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Spectroscopic ellipsometry characterization of amorphous carbon and amorphous, graphitic and fullerene-like carbon nitride thin films

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Carbon nitride (CN_x) and amorphous carbon (a-C) thin films are deposited by reactive magnetron sputtering onto silicon (001) wafers under controlled conditions to achieve amorphous, graphitic and fullerene-like microstructures. As-deposited films are analyzed by Spectroscopic Ellipsometry in the UV-VIS-NIR and IR spectral ranges in order to get further insight into the bonding structure of the material. Additional characterization is performed by High Resolution Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy, and Atomic Force Microscopy. Between eight and eleven resonances are observed and modeled in the ellipsometrically determined optical spectra of the films. The largest or the second largest resonance for all films is a feature associated with C-N or C-C modes. This feature is generally associated with sp³ C-N or sp³ C-C bonds, which for the nitrogen containing films instead should be identified as a three-fold or two-fold sp² hybridization of N, either substituted in a graphite site or in a pyridine-like configuration, respectively. The $\pi \rightarrow \pi^*$ electronic transition associated with sp² C bonds in carbon films and with sp² N bonds (as N bonded in pyridine-like manner) in CN_x films is also present, but not as strong. Another feature present in all CN_x films is a resonance associated with nitrile often observed in carbon nitrides. Additional resonances are identified and discussed and moreover, several new, unidentified resonances are observed in the ellipsometric spectra.

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1. Introduction

Carbon-based materials have received considerable attention during the past decades ever since the theoretical prediction of a crystalline phase of β - C_3N_4 by Liu and Cohen [1,2]. Numerous types of structures of C and CN_x have been produced since then and several of the structures show interesting mechanical, tribological, electronic and optical properties making them promising candidates e.g. as tribological coatings [3], as protective layers on magnetic hard disks [4], as filler in electrical conductive adhesives [5], and as a biomaterial [6,7]. In the context of biomaterials, one group of carbon-based materials should be mentioned in particular, the fullerene-like CN_x , discovered in 1995 [8-10]. It is a nano-scaled material consisting of bent and intersecting, cross-linked nitrogen containing graphene sheets, exhibiting a combination of high hardness and extreme elasticity and might be a candidate aimed e.g. for replacements of hips and joints.

The films studied in this work are grown by physical vapor deposition in a magnetron sputtering system and are representatives of amorphous carbon (a-C), amorphous carbon nitride (a- CN_x), graphitic carbon nitride (g- CN_x) and fullerene-like carbon nitride (FL- CN_x). The amorphous films exhibit a microstructure without order, whereas the graphitic structure is described with large graphitic domains with less curvature as compared to the fullerene-like (FL) structure which consists of smaller domains and a more pronounced curvature. The ordered films exhibit no long range order. The bonding structure of carbon-based films predominantly consists of sp^2 and sp^3 hybrids of C-C and C-N bondings, where the sp^2 hybrids are dominating in CN_x films as nitrogen bonded in a substitutional site in the graphite network or as nitrogen bonded in a pyridine-like manner. The latter is established in earlier studies on the same type of films [10-12]. The size and arrangement of the sp^2 domains, composed of a mixture of chains and rings, are important for the understanding of the electronic and optical properties of a material [13].

The objective of this work is to use Spectroscopic Ellipsometry (SE) to determine and analyze optical properties of the carbon-based films in the UV-VIS-NIR and IR spectral ranges. There is a high motivation employing SE on these materials, since SE-data contains quantitative structural information in terms of resonance energies, broadenings and magnitude of absorption bands and, especially in the IR and NIR regions (below 8000 cm^{-1} or 1 eV), SE-data are rarely available in the literature. The

structure, as analyzed by X-ray Photoelectron Spectroscopy (XPS) and High Resolution Transmission Electron Microscopy (HRTEM) is used to correlate the structure as detected from the ellipsometric measurements.

