Bonding in hard and elastic amorphous carbon nitride films investigated using $^{15}$N, $^{13}$C, and $^1$H NMR spectroscopy

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The nitrogen bonding in hard and elastic amorphous carbon nitride ($\alpha$-CN$_x$) films is examined with $^{15}$N, $^{13}$C, and $^1$H nuclear magnetic resonance (NMR) spectroscopy. Films were deposited by dc magnetron sputtering, in a pure nitrogen discharge on Si(001) substrates at 300 °C. Nanoindentation tests revealed an elastic recovery of 80%, a hardness of 5 GPa, and an elastic modulus of 47 GPa. The NMR results show that nitrogen bonding in this material is consistent with $sp^2$ hybridized nitrogen incorporated in an aromatic carbon environment. The data also indicate that the $\alpha$-CN$_x$ prepared for this study has very low hydrogen content and is hydrophilic. Specifically, analysis of $^{15}$N and $^{13}$C cross polarization magic angle spinning and $^1$H NMR experiments suggest that water preferentially protonates nitrogen sites.

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INTRODUCTION

Incorporating nitrogen into carbon films can improve their mechanical properties. When deposited under suitable conditions, amorphous carbon nitride ($\alpha$-CN$_x$) films are fabricated with low elastic modulus but with high strength and high elastic recovery. Early work on $\alpha$-CN$_x$ proposed that a turbostratic structure consisting of cross-linked buckled graphitic layers accounts for its strength and high elasticity. A current research focus is to identify unknown structures responsible for bending and cross linking the graphitic layers. However, the identity of these structures and nitrogen bonding in $\alpha$-CN$_x$ remain unknown.

Many publications have been devoted to the study of nitrogen bonding in $\alpha$-CN$_x$ films. In particular, x-ray photoelectron spectroscopy (XPS) and vibrational spectroscopy measurements have been the most common techniques used to investigate this subject. However, interpretation of these data varies widely in the literature. This is not surprising, since the varieties of different bonding configurations are too close in energy. Thus, one is faced with interpreting spectra with a multitude of overlapping peaks, which makes deconvolution problematic.

In this study, solid-state nuclear magnetic resonance (NMR) spectroscopy is used to elucidate the chemical bonding in $\alpha$-CN$_x$. The advantage of NMR is its high sensitivity to the electronic environment, which is reflected in the isotropic chemical shift. NMR chemical shifts are more sensitive than XPS values, and thus provide a better description of bonding. Taking advantage of this greater sensitivity, plausible chemical shift assignments are made, and the bonding configurations that play dominant roles in $\alpha$-CN$_x$ are determined.

Unfortunately, NMR has an inherent disadvantage in that a large amount of material (~100 mg) is required to make measurements—a requirement that is difficult to fulfill using film fabrication techniques. This presumably explains the limited attention NMR has received from the carbon nitride community. The few researchers who used NMR to investigate $\alpha$-CN$_x$ films have focused on hydrogenated materials or materials deposited at ambient temperature. However, $\alpha$-CN$_x$ materials deposited under these conditions have less robust mechanical properties. Mechanical testing results were not reported for the materials previously characterized by NMR, and it is doubtful if those were the highly elastic and mechanically hard material of interest.

In this study, our materials have been characterized by $^{15}$N, $^{13}$C, and $^1$H NMR measurements in addition to nanoindentation. The primary focus of this report is on the $^{15}$N NMR results, which elucidate the nature of nitrogen bonding in $\alpha$-CN$_x$. These results complement our previous $^{13}$C NMR study. In addition, results from $^{15}$N cross polarization (CP) and $^1$H magic angle spinning (MAS) NMR experiments suggest that nitrogen sites are susceptible to protonation from water absorbed during sample preparation for the NMR measurements. This result may be contrasted with our previous report, where we showed that the overall fraction of protonated carbons in our material is very low. Specifically, our results indicate that nitrogen sites are more susceptible to protonation than carbon sites. In an attempt to clarify this result, we have compared the contact time dependence of the $^{13}$C CPMAS spectra with our previous REAPDOR measurements. This comparison indicates that those carbons that are protonated are also more likely to be directly bonded to nitrogen. Finally, we present a film-structure model for hard and elastic $\alpha$-CN$_x$, which is based on the insights provided by the $^{15}$N NMR results as well as those from our previous $^{13}$C NMR study.

