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Spectroscopic determination of the structure of amorphous nitrogenated carbon films
Electronic structure of hydrogenated carbon nitride films

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Hydrogen-induced changes on the electronic and structural properties of amorphous carbon nitride \((a\text{-}CN_x\text{:H})\) prepared by ion beam assisted deposition are investigated by x-ray photoelectron, ultraviolet photoelectron, infrared, and Raman spectroscopies. Two series of specimen are studied: films with a constant nitrogen content \((C/N=26\%)\) grown at 150 °C using different hydrogen partial pressures between 0% and 70% and samples deposited at different substrate temperatures \((150–500 \, ^\circ\text{C})\) with fixed \(H_2\) partial pressure of 60%. The pronounced changes of the N 1s and C 1s core level spectra on increasing hydrogen incorporation \((\text{up to 17 at. \%})\) are interpreted as due to the formation of terminating NH and CH bonds accompanied by modifications of the local C–N bonding structure. Corresponding changes are observed in the He II valence band spectra showing a recession of the leading edge of more than 0.9 eV while the optical band gap widens from 0 to more than 1 eV. Consistent with these results, the information obtained from the infrared and Raman spectra suggests a hydrogen induced transformation of the disordered \(sp^2/sp^3\) network into a polymerlike structure. With increasing substrate temperature a reversed process takes place. At 700 °C an increasing graphitization of the films is observed, but the effect of hydrogen on the structure influencing the growth kinetics is still present at this temperature. The nitrogen concentration \((N/C)\) of about 30% indicates high thermal stability of the CN material.

I. INTRODUCTION

Since the prediction of Liu and Cohen\(^1\) of a hypothetical covalent bonded material \(\beta\text{-}C_3N_4\) with a hardness comparable to that of diamond, considerable efforts have been made to synthesize nitrogen-rich carbon nitride films. Various methods have been applied and, although serious problems in producing a stoichiometric crystalline phase emerged, amorphous CN\(_x\) films exhibit useful optical and mechanical properties.\(^2\)–\(^4\) Much less attention was dedicated to studies of hydrogen containing carbon nitride films.\(^5\)–\(^8\) In the majority of these studies CN\(_x\):H films with different N concentrations were deposited in a glow discharge process without a systematic variation of the hydrogen concentration and the deposition temperature. As already demonstrated for amorphous hydrogenated silicon \((a\text{-}Si:H)\) and amorphous hydrogenated carbon \((a\text{-}C:H)\), the incorporation of hydrogen induces considerable changes in the electronic structure, in most cases improving the optical, electrical and mechanical properties of the material.\(^5\)–\(^10\) Furthermore, analogous to the synthesis of microcrystalline diamond, it cannot be excluded that at appropriate deposition conditions the addition of hydrogen may have similar importance for the formation of the \(\beta\text{-}C_3N_4\) phase. In a previous work, however, it was shown that H interrupts the connectivity of the network, probably preventing the formation of a stoichiometric phase.\(^11\) Moreover, in a recent study performed at a fixed temperature of 300 °C we presented results showing the effect of hydrogen on the electronic structure of CN\(_x\):H films deposited by ion beam assisted deposition (IBAD).\(^12\) Although from the analysis of the photoelectron and infrared spectra a tendency of a modification toward a polymerlike phase under the influence of hydrogen was detected, no further details about the film composition and changes of the mass density were available.

The present work was performed to get a better understanding of the chemical bonding arrangement of hydrogenated carbon nitride films with relative high N contents deposited at various conditions. It contains a detailed investigation of hydrogen induced changes on the local bonding structure by studying the core-level and valence band spectra of CN\(_x\) films deposited at a wide range of temperatures and with different concentrations of hydrogen. Infrared, visible and Raman spectroscopies were applied for further characterization of the material.

