Nitrogen driven structural transformation in carbon nitride materials

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Abstract

The variation of local bonding as a function of nitrogen concentration in plasma-assisted pulsed-laser deposited carbon nitride films has been systematically studied. Time-of-flight (TOF) mass spectroscopy and electron energy loss spectroscopy (EELS) were combined to identify ablation conditions that produce highly sp^3-hybridized diamond-like-carbon (DLC) for typical carbon nitride growth pressures. EELS studies of carbon nitride films grown using these optimal conditions demonstrate that there is a structural transformation from ~ 70 to 0% sp^3-bonded carbon as the nitrogen concentration increases from 12 to 17%. Density measurements show that this transformation is accompanied by a density decrease from 3.3 to 2.1 g/cm^3. Hartree–Fock and density functional calculations on nitrogen substituted diamond clusters show that there is a strong preference to form sp^2-bonded carbon when the local nitrogen concentration is larger than 12 atomic percent. These experimental results and calculations suggest that amorphous carbon nitride structures with highly sp^3-hybridized carbon are unstable. © 1998 Elsevier Science B.V.

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1. Introduction

Carbon nitride materials have been the focus of considerable attention since Cohen and coworkers proposed that β-C_3N_4, a carbon nitride material analogous to β-Si_3N_4, may have a hardness comparable to diamond [1]. Subsequent calculations have shown that other crystalline C_3N_4 structures should have stabilities comparable to or greater than β-C_3N_4 [2,3]. Many of these proposed C_3N_4 structures are expected to be quite hard (e.g., cubic-C_3N_4), although the energetically most stable rhombohedral-

C_3N_4 material, which has a graphite-like structure, is expected to be soft. The local structural property that distinguishes potential superhard and dense C_3N_4 structures from low-density, softer materials 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 analogous to that in amorphous DLC.

Extensive experimental effort has been placed on preparing superhard carbon nitride materials using thinfilm growth techniques [4]. The materials produced in these studies generally have been amorphous with nitrogen concentrations less than 50%

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[4–6]. Furthermore, in cases where the local coordination has been clearly defined using EELS, the carbon has exhibited predominantly sp^2 or sp^2/sp bonding [7,8]. These results raise the critical issue of whether it is possible to obtain a high-density, sp^3-bonded carbon nitride solid using thin film growth techniques. Indeed, previous studies of nitrogen-doped DLC indicate that carbon relaxed to sp^2 bonding for less than 5% nitrogen [9].

Herein, we have systematically characterized the local carbon coordination as a function of nitrogen composition in carbon nitride thin films. The materials were grown using a plasma-assisted pulsed laser deposition (PLD) approach described previously [4,5]. Combined TOF mass spectroscopy and EELS studies were used to identify experimental conditions that produce highly sp^3-hybridized DLC films at our standard carbon nitride growth pressures. Using these optimal conditions, we have found that nitrogen can be incorporated up to ~ 12 atomic percent without reducing the percentage of sp^3-bonded carbon. Further increases in the nitrogen composition produce a structural transformation to fully sp^2-bonded carbon nitride materials. This local transformation in the carbon bonding was accompanied by an abrupt reduction in sample density from 3.3 to 2.1 g/cm^3. The origin of this nitrogen-driven transformation has been investigated using Hartree–Fock and density functional calculations on model clusters. The calculations suggest that above $\sim 12\%$ nitrogen there are significant energetic and kinetic preferences for sp^2 vs. sp^3-bonded structures. The implications of these results to the preparation of superhard, sp^3-bonded carbon nitride materials are discussed.

2. Experimental

Carbon nitride thin films were prepared using a plasma-assisted PLD apparatus described previously [5,10]. Briefly, energetic carbon species are generated by ablating a carbon target with a KrF excimer laser (248 nm, 17 ns pulse width), and a r.f. plasma gun is used to produce atomic nitrogen. By adjusting the N_2 concentration in the plasma gas mixture (N_2/He), films with nitrogen concentration from 0% up to 50% can be controllably grown. TOF data were recorded using a Comstock TOF-101 spectrometer as described previously [11]. EELS data were recorded using a VG HB603 electron microscope equipped with a Gatan parallel EELS detector. The electron beam energy was 250 keV and the EELS resolution was 0.7 eV. The ratio of the intensities of the carbon $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions was used to calculate the percentage sp^3-bonded carbon [12,13]. The nitrogen composition in the samples was determined by EELS (N < 10%) [9,14] or by Rutherford backscattering spectroscopy (RBS) and EELS (N > 10%). Film density was determined using the thickness, which was measured directly, and areal density determined by RBS.

