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Nitrogen-driven sp^3 to sp^2 transformation in carbon nitride materials

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The coordination of carbon as a function of nitrogen concentration in energetically deposited carbon nitride films has been systematically studied. A structural transformation from primarily sp^3-bonded to sp^2-bonded carbon and a density decrease from 3.3 to 2.1 g/cm^3 were observed as the nitrogen concentration increases from 11 to 17 %. Calculations on nitrogen-substituted carbon clusters indicate that there is a preference to form sp^2-bonded carbon when the nitrogen concentration is larger than 12%. The implications for these results to the synthesis of superhard carbon nitride materials are discussed. [S0163-1829(98)51006-5]

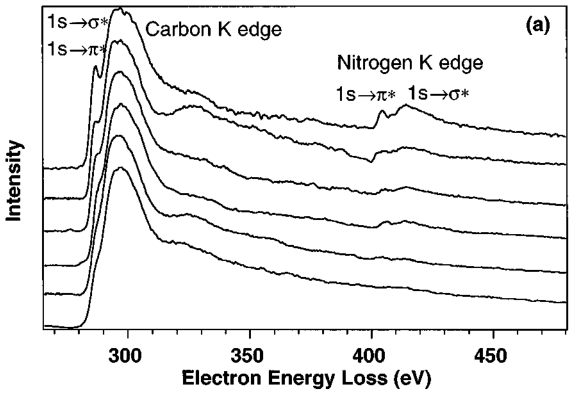
Carbon nitride materials have been the focus of considerable experimental and theoretical attention since Cohen and co-workers proposed that β-C_3N_4, a carbon nitride material analogous to β-Si_3N_4, should have a hardness comparable to that of diamond.[1] Subsequent calculations have shown that other crystalline C_3N_4 structures should have stabilities comparable to or greater than that of β-C_3N_4,[2,3] and that many of these structures should be quite hard (e.g., cubic C_3N_4). In addition, the energetically most stable material, rhombohedral C_3N_4, which has a graphitelike structure, is expected to be quite soft. The local structural property that distinguishes potentially superhard and dense C_3N_4 structures from low-density, softer material is the carbon coordination: hard materials require tetrahedral or sp^3-bonded carbon in the C_3N_4 network, while sp^2-bonded carbon will lead to much softer materials. This requirement of having sp^3-bonded carbon in a hard carbon nitride is completely analogous to that in amorphous diamondlike carbon (DLC).[4]

Extensive experimental effort has been placed on preparing carbon nitride materials using physical deposition and other techniques.[5–12] In general, the materials produced in these studies have been amorphous with nitrogen compositions less than 50%.[5–8] Early on our group[6] and others[7] reported the observation of small β-C_3N_4 crystallites on the basis of electron diffraction data. Unfortunately, these studies and subsequent ones have not identified the composition or local carbon bonding in the diffracting crystallites, and thus we do not think that this diffraction data provides strong evidence for sp^3-bonded β-C_3N_4. In support of this analysis, we note that all recent electron energy loss spectroscopy (EELS) studies, which provide an unambiguous determination of the local carbon coordination, have found dominant sp^2 or sp^2/sp carbon bonding.[9–12] Hence, it is important to ask whether it is possible to obtain high-density, sp^3-bonded carbon nitride solids using physical deposition techniques; that is, does the incorporation of nitrogen intrinsically favor low-density, sp^2-bonded carbon? Indeed, previous studies of nitrogen-doped DLC indicate that carbon relaxes to sp^2 bonding at less than 5% nitrogen composition.[13]

We have systematically characterized the local atomic coordination as a function of nitrogen composition in carbon nitride thin films prepared using energetic deposition conditions that produce metastable, sp^3-bonded DLC.[4] Pulsed laser deposition (PLD) was used to generate energetic carbon species and a plasma source[5,6] was used to create a controlled flux of reactive atomic nitrogen. Using optimal PLD conditions that produce 70% sp^3-hybridized DLC films, we find that carbon nitride materials containing up to 12% nitrogen can be grown without reducing the percentage of sp^3-bonded carbon. Further increases in the nitrogen composition, however, produce a structural transformation to carbon nitride materials in which carbon has predominantly sp^2 bonding. Measurements of the sample density further show that this structural transformation is accompanied by an abrupt reduction from 3.3 ± 0.3 to 2.1 ± 0.3 g/cm^3. The origin of this nitrogen-driven transformation has been investigated using *ab initio* Hartree-Fock (HF), density functional (DF) and semiempirical calculations on model clusters. These calculations suggest that above 12% nitrogen there are thermodynamic and kinetic preferences for sp^2- vs sp^3-bonded structures.