II. EXPERIMENT

The \(a\text{-}CN_x\text{:H}\) films were prepared by ion beam assisted deposition, shown schematically in Fig. 1. The main components of the system are two Kaufman ion sources of 3 cm diameter used as sputter and assisting guns and a high purity graphite target \((99.99\%)\). A removable heated \((\text{up to 1000} \, ^\circ\text{C})\) substrate holder allows for an easy transfer of the samples to the ultraviolet photoelectron spectroscopy/x-ray photoelectron spectroscopy (UPS/XPS) analysis system. The target was sputtered by nitrogen ions at a beam voltage of 1500 V using a total beam current of 90 mA. Simultaneously, a 75 V nitrogen-hydrogen ion mixture bombarded the growing film. The first series of samples was grown at a substrate temperature of 150 °C. The relative hydrogen partial pressure in the assisting gun \(p_{H_2}/(p_{H_2} + p_{N_2})\) was kept at

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0%, 40%, 60%, and 70% and the total assisting beam current was 1, 2, 5 and 10 mA, respectively. The increase of the assisting beam current was necessary to produce films with an almost constant nitrogen concentration but increasing hydrogen content. The second batch of films was grown at a constant hydrogen partial pressure of 60% and the substrate temperature was varied between 150 and 500 °C. For two films deposited at 700 °C, 0% and 15% hydrogen were used.

The assisting ion intensity, \( I_\mathrm{a} \), arriving at the substrate was measured by a probe placed at the position of the substrate biased at a voltage of −30 V. The carbon flux, \( A \), was calculated from the deposition rate without the assisting beam. The total deposition pressure was varied depending on the gas mixture between \( 2.5 \times 10^{-2} \) and \( 1.2 \times 10^{-1} \) Pa. The base pressure of the chamber pumped by a 450 l/s turbomolecular pump was about \( 2 \times 10^{-3} \) Pa. Polished Si (100) wafers and Corning glass were used as substrates.

After the deposition, the samples were transferred in situ to the XPS/UPS chamber \((<10^{-7} \text{ Pa})\) and measured without further treatment. For the XPS analysis, the Al K\( \alpha \) line was used \((h\nu=1486.6 \text{ eV}, \text{ width } 0.85 \text{ eV})\), and the mirror analyzer pass energy was 10 eV \((0.3 \text{ eV resolution})\). The elastic background of the C 1\( s \) and N 1\( s \) electron core-level spectra was subtracted using Shirley’s method. Further examination of the spectra was performed by a standard multiple Gaussian peak fitting procedure. No traces of oxygen were detected. The UPS valence band spectra were measured using the He \( \Pi \) line \((h\nu=40.8 \text{ eV})\) from a Vacuum Generation He resonant lamp with a total resolution of 0.3 eV. After the XPS and UPS experiments, the samples were analyzed by infrared, Raman and optical spectroscopies. The thickness of the films measured using a profilometer was between 100 and 300 nm. The atomic concentrations of hydrogen, carbon and nitrogen of the first series of films, listed in Table I were determined by elastic recoil detection analysis (ERDA) and Rutherford backscattering spectroscopy (RBS). The N/C values obtained by XPS analysis were in very good agreement with those of RBS giving a maximum error of less than 2%.

### III. RESULTS AND DISCUSSION

Section III is divided in two subsections, Sec. III A and Sec. III B. In Sec. III A, the study focuses on the structural changes induced by hydrogenation of carbon nitride containing a constant nitrogen content \((\text{N/C}=0.26)\) deposited at a fixed substrate temperature of 150 °C. In Sec. III B, the influence of the deposition temperature on the structural properties of the alloy is analyzed.

#### A. Dependence of the structural properties on the hydrogen concentration

1. **Deposition rate**

The deposition rate is an important parameter influencing many properties of amorphous films. In hydrogenated amorphous semiconductors, for instance, a suitable hydrogen dilution of the starting gases decreases dramatically the deposition rate producing, among other things, microcrystallinity.\(^{13}\) Since hydrogen may have a crucial effect on the deposition rate of CN, we shall pay special attention to this subject. In particular, as the incorporation of N may be severely limited by the presence of H, we shall discuss the most favorable experimental conditions for the purposes of this work.

Figure 2 displays the dependence of the deposition rate \((\text{DR})\) on the hydrogen partial pressure for films grown with and without being bombarded by a mixture of hydrogen and nitrogen ions. At a substrate temperature of 150 °C, the presence of an increasing amount of \( \text{H}_2 \) reduces the deposition rate by a factor of 2. The decrease is more drastic when the film is exposed to the assisting beam of 75 V \((\text{factor of } 3)\). This effect is attributed to chemical etching induced by the formation of volatile cyano, amino and \( \text{CH}_3 \) compounds \((\text{CN radicals, HCN and C}_2\text{N}_2)\) during film growth. Recent studies showed\(^{14}\) that the chemical etching effect is also present without the addition of hydrogen and is considered as one of the most important factors that limits the nitrogen concentration in CN films. On the right-hand axis of Fig. 2 the ion to atom arrival ratio \( I/A [(\text{N}_2^+ + \text{H}_2^+)/\text{C}] \) is plotted for the films grown at different \( \text{H}_2 \) partial pressures. Above, at a very low value of \( I/A=0.5 \), no film formation occurs. This ratio is about four times smaller than the critical \( I/A \) values.
ratio previously reported for 100 V nitrogen assisting \([I/A]_{\text{crit.}}=2\). As a consequence the H\textsubscript{2} partial pressure limited both the H and N concentrations of the films to the values given (see Table I).