3. Results and discussion

Fig. 1 summarizes the TOF mass spectroscopy data recorded on carbon ions produced by ablation at 248 nm using a KrF excimer laser. For laser power densities from 2×10^8 to 6×10^8 W/cm^2, the fraction of C^+ increases monotonically and becomes the dominant ion species in the laser plume (Fig. 1a). With increasing power density, the C^+ kinetic energy distribution broadens and becomes clearly bimodal at high power densities (Fig. 1b). The average kinetic energy of the C^+ fast component increases from several eV to more than 40 eV with increasing power density (Fig. 1c), although the average kinetic energy of the entire distribution saturates at higher power densities. EELS studies of carbon films grown at somewhat higher pressures (1×10^{-4} vs. 2×10^{-8} Torr) show that the percentage of sp^3-bonded carbon increases rapidly, and then saturates between 60 and 70% with increasing power density. TOF studies show that the major effect of this small increase in pressure is to shift the distribution ~ 5 eV lower in energy. The saturation does, however, correlate well with the observed saturation in average kinetic energy.

We have used the optimal ablation conditions determined from these studies to prepare carbon nitride films containing up to 50% nitrogen. Typical EELS data from these carbon nitride films (Fig. 2) show the carbon $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ core-level transitions. The relative intensities of the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions provide a robust measure of the percentage sp^2-bonded carbon [8,15]. In the pure carbon film, the $1s \rightarrow \pi^*$ peak is small and almost buried under the higher energy broad peak
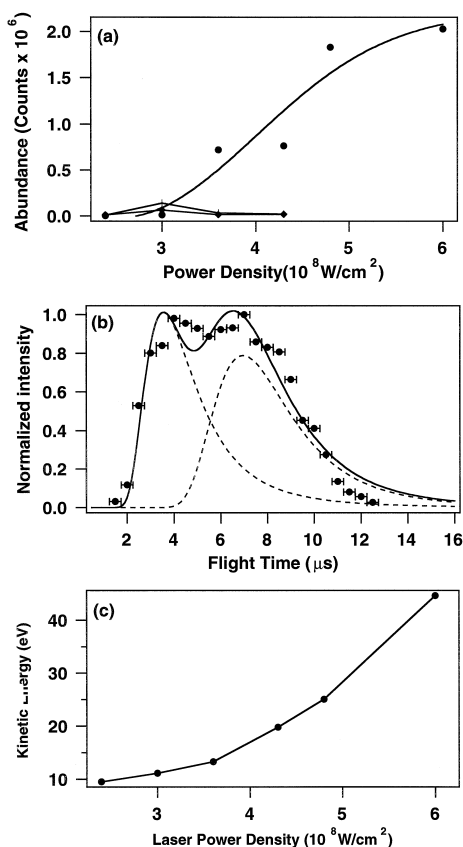
Fig. 1. TOF mass spectroscopy data recorded on carbon ablation plumes. (a) Relative abundance of C^+ ($\bullet$), C_2^+ ($\blacklozenge$), and C_3^+ ($+$) ions as a function of laser power density. (b) TOF distribution ($\bullet$) for C^+ ions produced with a power density of 4.8×10^8 W/cm^2. The smooth dashed curves correspond to the two maxwellian distributions of fast and slow components used to fit the TOF data. (c) Kinetic energy of the C^+ fast component as a function of laser power density.

that corresponds to the $1s \rightarrow \sigma^*$ and higher energy transitions. Qualitatively, the $1s \rightarrow \pi^*$ peak increases with nitrogen concentration for nitrogen $>$ 10% and becomes well separated from the $1s \rightarrow \sigma^*$ transition in carbon nitride samples containing more than 20% nitrogen. EELS spectra from samples containing 25–50% nitrogen show little change from the sample with 25% nitrogen. We have also quantitatively analyzed this EELS data to determine the percentage sp^3-bonded carbon as a function of nitrogen concentration. Significantly, these results demonstrate that there is a relatively sharp transition in which the percentage sp^3-bonded carbon drops

from $\sim 70\%$ to almost zero as the nitrogen concentration increases from 12 to 17% (Fig. 3a). The midpoint of this transition is approximately 14%.

