Review

Structure and properties of pulsed-laser deposited carbon nitride thin films

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Abstract

Carbon nitride (CN_x) thin films were deposited on silicon (100) and (111) substrates at 300 °C by laser ablation of a graphite target using a pulsed Nd:YAG laser in a nitrogen atmosphere. The composition and structural properties of the films were investigated as functions of gas pressure and laser fluence. X-ray photoelectron spectroscopy (XPS) revealed a strong dependence of the amount of structurally incorporated nitrogen upon gas pressure. A maximum was observed at the highest laser fluence of 10 J/cm^2 and at an intermediate pressure of 4 Pa. Further analyses of the XPS N 1s core level spectra of the CN_x films, exhibiting the highest elasticity in nanoindentation experiments, revealed a typical double-peak arrangement; most pronounced for the highest laser fluence at low pressures. These two peak components indicate that the nitrogen bonded onto a graphitic structure dominates over the two-fold coordinated pyridine-like bonding configuration. This favors the growth of intersecting corrugated graphene structures that may be considered to have "fullerene-like" microstructures. Additionally, Fourier Transformed Infrared Spectroscopy analyses of films deposited at different pressures show the presence of 2229 and 2273 cm^{-1} stretching peaks associated with CN triple bonds (C≡N) of nitriles and isocyanides, 1640 cm^{-1} and 1545 cm^{-1} associated with the C=C and C=N and a peak at 1730 cm^{-1}, which is connected to the C=O carbonyls groups. Films grown at 0.66 Pa revealed the strongest C≡N peak.

Contents

1. Introduction

Pulsed-laser deposition (PLD) is a well-established technique for the synthesis of carbon-based amorphous materials [1] such as diamond-like carbon [2] boron carbides [3] and carbon nitrides (CN_x) [4,5]. Deposition of CN_x materials has

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proven to be particularly challenging because of the difficulty of incorporating nitrogen in the growing amorphous carbon matrix. In many papers, the nitrogen content is reported, in most cases, it is between 30 and 40 at.% [6–8], considerably lower than the concentration of 57 at.% required for C_3N_4. For that material, several groups [5–9] have opted for performing ion- or plasma-assisted PLD in an attempt to increase nitrogen incorporation in the material. Extensive literature can be found on the effect of the process parameters, such as laser fluence [8,10], pressure [4,11,12], and substrate temperature [13].

In general, CN_x films contain a mixture of carbon sites characterized by 'diamond' sp^3, 'graphite' sp^2 and, to a lesser extent, 'nitrile' sp^1 hybrid configurations. Amorphous CN_x thin films are currently being extensively studied as to their potential tribological application—owing to their favorable mechanical and tribological properties [14]. Deposited under appropriate deposition conditions, hard and elastic CN_x films with outstanding elastic recovery can be synthesized [15–17]. The beneficial properties are most evident in films having a, so-called, "fullerene-like" microstructure, consisting of nitrogen containing, corrugated and frequently intersecting graphene sheets [16]. These are commonly synthesized by magnetron sputtering [16], where the structure formation mechanisms have been under recent investigation [18–20]. Interestingly, Voevodin et al. [17] uncovered striking similarities between sputtering and PLD with respect to the existence of preformed CN species in the deposition flux, which can serve as building blocks for the formation of corrugated sheet-like structures [19,20].

The properties of CN_x thin films are mainly determined by the chemical bonding structures among the constituent atoms. Therefore, it reveals a compound nature. The most widely accepted model proposes that CN_x is based on a structure of buckled graphene segments with incorporated nitrogen, in which the segments are more or less cross-linked [15,16,21]. Depending on the length and packaging of such structures, the material may appear textured or amorphous (glassy carbon) in X-ray or electron diffraction. An important parameter characterizing carbon-based films prepared under different deposition conditions is the sp^3/sp^2 ratio. For instance is the hardness of diamond-like C strictly correlated to the increase of the sp^3 concentration in the films [22,23]. For CN_x, however, the existence of sp^3-coordinated carbon is uncertain [24]. In that case, nitrogen promoted cross-linking between graphene sheets by sp^2 C or $sp^2–sp^3$ hybridized C will yield, in particular, the fullerene-like CN_x material with high strength [16] as compared to diamond-like carbon (DLC); while its toughness originates from an extreme elasticity due to the additional degrees of freedom for bond-bending in this less dense material.

In this study, we investigated the influence of deposition parameters during PLD of CN_x such as laser fluence and gas pressure onto the film composition and microstructure. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) are used to determine how the Nd:YAG laser fluence and gas pressure influence the bonding structure and properties of CN_x films grown by PLD.