2. Structural analysis by photoelectron spectroscopy

Figure 3 shows the evolution of the N 1s core-level spectra for three films of the 150 °C batch (\(\alpha\)-CN\textsubscript{0.26}:H) deposited by assisting the sputtered carbon film by an increasing amount of hydrogen in the ion beam. No significant differences were observed between samples CN26 and CN27. Therefore, we have plotted only the results corresponding to CN27. The partial pressure of N\textsubscript{2} was kept constant. The atomic hydrogen concentration values \(c_H\) determined by ERDA are reported in Table I. The best fits of individual components are included in the spectra using Gaussian curves with a constant full width at half maximum (FWHM) of 1.9 eV. The deconvoluted spectrum of the unhydrogenated film shows two well resolved peaks at 398.3 and 400.6 eV and two small peaks at 402.6 and 404.6 eV. Recently, the assignment of the main components was performed by numerical simulations applied to representative N containing molecules having structures which include \(sp, sp^2,\) and \(sp^3\) carbon hybridization and fragments of the theoretically predicted \(\beta\)-C\textsubscript{3}N\textsubscript{4} phase. According to these results the peak at lower binding energy (398.3 eV) is due to N atoms bonded to \(sp^3\) hybridized C with isolated lone pair electrons, as in \(\beta\)-C\textsubscript{3}N\textsubscript{4}. The peak located at higher binding energy (400.6 eV) is attributed to substitutional N atoms in a graphitic-like configuration with lone pair electrons now involved in aromatic \(\pi\) bonding. Components representing N bonded to \(sp^2\) C in nonaromatic structures and the nitrile an isonitrile bonding configuration (C=N) are expected close to 399 eV. These findings are in agreement with results obtained by an extensive XPS study on CN\textsubscript{1} films by Baker and Hammer. The origin of the peaks at higher binding energy is not clear, but the structures probably result from the planar N–N bonding configuration and from N\textsubscript{2} molecules trapped in the film. As previously reported, the incorporation of hydrogen leads to the evolution of a new peak at about 399.1 eV interpreted as a contribution of H bonded to N. As is shown later, the presence of NH bonds is confirmed by the infrared spectra (see Fig. 7). Increasing the H\textsubscript{2} partial pressure up to 70% (17 at. % H) increases the intensity of this component at the expense of both the N bonded to \(sp^2\) C (N–sp\textsubscript{2} C) and the N bonded to \(sp^3\) C (N–sp\textsubscript{3} C) structures, demonstrating profound changes in the bonding structure of the films. In Fig. 4 the relative peak intensities of the three N 1s components \(A_{N–sp^2C}\) (400.6 eV), \(A_{N–sp^3C}\) (398.3 eV) and \(A_{N–H}\) (399.1 eV) are plotted as a function of the H content. The value of \(A_{NH}\) increases to more than 50% while the peak area ratio \(A_{sp^3C}/A_{sp^2C}\) decreases from a value of 1.2 to 0.3. Also, the total peak width (FWHM) reduces from 4.1 to 3.1 eV. In a recent study of CN\textsubscript{0.23}:H films deposited at 300 °C we reported similar results although with less pronounced changes. It was observed that at a deposition temperature of 300 °C, the \(A_{NH}\) represents 35% of the total contribution for a hydrogen concentration of 15 at. %. This result shows that at a higher deposition temperature films with lower hydrogen concentrations are produced. This is due to enhanced effusion of hydrogen containing volatile species. Furthermore, as expected, lowering the substrate temperature to 150 °C allows a more effective H incorporation, enhancing the modifications of the structural properties of the material.
The XPS C 1s results for the hydrogen free film (CN23) and that with the highest hydrogen content (CN27) are presented in Fig. 5. For discussion purposes, spectra of a-C and a-C:H films, grown as far as possible under similar conditions replacing nitrogen by argon ($p_{\text{H}_2}/p_{\text{tot}}=40\%$), are included. The C 1s peak position of the a-C film located at 284.4 eV is very close to that determined for graphite at 284.35 eV. A minor component at about 285.6 eV is attributed to a small fraction of $sp^2$ carbon. The incorporation of hydrogen in a-C has two effects. First, there is a shift of the peak position up to 284.8 eV as can be seen in the a-C:H spectrum. Second, the C 1s peak is narrower and more symmetric. The shift stems from hydrocarbon components located at about 284.9 eV while the narrowing is caused by the decrease of the graphitic and apparently also of the $sp^3$ (285.6 eV) component.