EXPERIMENTAL

The $\alpha$-CN$_x$ films were deposited by dc magnetron sputtering in a pure nitrogen discharge at 1.2 Pa on 75 mm diam. Si(001) substrates, using a 50-mm, sputtering gun (Mighty-Mak U.S. Inc.). The target was a 99.999% pure graphite disk with 50 mm diameter and 6.4 mm thickness. The sample was mounted on a radiatively heated substrate holder, which was positioned 8 cm from the target face. During film deposition,
the substrate was electrically grounded and heated to 300 °C, and the target discharge current was limited to 300 mA. The ultimate pressure of the vacuum system was 3 × 10⁻⁵ Pa at room temperature. An ¹⁵N₂ and ¹⁴N₂ feedstock gas mixture was used to enrich the material fabricated for the ¹⁵N NMR measurements. The total gas-flow was regulated by a precision gas-flow controller at 10 sccm with flow rates set at 4 and 6 sccm for the ¹⁵N₂ and ¹⁴N₂ gases, respectively. However, for the ¹³C and ¹H measurements, experiments were carried out on the unenriched a-CN₃ sample used in our previous NMR study. The deposition rate of the material was determined to be ~1 µm/h, as determined by a thickness profile measurement using scanning electron microscopy.

For the NMR measurements, 180 mg of material was prepared by depositing four, 8 µm-thick films. The material was scraped off the substrates, ground to a fine powder using a mortar and pestle, and packed into a 5 mm zirconia rotor. All solid-state NMR measurements were made with a custom-built spectrometer operating at 7 T (¹H Larmor frequency of 300.07 MHz) with a ¹³C frequency of 75.46 MHz and an ¹⁵N frequency of 30.41 MHz. The 90° pulse width for the ¹H, ¹³C, and ¹⁵N detection experiments were 5, 4, and 4 µs, respectively. For proton decoupling, a radio frequency field-strength of 71.4 kHz was used for proton decoupling.

Magic angle spinning (MAS) (νₘ = 8–9 kHz) NMR direct-detection and cross polarization (CP) spectra were obtained using a Hahn-echo pulse sequence (90° − τ − 180°) for the ¹⁵N and ¹³C measurements, and a solid-echo sequence (90° − τ − 90°) for the ¹H experiments. Comparison between spectra collected by direct detection versus cross polarization provided valuable insight into the extent of hydrogen bonding in the material. The cross polarization experiments are double resonance techniques in which the signal is obtained by the transfer of spin polarization from protons to the detected spins (here, ¹³C or ¹⁵N). Since in spin polarization transfer from ¹H to the detected spins is mediated by the strength of the dipolar coupling (and therefore inter-nuclear distances), the proton connectivity associated with particular carbons or nitrogen in the spectrum can be inferred. Specifically, sites with associated with directly bonded protons can be readily discerned from those with remotely coupled protons.

Cross polarization with population inversion (CPPI) was used to provide partial spectral editing of the ¹⁵N spectra. All NMR spectra were obtained at room temperature except for the ¹H spectra, which were obtained at both room temperature and 150 °C. For the ¹H NMR experiments at high temperature, the sample was first heated for 20 min at 150 °C, and then data were acquired at 150 °C for an additional 22 min. Additional experimental details of recycle delays (τₕ), echo spacing times (τₑ), spinning speeds (νₛ), number of scans (NS), and apodization by Lorentzian line broadening (LB) are included in the figure captions. The reported ¹H chemical shifts are referenced to labeled glycine at ~348 ppm on the nitromethane scale (CH₃NO₂ at zero ppm), and the ¹³C chemical shifts are referenced to the carboxyl carbon of glycine at 176 ppm on the tetramethylsilane scale (TMS at zero ppm). The ¹H chemical shifts are referenced to water at 5.3 ppm (TMS at zero ppm).