Carbon nitride thin films were prepared by plasma-assisted PLD.[6,14] Briefly, energetic carbon species were generated by ablating a carbon target with a KrF excimer laser (248 nm, 17 ns pulse width), and atomic nitrogen was produced using a rf discharge. By adjusting the N_2 concentration in the N_2/He plasma gas mixture, carbon nitride films with nitrogen compositions between 0 and 50 % were controllably grown. The optimal laser power density for producing DLC at typical carbon nitride growth pressures (1×10^9 W/cm^2 at $0.5-2\times10^{-4}$ Torr) was determined using combined time-of-flight mass spectroscopy and EELS studies.[15] All samples were grown at 77 K. EELS was used to determine the local coordination of carbon and nitrogen in the carbon nitride films.[16,17] The EELS data were recorded using a VG HB603 scanning transmission electron microscope equipped with a Gatan parallel EELS detector. The nitrogen composition was determined by EELS ($[N]<10\%$) or by Rutherford backscattering spectroscopy (RBS) and EELS ($[N]>10\%$).

The central results of our studies are shown in Fig. 1. In Fig. 1(a), EELS data showing the $1s\rightarrow\pi^*$ and $1s\rightarrow\sigma^*$ transitions for carbon and nitrogen are displayed for carbon nitride samples containing up to 25% nitrogen. The samples were grown under similar conditions (i.e., laser power density, pressure, and substrate temperature) that produce 60–70 % sp^3-bonded carbon in the absence of nitrogen in the



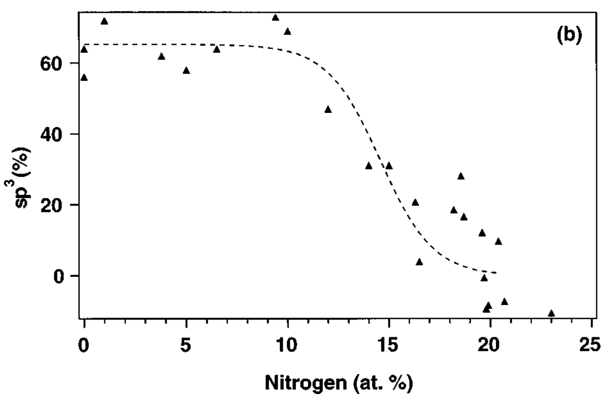


FIG. 1. (a) EELS spectrum of carbon and nitrogen K edges recorded in films with nitrogen percentages of <1, 5, 8, 12, 15, and 25 % (bottom to top). The EELS data were recorded with an electron beam energy of 250 keV; the detector resolution was 0.7 eV. (b) The percentage of sp^3-bonded carbon vs nitrogen composition.

plasma source. The relative intensities of the $1s\rightarrow\pi^*$ and $1s\rightarrow\sigma^*$ transitions in both the carbon K edge and nitrogen K edge provide a good measure of the percentage of sp^2-bonded carbon and nitrogen, respectively.[4,12,18] In pure carbon films grown under these conditions, the carbon $1s\rightarrow\pi^*$ transition appears as a low-energy shoulder on the broad peak that arises from the $1s\rightarrow\sigma^*$ and higher energy transitions. Qualitatively, the spectra in Fig. 1(a) show that the intensity of the $1s\rightarrow\pi^*$ peak remains unchanged for nitrogen compositions ≤10%, but then increases with increasing nitrogen composition; well-defined $1s\rightarrow\pi^*$ peaks are observed in carbon nitride samples containing more than 20% nitrogen. On the other hand, well-defined nitrogen $1s\rightarrow\pi^*$ peaks are found in all of the samples. These nitrogen K-edge results suggest that nitrogen has sp^2 bonding independent of its percentage in the films.[19]

