

Phases and physical properties of carbon nitride thin films prepared by pulsed laser deposition

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Abstract

Pulsed laser deposition combined with atomic beam techniques have been exploited to grow carbon nitride thin films with controlled nitrogen composition. The nitrogen composition in the thin films was found to increase as the laser fluence was decreased for laser ablation at both 532 and 248 nm wavelengths. Analysis of these carbon nitride materials shows that over a wide range of conditions the film growth rate determines the overall nitrogen composition, although at the lowest growth rates the composition saturates at a value close to 50% nitrogen. Infrared spectroscopy indicates that a cyanogen-like impurity is present in all of the films with nitrogen composition greater than 30%, and that the amount of this impurity increases with increasing nitrogen content. However, the cyanogen-like impurity phase was eliminated by a thermal annealing process to yield a single phase material. Systematic studies of the carbon nitride film electrical resistivity and thermal conductivity as a function of nitrogen composition will be discussed.

Keywords: Pulsed laser deposition; Carbon nitride; Atomic beam techniques

1. Introduction

Currently there is a great interest in the fundamental properties and potential applications of a new class of materials called carbon nitride solids [1]. This interest in carbon nitride solids was initially stimulated by theoretical studies of a hypothetical compound having a structure analogous to silicon nitride, β -C₃N₄ [2]. This theoretical work suggested that β -C₃N₄ should be reasonably stable and have a hardness comparable to or greater than diamond. Experimentally, a variety of approaches have been used in efforts to synthesize β -C₃N₄. Polymeric C–N–H materials have been obtained by plasma-assisted chemical vapor deposition using CH₄ and N₂ and pyrolysis of organic materials in a nitrogen atmosphere [3,4]. Shock wave compression of organic compounds containing C, N and H did not generate β -C₃N₄ but did yield well-ordered diamond [5]. This latter work indicates that diamond is more stable at high pressures and high temperatures than carbon nitride. These early attempts suggest that there are several key factors which must be considered in order to achieve a successful synthesis of carbon nitride, includ-

ing: (1) the purity of the carbon and nitrogen reactants (e.g., to avoid the formation of C–N–H polymers) and; (2) control of the carbon and nitrogen reactant energies (i.e., to kinetically trap this metastable phase).

Laser ablation and reactive sputtering are two techniques in which reactant purity and energy can be well-controlled in principle. Indeed, evidence for nanocrystalline β -C₃N₄ has been obtained for materials prepared by laser ablation [6,7] and reactive sputtering [8]. However, the nitrogen composition in these samples has been significantly lower than expected for a β -C₃N₄ stoichiometry [6–8], and further, many of these materials have contained significant quantities of oxygen [8,9]. The fact that the experimentally observed nitrogen compositions have been lower than originally predicted suggests that other stoichiometries and/or structures may be possible for binary carbon nitride. This idea is supported by recent theoretical studies which have shown that two other hypothetical C₃N₄ structures, a defect zinc-blende and a rhombohedral graphite-like one, should have a thermodynamic stability similar to or greater than β -C₃N₄ [10].

To address the critical issue of what carbon nitride phase or phases can be prepared requires systematic data addressing the carbon–nitrogen composition range and corresponding structures. Further, to evalu-

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ate potential applications of the new carbon nitride materials requires an understanding of key carbon nitride physical properties, such as the electrical and thermal conductivities, and how they correlate with composition and phase. Herein we address both of these points through systematic studies of growth and properties of carbon nitride solids prepared using a recently developed laser ablation/atomic beam deposition technique [6]. This experimental approach provides pure carbon and nitrogen reactants and the ability to control independently the energy of each reactant source. The nitrogen composition range, phases, and physical properties of thin film carbon nitride materials have been systematically studied. We find that as the laser fluence is decreased the nitrogen composition increases to a limiting value of close to 50% for laser ablation at 532 and 248 nm. Infrared spectroscopy indicates that a cyanogen-like impurity is present in all of the films with nitrogen compositions greater than 30%, and that the amount of this impurity increases with increasing nitrogen content. The cyanogen-like impurity phase can be eliminated by a thermal annealing process to yield a single phase material. Systematic investigations of the electrical and thermal conductivities of these carbon nitride films indicate that this material may be useful in microelectronics applications.