RESULTS

The mechanical properties of this material have been reported in an earlier publication. To summarize, nanoindentation tests gave a hardness of 5 GPa and an elastic modulus of 47 GPa for an indentation depth of 100 nm, as obtained by the method of Oliver and Pharr. The a-CN₃ films exhibit a high elastic recovery of 80% at 1.0 mN maximum load. We also demonstrated that the mechanical properties are uniform across the entire diameter of the 75 mm substrate, which proves the integrity of our deposition method for producing the large quantity of material needed for the NMR experiments. The direct-detection ¹⁵N MAS spectrum (Fig. 1) was obtained with 11 160 scans using a 30 s recycle delay. By comparing spectra obtained at 20 and 30 s recycle delays, the spin-lattice relaxation time was estimated: T₁ ≈ 15 s. The broad, low-intensity features positioned symmetrically around the central portion of the spectrum are spinning side bands (296 ppm ~9 kHz).

FIG. 1. ¹⁵N Hahn-echo MAS spectrum with proton decoupling (τᵣ = 30 s, τₑ = 111.1 μs, νₛ = 9 kHz, NS = 11 160 transients, and no apodization). The shape of the spectrum suggests at least five bonding configurations at the following estimated positions: −120, −160, −255, −295, and −358 ppm. The vertical lines indicate the calculated chemical shift of the two nitrogen-sites in graphitic C₃N₄ (Ref. 23).

Hahn-echo ¹⁵N MAS spectra obtained using direct detection and cross polarization experiments are compared in Fig. 2. The direct-detection spectra obtained with (solid line) and without (dotted line) proton decoupling are indicated in the top traces; proton decoupling has the greatest affect on the intensity of the broad shoulder in the range between −210 to −330 ppm. Without proton decoupling, the spectral feature centered approximately at −295 ppm (top traces) is notably dephased. For comparison, a CP spectrum obtained using a 1 ms contact time (dashed line in lower portion of Fig. 2) is
also displayed. Notice that the highest cross polarization efficiency is observed at $-295$ ppm (gray line), precisely where the direct detection spectrum exhibits the largest dephasing with out proton decoupling. This is to be expected since in the absence of decoupling the $^{15}$N and $^1$H will be dipolar coupled.

CPMAS $^{15}$N spectra obtained at 0.1, 1.0, and 5.0 ms contact times are shown in Fig. 3(a). Evolution of the $^{15}$N CPMAS spectra with contact time suggests at least two $^{15}$N-$^1$H dipolar coupling strengths for polarization transfer. Cross polarization is very effective at short contact times (0.1 ms) for the high intensity feature centered near $-275$ ppm, indicating dipolar coupling to directly bonded protons. However, cross polarization is not efficient for the low-intensity broad shoulder centered near $-160$ ppm. The intensity of this shoulder increases up to 1 ms contact time, and remains constant out to at least 5 ms. The low relative intensity and slow build-up of the polarization indicates that these nitrogens have no directly bonded protons, which is consistent with the behavior shown in Fig. 2; the portion of the direct-detection spectra near $-160$ ppm is insensitive to the dipolar dephasing time period.

The shape of the peak centered near $-275$ ppm [Fig. 3(a)] suggests at least two nitrogen bonding configurations. To distinguish these, CPPI measurements were performed using a 1 ms initial contact time, as shown in Fig. 3(b). As indicated by the gray vertical lines in the CPPI spectra, the high-intensity feature in the CPMAS spectrum is composed of two nitrogen bonding types, which are centered at approximately $-255$ and $-295$ ppm. The inversion time for the peak at $-295$ ppm occurs between 0.5 and 1.0 ms PI times, while the other portions of the spectrum retain a positive intensity for PI times greater than 3.0 ms.

