

## **GROWTH AND PROPERTIES OF CARBON NITRIDE THIN FILMS**

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### **ABSTRACT**

Recent research on carbon nitride thin films grown using pulsed laser deposition combined with atomic beam techniques is reviewed. The composition, growth mechanism and phases of these films have been systematically 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 wavelengths. Time of flight mass spectroscopy investigations of the ablation products have shown that the fluence variations affect primarily the yield of the carbon reactant. These experiments demonstrate that the overall film growth rate determines the average nitrogen composition, and furthermore, suggest that a key step in the growth mechanism involves a surface reaction between carbon and nitrogen. Infrared spectroscopy has been used to assess the phases present in the carbon nitride thin films as a function of the overall nitrogen content. These measurements have shown that a cyanogen-like impurity occurs in films with nitrogen compositions greater than 30%. Studies of thermal annealing have shown, however, that this impurity phase can be eliminated to yield a single phase  $C_2N$  material. In addition, systematic studies of the electrical resistivity and thermal conductivity of the carbon nitride films are discussed.

### **I. INTRODUCTION**

Carbon nitride materials represent an exciting challenge to both fundamental and applied research [1]. Basic research is needed to develop new preparative methods for combining rationally carbon and nitrogen into solid materials and to elucidate the structures and physical properties of these new materials. In addition, applications of carbon nitride solids are being actively pursued since simple bonding arguments and more rigorous theoretical calculations suggest that these materials should have attractive properties, such as extreme hardness and thermal conductivity.

Early theoretical investigations of carbon nitride solids focused on a hypothetical binary carbon-nitrogen compound,  $\beta\text{-C}_3\text{N}_4$ , that has the  $\beta\text{-Si}_3\text{N}_4$  structure [2]. The results from this theoretical work suggested that  $\beta\text{-C}_3\text{N}_4$  should have a reasonably large cohesive energy and thus should be metastable. More recent theoretical studies have also investigated the stability and properties of  $\text{C}_3\text{N}_4$  compounds that have structures distinct from that of the  $\beta\text{-Si}_3\text{N}_4$  structure [3]. Significantly, these latter studies have found that carbon nitride  $\text{C}_3\text{N}_4$  materials having either defect zinc-blende or rhombohedral graphite-like structures should have stabilities comparable to or greater than  $\beta\text{-C}_3\text{N}_4$ . Because there is also no reason to assume that carbon nitride must have a  $\text{C}_3\text{N}_4$  stoichiometry, there is many metastable C-N phases that must be carefully considered in experimental studies of this new class of materials.

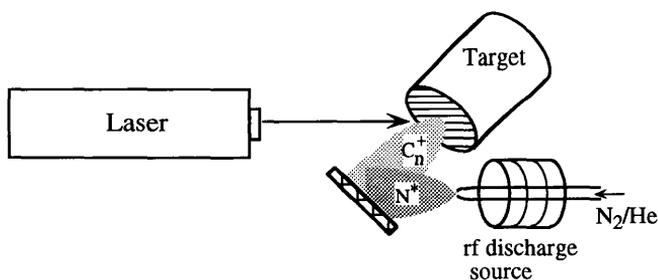
Experimental approaches to the synthesis of carbon nitride have utilized a variety of techniques, including plasma-assisted chemical vapor deposition [4], thermal pyrolysis [5], shock wave compression [6], reactive sputtering [7-9], and laser ablation [1,10-12]. Although evidence for nanocrystalline  $\beta\text{-C}_3\text{N}_4$  has been obtained for materials prepared by laser ablation [10,12] and reactive sputtering [7], the overall nitrogen composition of these materials has been significantly less than the  $\text{C}_3\text{N}_4$  stoichiometry [13]. Furthermore, we have noted that the reported diffraction data are not unique to the  $\beta\text{-C}_3\text{N}_4$  structure but can also be explained by a tetragonal-CN phase analogous to the high-pressure form of GeP [1,11]. To clarify this uncertain experimental situation requires systematic studies of the composition and phases of carbon nitride. Furthermore, to advance rationally this material for applications requires an understanding of the relationships of nitrogen composition and key physical properties.

