

Growth and composition of covalent carbon nitride solids

Z. John Zhang, Shoushan Fan, and Charles M. Lieber^{a)}

Division of Applied Sciences and Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 6 February 1995; accepted for publication 7 April 1995)

The composition, growth mechanism, and phases of carbon nitride thin films obtained from the reaction of laser ablated carbon and atomic nitrogen have been investigated. The nitrogen composition was found to increase to a limiting value of 50% as the fluence was decreased for laser ablation at both 532 nm and 248 nm. Analysis of these data shows that the overall growth rate determines the nitrogen composition, and suggests that a surface reaction between carbon and nitrogen represents a key step in the growth mechanism. Infrared spectroscopy has also been used to assess the phases present in the carbon nitride thin films. The implications of these results to the stoichiometry of covalent carbon nitride are discussed. © 1995 American Institute of Physics.

Carbon nitride solids, which may represent a new class of superhard materials, have been the focus of considerable research effort.¹⁻³ Early theoretical studies suggested that a carbon nitride solid analogous to β -silicon nitride, β -C₃N₄, should be reasonably stable and possess a hardness comparable to or greater than diamond.³ A number of groups have subsequently attempted to prepare β -C₃N₄ using a variety of techniques, including laser ablation and reactive sputtering.^{2,4-10} Although diffraction data consistent with the β -C₃N₄ structure have been obtained in several recent studies,^{4,6,9} the overall C/N composition has varied significantly from that proposed for this material. The clear differences in the experimentally observed and theoretically predicted stoichiometries and incomplete diffraction data suggest that β -C₃N₄ may not be the most stable structure or stoichiometry for binary carbon nitride phases. Indeed, recent theoretical studies have demonstrated that two other hypothetical C₃N₄ structures, which resemble defect zincblende and rhombohedral graphitelike structures, should have a stability similar to that of β -C₃N₄.¹¹

To address the current uncertainty in the stoichiometry of stable carbon nitride phases, we herein report systematic studies of nitrogen composition range, growth mechanism, and phases of these materials. Carbon nitride thin films were prepared using an approach recently developed in our laboratories that combines pulsed laser ablation of graphite and an atomic nitrogen beam source.^{2,4} Briefly, ablation of high-purity pyrolytic graphite was carried using either a frequency-doubled Nd:YAG laser (532 nm, 6 ns pulse width) or a KrF excimer laser (248 nm, 23 ns pulse width). The reactive nitrogen atom beam ($>10^{18}$ atoms/sr s) intersects the laser-generated carbon species at the substrate surface.¹² In this work, we use nitrogen beam conditions optimized for maximum nitrogen incorporation.^{2,4} The films were grown on HF-etched Si (100) surfaces at $\sim 200^\circ\text{C}$.

To probe the composition range and growth mechanism, we have prepared carbon nitride thin films as a function of the laser fluence and wavelength. In general, we find that the nitrogen composition increases as the laser fluence decreases. For ablation at 532 nm, Rutherford backscattering spectroscopy (RBS) shows that a carbon nitride film grown by ablating graphite target with a relatively high fluence of 3.5 J/cm² has a nitrogen content of 28% [Fig. 1(a)], while a film obtained using a lower fluence of 0.86 J/cm² contains 47% nitrogen [Fig. 1(b)]. However, as the laser fluence is decreased below about 0.8 J/cm², the nitrogen composition in the films does not increase further.¹³ Similar results have also been observed for carbon nitride films grown at 248 nm [Figs. 1(c), (d)]. For example, RBS analyses show that films grown using 11 and 3.6 J/cm² fluence contain 33% [Fig. 1(c)] and 47% nitrogen [Fig. 1(d)], respectively.