MAS $^{13}$C NMR spectra of $\alpha$-CN$_x$ as obtained by rotational-echo, adiabatic-passage, double-resonance (REAPDOR), and Hahn-echo CPMAS are compared in Fig. 4. The results from the REAPDOR experiment (upper traces) were published in our previous $^{13}$C NMR study; the full spectrum (filled squares) is compared to the attenuated spectrum (open circles). The attenuated spectrum is obtained by applying a dipolar dephasing pulse to the $^{14}$N channel. Since the strength of the dipolar interaction is inversely proportional to the cube of the internuclear bond distance, those $^{13}$C bonded closest to $^{14}$N experience the strongest dipolar dephasing. Thus the highest dephasing efficiency (signal attenuation) is observed for carbons directly bonded to nitrogen. The gray shaded region indicates the portion of the $^{13}$C spectrum that is coupled to $^{14}$N nuclei. The largest dephasing occurs at 150 ppm, as indicated by the solid vertical line. The REAPDOR spectra are also compared with $^{13}$C CPMAS measurements (lower traces) obtained using contact times of 1 ms (dashed line) and 5 ms (solid line). Note that at short contact times (1

FIG. 2. $^{15}$N Hahn-echo MAS spectra obtained by direct-detection and cross polarization experiments. The direct-detection spectra ($\tau_d$ = 30 s, $\tau_p$ = 111.1 $\mu$s, $\nu_p$ = 9 kHz, NS = 2480, and LB = 50 Hz) obtained with and without proton decoupling are indicated by the solid line and dotted line, respectively. A CPMAS spectrum with 1 ms contact time ($\tau_d$ = 1 s, $\tau_p$ = 111.1 $\mu$s, $\nu_p$ = 9 kHz, NS = 2480, and LB = 50 Hz) is displayed at the bottom (dashed line) for comparison. The spectral feature near $-295$ ppm (gray line) is markedly dephased in absence of proton decoupling, and this feature coincides with the highest cross polarization efficiency.

FIG. 3. (a) $^{15}$N CPMAS spectra ($\tau_d$ = 1 s, $\tau_p$ = 111.1 $\mu$s, $\nu_p$ = 9 kHz, NS = 2480, and LB = 50 Hz) obtained at 0.1, 1.0, and 5 ms contact times. The efficient cross polarization of the feature centered at $-275$ ppm at short contact times indicates that this nitrogen bonding site is protonated. (b) $^{15}$N CPPI MAS spectra ($\tau_d$ = 1 s, $\tau_p$ = 111.1 $\mu$s, $\nu_p$ = 9 kHz, NS = 600, and LB = 200 Hz) for various PI times ranging from 0.5 to 3.0 ms following an initial 1 ms contact time. Peak positions estimated from the CPPI measurement are indicated by the gray lines at $-295$ and $-255$ ppm.
ms), the CPMAS spectra exhibit a sharp peak at $\sim 150$ ppm, precisely where the REAPDOR spectra exhibit the largest dephasing.

The temperature dependence of the $^1$H MAS NMR spectra of $a$-CN$_x$ was also investigated, as shown in Fig. 5. The data were first collected on the as-prepared sample (solid line). Then, the sample was heated inside the probe for 20 min. at 150 °C, and this temperature was maintained during data acquisition ($\sim 22$ min). The heat treatment caused a large reduction of the $^1$H MAS spectral intensity (dashed line) and revealed a previously unresolved feature near 0 ppm.