The inclusion of N in the a-C system (0% H$_2$) has the effect of widening and shifting the C 1s spectrum to higher energies. Different C-N binding environments ($sp^2$ C bonded to N and $sp^3$ C bonded to N) can produce these effects. Indeed, the higher electronegativity of nitrogen is expected to increase the binding energy of the C 1s electrons. Also, a component from aromatic structures (pure graphitic) at ~284.4 eV contributes to the final shape of this band.

Upon hydrogenation (17 at. % H), the graphitic component diminishes and some C-N bonds are substituted by C-H bonds having a lower binding energy. Therefore, a narrower spectrum is generated. The FWHM is reduced from 2.8 to 2.3 eV. We wish to remark, however, that some effect on the observed narrowing could be attributed to the lower amount of N content of the hydrogenated sample (see Table I).

The UPS, He II valence band (VB) spectra for the 150 °C film series with different H contents are shown in Fig. 6. As before, a-C and a-C:H spectra of films grown at similar conditions are included. The origin of the four main structures of the hydrogen free film (CN23) located at about 0–3.5, 3.5–5,
6.5, and ~9 eV are assigned as follows. The band located at about 0–3.5 eV is associated with C–C π bonds due to C 2p electrons. The structure between 3.5 and 5 eV is attributed to nitrogen lone pair electrons (sp² hybridized nitrogen) and to C–C π states. The origin of the dominant structure at 6.5 eV is a contribution of C 2p and N 2p electrons associated with π bonds superimposed on the C 2p electrons σ-bond feature located at about 7 eV (see Fig. 6, a-C film). The band located at about 9 eV is due to C 2p and N 2p electrons shared in the σ bonds.

Upon hydrogenation several effects are evident. There is a recession of the valence band leading edge E_{LE} of more than 0.9 eV (see also Table I). Here, E_{LE} is the energy defined at the intersection of the linear extrapolation of the valence band tail with the energy axis. This recession is attributed to a reduction of the C–C π states close to the Fermi level, as suggested by a-C:H film spectrum. Moreover, as discussed before, the reduction of the graphitic component observed in the C 1s spectra confirms this interpretation (see Fig. 5). Another consequence of the reduced π state density upon hydrogenation is the increasing value of the optical band gap E_{Tauc} (see Table I). As already mentioned, hydrogen induces a reduction of the nitrogen incorporation in the alloy. Therefore, the intensity associated with the nitrogen lone pair electrons (~4.2 eV) is slightly reduced as the N concentration changes from 22 to 16 at. %. Furthermore, the main feature at 6.5 eV (C–N π bonds) is subsequently replaced by a new component located at 7.6 eV. This modification is associated with the increasing number of C–H and N–H bonds discussed in relation to the XPS spectra (Figs. 3, 4 and 5).

3. Structural analysis by infrared and Raman spectroscopies

Further information about the chemical bonding structure was obtained by infrared (IR) spectroscopy, shown in Fig. 7. For the hydrogen free film (CN 23) the unresolved band between 1000 and 1600 cm⁻¹ is mainly associated with graphitelike structures. As hinted by the broad shoulder above ~1300 cm⁻¹ and in analogy to the Raman spectra (shown later), two broad bands can be identified. They are associated with vibration modes of N bonded to sp² C in small disordered domains (D band, ~1350 cm⁻¹) and of N containing aromatic ring structures (G band, ~1550 cm⁻¹). Also, around 1100 cm⁻¹ contributions of sp³ C bonded to N (C–N stretching vibrations) are present. Four effects are observed in the IR spectra on increasing H incorporation. (1) The absorption associated with the D and the G bands becomes less active; (2) a new band associated with olefinic CN bonds (imines: >C=N–C, >C=N–H) and possibly NH₂ bending vibrations appears at 1600 cm⁻¹; (3) the CH stretching modes (~2900 cm⁻¹) and the nitrile or isonitrile band (C≡N) at 2200 cm⁻¹ remain very weak for all the samples studied; and (4) an apparently increasing activity of N–H stretching vibrations between 3200 and 3500 cm⁻¹ is observed. However, recent experiments show that a strong band remains at 3350 cm⁻¹ after replacing H₂ by D₂, an incompatible result with the expected isotopic effect of deuterium. Therefore the main contribution for the 3200–3500 cm⁻¹ absorption band is probably due to OH stretching vibrations caused by absorbed oxygen after exposing the sample to the atmosphere. An explanation for the presence of OH in the bulk of the hydrogenated samples could be the porosity of the material, as suggested by the decreasing film density ρₘ (see Table I). This is another indication of structural changes taking place when, as discussed before, an increasing hydrogen content promotes more terminating NH and CH bonds favoring the evolution of voids.