This brief review summarizes our recent systematic studies of the nitrogen composition range, phases, and physical properties of thin film carbon nitride materials prepared using a laser ablation/atomic beam deposition technique. We find that the nitrogen composition increases to a limiting value of 50% as the laser fluence is decreased at both 532 nm and 248 nm. Analysis of these experiments and time of flight mass spectroscopy results show that the growth rate determines the overall nitrogen composition, and furthermore, suggests that a key step in the growth mechanism involves a surface reaction between carbon and nitrogen. Infrared (IR) spectroscopy has been used to study the phase purity in these carbon nitride films, and show that a cyanogen-like impurity occurs in films with nitrogen compositions greater than 30%. The cyanogen-like impurity phase can, however, be eliminated by thermal annealing to yield a single phase  $\text{C}_2\text{N}$  material. In addition, systematic measurements of the electrical resistivity and thermal conductivity of

the carbon nitride films indicate that this material may be an attractive candidate for electronic applications.

## II. EXPERIMENTAL

Our approach to the synthesis of carbon nitride materials combines pulsed laser ablation with an atomic beam source. A schematic diagram of our experimental set-up is shown in Figure 1. Carbon fragments are produced by ablation of high-purity pyrolytic graphite in a vacuum chamber using either a frequency-doubled Nd:YAG laser (532 nm) or a KrF excimer laser (248 nm). A N<sub>2</sub>-seeded He flow was passed through a radio frequency (rf) discharge source to generate a reactive nitrogen beam consisting primarily of relatively high kinetic energy atomic nitrogen [14]. The reactive nitrogen atom beam ( $>10^{18}$  atoms/sr-s) intersects the carbon ablation plume at the substrate surface. Using this experimental apparatus only pure carbon and nitrogen reactants are produced, and thus elemental impurities such as hydrogen and oxygen are eliminated.

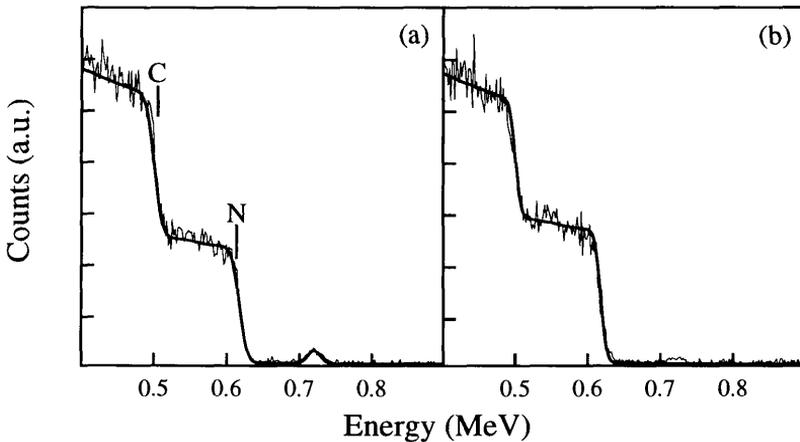


**Figure 1.** A schematic diagram of the experimental set-up for the carbon nitride growth. The substrate, rotating graphite target and atomic nitrogen source are all contained within a vacuum chamber that is evacuated by a liquid nitrogen trapped 5000 l/s diffusion pump.

The carbon nitride thin films were grown on quartz or HF-etched Si (100) surfaces at  $\sim 200$  °C. The nitrogen beam conditions used in these studies were optimized through variations in the N<sub>2</sub>:He ratio and rf power to yield the maximum nitrogen composition under fixed ablation conditions [10,11]. The base pressure of deposition chamber is less than  $10^{-8}$  torr; however, with the nitrogen beam source operating the pressure usually rises to between  $10^{-5}$  to  $10^{-4}$  torr during film growth.

### III. RESULTS AND DISCUSSION

We have systematically grown a series of carbon nitride films under different the laser fluences and wavelengths, and employed Rutherford backscattering spectroscopy (RBS) to determine the chemical composition in these films. In general, we find that the nitrogen composition of the film increases as the laser fluence decreases. This trend is illustrated in Figure 2. These RBS spectra show different composition carbon nitride films grown by 532 nm wavelength laser ablation of a graphite target at different fluences.

