Carbon Nitride Deposited Using Energetic Species: A Two-Phase System

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Carbon nitride films deposited by three different methods have been analyzed using *in situ* Auger electron spectroscopy and *ex situ* x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry. The XPS data for all 27 samples indicate that these films have a similar composition consisting of two phases. One phase has a stoichiometry near C_3N_4 and is identified as a tetrahedral component. The other phase has a variable stoichiometry from C_5N to C_2N and is identified as predominantly an sp^2 bonded structure. For a film composition of $[N]/[C] < 1$, the tetrahedrally bonded component grows only moderately as the nitrogen content of the films is increased.

In 1990, Liu and Cohen presented a pseudopotential study [1] of the structural and electronic properties of β-C_3N_4, a hypothetical compound, and of β-Si_3N_4, a compound with well-known properties. The good agreement between calculated and experimental data for the latter compound lends credibility to the findings of this study concerning the exciting properties of the unknown C-N compound. The calculated bulk modulus of β-C_3N_4 was found to be comparable to that of diamond. In addition, the velocity of sound in the C-N compound was predicted to be about 1.1×10^6 cm/s, suggesting a high thermal conductivity. It was suggested that β-C_3N_4 may be metastable because of its moderately large cohesive energy.

Synthesis of β-C_3N_4 has recently been claimed [2] on the basis of electron diffraction data but the overall composition of the films in this, as in most other experiments [3–6], is not stoichiometric: the N-to-C concentration ratio attained in most cases is about $[N]/[C] = 0.7$. We propose that the reason for this discrepancy, which may raise questions about the results of Niu, Lu, and Lieber [2], is that for the deposition methods investigated, β-C_3N_4 forms only in very small crystallites that are embedded in amorphous sp^2 bonded C_xN_y where y/x is typically between 0.2 and 0.5, depending on deposition conditions. Furthermore, we present x-ray photoelectron spectroscopic (XPS) data which shows that these two carbon nitride phases can be distinguished by their binding energies. Such a distinction provides researchers with a tool to assess quickly and effectively the quality of their films not simply on the basis of the overall nitrogen content, but rather based on the nitrogen and carbon that are in proper binding states. If pure β-C_3N_4 were readily available, it would be a simple routine procedure to establish characteristic binding energies for this purpose. At the present time, however, the precise knowledge of the binding energies has to *precede* the production of β-C_3N_4 in a purer form. Although some of the cited authors include references to XPS characterization of their films, the data presented are not adequate. For example, Niu, Lu, and Lieber observed the C $1s$ line at 284.6 eV and the N $1s$ line at 399.1 eV [2], however, they gave no

description of the line shapes and widths. Yeh *et al.* [3] published carbon $1s$ spectra for a pure carbon film and a nitrogen containing film, but their interpretation of these spectra was limited to pointing out that the latter film may have more sp^3 character than the carbon film.

In the Letter, we report XPS data obtained on carbon nitride films from three different laboratories that were deposited by three different methods: (i) We synthesized carbon nitride using ion beam deposition (IBD) at room temperature. Our low-energy IBD system [7, 8] was designed specifically to accomplish compound deposition from two mass-selected ion sources under well controlled conditions. Typical ion beam current densities at energies 5 to 55 eV were 1 μA/cm^2 for C$^+$ ions and 2 μA/cm^2 for N$^+$ ions. The C$^+$ and N$^+$ ion energies used during the deposition were the same. An arrival ratio of C:N = 3/8 was used in most experiments. Typical film thicknesses ranged from 5 to 50 nm. The films were analyzed *in situ* by Auger electron spectroscopy (AES) using a double-pass cylindrical mirror analyzer with a coaxial electron source. The data were evaluated using published sensitivity factors. Preliminary results of these experiments have been reported [9] and a full paper is in preparation. (ii) At the Texas Center for Superconductivity, films were deposited using dc magnetron sputtering [10]. The sputtering was carried out with 50 V bias in 200 mTorr He-N_2 mixture with various N_2 partial pressures up to 100% N_2. The film thicknesses were in the 100 nm range and some of the films were annealed at 700 °C in nitrogen. (iii) A combination of carbon *e*-beam evaporation with an electron cyclotron resonance (ECR) nitrogen ion source was used at the Space Vacuum Epitaxy Center [11] for film deposition. The ion energy in this system is about 25 eV. The arrival ratio of the species was varied using increasing current densities from the ion source; these films are about 100 nm thick.

