

Research News

Synthesis of Covalent Carbon–Nitride Solids: Alternatives to Diamond?

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A central challenge of solid-state chemistry is to rationally synthesize new materials possessing useful mechanical, electrical, optical, and/or magnetic properties. To achieve this goal requires the development of synthetic methods for the assembly of atoms and clusters into predetermined three-dimensional arrays. Traditional inorganic materials synthesis techniques, which require high-temperature reactions in order to facilitate diffusion, generally preclude the rational assembly of atoms into specific arrays since the products are restricted to those phases stable at high-temperature.^[1] For example, heating graphite in molecular nitrogen does not provide carbon–nitride solids, thus suggesting that carbon–nitride phases are thermodynamically unstable relative to graphite and N_2 at temperatures sufficiently high that they might react.

Binary carbon–nitride solids are, however, an important synthetic goal since they are expected to possess unique and useful properties.^[2, 3] Liu and Cohen predicted using *ab initio* calculations that the hypothetical carbon–nitride solid β - C_3N_4 should be metastable and have a hardness comparable to or greater than diamond.^[4, 5] This solid was proposed to adopt the structure of β - Si_3N_4 thereby consisting of an infinite three-dimensional network of covalent carbon–nitrogen bonds (Fig. 1).

After considering the stability of graphite and molecular nitrogen, it is perhaps not unexpected that traditional high-temperature reactions between these species fail to yield the β - C_3N_4 structure. To overcome the limitations imposed by classical methodologies of solid-state chemistry and provide access to these potentially exciting materials requires better control of the reactants and reactions that might lead to β - C_3N_4 . To this end we have implemented a new experimental approach that combines pulsed laser ablation (to generate reactive carbon fragments) and a high-flux atomic nitrogen beam (a reactive nitrogen source). Employing this approach it has been possible to prepare covalent carbon–nitride for the first time.^[6]

The synthesis of covalent carbon–nitride solids has been explored previously, although little success was achieved. For example, plasma decomposition of methane and molecular nitrogen led to the formation of amorphous C–N–H

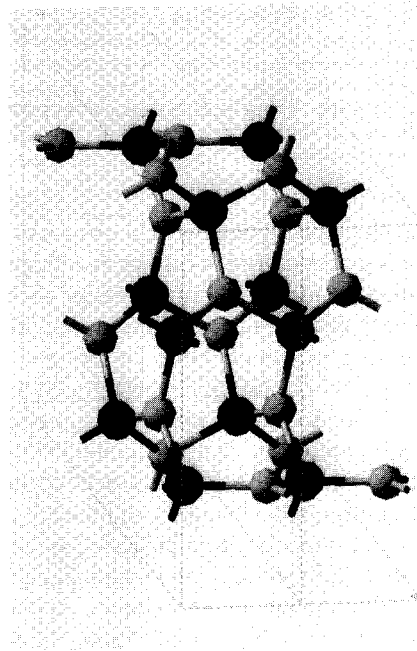


Fig. 1. Computer model of β - C_3N_4 displaying two unit cells. Each sp^3 hybridized carbon atom (black) is bonded to four nitrogen atoms (gray) in a distorted tetrahedral geometry, while each sp^2 hybridized nitrogen is bonded to three carbon atoms in a trigonal planar geometry.

solids and no evidence of β - C_3N_4 .^[7] Similar products were also obtained by pyrolytic decomposition of C–N–H organic materials.^[8] These results suggest that the thermodynamic stability of C–H and N–H products (versus C–N and H_2) under the above reaction conditions preclude the formation of β - C_3N_4 .

Shock-wave compression of organic C–N–H precursors has also been used in attempts to prepare carbon–nitride.^[9] However, the only crystalline product observed from shock compression was diamond. This observation indicates that at ultrahigh pressure diamond and N_2 are more stable than C_3N_4 . In addition, reactive sputtering of graphite with N_2 and laser ablation of graphite in N_2 have been used to prepare nitrogen-containing carbon films.^[10–13] The materials obtained in these studies do not appear, however, to be crystalline carbon–nitride, β - C_3N_4 .^[12]

The new synthetic approach adopted by us^[6] is outlined schematically in Figure 2. A pulsed laser is used to ablate a

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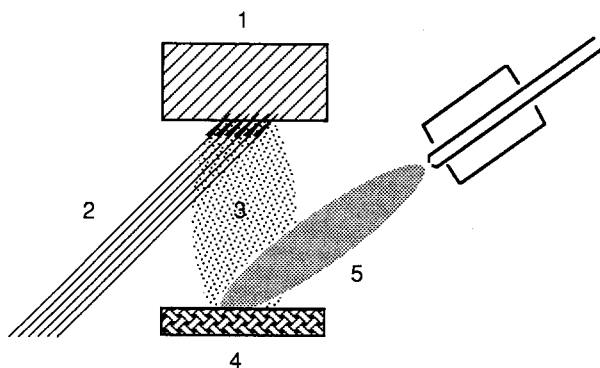