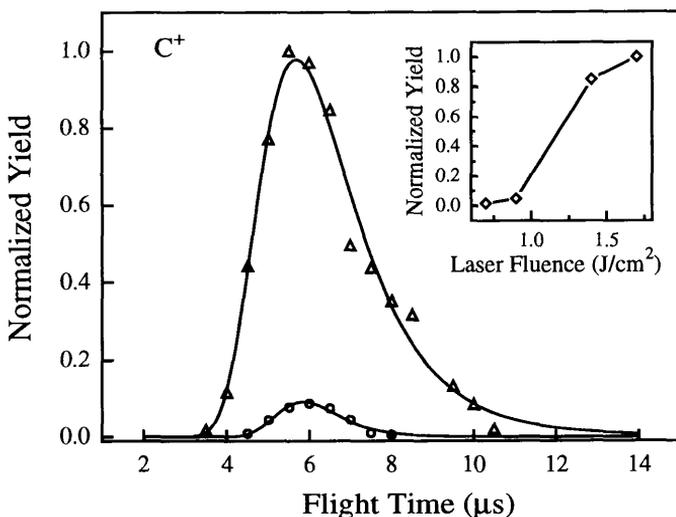


**Figure 2.** RBS spectra (General Ionics Model 4117, 2.0 MeV He ion beam) of carbon nitride films. The C and N compositions were determined from fits (smooth lines) to the experimental data. The films in (a) and (b) are 2.0 and 2.2  $\mu\text{m}$  thick, respectively.

Figure 2a corresponds to data obtained from a carbon nitride film that was prepared using a laser fluence of 1.4  $\text{J}/\text{cm}^2$ ; this film contains 37% nitrogen. When the fluence is decreased to 0.9  $\text{J}/\text{cm}^2$ , RBS data shows the nitrogen composition increased to 45% (Fig. 2b). No further increase in nitrogen composition was observed, however, for fluences less than 0.8  $\text{J}/\text{cm}^2$ . Similar results have also been obtained for carbon nitride films grown by laser ablation at 248 nm [11].

Time-of-flight (TOF) mass spectroscopy has been employed to explore the origin of the dependence of the nitrogen composition on laser fluence. Preliminary results show that the carbon fragments in our laser ablation plume consist primarily of one to four carbon atom species, and of these species one carbon fragments are dominant. Hence, we have used

this dominant species as an indicator of the total carbon yield under different ablation conditions. We find that the carbon yield for ablation using a 1.4 J/cm<sup>2</sup> fluence is significantly greater than the yield obtained using 0.9 J/cm<sup>2</sup> laser fluence (Fig. 3). More generally, these experiments show that the carbon yield increases systematically with laser fluence, although the increase is non-linear [15]. Preliminary analysis of this data also indicates that there is very little change in the kinetic energy of the carbon fragments for the range of fluences studied.

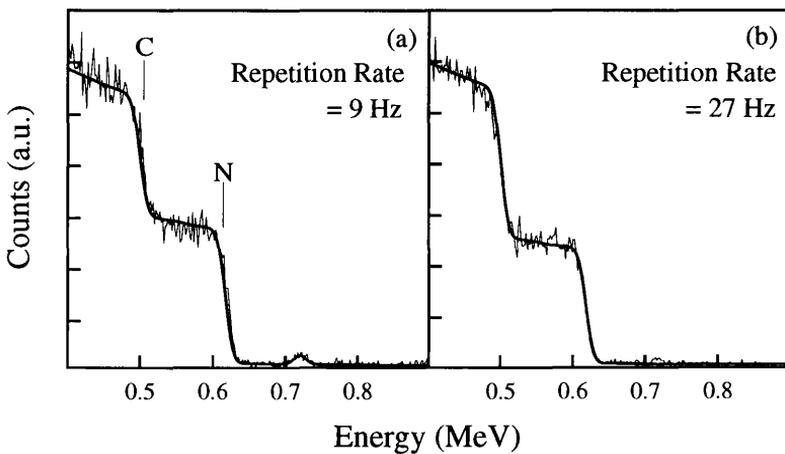


**Figure 3.** TOF distributions for C<sup>+</sup> produced with laser ablation fluences of 0.9 J/cm<sup>2</sup> (O) and 1.4 J/cm<sup>2</sup> (Δ). The inset is a plot of total yield of C<sup>+</sup> versus laser fluence.

The correlation between carbon yield and laser fluence indicates that the growth rate may determine in large part the carbon nitride composition. For example, the carbon nitride films grown with 1.4 and 0.9 J/cm<sup>2</sup> have the growth rates of 3.1 and 1.4 Å/s and compositions of 37% and 45% nitrogen, respectively. To confirm that the growth rate determines composition and not for example the energy of the carbon fragments, we have also prepared carbon nitride films using a constant laser fluence at different pulse repetition rates. RBS analyses of two carbon nitride films prepared using 248 nm ablation at a constant laser fluence of 3.4 J/cm<sup>2</sup> and different repetition rates of 9 and 27 Hz are shown in Figure 4. Significantly, the film grown using the lower repetition rate (growth rate of 1.6 Å/s) had a nitrogen composition of 45% (Fig. 3a), while the film grown using a higher 27 Hz repetition rate (i.e.,

and higher growth rate of 4.0 Å/s) had a lower nitrogen composition of 36% (Fig. 3b).