In situ analytical information is available only for the films deposited by IBD. The composition of some films was determined *ex situ* using resonance enhanced Rutherford backscattering spectrometry (RBS). Such ex-

periments confirmed the *in situ* AES data within a few at. %, i.e., within the limits of accuracy of both techniques. XPS measurements were carried out *ex situ* in a Perkin-Elmer Model 550 using Mg $K\alpha$ x-rays at 0.5 eV spectrometer resolution. At this resolution the spectral linewidth is limited by the x ray source linewidth, i.e., about 0.8 eV. The widths of photoemission lines from a solid at these conditions are determined by the dispersion in binding energies. The narrowest lines observed are about 1.3 eV FWHM. An example of such a narrow line is the Au $4f_{7/2}$ which was used for calibration.

We will report data for films of various origins together because the differences between these groups of materials revealed by XPS are not significant. Films deposited by other groups have also been obtained using energetic particles; thus it is expected that the fundamental properties of all these films are quite similar to those included in this study. All films were found to be amorphous, with the notable exception of those reported by Niu, Lu, and Lieber [2] which contained small crystallites with grain sizes <10 cm. Note that although the carbon nitride films deposited by Niu, Lu, and Lieber [2] were obtained from species that arrived at the substrate at lower kinetic energies than any of those used in the methods reported here, these species, nevertheless, had hyperthermal energies. The overall composition of their films is about the same as some of the films in this Letter.

Examples of C $1s$ and N $1s$ XPS lines are shown in Fig. 1 for a carbon nitride film. As for most of the films, there are four distinguishable features in the carbon spectrum and three in the nitrogen spectrum. The carbon peak at the binding energy 284.6 eV is identified as originating from adventitious carbon and surface carbon that may have lost its nitrogen neighbors due to reaction with O_2 and/or CO from the air. The peak at 289.5 eV is identified as originating from CO type bonds. These two peaks are incidental and are excluded from further consideration. The above peak assignment
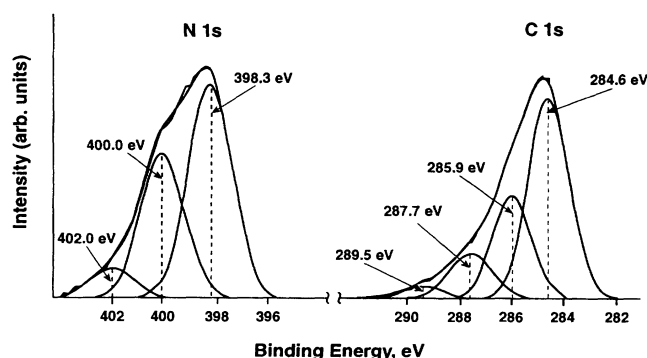

FIG. 1. Typical nitrogen and carbon $1s$ XPS spectra obtained with Mg $K\alpha$ x rays at 25 eV pass energy. The data are presented after inelastic background subtraction and using Gaussian fits. The intensity scales for the N and C spectra are not the same.

is also substantiated by data from low exit angle XPS measurements which show a significant enhancement of these peaks relative to the others. The remaining two carbon peaks at 285.9 and 287.7 eV reflect two different binding states between carbon and nitrogen. Correspondingly, there are two nitrogen peaks at 400.0 and 398.3 eV for these two binding states, while the peak at 402.0 eV is identified as originating from N-O or N-N bonds and is not considered further.

In the assumed β-C_3N_4 structure, the carbon atoms are in tetrahedral sites and the nitrogen atoms are in threefold positions. Diamond, the tetrahedral allotrope of carbon, has about the same binding energy as other pure carbon forms and hydrogenated carbons [12, 13]. The binding energy of the $1s$ electrons is quite insensitive to the coordination as long as the bonds are nonpolar. Even moderate polarization of carbon bonds leads, however, to significant binding energy changes. For example, in pyridine (C_5H_5N) which is a π-bonded aromatic ring with only one nitrogen atom, the carbon binding energy is 285.5 eV [14]. In the tetrahedrally bonded nitrogen-containing compound urotropine (hexamethylene-tetramine; $C_6H_{12}N_4$), the carbon binding energy is 286.9 eV [15]. The shift is probably due to the higher degree of polarization of the urotropine bonds. The nitrogen binding energies in these compounds are 399.8 eV for pyridine [16] and 399.4 eV for urotropine [17]. Note that the latter compound contains the nitrogen and carbon atoms in positions closely resembling those in the predicted β-C_3N_4 structure. The difference between this molecule and a subnanometer size crystallite of β-C_3N_4 is mainly that carbon dangling bonds are hydrogen terminated, although the nitrogen atoms in urotropine are in tetrahedral, rather than in trigonal sites. It is then to be expected that in amorphous carbon nitride, the carbon and nitrogen atoms in positions resembling β-C_3N_4, (to be referred to as phase 1, or C^1 and N^1) will have similar binding energies to those in urotropine. However, since the nitrogen atoms are now in trigonal positions, the extra electron pairs will contribute more effectively to screening of the $1s$ orbitals and this should lead to some decrease of the N $1s$ binding energy. Atoms in "defective" positions, i.e., in areas with excess carbon (phase 2, or C^2 and N^2), will have binding energies closer to those in pyridine. In keeping with this analysis, we assign the peaks at 287.7 and 398.3 eV as C^1 and N^1 peaks, respectively, and the peaks at 285.9 and 400.0 eV as C^2 and N^2 peaks, respectively.