The carbon K-edge EELS data have been analyzed to determine quantitatively the relationship between local carbon bonding and nitrogen concentration in the carbon nitride samples.[16,17] In this analysis, the ratio of the intensities of the carbon $1s\rightarrow\pi^*$ and $1s\rightarrow\sigma^*$ transitions in the carbon nitride samples relative to a standard containing 100% sp^2-bonded carbon was used to calculate the percentage of sp^3-bonded carbon. Significantly, our results demonstrate that there is a relatively sharp transition with increasing nitrogen composition in which the percentage of sp^3-bonded carbon drops from 60–70 % to almost zero as the nitrogen concentration increases from 11 to 17 %. The midpoint of this transition is

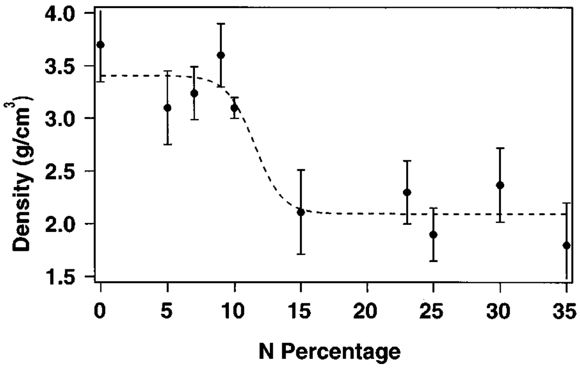


FIG. 2. The density of carbon nitride films vs nitrogen composition. Film density was calculated directly from the thickness and areal atom density determined by cross-sectional scanning electron microscopy and RBS, respectively.

around 14% [Fig. 1(b)]. Although there is some uncertainty in the absolute percentages determined by EELS, the large change in percentage sp^3-bonded carbon at the transition point is robust. Furthermore, analysis of EELS spectra from samples containing 25–50 % nitrogen showed no evidence for sp^3-bonded carbon within the uncertainties of the measurements.

We have also characterized the densities and infrared (IR) spectra of these materials as a function of nitrogen composition to obtain greater insight into the nature of this sp^3 to sp^2 transition. Figure 2 shows the density of the carbon nitride samples vs nitrogen composition. There is a sharp decrease in density from 3.3±0.3 to 2.1±0.3 g/cm^3 as the nitrogen composition increases from 10 to 15 %. This transition to lower density materials thus occurs over the same range of nitrogen compositions where we observe the local carbon coordination to change from sp^3 to sp^2. These observations are consistent with calculated and measured density changes for different atomic coordination. In proposed crystalline carbon nitride materials, the densities of structures with sp^3-bonded carbon (e.g., β-C_3N_4: 3.57 g/cm^3) are similar to that of diamond but larger than the density of rhombohedral C_3N_4 with sp^2-bonded carbon (2.55 g/cm^3). In addition, tight-binding molecular dynamics calculations of the cohesive energy vs density for different composition amorphous carbon nitride materials suggest a similar trend.[20] We believe that our microscopic and macroscopic results provide unambiguous experimental evidence for a nitrogen driven relaxation of sp^3-bonded carbon to sp^2-bonding at approximately 14% nitrogen.

To further confirm that the sharp decrease in sp^3-bonded carbon is not due to the formation of cyanogen-like (i.e., C≡N), sp bonding, we have recorded IR spectra on these samples. In general, the IR spectra of carbon nitride materials exhibit a broad band between 1550 and 1350 cm^{-1}, which corresponds to C═N and C—N stretching modes, and may also exhibit a band at ~2200 cm^{-1} corresponding to the C≡N stretching mode.[8] Figure 3 shows that there is little if any C≡N bonding in carbon nitride samples with nitrogen compositions ≤25%; however, further increases in nitrogen composition do produce significant C≡N structure.[10] These IR data thus strongly suggest that