Our investigations of the laser fluence and repetition rate effects and TOF mass measurements indicate clearly that the overall growth rate determines the nitrogen composition in these carbon nitride films. We suggest that this correlation arises from a growth mechanism that involves as a key step the reaction between carbon and nitrogen at the growth surface. If on the other hand gas phase reactions were important, the nitrogen composition would not have changed with variations in the repetition rate since the reaction time between carbon and nitrogen in the gas phase is same for both repetition rates.

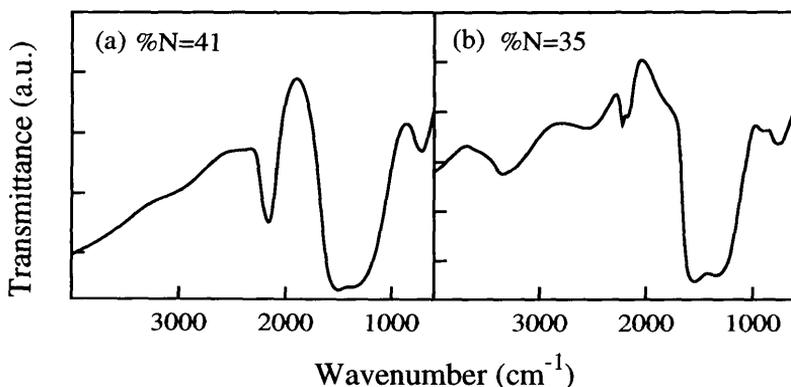


**Figure 4.** RBS spectra of carbon nitride films grown at 248 nm laser wavelength with repetition rates of (a) 9 and (b) 27 Hz. The films were 2.3 and 2.1  $\mu\text{m}$  thick, respectively.

We have used this knowledge of the growth mechanism to explore systematically the nitrogen composition limits of carbon nitride. Significantly, we have found that the nitrogen composition in carbon nitride films saturates at a value close to 50% [11]. This saturation value implies that a possible stoichiometry of carbon nitride is CN (and perhaps not  $\text{C}_3\text{N}_4$ ), although this assignment requires that the 50% nitrogen thin films contain a single phase. To evaluate the phases present in these carbon nitride materials we have used infrared (IR) spectroscopy. A typical IR spectrum recorded on a carbon nitride film containing 41% nitrogen is shown in Figure 5a. This spectrum exhibits two overlapping bands at  $\sim 1500$  and  $1350\text{ cm}^{-1}$  and a third stretching mode at  $\sim 2200\text{ cm}^{-1}$ . The overlapping bands at  $\sim 1500$  and  $1350\text{ cm}^{-1}$  are believed to

correspond to C=N and C-N stretching modes [16], and are consistent with an extended inorganic carbon nitride solid.

The third band occurring at  $\sim 2200\text{ cm}^{-1}$  corresponds to a  $\text{-C}\equiv\text{N}$  or cyanogen-like stretching mode [17]. This  $\text{-C}\equiv\text{N}$  bonding arrangement precludes an extended inorganic carbon nitride solid and represents a cyanogen-like impurity phase in these materials. The cyanogen-like impurity increases very little as the nitrogen composition increases from 30 to 35%. However, as the nitrogen composition increases above 35%, the intensity of the  $\sim 2200\text{ cm}^{-1}$  band increases dramatically. These observations imply that increases in the carbon nitride nitrogen composition above about 35% occur in large part at the expense of forming a  $\text{-C}\equiv\text{N}$  impurity phase. Hence, we conclude that the nitrogen composition of the dominant carbon nitride phase present in these thin films is less than 50%.



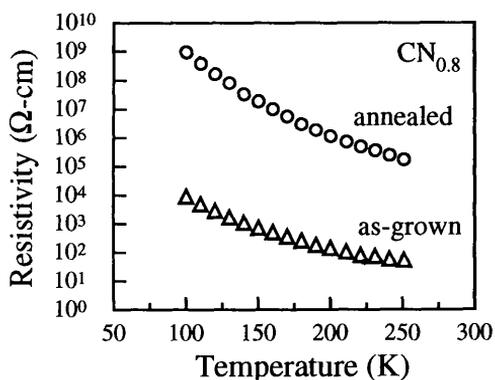
**Figure 5.** IR spectra of carbon nitride films recorded before (a) and after vacuum annealing at  $550\text{ }^{\circ}\text{C}$  (b). The nitrogen compositions both before and after the annealing procedure were determined by RBS.