2. Experimental details

The experimental growth set-up is shown schematically in Fig. 1 [6]. Carbon fragments of C_n ($n = 1-4$) were 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_2 -seeded He flow was passed

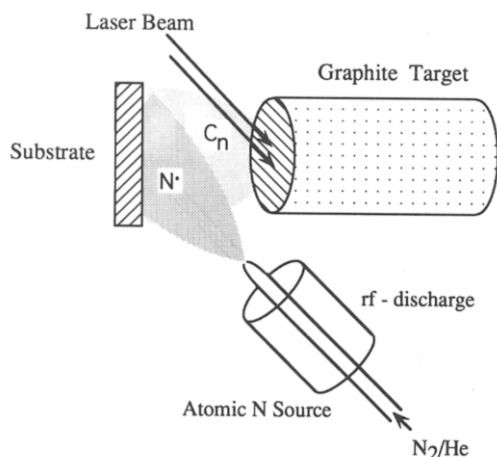


Fig. 1. Schematic diagram of the experimental set-up for carbon nitride growth. The apparatus is contained within a vacuum chamber that is evacuated by a liquid nitrogen trapped 5000 l s⁻¹ diffusion pump.

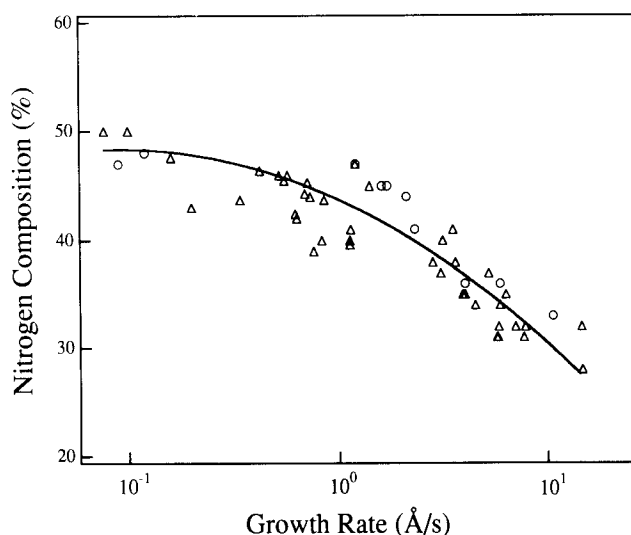


Fig. 2. Plot of the nitrogen composition in carbon nitride thin films versus growth rate at ablation laser wavelengths of 532 nm (Δ) and 248 nm (O).

through a radio frequency (rf) discharge source to generate a reactive nitrogen beam consisting primarily of atomic nitrogen. This reactive nitrogen atom beam ($>10^{18}$ atoms/sr-s) intersects the carbon ablation plume at the substrate surface. The optimal nitrogen beam conditions used in these studies were determined in our previous work [6]. The base pressure of the growth chamber is below 10^{-8} torr, and the working pressure with the atom nitrogen source is between 10^{-5} and 10^{-4} torr. The carbon nitride thin films were grown on quartz or HF-etched Si (100) substrates at ~ 200 °C.

3. Results and discussion

A series of carbon nitride films have been grown using different laser fluences at both 532 and 248 nm wavelengths. The compositions of these carbon nitride thin films were determined by Rutherford backscattering spectroscopy (RBS). In general, we find that the nitrogen composition increases as the laser fluence decreases [11]. For instance, when the graphite target was ablated with a relatively high fluence of 2.2 J cm^{-2} at 532 nm wavelength, the deposited film had a nitrogen composition of 32%. However, when the laser fluence was reduced to 1.0 J cm^{-2} the thin film contained 42% nitrogen. The inverse dependence of the nitrogen composition on laser fluence indicates that the growth rate is a critical factor determining carbon nitride composition since the fluence affects strongly the total flux of carbon [12,13]. Calculations of the growth rates for the carbon nitride film produced under a variety of conditions are consistent with this proposal. These results,

which are summarized in Fig. 2, show that as the film overall growth rate decreases, the nitrogen composition increases in the carbon nitride films. We suggest that this correlation of the nitrogen composition with film growth rate implies that a key step in carbon nitride growth mechanism involves a reaction between carbon and nitrogen at the growth surface and not in the gas phase.