The inverse dependence of nitrogen composition on laser fluence indicates that the growth rate is critical in determining carbon nitride composition since the fluence affects primarily the total flux of carbon.¹⁴ Notably, calculation of the growth rates for the samples shown in Fig. 1 shows that rates of 14.7, 1.2, 10.6 and 1.2 Å/s have produced the films containing 28%, 47%, 33%, and 47% nitrogen, respectively.

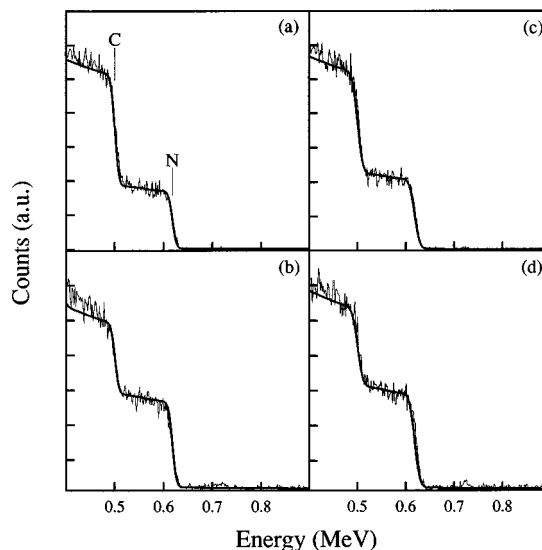


FIG. 1. RBS spectra (General Ionics Model 4117, 2.0 MeV He ion beam) of carbon nitride films. The C and N compositions were determined from fits (smooth lines) to the experimental data. The films in (a), (b), (c) and (d) were 2.3, 1.7, 1.9 and 2.2 μm thick, respectively.

^{a)}Electronic mail: cml@cmliris.harvard.edu

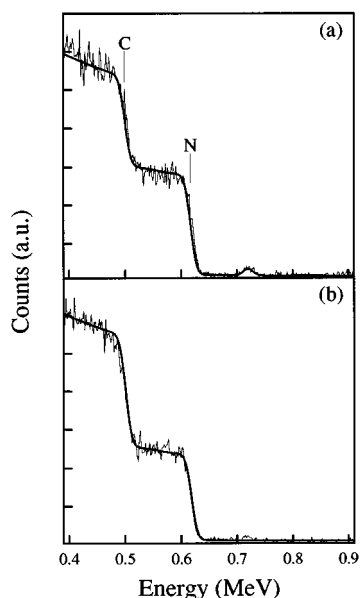


FIG. 2. RBS spectra of carbon nitride films grown at (a) 9 and (b) 27 Hz. The films were 2.3 and 2.1 μm thick, respectively.

To confirm the importance of the film growth rate, we have also prepared materials as a function of the laser pulse repetition rate while keeping other parameters constant. RBS data for two carbon nitride films grown at 248 nm (3.4 J/cm^2) using repetition rates of 9 and 27 Hz are shown in Fig. 2. Significantly, the material grown at the lower repetition rate (growth rate = 1.6 \AA/s) has a larger nitrogen content than in the film produced at the higher repetition rate (growth rate = 4.0 \AA/s): 45 versus 36% nitrogen. In addition, RBS spectra obtained for these thick ($>1.5 \mu\text{m}$) films show that the materials consist of almost purely carbon and nitrogen, and do not contain significant amounts of other elemental impurities.¹⁵

Our studies of laser fluence and pulse repetition rate suggest that the growth rate determines the nitrogen composition in these materials. The relationship between growth rate and composition is shown explicitly in Fig. 3. This plot, which contains data from numerous experiments carried out using 532 and 248 nm ablation, demonstrates that the nitrogen content increases and then saturates as the growth rate is reduced below 0.5 \AA/s . Hence, for the range of fluences and repeti-

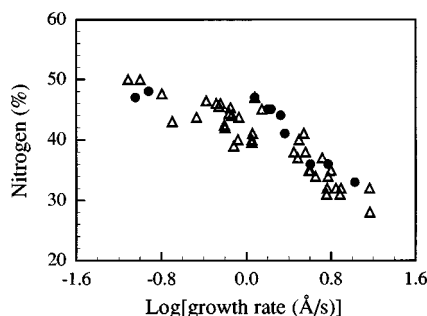


FIG. 3. Plot of the percentage nitrogen in carbon nitride solids vs growth rate for materials prepared by laser ablation at 532 nm (Δ) and 248 nm (\bullet).