2. Experimental details

Carbon and carbon nitride films were grown to a nominal thickness of 200 nm on silicon (001) wafers in a d.c. magnetron sputter deposition system at a base pressure below 1×10^{-9} Torr (1.3×10^{-7} Pa) and a bias voltage of -25 V. By changing the deposition parameters (substrate temperature and fraction of nitrogen in the discharge), films of a-, g- and FL-CN_x as well as a-C were grown. Some details of the deposition parameters and properties of the films are listed in Table 1. Further details about the deposition technique can be found elsewhere [14,15].

Directly after deposition, the films were analyzed by XPS regarding bonding configuration and elemental composition using a VG Microlab 310F instrument with a non-monochromated Mg K_{α} ($h\nu=1253.6$ eV) X-ray without initial “sputter cleaning”. The microstructure was characterized by HRTEM using a Jeol 3010 transmission electron microscope operated at 300 kV and a resolution of 1.7 Å. Furthermore, surface roughness was determined by Atomic Force Microscopy (AFM) using a Nanoscope IIIa from Digital Instruments operating in tapping mode and equipped with a silicon tip having a cone angle of 22°. Root mean square roughness (RMS) and average roughness (Ra) were evaluated from $1 \times 1 \mu\text{m}^2$ scans. Ellipsometric studies were performed with a Variable Angle Spectroscopic Ellipsometer (VASE) from J. A. Woollam Co. Inc. in the UV-VIS-NIR range 230-1690 nm at angles of incidence of 60° - 75° as well as in the IR range 2000-30 000 nm at angles of incidence of 50° - 70° using an Infrared Spectroscopic Ellipsometer (IRSE) from the same company. Both instruments provide spectral Ψ and Δ data and all modeling of ellipsometric data was performed using the WVASE software [16]. The non-linear regression algorithm provides values on the fitting parameters, 90% confidence intervals and mean squared errors (MSE). To be noticed is that the spectral ranges of the two instruments do not overlap according to their specifications and therefore leaves a gap with no data between 1690 and 2000 nm. The energy positions of the optical features are presented in units of cm^{-1} or eV and

the UV-VIS-NIR and IR ranges correspond to 5917-43 480 cm^{-1} (0.73-5.39 eV) and 333-5000 cm^{-1} (0.041-0.62 eV), respectively.

Since carbon atoms in carbon-based materials can exhibit a large variety of local bonding environments and thus can give rise to a large variation in bonding vibrations, the analysis of the optical properties of carbon-based materials becomes challenging. In addition there are very few references on this subject found in the literature for solely sp^3 or sp^2 bonded materials. In this work, experimental ellipsometric data from UV-VIS-NIR and IR measurements were modeled in the range 336-29 400 cm^{-1} (0.0417-3.64 eV) as exemplified in Fig. 1 for the a-CN_x film.

The films were sufficiently thick to use a two-phase model in which the film corresponds to the substrate and air is ambient. An optical model with Lorentz oscillators was used for fitting of the complex-valued model dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ to experimental Ψ and Δ data. The following form of the Lorentzian function was used

$$\varepsilon = \varepsilon_\infty + \sum_j \frac{A_j \Gamma_j E_{0j}}{E_{0j}^2 - E^2 - i\Gamma_j E} \quad (1)$$

where ε_∞ is an offset taking care of resonances at larger energies, A_j , Γ_j , and E_{0j} are the amplitude, broadening and resonance energy of resonance j and E is the photon energy. The amplitude A_j is equal to the peak height of ε_2 at the center energy E_{0j} . The refractive index is obtained as $N = n + ik = \sqrt{\varepsilon}$.

A few resonances showed a double peak behavior and in these cases the fitting was improved by using a Gauss-Lorentz Asymmetric Doublet (GLAD) oscillator. The GLAD feature is included in the WVASE software and allows modeling of two over-lapping peaks in terms of a center energy and a splitting equal to the distance between the energy positions of the two peaks. This considerably reduces correlation between the parameters of the two peaks compared to modeling them individually [16]. In addition, the shape of the peaks can be optimized by using a mix of a Lorentzian and a Gaussian line-shape.

Figure 1 Experimental (symbols) and modeled (dashed curves) SE-data of the $a\text{-CN}_x$ film. Notice that different angles of incidence were used in IR and UV-VIS-NIR spectral ranges.