We have also characterized the densities of these materials as a function of nitrogen concentration to obtain greater insight into the nature of this sp^3 to sp^2 transition. These results are summarized in Fig. 3b. Significantly, we find that there is a sharp decrease in density from 3.3 ± 0.3 to 2.1 ± 0.3 g/cm^3 as the nitrogen concentration increases from 10 to 15%. These observations are consistent with calculated and measured density changes for different atomic coordination. In calculated carbon nitride structures, the density of structures with sp^3-bonded carbon (e.g., β-C$_3$N$_4$: 3.57 g/cm^3) is similar to diamond but larger than the density of rhombohedral-C$_3$N$_4$ with sp^2-bonded carbon (2.55 g/cm^3). These macroscopic and microscopic experimental results demonstrate that there is a nitrogen driven relaxation of sp^3-bonded carbon to sp^2-bonding that begins at approximately 12 atomic percent nitrogen. As discussed below, we believe that this transformation in the local carbon bonding with increasing nitrogen concentration has significant implications.

To obtain greater insight into the origin of this nitrogen-driven transformation, we have used ab initio Hartree–Fock (HF) and density functional (DF) calculations to evaluate the properties of two model
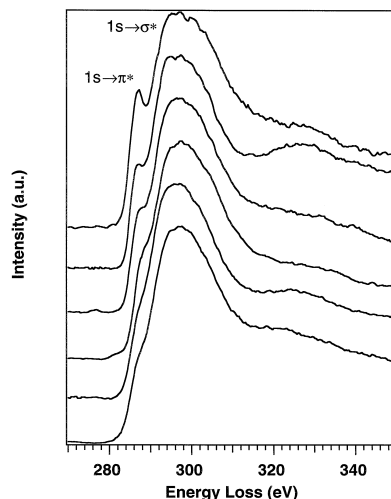

Fig. 2. EELS spectra of the carbon K-edge for carbon nitride samples containing $<1\%$, 5%, 8%, 12%, 15%, and 25% nitrogen (bottom to top). The substrate growth temperature was 77 K.
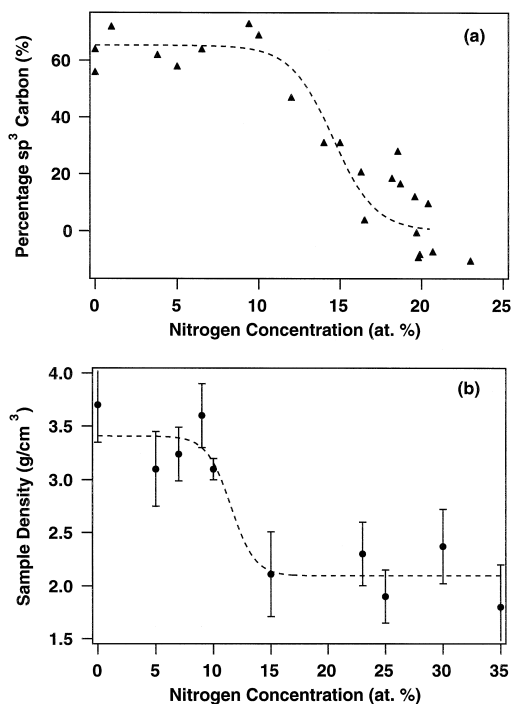
Fig. 3. (a) The percentage of sp^3-bonded carbon vs. nitrogen concentration in the carbon nitride films. The sp^3 percentage was calculated from EELS data using an e-beam evaporated carbon sample as reference for 100% sp^2 bonding. (b) The density of carbon nitride films vs. nitrogen concentration.

clusters [16]. The 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 we experimentally observe the structural transformation, we replace two carbon atoms in the cluster with nitrogen atoms. The two nitrogen atoms were put within one diamond unit cell with a separation that yields a local nitrogen concentration of about 12%. Two distinct structures were formed to compare energy differences. In structure-1, all the atoms remain single bonded despite some distortion due to the incorporation of nitrogen (Fig. 4a). This structure represents an intermediate that could be formed when first inserting nitrogen atoms into the carbon lattice and creates 1-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. 4b). HF and DF