Significantly, these growth versus composition studies also show that the nitrogen composition of carbon nitride films eventually saturates at a level close to 50% nitrogen. This saturation value suggests a possible stable carbon nitride phase that has a stoichiometry of CN. To determine whether CN is a stable phase requires knowledge of the phase purity of these thin films. We have addressed this issue using infrared (IR) spectroscopy. Typical IR spectra of carbon nitride films containing different overall nitrogen compositions are shown in Fig. 3. These spectra exhibit two overlapping bands at ~ 1500 and 1350 cm^{-1} and a third stretching mode at $\sim 2200\text{ cm}^{-1}$. The overlapping bands at \sim

1500 and 1350 cm^{-1} are believed to correspond to C=N and C–N stretching modes [11], and are consistent with an extended inorganic carbon nitride solid. The third band at $\sim 2200\text{ cm}^{-1}$ corresponds to a $\text{—C}\equiv\text{N}$ (cyanogen-like) stretching mode [11,14]. The cyanogen-like mode increases dramatically as the nitrogen composition in the film increases from 31 (Fig. 3(a)) to 45% (Fig. 3(b)). This $\text{—C}\equiv\text{N}$ bonding arrangement precludes an extended inorganic carbon nitride solid and represents an impurity phase. Hence, the increase in the nitrogen composition to $\sim 50\%$ must be due in part to the formation of this $\text{—C}\equiv\text{N}$ impurity phase, and thus we are forced to conclude that the carbon-nitrogen stoichiometry of the dominant carbon nitride phase should be less than 1:1.

Since cyanogen-like materials typically have a low thermal stability [14], we have also investigated the effects of thermal annealing on the composition and phases of these carbon nitride thin films. IR spectra recorded on the same carbon nitride thin film both before and after annealing at 550°C in vacuum for 3 h are shown in Figs. 3(b) and 3(c), respectively. Significantly, the intense $\text{—C}\equiv\text{N}$ mode at 2200 cm^{-1} observed in the as-grown film is nearly almost eliminated by this annealing process. RBS analysis shows that the annealing process reduced the overall nitrogen composition in this film from 45% to 34%. Systematic studies of the thermal annealing process carried out on a number of independent carbon nitride thin films show: (1) that the cyanogen-like impurities can be eliminated and; (2) that the nitrogen composition in the films initially containing more than 40% nitrogen reaches a common, stable composition of $\sim 35\%$ nitrogen. These results indicate that a single phase C_2N material can be prepared by our post-annealing process.

We have investigated the correlation between the nitrogen composition and the electrical properties of the carbon nitride materials. Carbon nitride thin films deposited on insulating quartz substrates were used in the resistivity measurements. In general, the resistivity of these materials increases with decreasing temperature, as expected for an insulator. We also find that resistivity increases systematically with increasing nitrogen composition, although this increase is highly non-linear. Using measurements at 200 K as an example, the resistivity initially increases slowly from approx. 0.2 to $0.8\text{ }\Omega\text{ cm}^{-1}$ as the nitrogen concentration increases from 0 to $\sim 30\%$. Further increases in the nitrogen composition lead to a rapid increase and saturation in resistivity at a value of $1\text{--}5 \times 10^3\text{ }\Omega\text{ cm}^{-1}$ at a nitrogen composition of $\sim 45\%$. We believe that the initial slow increase in resistivity corresponds to electron transport dominated by amorphous carbon, and that the saturation value represents the resistivity of carbon nitride. Because these measurements were made on materials containing cyanogen-like impurities, we believe that the

