Nitrogen 1s Electron Binding Energy Assignment in Carbon Nitride Thin Films with Different Structures

Niklas Hellgren  
*Messiah University*, nhellgren@messiah.edu

Wei Tao Zheng

Ke Zhao Xing

Michael Lögdlund

Åsa A. Johansson

See next page for additional authors

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Authors
Niklas Hellgren, Wei Tao Zheng, Ke Zhao Xing, Michael Lögdlund, Åsa A. Johansson, U Gelivs, William R. Salaneck, and Jan Eric Sundgren
Abstract

Carbon nitride thin films deposited by dc unbalanced magnetron sputtering have been analyzed by high-resolution X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The XPS data show that N 1s binding states depend on substrate temperature ($T_s$). By comparison with the Raman spectra, N 1s binding states are assigned in which nitrogen atoms are mainly bound to sp$^2$ and sp$^3$ carbon atoms at $T_s = 100^\circ$C, whereas at $T_s = 500^\circ$C nitrogen atoms are mainly bonded to sp$^2$, sp$^3$ and sp$^4$ carbon atoms. © 1997 Elsevier Science B.V.

Keywords: Carbon nitride film; XPS; Raman spectrum; N 1s binding energy

Since Liu and Cohen [1] theoretically predicted the possible existence of superhard $\beta$-C$_3$N$_4$ phase carbon nitride, many groups have tried to deposit thin films of carbon nitride by using different techniques [2–8]. No convincing evidence for the existence of the $\beta$-C$_3$N$_4$ phase has been presented so far, since most of the films show an amorphous structure. In order to charac-terize such materials, the composition, chemical bind-ing state and the local order should be determined. Generally, the chemical binding states can be charac-terized by X-ray photoelectron spectroscopy (XPS) [2,3]. However, even though many investigators have demonstrated that the C 1s and N 1s lineshapes are composed of multiple components [2–6], there are discrepancies in the binding energy assignments. For instance, Marton et al. [2] deposited carbon nitride films by ion beam deposition and deconvoluted N 1s XPS spectra into three peaks with the main N 1s binding energies: at 398.3 eV, attributed to $\beta$-C$_3$N$_4$ bonds, and at 400.0 eV, attributed to C=N bonds. Rossi et al. [3] prepared carbon nitride films grown by ion-beam-assisted deposition and deconvoluted the N 1s XPS signal into two peaks at 398.2 and 400.2 eV, but they attributed these two peaks to N≡C and N=C, respectively. Gouzman et al. [4] implanted 500 eV N$_2^+$ ions in graphite as well as diamond to obtain carbon nitride and deconvoluted the XPS N 1s into three peaks at 402.0, 400.0 and 398.0 eV, denoted by $\alpha$, $\beta$ and $\gamma$. They assigned the main peaks $\beta$ and $\gamma$ to unpolarized $\beta$-C$_3$N$_4$ bonding and N≡C bonding, respectively. In contrast, Diani et al. [5] made in situ XPS measurements on carbon nitride films deposited by ECR plasma deposition and assigned the two N 1s peaks at 398.0 and at 399.8 eV to Si−N and C=N bonding. While the observed differences, of course, could be attributed to different structures of the ana-lyzed films, it is clear that further studies are needed on film structures that have been structurally and chemically characterized by other techniques as well. Also, measurements with as high an energy reso-lution as possible are needed in order to obtain as reliable a deconvolution as possible.

In this paper, high-resolution XPS spectra of CN$_x$ thin films grown at substrate temperatures, $T_s$, of 100° C and 500°C are presented. The films, which con-tained a nitrogen concentration of ~25 at.% and ~20 at.% respectively, were previously [8,9] charac-terized structurally by high-resolution transmission electron microscopy and Fourier transform infra-red spectroscopy. While the film grown at $T_s = 100^\circ$C was predominantly amorphous, the film grown at $T_s = 500^\circ$C had a ‘fullerene-like’ or ‘turbostratic-like’ structure with nm-sized areas composed of curved and crosslinked graphite planes [9]. The XPS results show that the nitrogen peaks are well separated, and the intensities of the nitrogen peaks depend on the struc-ture of the films. By comparison with Raman spectra from the same films, an assignment of the N 1s bind-ing energies is made.

Deposition of carbon nitride thin films on Si(100) substrates was carried out in a dc unbalanced mag-netron sputtering system. The vacuum chamber was evacuated to a base pressure of $8 \times 10^{-8}$ torr. A high-purity 99.999% pyrolytic graphite and 99.9999% pure nitrogen were used as a target and sputtering gas, respectively. The growth temperature of the films was kept at room temperature and $T_s = 500^\circ$C, whereas the nitrogen partial pressure was held con-stant at 2.5 mtorr. At room temperature, although no intentional substrate heating was used, the film growth temperature was recorded to be approximately 100°C. The thickness of the grown films with nitrogen content ranging from 20 to 25 at.% was between 300 and 1000 nm.