For the same films corresponding results to the infrared analysis were obtained by Raman spectroscopy in the region between 800 and 2000 cm⁻¹. The normalized spectra were quantitatively analyzed by a deconvolution procedure using a combination of Gaussian and Lorentzian line shapes (Fig. 8). The spectra show significant changes on H incorporation, although some of the spectral features are not present or are less evident than in infrared case. The main features are the D band located at 1365 cm⁻¹ (FWHM=280 cm⁻¹) and the G band at 1565 cm⁻¹ (FWHM=175 cm⁻¹). We note that the 1110 cm⁻¹ band (FWHM=170 cm⁻¹), attributed to N bonded to sp³ C, is less marked than the corresponding band in the infrared spectra of the hydrogen free film (CN23).

The main change upon increasing hydrogen content occurs at higher energy. A new component at 1590 cm⁻¹ (FWHM =95 cm⁻¹) has to be included to fit the spectra. Exclusion of this component causes a shift of the G band to a value of 1585 cm⁻¹ giving a poor fit even without restrictions for the fitting parameters of the D band. The new component can be attributed to the formation of the olefinic C≡N–H bonds already discussed in the infrared spectra. The infrared structure visible as a shoulder of the 17 at. % H film (CN27) at ~1700 cm⁻¹ (see Fig. 7), probably due to C=O stretching vibrations, is not active in the Raman spectra.
Finally, although the integrated intensity ratio of the \(D\) and \(G\) bands remains almost constant \((I_D/I_G=2.0)\), the relative intensity of both peaks decreases by 10\% upon hydrogenation. It is well known that aromatic structures have a rather high Raman scattering efficiency, masking all other emerging features in the spectra.\(^{23}\) This is a setback when analyzing standard Raman spectra. On the contrary, due to the more equilibrated transition matrix elements, relatively small spectral changes are observed much better in the infrared and Raman spectra. Therefore, upon hydrogen incorporation a much stronger reduction of the relative \(G\) and \(D\) band intensity can be detected.

![Raman spectra of amorphous CN\(_{26}\) films deposited at 150 °C with hydrogen concentrations of 0 (CN23), 10 (CN25) and 17 at. % (CN27).](image)

**Fig. 8.** Raman spectra of amorphous CN\(_{26}\) films deposited at 150 °C with hydrogen concentrations of 0 (CN23), 10 (CN25) and 17 at. % (CN27).

4. **Combined interpretation of the results**

From the above results the following conclusions can be drawn. (1) The amorphous hydrogen free CN\(_x\) network consists mainly of small aromatic ring domains \((G\) and \(D\) bands, see Figs. 7 and 8) interconnected by a smaller fraction of tetrahedrally bonded C atoms. (2) As deduced from the analysis of the N 1\(s\) and C 1\(s\) spectra, the \(sp^2\) hybridized nitrogen is preferentially bonded to \(sp^3\) hybridized carbon and also occupies sites within aromatic rings by substitution of C atoms. In both cases N has a lone electron pair.