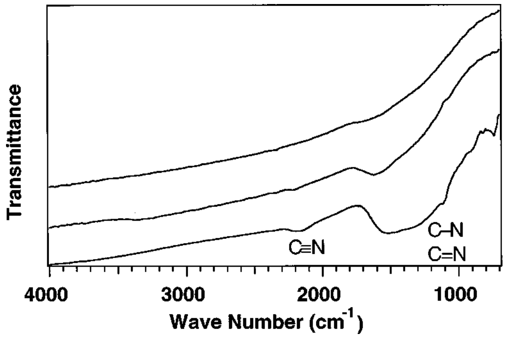


FIG. 3. IR spectrum of carbon nitride films with 38, 25, and 10 % nitrogen (bottom to top). The broad band between ~1550 and 1350 cm $^{-1}$ corresponds to C═N and C—N stretching modes. The band at ~2200 cm^{-1} corresponds to the C≡N stretching mode.

the formation of cyanogenlike structures do not drive the observed sp^3 to sp^2 transformation in carbon bonding above 12% nitrogen composition.

To obtain greater insight into the origin of this nitrogen driven transformation, we have used *ab initio* HF, DF and semiempirical calculations to evaluate the properties of several model clusters. The primary clusters used in these calculations consist of a core of 38 carbon atoms that are capped by 40 hydrogen atoms to eliminate dangling bonds (Fig. 4). The basic core structure is that of crystalline diamond. To study the effect of nitrogen at the 12% level where the structural transformation is observed experimentally, we replace two carbon atoms within one diamond unit cell with nitrogen atoms. This yields a local (for the unit cell) nitrogen concentration of 12.5%; the remaining carbon atoms in the cluster were required to minimize finite size effects. The rationale behind this substitution strategy was to model locally the effect of two nearby nitrogens with separations that are similar to that in homogeneous films near the sp^3 to sp^2 transition point. Two distinct structures representative of those studied are shown (Fig. 4). In structure 1, all the atoms remain single bonded despite some distortion due to the incorporation of nitrogen [Fig. 4(a)]. This structure thus represents an intermediate that could form when first inserting nitrogen atoms into an sp^3-bonded carbon lattice, and formally has one unpaired electron on carbon/nitrogen. In structure 2, a double bond is formed between C_1 and C_3 to model the relaxation to a sp^2-bonded structure [Fig. 4(b)]. With regards to film growth, a crucial question is whether a plausible sp^3-bonded intermediate [Fig. 4(a)] is reasonably stable during growth relative to the sp^2-bonded structure [Fig. 4(b)]. HF and DF calculations with B3LYP/6-31G(d)//HF/STO-3G methods[21] were used to optimize geometry and calculate the total energies of both structures. We first tested this approach by reinvestigating the structural relaxation induced by one nitrogen atom in a diamond lattice, and found excellent agreement with previous calculations.[22,23]

The optimized cluster structures with two nitrogens show some similarities to previous studies of the relaxation around single nitrogen centers in diamond. In structure 1 [Fig. 4(a)], the repulsion between the nitrogen lone pair and the carbon dangling bond produces an increase in the bond length of C_1-N_1 and C_2-N_2 to ~2.38 Å (from 1.54 Å in diamond), although carbon and nitrogen are otherwise connected by single bonds. In structure 2 [Fig. 4(b)], the C_1-N_1 and C_3-N_2 distances increase to about 2.38 Å and a double bond is formed between C_1 and C_3. We find that the total energy of structure 2, which contains the carbon-carbon double bond, is 0.89 eV lower than that of the intermediate structure 1. DF calculations carried out on the two analogous structures in which the nitrogen atoms were placed on the same side (i.e., with a somewhat smaller N-N separation) also showed that the carbon double structure is significantly favored.[22] More importantly, the formation of the double bond structure can occur by small concerted displacements of C_1, C_3, N_2, and C_2, and thus should have a moderate barrier; that is, intermediate structure 1 can convert readily to the energetically favored structure 2.[24] In addition, semiempirical (AM1) calculations were carried out on a 50 carbon atom cluster to explore how the energy difference between the two basic structure types varies with N-N separation or the effective nitrogen composition.[23] These calculations show that the energy difference decreases for a lower, 10% nitrogen composition, and furthermore, that the formation of the double bond structure should involve a large kinetic barrier associated with large displacive motion of several atoms in order to generate a double bond structure. Our calculations thus suggest that the formation of the double bond structure from a plausible growth intermediate like structure 1 involves only a small energetic barrier for >12% nitrogen, and thus that