As a result of analyses performed on 27 films we found that the binding energies in the two carbon nitride phases are the following: C^1, 287.7 $\pm$ 0.2 eV; N^1, 398.5 $\pm$ 0.2 eV; C^2, 286.1 $\pm$ 0.2 eV; and N^2, 400 $\pm$ 0.3 eV. This narrow distribution of the binding energies in films of diverse origin is convincing evidence for the existence of the two said phases. This analysis of the carbon and nitrogen lines allows us to make some

further evaluation of the film composition. We will characterize the films according to their average composition. $[N]/[C] = ([N^1] + [N^2])/([C^1] + [C^2])$, the composition of phase 1, $[N^1]/[C^1]$, and the fractional concentration of phase 1, $([N^1] + [C^1])/([N^1] + [C^1] + [N^2] + [C^2])$. The $[N^1]$, $[N^2]$, $[C^1]$, and $[C^2]$ concentrations were calculated from areas under Gaussians fitted as in Fig. 1 using published sensitivity factors.

First, in Fig. 2 we compare the composition results $[N]/[C]$ obtained from XPS with composition data obtained from RBS and *in situ* AES analyses. The figure shows that our method, while close, may slightly overestimate the nitrogen content of the films. For the 16 data points plus the (0,0) point, the slope of the line representing $([N]/[C])_{XPS}$ versus $([N]/[C])_{RBS,AES}$ is 0.852 with a regression coefficient of $r = 0.927$. Remarkably, the deviation from the ideal correspondence of the XPS data to the RBS and AES is most significant at low concentration ratios. One reason for underestimating the carbon content of carbon-rich films may be that in these films some carbon atoms are in nearly perfect graphitic rings where they would give rise to a peak at 284.6 eV binding energy and this peak is omitted from the XPS evaluation. The relatively low regression coefficient is not surprising in view of the quite limited accuracy of all the analytical methods used. Both the RBS and AES data are estimated to have an error of ±10% in $[N]/[C]$.

Our assignment of the binding energies implies that the N^1 to C^1 concentration ratio should be close to the C_3N_4

stoichiometry, at least for samples with relatively high nitrogen content. Indeed, the nitrogen to carbon ratio of this phase $[N^1]/[C^1] = 1.23 \pm 0.18$ for the 21 samples with $[N]/[C] > 0.4$. For 9 samples with $[N]/[C] > 0.7$, $[N^1]/[C^1] = 1.29 \pm 0.15$. Although the scatter of the data is significant, the average agrees reasonably well with the expected 1.33 value. For the total sample pool $[N^2]/[C^2] = 0.40 \pm 0.17$, i.e., the phase with low nitrogen content has a composition that may vary from C_5N to C_4N_2 and beyond. For the 9 samples with high nitrogen content, $[N]/[C] > 0.7$, $[N^2]/[C^2] = 0.57 \pm 0.09$, indicating that these samples are probably composed of a mix of C_3N_4, C_4N_2, and CN.