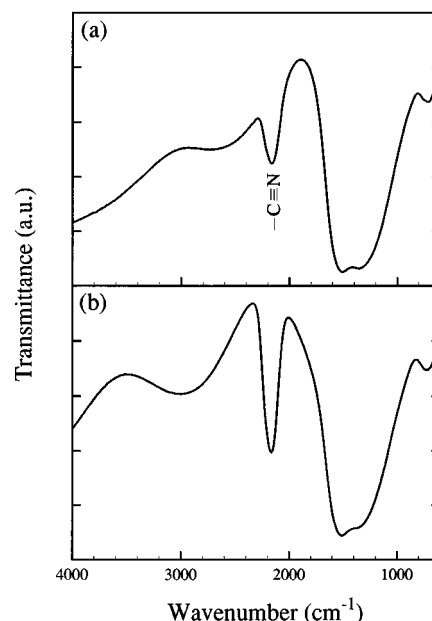


FIG. 4. Infrared spectra of carbon nitride films (Nicolet, Model 5PC). The films in (a) and (b) contain 40% and 46% nitrogen, respectively.

tion rates used in these studies it is clear that the nitrogen composition is determined solely by the average growth rate.

We believe that the correlation of the nitrogen composition with film growth rate suggests that a key step in the carbon nitride growth mechanism involves a reaction between carbon and nitrogen at the growth surface and not in the gas phase. If gas phase reactions controlled the nitrogen composition, then the nitrogen composition would not have changed with variations in the repetition rate since the gas phase reaction time is much shorter than the time between laser pulses. In addition, productive gas phase reactions between atomic N and C are unlikely without the presence of a third body. While further studies are obviously required, we believe that an understanding of the growth mechanism will be crucial to controlled preparation of crystalline carbon nitride in the future.

The plot in Fig. 3 also shows that the nitrogen composition in our pure carbon nitride materials saturates close to 50% and not the 57% level expected for C_3N_4 .¹⁶ This implies that the stoichiometry of one stable carbon nitride phase could be CN. However, a CN stoichiometry cannot be concluded without knowledge of the phase purity in these materials. To address this issue, infrared (IR) spectroscopy has been employed to probe the structure and bonding in the carbon nitride films. IR spectra typically exhibit bands at ~ 2200 , 1500 and 1350 cm^{-1} (Fig. 4). The broad bands at ~ 1500 and 1350 cm^{-1} are believed to correspond to C=N and C-N stretching modes,¹⁷ and are consistent with an extended inorganic carbon nitride solid. The band at $\sim 2200 \text{ cm}^{-1}$ corresponds to a C \equiv N stretching mode.¹⁸ This C \equiv N bonding arrangement is incompatible with an extended inorganic solid and represents an impurity phase. Significantly, we find that the amount of this C \equiv N impurity phase increases with the overall nitrogen composition (Fig. 4), and thus we suggest that the composition of the inorganic carbon

nitride phase must be less than the saturation level of 50%.

In summary, systematic studies of the growth of carbon nitride thin films have been carried out. The nitrogen composition was found to increase to a limiting value of 50% as the fluence was decreased for laser ablation at both 532 nm and 248 nm. Analysis of these data shows that the overall growth rate determines the nitrogen composition, and suggests that a key step in the growth mechanism of carbon nitride involves a surface (versus gas-phase) reaction between carbon and nitrogen. Although the saturation nitrogen composition of 50% is suggestive of a CN stoichiometry, IR analyses have shown that a C \equiv N impurity phase increases in concentration as the overall nitrogen composition increases to 50%. These results thus suggest that the dominant inorganic phase in thin-film carbon nitride materials has <50% nitrogen.