We have also investigated the effects of thermal annealing to our carbon nitride thin films since cyanogen-like materials, which represent the impurity phase, typically have low thermal stabilities [17]. The effect of thermal annealing on the structure and composition of the carbon nitride thin films was evaluated by recording IR and RBS spectra before and after the annealing process. For example, Figure 5b shows the IR spectrum of the film used to record Figure 5a after it was annealed in vacuum at  $550\text{ }^{\circ}\text{C}$  for three hours. Notably, we find that the annealing process nearly eliminates the intense  $\text{C}\equiv\text{N}$  mode at  $2200\text{ cm}^{-1}$  which was found in the as-grown film. RBS analysis also shows that the nitrogen composition in the annealed film is reduced from 41% to 35%. Systematic RBS studies of the film composition before and after annealing

demonstrates that the nitrogen composition in films initially containing more than 40% nitrogen decreases during the annealing process and reaches a common, stable composition of ~35%. Furthermore, IR spectra recorded on these same materials show that the  $-C\equiv N$  impurity phase is essentially eliminated in all of the films that have been annealed to yield the common, stable composition of ~35% nitrogen. These results indicate that a nearly single phase  $C_2N$  material containing 35% nitrogen and both C-N and C=N bonding can be prepared by our post-annealing process.

The thermal annealing process also results in profound changes in electrical properties of our carbon nitride films. Resistivity measurements made on thin films that were deposited on insulating quartz substrates have shown that the resistivity of the carbon nitride films increases systematically with nitrogen composition, although this increase is highly nonlinear. The resistivity at 200 K initially increases slowly until the nitrogen composition reaches 30%, and then increases much more rapidly until it ultimately saturates at  $1.5 \times 10^3 \Omega\text{-cm}$  in films with a nitrogen composition of ~45%. We believe that the initial slow increase in resistivity corresponds to transport dominated by amorphous carbon, and that the saturation value corresponds to the resistivity of the carbon nitride (but a form that also contains a  $-C\equiv N$  impurity phase).

Significantly, carbon nitride films containing initially  $\geq 40\%$  nitrogen exhibit a much high resistivity after our vacuum annealing treatment. Temperature dependent resistivity measurements made on a carbon nitride film containing 45% nitrogen before annealing and 35% nitrogen after vacuum annealing at 550 °C are shown in Figure 6.



**Figure 6.** Temperature dependent resistivity measurements recorded on a carbon nitride thin film with 45% nitrogen before ( $\Delta$ ) and after vacuum annealing (O) at 550 °C.

The resistivity of the film increased 3-5 orders of magnitude after the annealing process. We believe that the enhancement in resistivity values for the post-annealed carbon nitride films is due to the elimination of the cyanogen impurity phase since this phase can increase the density of states at the Fermi level [18]. Importantly, the stability of the carbon nitride electrical properties to thermal processing make this material an attractive candidate for microelectronics applications.

We have also investigated the thermal conductivity of these films since the ability of carbon nitride to transport heat efficiently is an important consideration for potential applications such as microelectronics. The thermal conductivity of these carbon nitride thin films has been measured using an well-established ac ( $3\omega$ ) electrical technique [19]. In our measurements, a thin and narrow gold line was deposited onto carbon nitride thin films grown on silicon substrates, and this metal line, which served as both a heater and temperature sensing element, was used to determine the thermal conduction through the film. Significantly, the thermal conductivity calculated for the carbon nitride film from this data, 0.8 to 1.3 W/m-K, is among the highest observed for any type of amorphous material [19,20].

#### **IV. SUMMARY**

Carbon nitride thin films have been prepared by combining pulsed laser deposition and atomic beam techniques. The nitrogen composition was found to increase to a limiting value of 50%, and the composition was shown to be controlled by the overall film growth rate. Analysis of these results suggests that a key step in the growth mechanism involves a surface reaction between carbon and nitrogen. IR spectroscopy was used to elucidate the phases present in these carbon nitride films, and demonstrated that a cyanogen-like impurity occurs in films with nitrogen compositions greater than 30%. A thermal annealing process has been developed, however, to eliminate this impurity and yield a single phase C<sub>2</sub>N material. Systematic investigations of the electrical resistivity and thermal conductivity of the carbon nitride films reveal that this material is a good electrical insulator and thermal conductor. Furthermore, thermal annealing process was found to enhances significantly the resistivity without degrading the thermal conductivity. The new understanding of carbon nitride properties obtained from these studies provides a strong basis with which to assess the use of this material in high-performance application.

**ACKNOWLEDGMENTS.** We acknowledge some experimental help from Drs. Shoushan Fan and 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 Number DMR-9400396.

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