3. Results and discussion

3.1. Microstructure

XPS was used to study chemical composition and bonding in the deposited films whereby the ratio between the peak for nitrogen bonded in a pyridine-like manner

(PL) and the peak for nitrogen substitutionally bonded into graphite (SB) could be determined (both types of bondings are sp^2 hybridized) and used as a fingerprint of the microstructure [14]. The XPS spectrum in Fig. 2 shows that the value of the ratio PL/SB is decreasing with a decreased nitrogen fraction and also with an increased deposition temperature at the same time as the separation between the peaks are increasing. A low PL/SB ratio indicates a pronounced FL microstructure [15]. The PL/SB ratio is determined by dividing the peak areas after normalization to the same maximum intensity and fitting the background according to Shirley [17] and is, along with N concentrations in the films, given in Table 1. Also to be noticed is that an increased amorphization of the structure leads to merging of the two peaks which is apparent for the a-CN_x film as seen in Fig. 2. The peak separation of the FL-CN_x film is ~2 eV. A minor contribution from a third peak was identified at ~399.5 eV which most likely corresponds to nitrile (sp -hybridized nitrogen) and is largest for the a-CN_x film and smallest for the FL-CN_x film.

Figure 2 Nitrogen 1s XPS-spectrum for the a-C and CN_x films with vertical lines schematically showing the fitted positions using a Shirley type [17] background (Fitted curves not shown).

Table 1: Deposition parameters, and properties as measured by XPS, of the sputtered films.

Denomination	a-C	a-CN _x	g-CN _x	FL-CN _x
N ₂ partial pressure	0	1	1	0.16
Deposition temperature (°C)	150	150	450	450
XPS N conc. (at%) $\pm 10\%$	0	28.5	18.1	10.4
Ratio of PL/SB (see text for def.)	--	1.3	1.1	0.75

The amorphous, graphitic and fullerene-like microstructures were confirmed by HRTEM as shown in Fig. 3. The two amorphous films display a typical amorphous microstructure, whereas the graphitic and the fullerene-like films show a more ordered microstructure with bent and intersecting nitrogen-containing graphene sheets and an interplanar lattice spacing of ~ 0.35 nm. In the FL film the cross-linking of the graphene sheets is more pronounced with smaller radii of curvature and more frequent intersection of the planes. From the selected area electron diffraction patterns (not shown) of the amorphous films, two diffuse rings can be discerned at 1.2 and 1.95 Å, characteristic of amorphous allotropes of C and CN_x. The g-CN_x and FL-CN_x films exhibit an extra ring at 3.5 Å and occasionally at ~ 1.75 Å (0002 and 0004 reflections of graphite, respectively). The appearance of the ring at ~ 3.5 Å is in accordance with the presence of packages of curved basal planes in the HRTEM images [15]. For the FL film the ring at 3.5 Å is not complete, but has an arc-like appearance indicating texture, in terms of a preferred orientation (standing position) of the basal planes.

The surface morphology of the films was studied by AFM and indicated low surface roughness for all films except for the g-CN_x film showing a slightly rougher surface (RMS=13 nm) compared to g-CN_x films grown earlier with values around 1 nm [18]. The RMS and Ra values are listed in Table 2.

3.2. Analysis of optical spectra

3.2.1. Analysis and overview

As seen in Fig. 1, the fit is very good for the a-CN_x data and similar fit quality is obtained for the other films. The mean squared errors (MSE), which can be used as a figure of merit of the quality of a fit, were 1.3 ± 0.2 for all films. For the graphitic film, modeling of the surface roughness with a Bruggeman effective medium layer

Figure 3 HRTEM micrographs of (a) a-C, (b) a-CN_x, (c) g-CN_x and (d) FL-CN_x films.

Table 2: Surface roughness as measured by AFM.