Upon hydrogenation several effects are observed: (1) an increasing optical band gap together with a recession of the He II valence band; (2) the appearance of a new band associated with olefinic structures in the infrared and Raman spectra; and finally (3) the strong changes in the N 1\(s\) spectra are evidence of structural modification of the material. They are interpreted as being caused by a reduction of the size and number of aromatic domains by the formation of terminating C–H and N–H. The consequence is a decreasing density of C–C \(\pi\) states close to the Fermi level (see Fig. 6) accompanied by an increasing transparency of the films. Furthermore, as can be concluded from the strong increase of the NH component of XPS N 1\(s\) spectra, H appears to be preferentially bonded to N in the network between the \(sp^2\) domains causing a significant reduction in the N–\(sp^3\) C component. Thus, the former N–\(sp^3\) C bonded matrix is mostly transformed into a polymeric configuration containing \(sp^2\) structures like >C=\(N\text{-C}\) and =C=\(N\text{-H}\). Formation of terminating CH, NH and C=\(N\) bonds favors the creation of voids hence reducing the mass density of the hydrogenated material.

B. **Dependence of the structural properties on the deposition temperature**

1. **Deposition rate**

As was remarked above, temperature is an important parameter influencing the growth kinetics and consequently the film structure. Films deposited at a substrate temperature between 150 and 500 °C and constant partial pressure \((p_{H_2}/p_{tot}=60\%)\) show an almost linear decrease of the deposition rate down to 0.5 nm/min (see Table II). Indeed, at elevated temperatures both a less effective film growth and H

<table>
<thead>
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<th>Film No.</th>
<th>(T_1) (°C)</th>
<th>(p_{H_2}) (%)</th>
<th>DR (nm/min)</th>
<th>N/C (%)</th>
<th>(A_{SH}) (%)</th>
<th>(A_{N-sp^2}) (%)</th>
<th>(A_{N-sp^3}) (%)</th>
<th>(E_{Tauc}) (eV)</th>
<th>(E_{LE}) (eV)</th>
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<td>150</td>
<td>60</td>
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<td>27.5</td>
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<td>41.0</td>
<td>0.75</td>
<td>0.50</td>
</tr>
<tr>
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<td>60</td>
<td>1.5</td>
<td>22.0</td>
<td>23.0</td>
<td>32.5</td>
<td>44.5</td>
<td>0.65</td>
<td>0.10</td>
</tr>
<tr>
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<td>400</td>
<td>60</td>
<td>1.2</td>
<td>21.5</td>
<td>15.0</td>
<td>38.5</td>
<td>46.5</td>
<td>0.55</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.5</td>
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<td>0.35</td>
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<tr>
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<td>15</td>
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<td>30.0</td>
<td>(6.0)</td>
<td>51.0</td>
<td>43.0</td>
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<td>−0.60</td>
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<tr>
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<td>49.0</td>
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<td>−0.60</td>
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</table>
incorporation are expected to be caused by increasing out diffusion of CNH species. Therefore, to study the effect of hydrogen at the highest temperature reached, 700 °C, the H2 partial pressure was reduced to 15% giving a deposition rate of 0.4 nm/min. In these experimental conditions we were able to obtain films with N/C of about 30%. A strong decrease of the N concentration above 600 °C reported by Lopez et al. for their dc magnetron sputtered CN samples was not observed. This may be due to the difference of deposition parameters and to the technique used.

2. Structural analysis by photoelectron spectroscopy

The evolution of the XPS N 1s core-level spectra of films grown at different substrate temperatures is presented in Fig. 9. As can be observed, increasing the deposition temperature is almost equivalent to decreasing the hydrogen content in the films (see Fig. 3). The progressive separation of the two main components (N–sp2 C and N–sp3 C) indicates a less efficient incorporation of hydrogen in the material at higher temperatures. For the sake of clarity the film deposited at 300 °C (CN14) is not shown in Fig. 9. Following a similar fitting procedure to that in Sec. III A 2, the adjusted NH component located at 399.1 eV was determined. According to these authors, nitrogen is preferentially bonded to sp3 C sites for films with N/C≥20%. This finding seems to also be valid for the intensity ratio \( \frac{A_{N-sp^3 C}}{A_{N-sp^2 C}} \) found for hydrogenated films with different N/C ratios grown between 400 and 700 °C (see Fig. 9).

More physical insight is gained by comparing the spectra of films deposited at 700 °C with and without hydrogen in the assisting beam. First, in the hydrogenated film, the two peaks are less resolved than that in the hydrogen free material (see Fig. 9). Second, in the hydrogenated sample, the component associated with N–sp3 C is smaller than that in the hydrogen free film. To explain these experimental facts we note that hydrogen is rather unlikely to remain bonded in the solid at 700 °C. Therefore, the 6% contribution to the area associated with NH (399.1 eV) for the hydrogenated sample deposited at 700 °C is probably physically meaningless (see Table II). Hence, we suggest that the difference in the N 1s spectra between these films may be attributed to changes in the growth kinetics induced by the presence of hydrogen.