calculations (B3LYP/6-31G(d)//HF/STO-3G) [16,17] were used to optimize the geometry and calculate the energies of structure-1 and structure-2. We find that the total energy of structure-2 is 0.89 eV lower than that of structure-1. We also note that the formation of the double-bond structure (structure-2) from structure-1 can occur by small concerted displacement of C_1, C_3, N_2, and C_2, and thus should have a very small barrier. Hence, during growth the intermediate structure-1 should rearrange with little kinetic barrier to the thermodynamically favored sp^2-bonded structure. We have also used semi-empirical calculations to investigate several different nitrogen compositions [16]. At lower (10%) nitrogen compositions there is no longer a large thermodynamic preference for the sp^2-bonded structure, and furthermore, formation of this structure involves a large kinetic barrier associated with large displacive motion of several atoms in order to generate a double bond structure. We thus believe that these calculations provide additional support for the
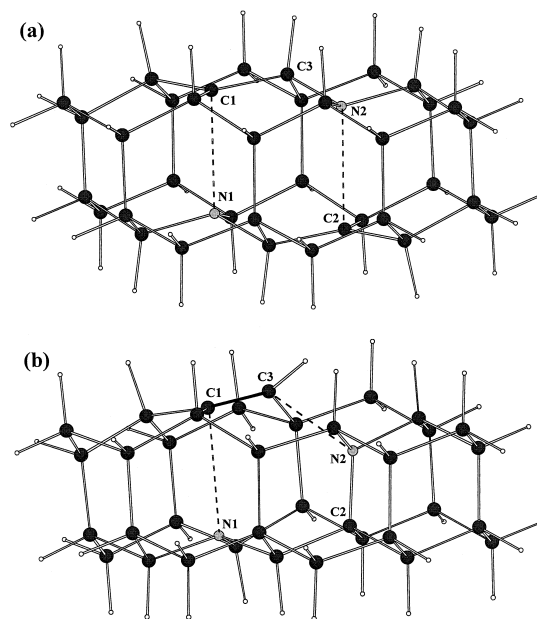

Fig. 4. Carbon nitride model clusters containing two nitrogen atoms. In structure-1 (a), the distance between C_1 and N_1, and that between C_2 and N_2 increase due to the repulsion between carbon and nitrogen lone pairs. However, all atoms are connected by single bonds. In structure-2 (b), the distances 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.

idea that nitrogen incorporation at the 12% level in carbon nitride materials strongly favors the formation of sp^2-bonded carbon.

The experimental results and calculations have significant implications for the synthesis of proposed high density, sp^3-bonded C_3N_4 materials. First, these data suggest that it will be difficult to prepare superhard, amorphous carbon nitride materials containing large amounts of nitrogen using thin-film growth techniques. Alternatively, a crystalline structure of C_3N_4 may be metastable, however, the elevated growth temperatures required to achieve crystalline growth are problematic. For example, a number of studies have shown that carbon nitride materials decompose to molecular nitrogen and other carbon products above $\sim 600°C$ [4]. Even at the very high-pressure of 20 GPa, the decomposition temperature increases to only 750°C [18]. These facts lead us to question recent claims of crystalline C_3N_4 produced at high-temperature [19,20].

4. Conclusions

In summary, we have systematically characterized the local carbon coordination as a function of nitrogen composition in carbon nitride thin films. Using growth conditions that produce highly sp^3-hybridized DLC, a structural transformation to sp^2-bonded carbon is observed as the nitrogen concentration increases from 12% to 17%. This transformation is also accompanied by a decrease in density from 3.3 to 2.1 g/cm^3. Theoretical calculations on model clusters show that there are significant energetic and kinetic preferences for sp^2 vs. sp^3-bonded structures when the nitrogen concentration increases above 12%. These experiments and calculations thus suggest that amorphous carbon nitride materials containing large amounts of nitrogen will likely have low-density, sp^2-bonded structures.

In the future, there are several directions that can be pursued to achieve superhard, sp^3-bonded carbon nitride materials with larger nitrogen concentrations. First, it will be advantageous to eliminate the low-energy component of carbon produced by laser ablation (e.g., Fig. 1c), since this component limits the fraction of sp^3-bonded carbon in DLC. The use of shorter wavelength pulsed lasers, which can produce high kinetic energy species at moderate power densi-

ties, will be important to investigate in this regard [21]. Second, high pressure approaches are promising, because the decomposition temperature increases with pressure [18]. At sufficiently high pressure and temperature crystalline carbon nitride will become thermodynamically stable, and thus may be quenchable to ambient pressure and temperature.

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