**DISCUSSION**

The direct-detection $^{15}$N MAS spectrum with proton decoupling (Fig. 1) suggests at least five different bonding environments: these are positioned approximately at $-120$, $-160$, $-255$, $-295$, and $-358$ ppm. Estimates of the peak-center values near $-120$ and $-160$ ppm were obtained from the zero crossings of the first derivative spectrum. The values of $-255$ and $-295$ ppm were inferred from the CPPI measurements [shown in Fig. 3(b)], and the value of $-358$ ppm for the sharp feature was obtained from its point of maximum intensity. The black vertical lines (Fig. 1) indicate the calculated $^{15}$N chemical shifts of the two nonequivalent sites in graphitic C$_3$N$_4$, as obtained by Yoon et al.$^{23}$ These two nitrogen sites are on the perimeter of a vacancy defect: a nitrogen site bonded to two carbons (similar to pyridine) at $-166$ ppm together with a nitrogen site bonded to three carbons (similar to a substitutional site in graphite) at $-240$ ppm.$^{23}$ The $^{15}$N chemical shifts found in $a$-CN$_x$ indicate that these bonding types may account for the features observed at $-160$ and $-255$ ppm. This suggestion is consistent with our previous $^{13}$C NMR results,$^{16}$ from which we infer that $a$-CN$_x$ has an $sp^2$ carbon bonded structure, since the spectra rule out $sp^3$ bonded carbons. However, we point out that their calculated $^{15}$N chemical shift for pyridine is 43 ppm lower than its experimental value.$^{23}$ This suggests that the calculated value of $-166$ ppm for graphitic C$_3$N$_4$ is similarly shifted. Applying the same shift, the value of $-166$ ppm becomes $-123$ ppm; note that the value of $-123$ ppm is very close to the value for the feature at $-120$ ppm in $a$-CN$_x$.

We have also compared our experimental $^{15}$N MAS spectra (Figs. 1 and 2) with two compilations of $^{15}$N chemical shifts.$^{23,25}$ The isotropic chemical shifts listed in Ref. 24 are based on liquid state NMR measurements, while those in Ref. 25 are from solid-state measurements. In addition, Ref. 24 includes some $^{14}$N chemical shift data, and these results were included in the comparison. The reference chemical shift data$^{24,25}$ are schematically summarized in Fig. 6. For clarity, pyridinelike and pyrrolelike bonding types are depicted in Fig. 7. The chemical shifts for pyridinelike and pyrrolelike nitrogens were taken exclusively from measurements on solutions.$^{24}$ and specific examples are shown in Fig. 6. For compounds with both nitrogen types (as an example see Fig. 7), only those with $R \neq H$ were considered in this comparison. Since, if $R=H$, then the chemical shift between the two sites is averaged due to affects of proton tautomerism.

The comparison in Fig. 6 suggests that the spectral feature at $-120$ ppm is due to nitrogen bonded in a pyridinelike or nitrile bonding configuration. However, our previous Fourier transform infrared spectroscopy work indicates that the frac-

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**FIG. 4.** REAPDOR spectra (upper traces) were acquired with $\tau_d = 3$ s; $\nu_r = 8$ kHz; and NS = 26,000. The full spectrum (filled squares) and attenuated spectrum (open circles) are shown. The gray shading indicates the region of the spectra with carbons directly bonded to nitrogen. Hahn-echo CPMAS spectra (lower traces) obtained using contact times of 1 ms (dashed line) and 5 ms (solid line) ($\tau_d = 1$ s; $\tau_c = 111.1$ $\mu$s; $\nu_r = 9$ kHz; NS = 10,000, and LB = 200 Hz).

**FIG. 5.** Comparison of $^1$H MAS NMR spectra ($\tau_d = 1$ s, $\tau_c = 250$ $\mu$s, $\nu_r = 8$ kHz, NS = 1320, and LB = 100 Hz) between the as-prepared material (solid line) and after heating at 150 °C (dashed line). After heating, the spectral intensity centered at 6.5 ppm is greatly reduced, which suggests desorption of water.
FIG. 6. A schematic display of $^{15}$N isotropic NMR chemical-shift ranges for various bonding configurations (Refs. 24, 25). For ease of comparison, the $^{15}$N direct-detection spectra from Fig. 2 are shown.

FIG. 7. Configurations of pyridinelike and pyrrolelike nitrogen (Ref. 24).

range of the gray-shaded bar shown in Fig. 6. If the gray region can completely account for this bonding contribution, then a region of equal intensity for the nitrogen neighbor that is directly bonded to the pyrrolelike N should also appear in the spectrum. These directly bonded nitrogen neighbor can be described as pyridinelike and has a chemical shift in that range (Fig. 6). To settle the question of N-N bonding, future experiments that exploit homonuclear dipole-dipole coupling are planned.