The temperature induced changes observed in the N 1s are evident also in the C 1s spectra for the corresponding samples (not shown). The shift of the main peak position from 285.3 [150 °C, (CN26)] to 284.9 eV [500 °C, (CN37)] indicates an increase of the graphitic component located at 284.35 eV. It must also be considered though that a part of this shift accounts for the lower N content of the 500 °C film reducing the number of CN bonds at the high energy side of the spectrum. Clear evidence of the increasing presence of graphitic C–C π states was obtained in the UPS He II spectra shown in Fig. 10. Comparing the samples deposited at 150 (CN26) and 700 °C (CN42), one sees that the value of the
leading edge $E_{LE}$ decreases by more than 1 eV. As shown in Table II, this effect is accompanied by the reduction of the optical band gap. We want to remark, however, that the position of the band associated with the nitrogen lone pair electrons (~4.2 eV) is only slightly shifted. This shift is probably due to the increasing C-C $\pi$ contribution to the spectrum rather than due to changes of the lone pair electron binding energy. On the other hand, the loss of hydrogen at high temperatures shifts the main feature located at 7.3 eV [C–N(H) $\pi$ bonds] subsequently towards 6.4 eV (C–N $\pi$ bonds). It should be noted that for both structures the peak intensity depends on the nitrogen concentration.

3. Structural analysis by infrared spectroscopy

The infrared spectra of samples deposited at 150, 400, and 500 °C are presented in Fig. 11 (the spectrum of the sample grown at 700 °C was not available due to the small thickness of the film). The changes introduced by increasing the substrate temperature in the region of the main absorption band (1000–1700 cm$^{-1}$) are evident. The modes assigned to olefinic CNH structures at 1600 cm$^{-1}$ although less active are still present at 500 °C. Simultaneously, a considerable increase of the D band (~1350 cm$^{-1}$) is observed, reflecting the more graphitelike character of the films. Furthermore, stretching modes representing the nitrile and isonitrile structures (C=≡N) at 2200 cm$^{-1}$, $sp^2$ C–H at 2900 cm$^{-1}$ and N–H/O–H at 3350 cm$^{-1}$ almost disappear from the spectra. The reduced activity of OH vibrations is probably related to the higher density and therefore reduced oxygen diffusion in the high temperature films.

4. Combined interpretation of the results

Upon increasing substrate temperature, the principal spectral changes observed by photoelectron spectroscopy are the strong decrease of the contribution from the NH component to the XPS N 1s spectra and a considerable increase of the C–C $\pi$ state density (He ii). Simultaneously, the optical band gap decreases. The infrared spectra show an enhanced activity of the D band indicative of the increasing number of disordered aromatic structures in the film. The reduced activity of the O–H vibrations suggests a densification of the structure. All these results represent a structural modification from a hydrogen-rich polymerlike material towards an almost hydrogen free predominantly $sp^2$ bonded phase. Even at high temperatures (700 °C), an efficient nitrogen incorporation is observed, reaching a concentration of 30% (N/C). However, the growth kinetics prevents the formation of hydrogen bonds by promoting a thermodynamically more stable nitrogen containing graphitelike structure.

IV. CONCLUSIONS

Two series of CN$_x$ films were deposited by the IBAD technique. One set of samples was grown at a constant substrate temperature of 150 °C, changing the H concentration. The second set was obtained at a constant H partial pressure and by varying the substrate temperature between 150 and 500 °C. The influence of hydrogen on the bonding structure was studied by XPS, UPS, infrared, Raman and visible spectroscopies. Incorporation of an increasing amount of hydrogen causes the evolution of new spectral features due to the formation of terminating CH and NH bonds. As a consequence, a transformation of a predominantly aromatic bonded amorphous $sp^2$/C–N network to a more polymerlike structure takes place. An increasing optical band gap and decreasing density of the material accompany this process. In turn, in films grown at high temperatures, the olefinic C≡N–H structures are almost entirely replaced by small graphitic domains. This process is induced by subsequent effusion of hydrogen and a changed growth kinetics. Furthermore, although without remaining in the material, experimental evidence was obtained that even at 700 °C the formation of the structure is influenced by hydrogen. Finally, the high N concentration (N/C=30%) demonstrates the high thermal stability of the amorphous CN$_x$ material.

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