Denomination	Ra [nm]	RMS [nm]
a-C	1.0	1.5
a-CN _x	0.2	0.3
g-CN _x	11	13
FL-CN _x	2.0	2.6

[16] decreased the MSE value from 1.20 to 1.19. The other films were not much affected by including a surface roughness layer in the model. This is relevant since

the graphitic film shows the largest surface roughness according to AFM measurements. The 90%-confidence limits for the lineshape parameters for most resonances in all films were lower than 7 %. A few reached values up to 11 % whereas the resonance at the lowest energy (outside the measurement range) in all films and the third resonance of the FL-CN_x film (width and amplitude) as well as the fifth resonance of the a-CN_x film (width and amplitude) reached higher values.

For the different films, eight to eleven resonances can be fitted to the experimental data. Some of the resonances can be identified whereas others can not be recognized in available literature data. The resonances are numbered C1, C2, C3, etc. for the a-C film and similar for the three other films using letters, A, G and F. GLAD doublets that belong together are indicated with prime or bis, e.g. A2' - A4' is one doublet and A7'' - A8'' is another. The broadening of a GLAD peak is the width of the doublet peak and not of each peak, giving the same Γ value for the two peaks.

Figure 4 shows the model dielectric functions for the four films studied. It is observed that the spectra of the imaginary and real parts of the complex dielectric function indicate that all four films are highly absorbing in the IR and NIR regions. Above IR (from 5500 cm⁻¹ (0.7 eV) towards higher energies), the spectra of the two ordered films (g- and FL-CN_x) look quite similar and are also comparable to those of films presented in earlier work [19,20]. The spectra of the two amorphous films show similarities to films in a study by Broitman et al. [21] although our a-CN_x film reaches higher values of ϵ_2 in the NIR region. All films show higher values of ϵ compared to magnetron sputtered films by Gioti et al. [22] which suggests higher probability for electronic transitions in our films. It might also be an indication of denser films. Gago et al. [19] presents one film grown at 673 K by vacuum arc deposition showing an increased value of ϵ_2 in NIR and explains this behavior with a higher conductivity. In another report Gago et al. [13] suggests the higher ϵ_2 values to be correlated with more cross-linking of the graphitic planes as well as a more pronounced FL microstructure. At a first glance of ϵ_2 in the IR range, two pairs of the four films might be discerned showing similarities in shape but deviating in amplitude. The a-CN_x and FL-CN_x films and the a-C and g-CN_x films, respectively, are comparable below 5500 cm⁻¹. Since ellipsometric data in the IR and NIR regions (below 8000 cm⁻¹) is rarely available in the literature, except for data presented in the region 900-2600 cm⁻¹ by Laskarakis et al. [23] and Kennou et al. [24], the

ellipsometric resonances observed in our work are also compared with resonances identified with Raman and Fourier transform infrared (FTIR) spectroscopy.

Figure 4 Real (a) and imaginary (b) parts of the model dielectric function for the four films in the study. Insets show the IR-region on an expanded energy scale, 0-9500 cm^{-1} .

3.2.2. Optical features common for the different films

Figure 5 shows ε_2 in part of the experimental spectral range for the four types of films studied in this work. Included are also decompositions into the individual resonances which are listed in Tables 3-6 with the identification numbers C1, C2,..., A1, A2,..., G1, G2..., and F1, F2 and so on. First we discuss some features which are of related origin in the films and in the next section we discuss more film specific optical features.

3.2.2.1. Range below 300 cm^{-1}

For all films the fits are improved by including a resonance at very low energies (below 300 cm^{-1}). Even though the confidence limits for their line-shape parameters are large, these resonances (C1, A1, G1 and F1) indicate a small free electron contribution of a Drude type in the optical spectra.

3.2.2.2. Range 1178-1308 cm^{-1}

The resonance with the largest amplitude for three of the films (C2', G3, F2') and the third largest resonance for the a-CN_x film (A2') is a feature in the range 1178-1308 cm^{-1} most often defined in literature as sp³ C-N bonds or sp³ C bonds [23-28]. For the nitrogen-containing films in this work, the resonance should instead be identified as a sp² C-N bond as established in earlier studies on the same type of films [10-12]. The sp² C-N bond is hybridized N in a substitutional graphite site (three-fold) or in a pyridine-like configuration (two-fold). Ferrari et al. suggest that all features in the region 1000-2000 cm^{-1} are originating from C=C modes or mixed C=N modes in CN_x. For the a-C film, a vibration is found at 1262 cm^{-1} (C2') and is suggested to be related to sp² hybridized C [29]. At a somewhat higher energy, Chalker et al. [25] identified a Raman peak at 1330 cm^{-1} as the presence of diamond (thus sp³ C-C) in polycrystalline diamond films, and Theye et al. [30] identified C-C bending modes in the range 1300-1350 cm^{-1} in amorphous carbon films.