XPS measurements were performed with the high-resolution SCIENTA ESCA300 X-ray photoelectron spectrometer. This spectrometer employs a high-power rotating anode and monochromated Al $K_{\alpha}$ X-ray source ($hv = 1486.6$ eV), and high-transmission electron optics. The spectra were recorded with a total (photoenergy and electron analyzer contribu-tions) energy resolution of 0.37 eV. The Raman
spectra were measured in the range of 600 to 2400 cm\(^{-1}\) with a Bruker IFS66 spectrometer. The samples were excited by a near infra-red Nd:YAG laser (\(\lambda = 1064\) nm). For the detection, a liquid-nitrogen-cooled germanium diode was used. The spectra were recorded at a resolution of 4 cm\(^{-1}\) and after being averaged over 128 scans.

Two types of carbon nitride film were studied; deposited at substrate temperatures of 100°C and 500°C. Overview (wide scan) spectra of these films indicated the presence of a very small O 1s content, in addition to the carbon and nitrogen constituents. The O 1s intensity decreased constantly with depth during sputter cleaning of the film surface with Ar\(^+\) ions, consistent with the presence of a small amount of oxygen-containing surface contamination.

Detailed (narrow scan) spectra of C 1s and N 1s regions are shown in Figs 1 and 2, respectively, for \(T_s = 100\)°C and \(T_s = 500\)°C. Each of the C 1s spectra consists of one major peak, centered near 284.5 eV, with an asymmetry on the high binding energy side.
indicating the presence of carbon atoms with at least three different binding energies. Since these peaks are not well resolved, curve decomposition was not attempted for the C 1s spectra.

The N 1s core-level spectra, shown in Fig. 2(a) and (b), indicate the presence of nitrogen atoms with at least two different binding energies. For a sample deposited at \( T_s = 100^\circ \text{C} \), two main spectral contributions are evident: at 400.0 eV (denoted by \( P_2 \), full width at half-maximum (FWHM) = 2.1 eV) and at 398.3 eV (denoted by \( P_3 \), FWHM = 1.5 eV). The very small feature seen on the higher binding energy side (denoted by \( P_1 \)) corresponds to electrons from a few nitrogen atoms in N=O bonds in the surface layer, and is excluded from further consideration. For \( T_s = 500^\circ \text{C} \) samples, the two main spectral contributions are observed at 400.7 eV (FWHM = 1.6 eV) and 398.0 eV (FWHM = 1.4 eV). In addition, by varying the take-off angle, \( \theta \), of the electron detected, from \( \theta = 90^\circ \) or “normal exit” for all other spectra shown to about \( \theta = 5^\circ \), in order to maximize signal from the outermost atoms, a third feature is clearly observed near 398.9 eV (denoted by \( P_4 \), FWHM = 1.0 eV), as illustrated in Fig. 3.

Furthermore, Fig. 2 shows that the relative intensity of \( P_2 \) increases with an increase in \( T_s \), whereas the intensity of \( P_3 \) decreases. As already mentioned, the assignment of the \( P_2, P_3 \) and \( P_4 \) peaks varies extensively in the literature [2–6]. On the other hand, the presence of N=N, N=O or N=Si bonds can be ruled out on the basis of Auger electron spectroscopy (AES) and infra-red spectroscopy (IR) analyses [8]. The only reasonably probable configuration is that the nitrogen atoms are bound to carbon atoms in different chemical states.

Raman spectroscopy was performed for the same films grown at \( T_s \) of 100°C and 500°C, and the results are shown in Fig. 4(a) and (b), respectively. It should be mentioned that the Raman signal from the film with 300 nm thickness grown at \( T_s = 500^\circ \text{C} \) was weaker. Different y-axis scales were used in Fig. 4(a) and (b). A broad peak between 1200 cm\(^{-1}\) and 1700 cm\(^{-1}\) and a small sharp peak at \( \sim 2330 \text{ cm}^{-1} \) were observed in both cases. Interestingly, a small but sharp peak at \( \sim 2100 \text{ cm}^{-1} \) is detected only at \( T_s = 500^\circ \text{C} \), see Fig. 3(b). The broad peak is due to the Raman-active G (1570 cm\(^{-1}\)) and D (1360 cm\(^{-1}\)) bands of amorphous carbon [10], while the small and sharp peak at \( \sim 2330 \text{ cm}^{-1} \) is caused by atmospheric nitrogen in the sample chamber of the Raman spectrometer.
Another small peak at \( \sim 2100 \text{ cm}^{-1} \) can be attributed to \( \text{C}=\text{N} \) triple bonds \[10\]. The broad peak in Fig. 4(a) and (b) is fitted by using two Gaussian lineshapes. The spectral shapes at \( T_s = 100^\circ \text{C} \) and \( 500^\circ \text{C} \) are evidently different. The peak positions, full width at half-maximum intensity (FWHMI) and integrated intensity ratio (/r) after a computer lineshape analysis are summarized in Table 1. An upshift of the G band, a downshift of the D band, and a decrease of the ratio /r are observed with an increase in \( T_s \).