Comparing literature values with our results (see Fig. 6) suggests that the features near $-255$ and $-295$ ppm might arise, in part, from nitrogen in amides or carbonyl derivatives. However, this assignment is implausible. If these features in the $^{15}$N spectra are associated with an amide then a corresponding feature due to C=O should appear in the $^{13}$C spectra near 168–177 ppm (Fig. 4). This feature is not evident in the $^{13}$C spectra (also see our previous report, Ref. 18), ruling out the presence of carbonyl groups. In addition, the spectral region covered by amines slightly overlaps with the intensity near $-295$ ppm. Finally, the sharp feature at $-358$ ppm falls in the range of amines, ammonium ions, or isocyanate structures. Since this feature ($-358$ ppm) makes up a small percentage of the overall integrated intensity, it will not be discussed further. In summary, comparison to reference chemical shift data suggests that nitrogen bonding in $a$-$CN_2$ is predominately $sp^2$ and exists in pyridinelike or pyrrolelike configurations. Unfortunately, experimental $^{15}$N chemical shifts are unavailable for nitrogen coordinated to three carbons in graphene segments.

In the direct-detection $^{15}$N spectra without proton decoupling (Fig. 2), the spectral feature near $-295$ ppm is considerably dephased, and this feature coincides with the highest intensity of the $^{15}$N CPMAS spectrum. These observations show that this nitrogen site is protonated; this conclusion is further supported by the observation that the CPMAS spectra show the highest efficiency for short contact times [Fig. 3(a)]. It is important to note that the other portions of the direct-detection spectra (Fig. 2) are either unaffected or at most slightly influenced by proton decoupling. Indeed, the overall resolution of the spectra is not greatly affected by proton decoupling. These results suggest that water adsorption during NMR sample preparation is the most likely source of proton contamination. If the majority of protons had been introduced during film deposition, one would expect that the entire $^{15}$N spectrum to be influenced by proton decoupling. However, we estimate an 8% relative intensity loss due to proton dipolar dephasing, which shows that only a small fraction of the nitrogen are protonated. In addition, this small change indicates that not all of the intensity near $-295$ ppm (direct detection spectra in Fig. 2) arises from protonated nitrogen.

If hydrogenation of the material is due to adsorbed water, the portions of the $^{15}$N direct-detection spectrum (Fig. 2) that are affected by proton decoupling (region between $-210$ and $-330$ ppm) may arise from a chemical shift due to protonation by water of the less-shielded portions of the spectrum (regions between $-30$ and $-210$ ppm). For example, one possible explanation is due to protonation of pyridine-like nitrogen, which would strongly shield the nitrogen site and
yield a chemical shift of approximately 100 ppm. The $^{15}$N CP MAS spectra [Fig. 3(a)] exhibit two major features separated by approximately 100 ppm: a peak centered near $-275$ ppm and a broad shoulder centered near $-160$ ppm. This may indicate that the peak near $-275$ ppm arises from protonation of the species associated with the region near $-160$ ppm. The observed cross polarization behavior of these peaks [Fig. 3(a)] is consistent with this idea. The slow build-up of the CPMAS intensity in the region near $-160$ ppm, as a function of contact time, indicates remote, weakly coordinated protons. While, the high cross-polarization efficiency of the intense peak in the region near $-275$ ppm originates from protonated or hydrated species. The possibility of water absorption is currently being explored; CPMAS and direct detection intensities are being recorded as a function of temperature and time.

