

Pulsed Laser Deposition and Physical Properties of Carbon Nitride Thin Films

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Carbon nitride thin films were grown using an approach that combines pulsed laser deposition and atomic beam techniques. The composition and phases of the carbon nitride materials obtained from the reaction of laser ablated carbon and atomic nitrogen 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 and 248 nm. Analysis of these experiments show that the growth rate determines the overall nitrogen composition, and thus suggests that a key step in the growth mechanism involves a surface reaction between carbon and nitrogen. Infrared spectroscopy has also been used to assess the phases present in the carbon nitride thin films. This spectroscopic measurement indicates that a cyanogen-like impurity occurs in films with nitrogen compositions greater than 30%. Investigations of the effects of thermal annealing have been carried out, and show that the impurity phase can be eliminated to yield a single phase material. In addition, systematic measurements of the electrical resistivity and thermal conductivity of the carbon nitride films were made as a function of nitrogen content. The implications of these results are discussed.

Key words: Carbon nitride, pulsed laser deposition, thin films

INTRODUCTION

Carbon nitride solids are an exciting class of materials that have been the focus of both basic and applied research.¹⁻³ Interest in carbon nitride materials was first stimulated by theoretical studies of a solid analogous to β -silicon nitride, β -C₃N₄.³ This work suggested that β -C₃N₄ should be a reasonably stable material and possess a hardness comparable to or greater than diamond. Experimental efforts directed toward the synthesis of β -C₃N₄ have employed a variety of techniques, including plasma-assisted chemical vapor deposition, shock wave compression, thermal pyrolysis, reactive sputtering, and laser ablation.^{2,4-10} Although evidence for nanocrystalline β -C₃N₄ has been obtained for materials prepared by laser ablation^{2,4,6} and reactive sputtering,⁹ the overall

nitrogen composition of these materials has been significantly less than the C₃N₄ stoichiometry. Furthermore, we have pointed out that the reported diffraction data are not unique to the β -C₃N₄ structure but can also be explained by a tetragonal-CN phase analogous to the high-pressure form of GeP.²

The clear difference between the theoretically predicted stoichiometry C₃N₄ and compositions observed experimentally suggests that other stoichiometries and/or structures may be possible for binary carbon nitride. Indeed, more recent theoretical studies 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 -C₃N₄.¹¹ There is little experimental data available, however, that either tests these new predictions or probes systematically the composition limits and phases of carbon nitride compounds. Furthermore, the key physical properties of carbon ni-

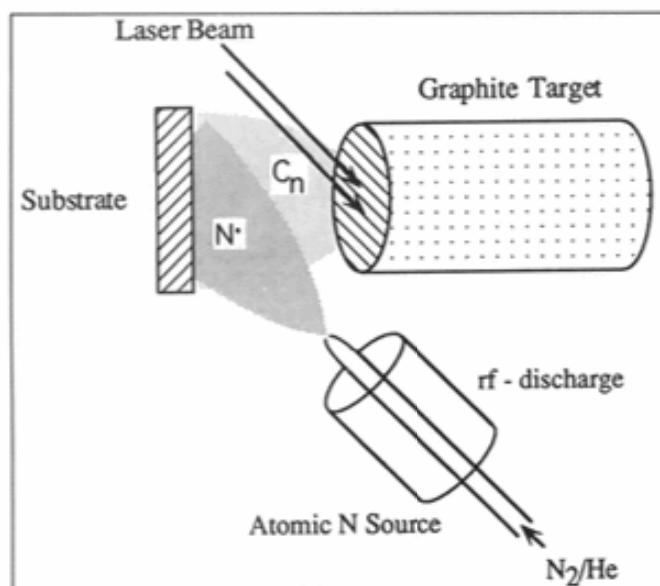


Fig. 1. Schematic diagram of the carbon nitride growth apparatus. The substrate, rotating graphite target, and atomic nitrogen source are all contained within a vacuum chamber that is evacuated by a liquid nitrogen trapped 5000 l/s diffusion pump.

tride, for example the electrical and thermal conductivities, have not been studied systematically as a function of composition and phase. Such latter work is particularly important in order to evaluate potential application of thin film carbon nitride materials.