Fig. 2. Schematic diagram of the carbon-nitride synthetic apparatus. A rotating graphite target (1) is irradiated with the focused output of a pulsed laser (2), and the resulting carbon ablation plume (3) is directed towards the substrate (4). The atomic nitrogen beam (5) intersects the carbon fragments at the substrate surface. Components 1, 3, 4, and the atomic beam source are housed within a stainless steel vacuum chamber.

graphite target thereby creating reactive carbon fragments. The size and energies of the carbon fragments can be controlled through variations in the laser wavelength and power density, thus providing significant flexibility in the properties of the carbon reactants. Of perhaps greater importance is the choice of nitrogen reactant used in the synthesis: to avoid thermodynamic constraints imposed by molecular nitrogen or nitrogen-hydrogen compounds, we utilize atomic nitrogen. In our apparatus an atomic nitrogen beam is generated using a radio frequency (rf) discharge within an alumina nozzle through which N_2 seeded in helium flows.^[6] This process can produce a very high flux of atomic nitrogen ($> 10^{18}$ atoms/sr-s). Furthermore, by varying the N_2 :He ratio and the rf power it is possible to control both the flux and energy of this critical reactant.

The synthetic control afforded using this approach is clearly evident from compositional analyses of thin films prepared using molecular nitrogen and varying fluxes of atomic nitrogen. The C-N stoichiometry in these materials was quantitatively determined using Rutherford backscattering spectroscopy (RBS). Materials prepared by laser ablation of graphite at a 532 nm wavelength with the rf discharge off or in a background of 200 mtorr nitrogen consisted only of amorphous carbon; that is, molecular nitrogen does not appear to react with the carbon fragments produced by laser ablation. However, the C:N ratio systematically decreases (increasing nitrogen content) as the flux of atomic nitrogen is increased (Fig. 3). The highest percentage nitrogen (40%) obtained in materials prepared using a frequency doubled Nd-YAG laser (532 nm) for ablation was, however, less than that expected (57%) for pure β - C_3N_4 . The stoichiometry determined by RBS represents an average, and thus, local regions of these carbon-nitride materials may contain higher or lower nitrogen concentrations than the average determined by RBS. Hence, some regions of these materials might have the predicted C_3N_4 stoichiometry.

This idea was tested using selected-area transmission electron diffraction to probe the structure of small regions of the

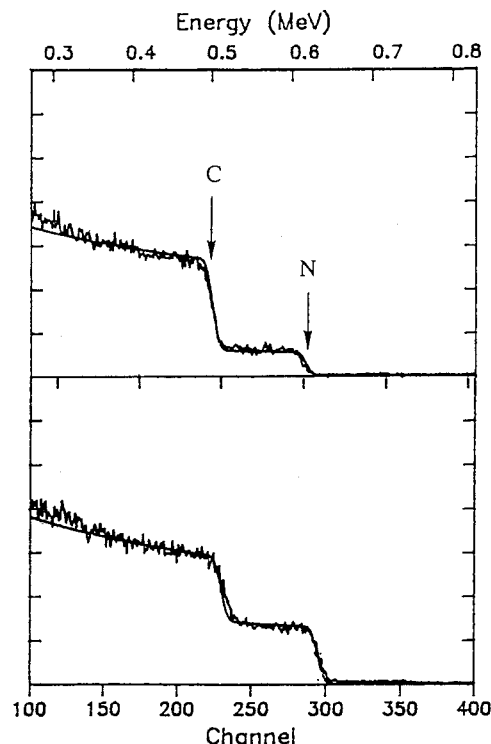


Fig. 3. RBS spectra recorded on carbon-nitride films produced using 1% (top) and 12% (bottom) molecular nitrogen seeded in He. Qualitatively, it is clear that the step height, which is proportional to concentration, for nitrogen increases relative to carbon in the solid prepared using the higher flux of nitrogen. Fits (smooth solid lines) to the experimental data show that the nitrogen content increases from 15 to 40% in these two films.

carbon-nitride materials.^[6] Overall, the carbon-nitride films prepared using the Nd-YAG laser at low-temperature ($T < 400^\circ C$) exhibited poor crystallinity, although diffraction rings are still observed from regions within these samples. Diffraction rings were not detected, however, from samples prepared using only molecular nitrogen. These data thus suggest that a crystalline carbon-nitride phase has been prepared from the reaction of ablated carbon fragments and atomic nitrogen.