3.2.2.3. Range 2028-2169 cm^{-1}

In the ellipsometric spectra of the amorphous, graphitic and FL-CN_x films, there are resonances at 2169 (A5), 2082 (G5) and 2028 (F4') cm^{-1} , respectively, possibly associated with nitrile [31] or isonitrile [23], triple bonds with sp¹ hybridization

Figure 5 (a)-(d) Imaginary parts of the dielectric function with all modeled resonances in the four films. The thick line represents the sum of all resonances. Unidentified resonances are denoted as described in the text and with references to Table 3-6. (The abbreviation s-m in Fig (b) means semi-metallic.)

Table 3: Ellipsometric determined resonances for a-C and suggested assignments.

Resonance	E_0 [cm ⁻¹ (eV)]	A [-]	Γ [cm ⁻¹]	Assignment	[Reference] Method
C1	141	25	161	-	
C2'	1262	6.3	993	C-C or C=C	[25] Raman [29,30] FTIR
C3'	1934	2.8	993	-	
C4	2571	2.8	1386	-	
C5	3388	1.4	1674	O-H	[33] FTIR
C6	7356	0.7	2480	-	
C7	9000	1.1	4433	-	
C8	31500 (3.9)	2.1	71250	$\pi \rightarrow \pi^*$	[19] SE

which is common in CN_x. This bond is generally described as a terminating configuration that hinders the growth of aromatic clusters and decreases with

increasing deposition temperature due to enhanced etching of C_2N_2 molecules through the reaction of the nitrile molecule $-C\equiv N$ with other particles to form volatile molecules that desorb from the surface. This is in contradiction with our result since these resonances are as large as the third largest in the spectrum of both $g-CN_x$ and $FL-CN_x$ films, which both are deposited at a higher temperature. Overlap from other features not identified might be an explanation. Rodil et al. [32] discuss water incorporation producing a broad band possibly extending from 2000 to 3600 cm^{-1} .

Table 4: Ellipsometric determined resonances for $a-CN_x$ and suggested assignments.

Resonance	E_0 [cm^{-1} (eV)]	A [-]	Γ [cm^{-1}]	Assignment	[Reference] Method
A1	12	172	176	-	
A2'	1305	3	603	C=N	[29] FTIR
A3	1576	3.1	368	C=N	[38,39] FTIR
A4'	1849	0.9	603	C=C	[24] IRSE
A5	2169	1.6	626	$-N\equiv C$	[23] IRSE
A6	2610	2	1259	-	
A7"	3199	4.8	2716	$=N-H$	[26,31,33] FTIR
A8"	4855	2.5	2716	-	
A9	6787	1.7	3677	-	
A10	16 300 (2.0)	1.8	14000	semi-metallic	[22] SE
A11	41 900 (5.2)	1.7	78000	$\pi\rightarrow\pi^*$	[36] SE

Table 5: Ellipsometric determined resonances for $g-CN_x$ and suggested assignments.

Resonance	E_0 [cm^{-1} (eV)]	A [-]	Γ [cm^{-1}]	Assignment	[Reference] Method
G1	50	199	105	-	
G2	833	9	811	sp^2 -domains	[38] FTIR
G3	1178	9.6	699	C=N	[29] FTIR
G4	1497	0.6	202	diamond precursor	[31,40] Raman
G5	2082	6	2485	nitrile	[31] FTIR
G6	6413	0.6	2281	-	
G7	9738	2.7	17600	unidentified	[22] SE
G8	31000 (3.8)	1.4	50000	$\pi\rightarrow\pi^*$	[19,37] SE

Table 6: Ellipsometric determined resonances for FL-CN_x and suggested assignments.