To this end, we describe herein 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 was decreased at both 532 and 248 nm. Analysis of these experiments show that the growth rate determines the overall nitrogen composition and suggests that a key step in the growth mechanism involves a surface reaction between carbon and nitrogen. Infrared spectroscopy measurements show that a cyanogen-like impurity occurs in films with nitrogen compositions greater than 30%, although this impurity phase can be eliminated by thermal annealing to yield a single phase 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.

EXPERIMENTAL

Carbon nitride thin films were prepared using an approach that combines pulsed laser ablation with an atomic beam source.^{2,4} The experimental setup is schematically shown in Fig. 1. Carbon fragments 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). The base pressure of this chamber is below 10^{-8} Torr, and the working pressure is usually between 10^{-5} to 10^{-4} Torr. A N_2 -seeded He

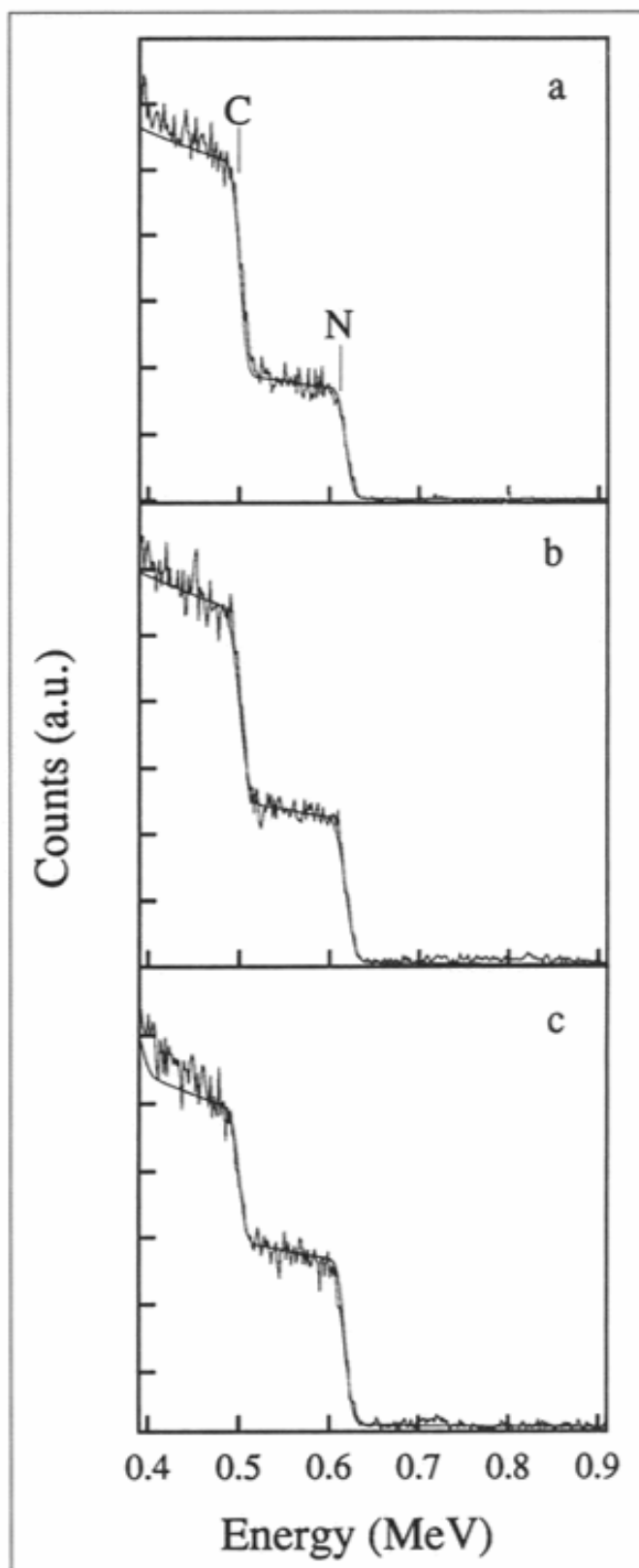


Fig. 2. RBS spectra (General Ionics Model 4117, 2.0 MeV He ion beam) of carbon nitride films. The C and N compositions were determined from fits (smooth lines) to the experimental data. The films in (a), (b), and (c) are 2.3, 2.1, and 1.7 mm thick, respectively.

flow was passed through a radio frequency (rf) discharge source to generate a reactive nitrogen beam consisting primarily of atomic nitrogen. This reactive