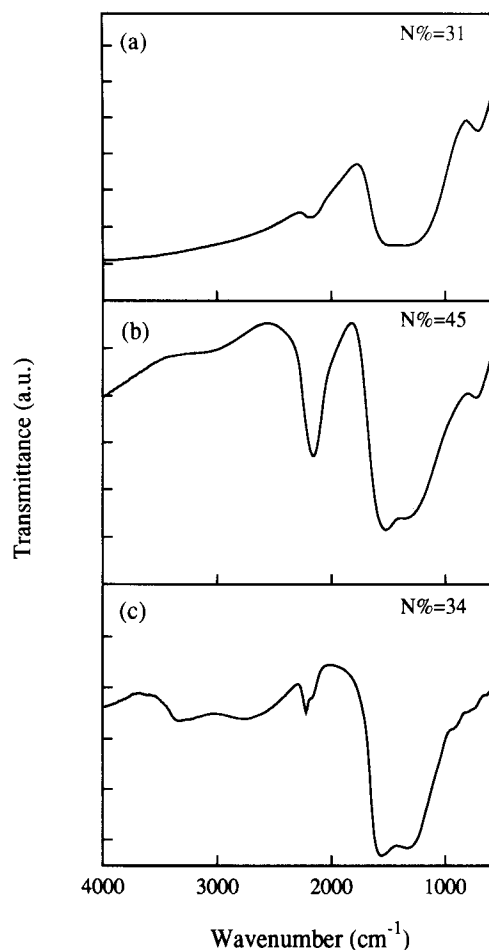


Fig. 3. IR spectra of carbon nitride films (Nicolet, Model 5PC). Spectra (a) and (b) were recorded on as-grown thin films. The spectrum in (c) was recorded on the same carbon nitride sample as in (b) but after annealing in vacuum for 3 h at 550°C . The nitrogen compositions of the films in (a)–(c) were determined by RBS.

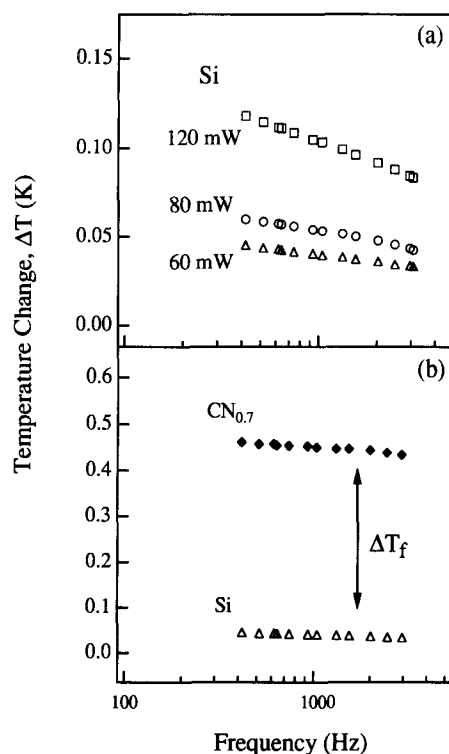


Fig. 4. (a) Change in temperature (ΔT) vs. frequency for a Si substrate at 298 K. The thermal conductivity values calculated for the three different input powers were similar. (b) Measured ΔT vs. frequency at 298 K for a bare Si substrate and a 2.1 μm thick carbon nitride film grown on a Si substrate. The data were recorded using an input power of 60 mW.

intrinsic resistivity of carbon nitride will be significantly higher.

The thermal conductivity of the carbon nitride thin films were measured using a well-established ac (3ω) electrical technique [15]. In this measurement, a 25 μm -wide, 1500 \AA -thick gold line was deposited onto clean silicon substrates or onto a carbon nitride film grown on silicon substrates; the gold line serves both as a heater and temperature sensing element to determine the thermal conduction through the sample. When an ac current passes through the metal line with a frequency of ω , the temperature change, ΔT in this metal line is related to the thermal conductivity of the sample underneath the metal line. For bulk samples or thick films, $\Delta T \propto (P/l\pi\Lambda) \ln(\omega)$, where P/l is the amplitude of the power per unit length generated by the ac current and Λ is the thermal conductivity of the sample. Fig. 4(a) shows plots of ΔT as a function of frequency and input power for a gold line deposited directly onto a bare Si (100) substrate. The thermal conductivity of Si determined from this data, 96 W/m-K, is consistent with the value reported for bulk silicon [16]. A thin film sample deposited onto a substrate behaves as a simple thermal resistance and adds a frequency-independent temperature shifting to the ΔT on the substrate. This temperature shift is $\Delta T_f = (P/l\Lambda_f)(t/2b)$, where Λ_f is the

thermal conductivity of the thin film, t is the film thickness and $2b$ is the width of the heating metal line [15]. Our measurements (Fig. 4(b)) of the carbon nitride films exhibited a frequency-independent shift in ΔT when compared to the Si substrate. Significantly, the thermal conductivity at 300 K 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 [17,18].

4. Conclusions

Pulsed laser deposition combined with atomic beam techniques has been used to successfully grow carbon nitride thin films with controlled nitrogen compositions. The nitrogen composition was found to increase to a limiting value of 50% as the fluence was reduced for laser ablation at both 532 nm and 248 nm wavelengths. These growth-composition studies indicate that the overall film growth rate determines the average nitrogen composition. Infrared 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%. However, thermal annealing was shown to eliminate this impurity and yield a single phase carbon nitride 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, and hence may be an attractive candidate for high-performance microelectronics applications.

Acknowledgements

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