In our previous $^{13}$C NMR study, we demonstrated that most of the carbons were unprotonated. This result was supported by much lower absolute intensity of the CPMAS spectra compared to direct-detection spectra, and was supported by the fact that the direct-detection spectra are unaltered by proton decoupling. In the present report, the influence of protonation in $a$-$\text{CN}_x$ is further explored by comparing $^{13}$C REAPDOR and variable contact time CP measurements (Fig. 4). The REAPDOR results (upper traces in Fig. 4) show the largest dipolar dephasing occurs near 150 ppm. Interestingly, the CPMAS $^{13}$C spectra (lower traces in Fig. 4) show that the intensity of the peak observed at 150 ppm (gray line) decreases as the contact time is lengthened from 1 ms to 5 ms. Together these results suggest that those carbons directly bonded to nitrogen are closest to protons. Moreover, these results are compatible with our observation that nitrogen sites exhibit the highest level of protonation.

Proton MAS NMR spectra, before and after annealing at 150 °C, are shown in Fig. 5. During the heating process, the integrated intensity of the proton spectra—centered at 6.5 ppm—dropped by 57%. This suggests that the spectral feature centered at 6.5 ppm is predominantly due to physisorbed water. After heating at 150 °C, the proton spectrum shows an additional small feature near 0 ppm. The origin of this small peak may be due to protons bonded to something less electronegative than oxygen, which is indicative of protons directly bonded to nitrogen sites in $a$-$\text{CN}_x$. This is plausible, since results from our previous $^{13}$C study spectra on hard and elastic $a$-$\text{CN}_x$ indicate that the carbons are not significantly hydrogenated. Alternatively, this small feature may be due, in part, to hydroxyl species.

Previous computational work by Johansson and Stafström suggested a bonding model for $a$-$\text{CN}_x$ that incorporates $sp^3$ carbons to explain the hardness of the material. However, our previous $^{13}$C NMR study demonstrated the absence of $sp^3$ carbons. Their model is thus inconsistent with our result. Furthermore, Johansson and Stafström proposed that the nitrogen bonded to $sp^3$ carbons are in a tertiary amine configuration, as in the model structure $N(C(CH_3)_3)$. However, our $^{15}$N results indicate that the amount of amine present is small (see comparison depicted in Fig. 6). Our work demonstrates that Johansson and Stafström’s bonding model is not applicable to hard and elastic $a$-$\text{CN}_x$. Collectively, our NMR and nanoindentation results imply that our $a$-$\text{CN}_x$ material has an aromatic carbon structure with nitrogen bonded in heterocyclic rings.

The calculated $^{15}$N and $^{13}$C chemical shifts of graphitic C$_3$N$_4$ are coincident with the range covered by our experimental spectra (Figs. 1 and 4), which suggests that N bonding at the perimeter of vacancy defects, as found in graphitic C$_3$N$_4$, may also occur in $a$-$\text{CN}_x$. Computational work by Snis and Matar on the model compound C$_{11}$N$_4$ demonstrates an XPS N(1$s$) chemical shift of $\sim 2$ eV between the two types of nitrogen sites on the perimeter of a single-atom vacancy in a graphitic layer: a site with nitrogen coordinated to two carbons and a site with nitrogen coordinated to three carbons. Their prediction is consistent with the experimental XPS chemical shift of the two main N(1$s$) bonding components observed in the spectra of hard and elastic $a$-$\text{CN}_x$. Thus, NMR and XPS data are compatible with the proposal that vacancy defects in graphitic layers occur in $a$-$\text{CN}_x$ films.

Previous transmission electron microscopy work indicates that hard and elastic $a$-$\text{CN}_x$ consists of buckled graphitic planes that are cross linked together. Furthermore, our experimental data suggest that nitrogen bonded in a pyrrolelike configuration is present in the material (Fig. 6). Incorporation of five-membered rings in the material, similar to pyrrole, would allow the graphitic planes to buckle. Thus, we propose a model that incorporates vacancy defects and pentagons; a schematic of one such model is shown in Fig. 8. This film-structure model allows for the incorporation of pyridineline nitrogen and for the buckling of graphitic planes. We propose that cross linking occurs at dangling bond (two-fold coordinated) sites on the perimeter of a vacancy. In particular, a pentagon placed next to a single-atom vacancy in a graphitic layer will have a two-fold coordinated vertex; such a site is anticipated to be very reactive due to high curvature.

