfect C_3N_4 composition. Moreover, the effect of the presence of a small amount of O (~5–10%) in these particles may also play a role in the structure of the crystals and the absence of some diffraction peaks in the TED pattern. The theoretical powder-diffraction pattern calculated with the shorter lattice parameters is presented in Table I in parentheses. A close match of the peak positions of the TED pattern with this calculated pattern is observed. The rings which correspond to the β-C_3N_4 diffraction are indexed in Fig. 3(b).

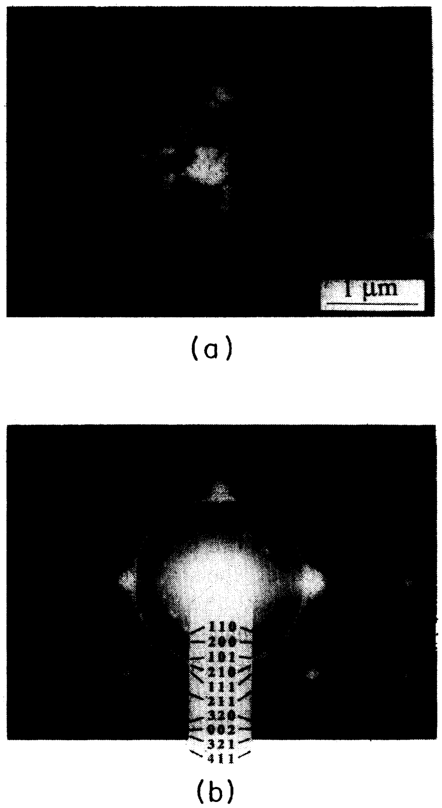

FIG. 3. (a) The transmission electron microscopy dark field image of the plan-view specimen from the CN#23 film on Si (100). (b) The corresponding electron-diffraction pattern of the crystals shown in (a). The lattice spacings measured from the diffraction rings are tabulated in Table I. The diffraction rings corresponding to the β-C_3N_4 phase are also indexed in the figure.

TABLE I. Comparison of the TED data of CN#23 on Si (100) with the calculated β-C_3N_4 powder-diffraction pattern. *s*, *m*, *w*, and vw represent strong, medium, weak, and very weak diffraction intensities. *d* spacings given in parentheses are calculated values using the lattice parameters extracted from the TED data (see text).

TED		Calculated β-C_3N_4 pattern		
d (Å)	Intensity	*d* (Å)	*hkl*	Intensity
		5.565 (5.46)	100	*m*
3.43(±0.05)	*w*			
3.15(±0.05)	*m*	3.213 (3.15)	110	*m*
2.65(±0.03)	vw	2.783 (2.73)	200	*s*
2.18(±0.02)	*s*	2.259 (2.18)	101	*s*
2.07(±0.02)	*s*	2.103 (2.06)	210	*m*
1.92(±0.02)	*w*	1.953 (1.90)	111	*m*
		1.855 (1.82)	300	*m*
1.76(±0.01)	*w*			
1.64(±0.01)	*w*			
1.56(±0.01)	vw	1.598 (1.56)	211	*w*
		1.543 (1.51)	310	*w*
		1.481 (1.45)	301	*w*
		1.345 (1.31)	221	*w*
1.25(±0.01)	*s*	1.277 (1.25)	320	*w*
1.17(±0.01)	vw	1.229 (1.19)	002	*w*
1.11(±0.01)	vw	1.133 (1.11)	321	*m*
		1.125 (1.09)	202	*w*
1.07(±0.01)	*m*	1.089 (1.06)	411	*w*

In summary we have performed RBS, PRS, SEM, XRD, and TEM measurements on C-N films deposited on Si and Ge wafers in the (100) and (111) orientations using rf diode sputtering. Small grains (~0.5–1 μm) are found in the film deposited on (100) Si. EDX, TEM, and TED analyses show that these grains are N-rich as compared to the film and strongly suggest that they are the theoretically predicted β-C_3N_4 phase. The fact that these grains only grow on (100) Si suggests that these crystals bear a specific orientation relationship with the substrate. The samples we have studied deposited by the standard procedure are far from ideal. We believe that by further varying the sputtering parameters systematically C-N films with a much larger quantity of crystalline β-C_3N_4 particles can be produced.

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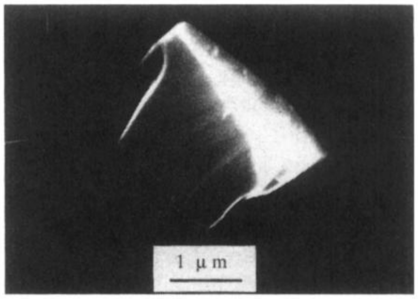

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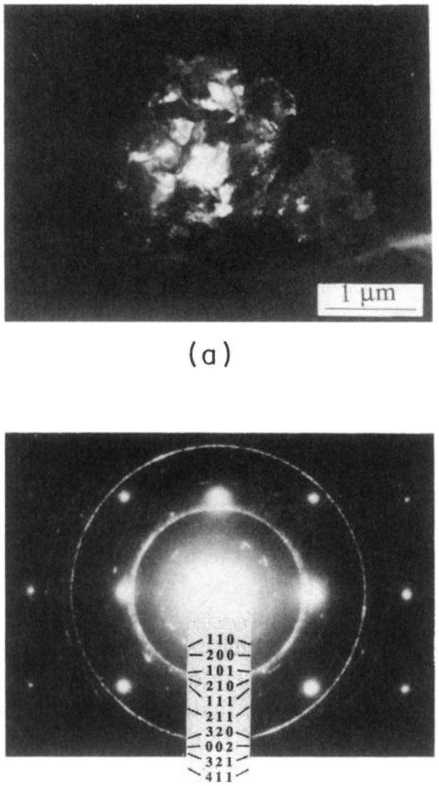

(a)

(b)

FIG. 3. (a) The transmission electron microscopy dark field image of the plan-view specimen from the CN#23 film on Si (100). (b) The corresponding electron-diffraction pattern of the crystals shown in (a). The lattice spacings measured from the diffraction rings are tabulated in Table I. The diffraction rings corresponding to the β-C_3N_4 phase are also indexed in the figure.