Resonance	E_0 [cm ⁻¹ (eV)]	A [-]	Γ [cm ⁻¹]	Assignment	[Reference] Method
F1	293	8.5	553	-	
F2'	1308	12.4	974	C=N	[29] FTIR
F3	1924	0.5	289	-	
F4'	2028	6.5	974	nitrile	[31] FTIR
F5''	2567	4.4	1033	-	
F6''	3187	1.6	1033	=N-H	[26,31,33] FTIR
F7	3945	7.7	3900	-	
F8	15100 (1.9)	3.1	24300	semi- metallic	[22] SE
F9	32450 (4.0)	1.3	30500	$\pi \rightarrow \pi^*$	[19,37] SE

3.2.2.4. Range 3187-3388 cm⁻¹

The resonances at 3388 (C5) [33], 3199 (A7'') and 3187 (F6'') [26,31,33] cm⁻¹ for a-C, a-CN_x and FL-CN_x, respectively, may be associated with stretching and bending modes of O-H (3200-3400 cm⁻¹ [33]) and N-H (3000-3300 cm⁻¹ [33] or 3100-3450 cm⁻¹ [26]) and indicate presence of hydrogen in the films. For the a-C and the FL-CN_x films this vibration is rather weak, but in the spectrum of a-CN_x this resonance is dominating which would mean there is a large amount of H in the film. Water uptake of carbon and CN_x has been investigated by Broitman et al. [34] using quartz crystal microbalance measurements and it was shown that amorphous structures of carbon and CN_x (with higher RMS-values compared to our films) adsorbed 10 times more water compared to nano-structured films. This was correlated to the nano-structure and the surface roughness (an amorphous structure with larger RMS gave an increased adsorption). The interpretation of those results might be an explanation to the dominating resonance for N-H stretch in the a-CN_x film. An alternative explanation described by Muhl and Méndez [35] is that hydrogen atoms incorporated during or after deposition form medium to strong hydrogen bonds with nitrogen in species having an unshared electron pair, e.g. pyridine-like rings.

Since no water vapor is present during deposition, the only possibility to incorporate larger amounts of H is if the film is highly porous and adsorbs water from the ambient after deposition. This is a little surprising since the refractive index, n , of

this film indicates a rather dense material (the highest density of the four films) with a refractive index value of 2.1 at 632 nm to be compared with 2.4 for diamond. The other films have values of n ranging from 1.6 for the g-CN_x film to 1.8 and 2.0 for the FL-CN_x and the a-C film, respectively. It is not fully clear, but our opinion is that the films most likely have adsorbed water after deposition, but perhaps not as much as the resonance for the a-CN_x indicates. Since the a-CN_x film according to the SE measurements has the highest density and at the same time the largest contribution from the N-H peak, the origin of the peak is probably not only explained by N-H stretching.

3.2.2.5. Range 31000-32450 cm⁻¹ (3.8-4.0 eV), $\pi \rightarrow \pi^*$

The $\pi \rightarrow \pi^*$ electronic transition associated with sp² bonds in graphitic structures, either as sp² C or sp² N (N in a pyridine-like configuration), was also present for all films, although the identification of the peak in the a-CN_x film is not fully clear. The peaks were not as strong as the C=N vibrational mode and also much broader. The resonance energy for $\pi \rightarrow \pi^*$ electronic transitions for crystalline graphite is found at 4.5 eV but the energy decreases when the amount of sp²-clusters in the matrix increases [36] or when the sp² sites exhibit a different arrangement [19]. This is in agreement with the lower resonance energies noticed for these films, located between 31000-32450 cm⁻¹ (3.8 and 4.0 eV), where the lowest energy is observed for the g-CN_x film (G8) and the highest for the FL-CN_x film (F9) [19,37]. The strongest peak for the $\pi \rightarrow \pi^*$ transition is noticed for the a-C film (C8) [19] and the weakest for the FL-CN_x film, which might be explained by a higher disorder in the sp² matrix for the FL and graphitic films which reduces the conjugation of the π electrons [13]. The XPS data reveal less amount of N bonded in a pyridine-like manner in the FL film, explaining the smaller amplitude of this resonance. For the a-CN_x film the resonance is either found at a higher energy, 5.2 eV (41900 cm⁻¹), where an unidentified peak (A11) is observed, or, possibly absent. A peak at 5.2 eV would mean a decreased amount of sp²-clusters in the matrix. A possible absence of the $\pi \rightarrow \pi^*$ transition peak could on the contrary be explained by a higher degree of clustering of the sp² hybrids (and/or higher disorder in the sp² domains) and not by the lack of sp² hybrids, as was similarly suggested for a magnetron sputtered FL-CN_x film by Gago et al. [13].