Comparing the XPS and Raman spectra of the films deposited at \( T_s = 100^\circ \text{C} \) and \( 500^\circ \text{C} \), the assignment of N 1s peaks in XPS can be made. The peaks P$_2$ and P$_3$ are attributed to nitrogen atoms bound to sp$^2$- and sp$^3$-coordinated carbon atoms, respectively, while P$_4$ is caused by \( \text{C}=\text{N} \) triple bonds (carbon atoms in sp$^1$ state). With the above assignment, the XPS spectra of \( \text{CN}_x \) films can be explained as follows: as \( T_s \) increases, the relative intensity of the N–C sp$^2$ binding state increases, whereas that of the N–C sp$^3$ binding state decreases. The contribution of the C=N binding state to the N 1s peak cannot be neglected at higher growth temperature. This is different from the assignment made by Marton et al. \[2\], although our assignment of N 1s peaks is in agreement with their report at lower growth temperature.

The films grown at \( T_s = 100^\circ \text{C} \) and \( 500^\circ \text{C} \) were previously \[8,9\] characterized structurally by high-resolution transmission electron microscopy. While the film grown at \( T_s = 100^\circ \text{C} \) was predominantly amorphous, containing nm-sized, diamond-like crystalline clusters, the film grown at \( T_s = 500^\circ \text{C} \) had a “fullerene-like” or “turbostratic-like” structure with nm-sized areas composed of curved and crosslinked graphite planes. The turbostratic microstructure can be described as built of basal structure units having a graphite-like structure, with the \( c \) planes rotated randomly with respect to each other, thus having crystalline ordering only between families of \( c \) planes. Since the nitrogen atom contains one more electron than the carbon atom, a buckling of otherwise flat, graphitic, six-membered rings is expected when substitutional nitrogen is present. Thus the different overall Raman spectrum is dominated by the G component, because the cross-section of the graphite stretching mode is much higher than that of the 1332 cm$^{-1}$ diamond mode \[3\].

### Table 1

<table>
<thead>
<tr>
<th>( T_s ) ((^\circ \text{C}))</th>
<th>( \omega_G ) (cm$^{-1}$)</th>
<th>( \omega_D ) (cm$^{-1}$)</th>
<th>/r</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1540</td>
<td>1330</td>
<td>3.03</td>
</tr>
<tr>
<td>( \pm 228 )</td>
<td>( \pm 408 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>1580</td>
<td>1270</td>
<td>0.81</td>
</tr>
<tr>
<td>( \pm 228 )</td>
<td>( \pm 408 )</td>
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local environments of the nitrogen atoms in CN$_x$ films with different structures may contribute the shifts in the N 1s binding energies in XPS spectra. Tamor and Wu [16] have proposed a graphite network model for diamond-like carbon. This model assumes “inter-planar (locally parallel graphitic sheets) links” through sp$^3$ bonding. Since the degree of fourfold-coordination carbon is limited by structural instabilities, the condition of low substrate temperature will minimize graphitization and preserve sp$^3$ carbon coor-dination. It seems that this is also the case for the CN$_x$ films, from the above analyses of XPS and Raman spectra. The creation of C–N triple bonds and cyanogen, C$_2$N$_2$, is thermodynamically favorable at elevated temperature. The appearance of a small sp$^1$hybridization in XPS and Raman spectra may indicate that reasonable quantities of the C–N species, pre-sumably terminal –C≡N, favorably exist in the surface layer. In summary, CN$_x$ thin films deposited by unbalanced magnetron sputtering have been analyzed by high-resolution XPS and Raman spectroscopy. The growth temperature has an influence on the binding states in CN$_x$ films. A detailed Raman spectrum analysis shows that the sp$^1$ bonding fraction in the films decreases with a rise in $T_s$, and the Raman band due to C≡N triple bonds only appears at higher growth temperature. By comparison with the Raman spec-tra, the assignment of N 1s peaks in XPS is made. For the film grown at $T_s = 100^\circ$C, the N 1s peaks at 400.0 and 398.3 eV are assigned to sp$^2$ and sp$^3$ CN bonding, respectively. In contrast, for the film deposited at $T_s = 500^\circ$C, the N 1s peaks at 400.7, 398.0 and 398.9 eV are attributed to sp$^2$, sp$^3$ and sp$^1$CN bonding.

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References