**CONCLUSIONS**

The $^{13}$C and $^{15}$N chemical shifts observed in direct-detection NMR spectra were compared with the calculated
chemical shifts of a variety of C₃N₄ structures and with tabulated compilations of experimental ¹⁵N chemical shifts from various organic molecules. Only the calculated ¹³C chemical shift of graphitic C₃N₄ (144 ppm) falls in the range of our experimental spectra. The graphic phase of C₃N₄ has two nonequivalent nitrogen sites on the perimeter of a single-atom vacancy. The calculated ¹⁵N chemical shifts are typically less than 0.33 ppm from various organic molecules. ¹⁵N chemical shifts for nitrogen that are threefold coordinated in a graphene sheet are unavailable, and other computational values are unavailable to compare with the feature at 240 ppm in graphitic C₃N₄. Moreover, literature reports indicate that the N/C ratios are typically less than 0.33 for amorphous carbon nitride (a-CN₄) fabricated by dc magnetron sputtering. This is clearly less than the N/C ratio found in graphitic C₃N₄. Nevertheless, similarities in bonding between the two materials may exist.

Further comparison of our data with tabulated ¹⁵N chemical shift values (Fig. 6) suggest that the spectral feature near -120 ppm is due to pyridine-like nitrogen; this is similar to the ¹⁵N assignment of the calculated chemical shift near -166 ppm in graphitic C₃N₄. In addition, this same comparison suggests an assignment of nitrogen bonded in a pyrrolic configuration for the features at -160 and -255 ppm. Cross polarization magic angle spinning (CP-MAS) ¹⁵N experiments suggest that portions of the feature near -295 ppm are protonated. However, it is unlikely that this feature is due to protonated nitrogens that are bonded adjacent to a carbonyl group, since carbonyl ¹³C chemical shifts typically fall in the range of 168–177 ppm and are unobserved in our ¹³C spectra (see Fig. 6 as well as results in Ref. 18).

As shown in our previous report, proton decoupling had a negligible effect on the direct-detection ¹³C spectra. Thus, it can be inferred that the majority of carbons in our a-CN₄ are not directly bonded to protons. This is further supported by the low efficiency of ¹³C CPMAS experiments. However in the ¹⁵N direct-detection spectra, proton decoupling has a notable influence on the spectral feature at -295 ppm. In particular, the dephasing and high cross polarization efficiency at short contact times indicate that nitrogens corresponding to portions of the spectrum near -295 ppm have protons in close proximity. The most likely proton source in a-CN₄ is adsorbed water. This conjecture is supported by ¹H NMR experiments, which indicate water desorption during sample heating. These results indicate that certain nitrogen bonding sites are hydrophilic, and are protonated by physisorbed water. In particular, we suggest that portions of the ¹¹N direct-detection spectrum that are affected by proton decoupling may arise from a chemical shift due to protonation by water of the less-shielded portions of the spectrum.

These multinuclear NMR results confirm our conclusions that the structure of a-CN₄ lacks s²p³ carbons and that the interconnecting structure is not hydrogen bonded. Considering our NMR and nanoindentation results from the same a-CN₄ material, the most consistent bonding model is an aromatic carbon structure with nitrogen bonded in heterocyclic rings. The similarity of the ¹⁵N chemical shifts in graphitic C₃N₄ and in hard and elastic a-CN₄ suggests that the same single-atom vacancy defects may occur in a-CN₄. This is consistent with the calculated x-ray photoelectron spectroscopy (XPS) chemical shifts of C₃N₄, which has a vacancy defect structure. Our experimental ¹⁵N data are also consistent with nitrogen bonded in a pyrrolic configuration. Thus, we propose a film-structure model that incorporates nitrogen bonding on the perimeter of vacancy defect structures and pentagons. Pentagon incorporation would account for the buckled graphitic layers observed by transmission electron microscopy.

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