Additional insight into the carbon-nitride solid produced by this approach was provided by diffraction investigations of materials containing varying average nitrogen contents (determined by RBS). This work showed that the same diffraction ring pattern was obtained from carbon-nitride samples with average nitrogen contents of 25–40%, and that the intensity of the rings increased with increasing nitrogen content. Taken together, the diffraction studies indicate that a single, crystalline carbon-nitride phase was obtained using our new synthetic strategy, although the solids as a whole were somewhat inhomogeneous in their local nitrogen content.

The structure of this crystalline carbon-nitride phase has been inferred from comparisons to the diffraction patterns calculated for hypothetical carbon-nitride structures. Notably, the six diffraction rings that are reproducibly observed can be consistently indexed as the (101), (210), (320), (002),

(411) and (611) reflections for the proposed structure of β - C_3N_4 .^[6] Other reasonable structural comparisons made to date do not, however, provide an adequate explanation of the experimental diffraction data. On this basis it seems likely that crystalline β - C_3N_4 has been at last produced, albeit in impure form.

What of the future? There remain a number of important questions that must be addressed. Foremost, can pure β - C_3N_4 (or another phase) be prepared? This lies at the heart of all work since pure materials are needed both for better structural characterization and unambiguous measurements of physical properties.

Notably, significant advances have been made towards achieving this goal. We previously speculated^[6] that incomplete reaction between the laser-ablated carbon fragments and atomic nitrogen could explain the observation that the carbon–nitride materials contain a single-crystalline phase distributed within an amorphous matrix. Our experimental approach provides, however, the flexibility to control carbon fragment size and thereby explore this hypothesis. Specifically, it is known from previous work^[14] that the mean distribution of carbon fragments produced by laser ablation decreases with decreasing laser wavelength.

We have found that carbon–nitride films prepared using an excimer laser (ArF, 193 nm) for graphite ablation and the same atomic nitrogen fluxes as used above have nitrogen contents typically in excess of 50% (Fig. 4). These results are quite exciting since the material composition is now approaching that of the proposed solid β - C_3N_4 . We thus believe there is significant promise that a pure phase will be obtained in the future, and with this in hand, it will then be possible to answer the question whether a material harder than diamond indeed exists.

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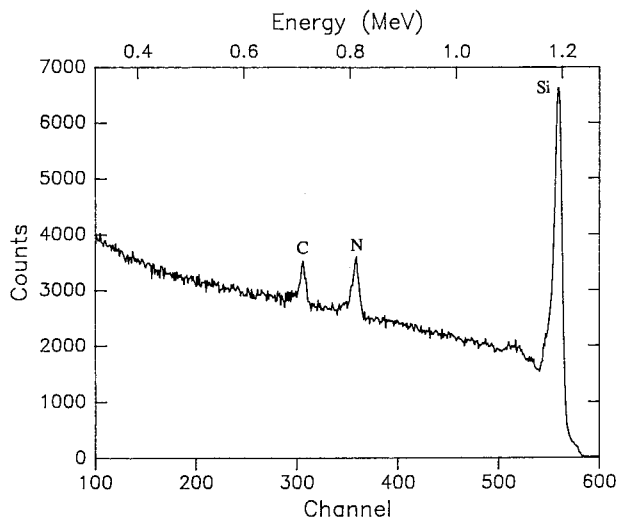


Fig. 4. RBS spectrum recorded in a glancing angle geometry for a film prepared using a 193 nm excimer laser. Analysis of the carbon and nitrogen peaks indicates that nitrogen content is in excess of 50%. The large Si peak corresponds to the substrate surface.

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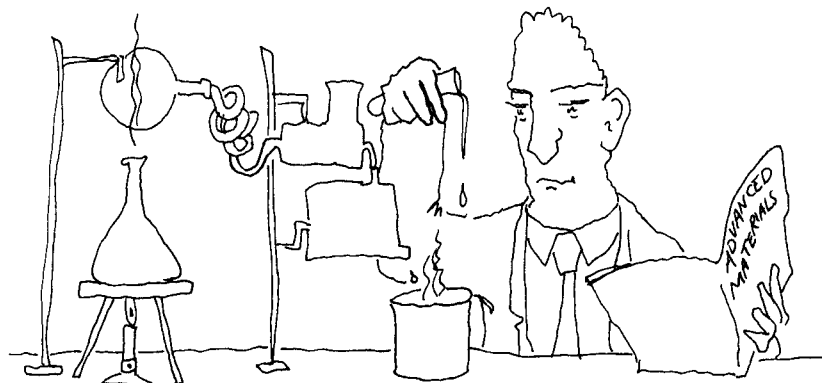
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