3.2.3. Optical features specific for each film

a-C: The dominating resonance (part of a double peak) for the a-C film is related to sp^2 or sp^3 hybrids of C (C2') followed by 3 equally large resonances of which two have not been identified (C3' and C4) whereas the third (C8) is associated with $\pi \rightarrow \pi^*$ electronic transitions from sp^2 C bonds in graphitic structures. A small feature indicating an O-H bond at 3388 cm^{-1} (C5) is also present. Two other resonances (C6 and C7) at energies above 7000 cm^{-1} could not be assigned.

a-CN_x: The dielectric function spectrum of a-CN_x is the most deviant of the four films and is dominated by a resonance at 3199 cm^{-1} (part of a double peak, A7'') that without further analyses only can be identified as hydrogen bonded to nitrogen [33] or possibly to carbon or oxygen [32]. The peak is rather broad and the possibility of overlapping from several peaks can not be disregarded. Furthermore, two equally rather large peaks can both be identified as C=N stretching originating from sp^2 hybrids, (A2') and (A3) [29,38,39]. Possibly the peak at 41900 cm^{-1} (A11) can be assigned to unsaturated bondings as $\pi \rightarrow \pi^*$ transitions at a higher resonance level. A resonance in the energy range 1.5-2 eV has, for an a-CN_x film, been ascribed a semi-metallic behavior of the material by Gioti et al. [22] and the resonance observed at 16300 cm^{-1} (2.0 eV) (A10) for our a-CN_x film might be attributed to the same behavior. This resonance is also found in the FL film at a slightly lower energy (F8). Three peaks in the spectrum remain unidentified. One of them (A6) appears also in the a-C and FL-CN_x films named C4 and F5'', respectively.

g-CN_x: The g-CN_x spectrum shows two equally strong and rather sharp peaks at 1178 cm^{-1} (G3) and 833 cm^{-1} (G2) representing C=N modes and the presence of large sp^2 domains, respectively [29,38]. The third largest resonance is found at 2082 cm^{-1} (G5) [31] in the spectral range for nitrile groups ($2065\text{--}2260\text{ cm}^{-1}$) and is surprisingly large, as mentioned earlier. The range for NH and OH groups is $2000\text{--}3600\text{ cm}^{-1}$ [32] and might also be a possible identification, but the peak is rather broad and the range covers only half of the peak, so it is not likely. This film, similar to the a-C and FL-CN_x films, shows a small resonance for $\pi \rightarrow \pi^*$ electron transitions (G8). A weak resonance at 1497 cm^{-1} (G4) can be identified either as a 'diamond precursor' as suggested by Ju et al. [31] for an a-C:H:N film at 1496 cm^{-1} or as a 5-membered ring

in fullerenes [40]. For this film the surface roughness was modeled and the RMS value was 14.2 nm.

FL-CN_x: The most obvious differences between the FL-CN_x and the g-CN_x film are the lack of the resonance for large sp² domains and the presence of a broad resonance at 15100 cm⁻¹ (1.9 eV) (F8) suggesting a semi-metallic behavior as in a-CN_x. On the other hand both films show a very high absorption below 4000 cm⁻¹ (0.5 eV) in the IR region which according to several authors, e.g. Gago et al. [13] and Roy et al. [41], might be attributed to the bending and cross-linking of graphene sheets in a more ordered microstructure. Both films also show a very strong resonance for C=N modes (F2') as well as a weaker resonance for $\pi \rightarrow \pi^*$ electron transitions (F9).