Figure 3 shows the relationship between the fraction of phase 1, which is mostly tetrahedrally bonded carbon nitride, and the overall N content of the films. The solid lines in Fig. 3 show the calculated change of the tetrahedral carbon nitride fraction with various assumptions for the other carbon nitride phase. In these calculations, phase 2 is assumed to have a fixed stoichiometry. As it is natural to expect, the experimental data show a tendency for the fraction of the phase 1 component to increase as the overall nitrogen content increases. The existence of such a correlation supports the intuition that samples with higher N content will be closer to the tetrahedrally bonded carbon nitride. Obviously, any change of the experimental parameters that leads to an increase of the nitrogen content in the films leads mostly to a change in the π-bonded phase 2, bringing it from graphitelike rings to such rings that contain two N atoms per ring and beyond. At that point perhaps there may be an increasing probabil-
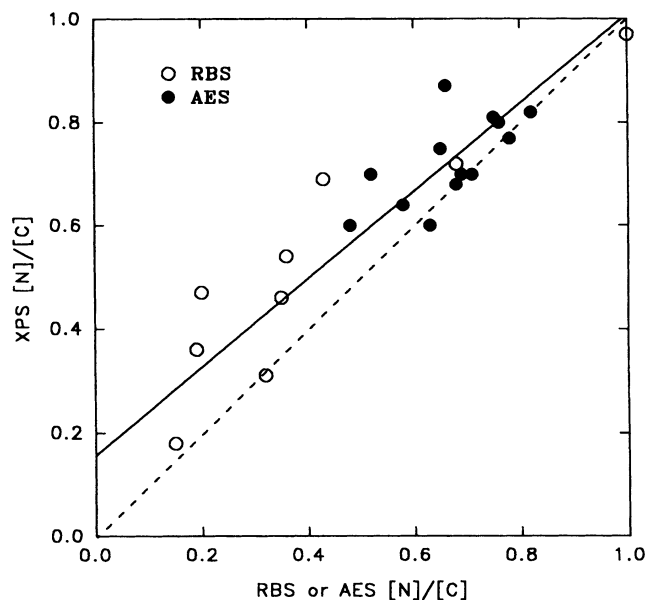

FIG. 2. Film composition data from XPS vs composition data from *in situ* AES and from RBS. AES and RBS data agree with each other when both are applied to the same sample. The solid line is the best fit to the data and the dashed line represents ideal correspondence between the methods.
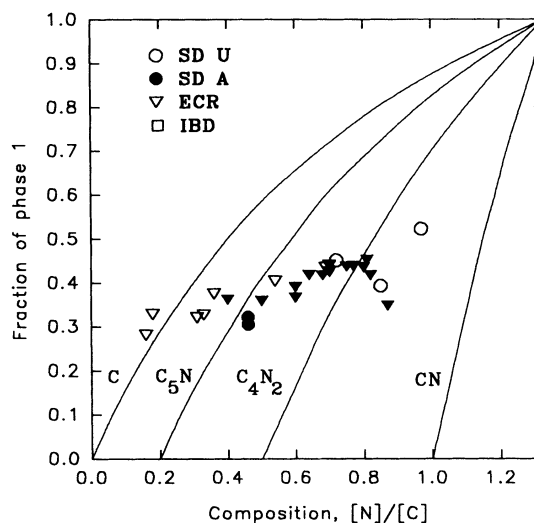

FIG. 3. Fraction of tetrahedrally bonded (phase 1) carbon nitride vs film composition from XPS. The lines represent the fractional changes assuming a constant composition for phase 2 as indicated. SDU: sputter deposition, unannealed; SDA: sputter deposition, annealed; ECR: combination of e-beam evaporation with ECR ion beam; IBD: direct ion beam deposition.

ity for the flat C-N rings to buckle and reorganize into a tetrahedral configuration.

The significance of the identification of two different binding states in carbon nitride deposited from energetic particles is that is allows us to evaluate success in any given systematic experiment based on the amount of the material in the tetrahedral state (phase 1) rather than the possibly less meaningful total concentration. Variations of different experimental parameters may lead to different changes in the two carbon nitride phases, resulting in different characters of the fraction of N^1 vs $[N]/[C]$ relationship. Indeed, in the ECR-evaporation experiment, where the main parameter varied was the N:C arrival ratio, the correlation between the phase 1 content and the $[N]/[C]$ concentration ratio is better than for other experiments where several parameters were varied.

Our analysis does not contradict the results of Niu, Lu, and Lieber [2] who observed β-C_3N_4 crystallites. They may have had no more than (40–50)% of this phase in films with $[N]/[C] \cong 0.7$. Whether or not the crystallites can be observed by electron diffraction depends on the average crystal size rather than on the concentration of the C_3N_4 phase. It would be most important to establish experimental conditions that facilitate the crystal growth. On the basis of experience with diamondlike films [18], we may assume that while the carbon nitride films deposited from energetic ions may always be amorphous, a highly sp^3 character can still be attained, and most of the exciting carbon nitride properties may be achieved.

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