We acknowledge helpful discussion with Dr. Jinlin Huang, and thank Dr. Arthur Moore of Union Carbide for providing pure graphite. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award No. DMR-9400396.

¹W. Schnick, *Angew. Chem. Int. Ed. Engl.* **32**, 1580 (1993).

²C. M. Lieber and Z. J. Zhang, *Adv. Mater.* **6**, 497 (1994).

³A. Y. Liu and M. L. Cohen, *Science* **245**, 841 (1989); A. Y. Liu and M. L. Cohen, *Phys. Rev. B* **41**, 10727 (1990).

⁴C. Niu, Y. Z. Lu, and C. M. Lieber, *Science* **261**, 334 (1993).

⁵F. Xiong, R. P. H. Chang, and C. W. White, *Mater. Res. Soc. Symp. Proc.* **285**, 587 (1993).

⁶J. Narayan, J. Reddy, N. Biunno, S. M. Kanetkar, P. Tiwari, and N. Parikh, *Mater. Sci. Eng. B* **26**, 49 (1994).

⁷M. Y. Ming, X. Lin, V. P. Dravid, Y.-W. Chung, M. S. Wong, and W. D. Sproul, *Surf. Coating Technol.* **54/55**, 360 (1992); M. Y. Chen, D. Li, X. Lin, V. P. Dravid, Y.-W. Chung, M.-S. Wong, and W. D. Sproul, *J. Vac. Sci. Technol. A* **11**, 521 (1993).

⁸P. G. Kosky, R. H. Wilson, and M. F. Carbauskas, G. E. Res. and Dev. Rep. No. 93CRD109 (1993).

⁹K. M. Yu, M. L. Cohen, E. E. Haller, W. L. Hansen, A. Y. Liu, and I. C. Wu, *Phys. Rev. B* **49**, 5034 (1994).

¹⁰H.-X. Han and B. Feldman, *Solid State Commun.* **65**, 921 (1988); M. R. Wixom, *J. Am. Ceram. Soc.* **73**, 1973 (1990); L. Maya, D. R. Cole, and E. W. Hagaman, *J. Am. Ceram. Soc.* **74**, 1686 (1991).

¹¹A. Y. Liu and R. M. Wentzcovitch, *Phys. Rev. B* **50**, 10362 (1994).

¹²J. E. Pollard, *Rev. Sci. Instrum.* **63**, 1771 (1992); S. J. Sibener, R. J. Buss, C. Y. Ng, and Y. T. Lee, *ibid.* **51**, 167 (1980).

¹³Film growth at a fluence below 0.8 J/cm² (532 nm) is irreproducible since the carbon deposition rate by ablation becomes comparable to the atomic nitrogen induced etching rate.

¹⁴J. T. Cheung and H. Sankur, *Crit. Rev. Solid State Mater. Sci.* **15**, 63 (1988).

¹⁵The small oxygen contamination peak at ~ 0.72 MeV [e.g., Fig. 2(a)] corresponds to only surface oxide layer on the film.

¹⁶Composition results are reported for thick films since the homogeneity and purity can be reliably assessed in these materials. Higher nitrogen compositions (up to 58%) have been observed in thin (0.1 μ m) films; however, in these films we believe that impurities at the substrate/film interface contribute to the measured nitrogen composition (Z. J. Zhang and C. M. Lieber, unpublished results).

¹⁷J. Kouvetakis, A. Bandari, M. Todd, B. Wilkens, and N. Cave, *Chem. Mater.* **6**, 811 (1994).

¹⁸D. Li, Y.-W. Chung, S. Yang, M. -S. Wong, F. Adibi, and W. D. Sproul, *J. Vac. Sci. Technol. A* **12**, 1470 (1994).