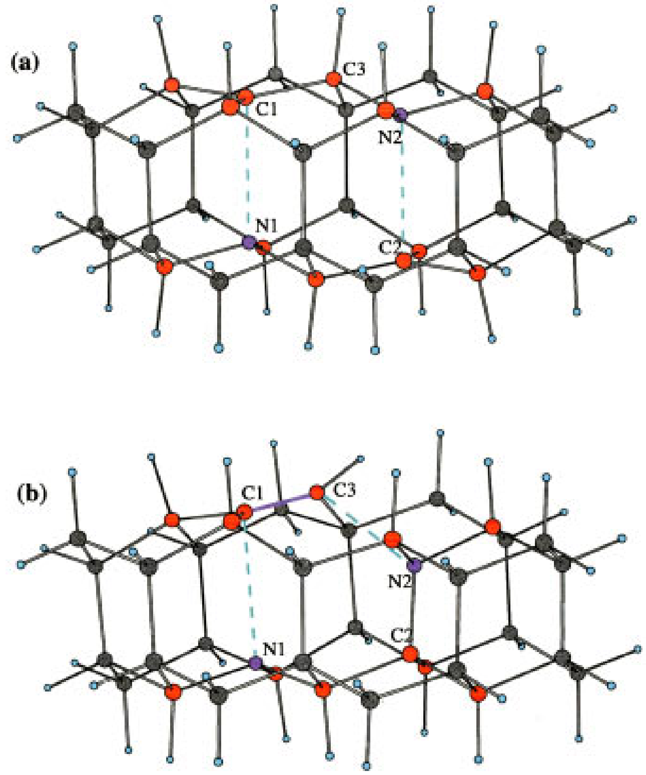


FIG. 4. (Color) Carbon nitride model clusters containing two nitrogen atoms. In intermediate structure 1 (a), the distance between C_1 and N_1, and that between C_2 and N_2 increase due to the repulsion between carbon and nitrogen lone pairs. However, all atoms are connected by single bonds. In structure 2 (b), the distances between C_1 and N_1, and N_2 and C_3 increase due to lone pair repulsion, and there is a double bond between C_1 and C_3. In both structures, the carbon atoms indicated in red undergo relaxation; nitrogen atoms are indicated in blue.

there is a strong kinetic preference for the observed sp^2-bonded products even under growth conditions that favor sp^3-bonded DLC.

Our experimental data and calculations have significant implications for the synthesis of proposed high-density, sp^3-bonded C_3N_4 materials. These data suggest that it will be difficult to prepare superhard, amorphous carbon nitride materials containing large amounts of nitrogen using physical deposition methods. Even at the low growth temperatures used in our studies it is apparent that the thermodynamic and kinetic preferences of sp^2-bonded structures dominate the product materials for nitrogen compositions >12%. We now believe that this is an intrinsic limitation that will be difficult to overcome unless intermediates like structure 1 can be stabilized. It is still likely that crystalline sp^3-bonded C_3N_4 structures can be formed, although we believe that different synthetic approaches will be required. For example, plasma-assisted chemical vapor deposition, which could potentially stabilize intermediates such as structure 1, has produced interesting crystalline materials,[25] although the composition and bonding within crystallites should still be clarified. In addition, we believe that high-pressure methods provide a most promising avenue for achieving superhard, sp^3-bonded carbon nitride materials.[26] At sufficiently high pressure and temperature crystalline carbon nitride will become thermodynamically stable,[3] and thus may be quenchable to ambient pressure and temperature.

In summary, we have systematically characterized the local carbon coordination as a function of nitrogen composition in carbon nitride thin films. A structural transformation in these materials from primarily sp^3 to sp^2-bonded carbon was observed as the nitrogen composition increased from 11 to 17 %. This transformation is also accompanied by a decrease in density from 3.3 to 2.1 g/cm^3. Hartree-Fock and DF calculations on model clusters show that there is a significant energetic preference for sp^2 vs sp^3-bonded structures, and that the formation of the sp^2-bonded structures will be kinetically facile when the nitrogen concentration increases above 12%. These experiments and calculations indicate that amorphous carbon nitride materials produced by physical deposition with large amounts of nitrogen will intrinsically favor low-density, sp^2-bonded structures. Other growth pathways, however, may lead to the formation of sp^3-bonded C_3N_4.

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