3.2.4. Additional unidentified resonances

A few resonances in the spectrum of each film can not be correlated to available literature data (including those already mentioned above), e.g. the peaks appearing at 2571 cm⁻¹ (C4), 2610 cm⁻¹ (A6) and 2567 cm⁻¹ (F5'') in the amorphous films and the FL-CN_x film. These peaks are rather large and quite broad. Another peak at 1924 cm⁻¹ (F3) and 1934 cm⁻¹ (C3') for the FL-CN_x film and the a-C film, respectively, could not be identified as well. Six peaks (C6, C7, A8'', A9, G6 and F7) are observed in the region 3500-9000 cm⁻¹, part of the IR and the NIR region, and could not be identified since no data in this region are available in the existing literature. The peak at 9738 cm⁻¹ (G7) in the g-CN_x film was found by Gioti et al. but was not identified [22].

4. Concluding remarks

SE, HRTEM and XPS analysis have been performed for an increased understanding of optical and microstructural properties of thin films of carbon and CN_x materials. The carbon and CN_x films, with typical amorphous, graphitic or fullerene-like structure are, according to the SE measurements dense and show a rich variety of absorption bands related to the materials local bonding structure.

The larger absorption at lower energies (<8000 cm⁻¹) observed for the graphitic and fullerene-like films might be attributed to the bending and cross-linking of graphene sheets in a more ordered microstructure and indicates that these films contain no sp³ bonds. All films show a strong resonance for C-C and/or C=C (in a-C) or C=N modes, which for the CN_x films most probably is originating from sp² C-N

bonds, either as N substituted in a graphite site and/or as N bonded in a pyridine-like manner. A $\pi \rightarrow \pi^*$ electronic transition associated with sp^2 C or sp^2 N (N in a pyridine-like configuration) bonds is also present for all films (the identification of $\pi \rightarrow \pi^*$ in the a-CN_x film is uncertain). The peak is weakest for the FL-CN_x film, which might be explained by a higher disorder in the sp^2 matrix for this film indicating a FL structure. The SE measurements also indicate that all CN_x films contain nitrile or iso-nitrile groups, but for the g-CN_x and FL-CN_x films this resonance might be overlapping with NH and OH groups. Another resonance was identified as N-H stretching and bending (O-H for a-C) and was present for all films except g-CN_x. This identification was for the a-CN_x film surprisingly the dominating resonance, which at this point is not easily explained. In addition, several new features (unidentified) have been observed in the ellipsometric spectra. These have not been presented elsewhere and remain so far unidentified.

The correlation between results from XPS and SE of the nitrile bond is not fully satisfying since XPS suggests low values of nitrile in the g-CN_x and FL-CN_x films and higher values in the a-CN_x film. The SE measurements and analyses show a strong contribution from nitrile in both g-CN_x and FL-CN_x, whereas it is not as strong but more reasonable in the a-CN_x film. An overlap from another feature of unknown origin, at least in the spectrum of the graphitic and FL films, is therefore probable. The $\pi \rightarrow \pi^*$ electronic transition is somewhat more correlated between the two techniques. Both XPS and SE show lower contribution from $\pi \rightarrow \pi^*$ transitions in the nano-structured films as well as a more significant contribution in the a-CN_x film if the resonance for the transition in a-CN_x is identified at a higher energy (5.2 eV). The XPS data reveals less amount of N bonded in a pyridine-like manner in the FL film, explaining the smaller amplitude observed for this resonance ($\pi \rightarrow \pi^*$ electronic transition) in the SE measurements. As the a-C film does not contain nitrogen we can not correlate the results from XPS and SE for this film.

The correlation of results from XPS, HRTEM and SE of the films in this paper is to a high extent satisfying, finding the correlation between HREM and SE of the bending and cross-linking of graphene sheets, as well as the correlation between XPS and SE for the bondings associated with $\pi \rightarrow \pi^*$ transitions and C=N modes. The nitrile contents are not as well correlated whereas the N-H and O-H bonding is not

possible to identify with neither XPS nor HRTEM. In addition, optical properties can not be recognized using XPS or HRTEM.

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