2. Experimental details

Two sets of CN_x films were deposited by pulsed-laser deposition (PLD) from a high-purity (99.99%) pyrolytic graphite target mounted in a vacuum chamber with background pressure of 0.13×10^{-4} Pa. The nitrogen gas pressure was varied from 0.13 Pa to 6.7 Pa, for further details see Ref. [25]. The distance between the target and the substrate was 3 cm. The target was placed on a support under a 45° angle to the substrate. An Nd:YAG laser, model INDI-30 Spectra Physics (wavelength 1064 nm, energy 500 mJ and pulsed-width of 7 ns) was used for ablation. The laser beam impacts onto the target surface at a 45° angle. To change the laser fluence, the laser beam was adjusted from focus to unfocused position, obtaining a larger fluence by focusing the laser beam onto a smaller irradiation spot. The laser fluence was set to 2 and 10 J/cm^2. Polished (100) and (111) oriented Si wafers were used as substrates and heated to 300 °C. XPS and FTIR analysis was carried out to characterize the compositional and structural properties of the films. XPS employed an Mg Kα 1253.6 eV X-ray (VG Microlab 310F) source. The samples were analyzed without initial sputter cleaning to avoid influencing the sensitive bonding structure in the uppermost atomic layers with the high-energy Ar ion bombardment [26]. Analysis of the core levels of C and N, characteristic of the chemical bonding, was carried out by multiple Gaussian fitting of the experimental spectra. FTIR measurements were performed on an 8400 Shimatzu FTIR spectrometer (350–4600 cm^{-1}), which uses a Nerst-type ceramic source.

High-resolution transmission electron microscopy (HRTEM) images were obtained using a Philips CM20 (UT) microscope operating at 200 kV. Cross-sectional TEM specimens were prepared by conventional Ar$^+$ ion milling technique using a BALTEC RES 010 ion miller. The milling process was carried out at 8 keV ion energy followed by an ion polishing process at 3 keV.

Mechanical properties of CN_x films such as hardness (H) and elastic modulus (M) were obtained by using a Hysitron Triboscope® nanoindenter connected to a Digital Instruments Nanoscope IIIa atomic force microscope. The system is equipped with a cube corner diamond tip (three-sided pyramid with 90° total included tip angle). The maximum penetration depth was set below 15% of the film thickness (approximately 150 nm). In order to obtain reliable H and E values for the extremely shallow indents, the tip shape was carefully calibrated using the Oliver and Pharr approach [27]. At least five indentations were made for the (10 J/cm^2 and 0.13 Pa at 300 °C substrate temperature) sample, with loads ranging from 5 μN up to 2000 μN. From the stiffness, indentation hardness and reduced Young's modulus of the film–substrate system were calculated [27].

3. Results and discussion

Ocular inspection of as-deposited CN_x films revealed that they were dense and well adherent with a grey and shiny appearance. Fig. 1 is a cross-sectional TEM micrograph
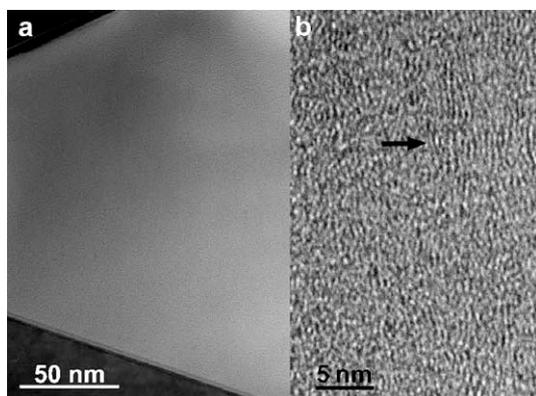
Fig. 1. Cross-sectional TEM micrographs of a CN_x thin film deposited by PLD of graphite on a Si (100) substrate at 300 °C, 10 J/cm² and 0.13 Pa N₂. (a) represents an overview and (b) high-resolution image from the regions containing bundles of corrugated graphene planes (marked by an arrow).

showing the microstructure of a typical CN_x film deposited at 10 J/cm², 0.13 Pa and 300 °C. The film was dense and homogeneous as seen from the lack of contrast in the overview image (a). Yet, texture is revealed in (b) from standing bundles of corrugated planes of 3.5 ± 0.2 Å spacing, as determined by fast Fourier transformation. This corresponds closely to the plane separation of (0002) graphite hexagonal basal planes. Such a structural signature in TEM is consistent with a fullerene-like structure [18]; although this must be confirmed by the bonding signature as seen in [28].

The N 1s and C 1s XPS spectra of the CN_x films show two major binding energy bands centered at about 400 eV and 285 eV, respectively. These bands are characteristic for the bonding structure of nitrogen and carbon. The evolution of the N 1s level spectra of carbon nitride films deposited at different pressures at a laser fluence of 2 and 10 J/cm² is shown in Fig. 2. The width and asymmetry of the N 1s XPS peaks indicate the presence of different bonding types and configurations associated to nitrogen within the films, whose relative intensities vary with the laser fluence. Up to four contributions can be fitted and are labelled as follows: Peak I (398−399 eV), Peak II (400.0−400.8 eV), Peak III (∼ 402.5 eV), and Peak IV (∼ 399 eV). Until recently, there has been controversy in the literature [21,29,30] on the assignment of the respective bonding configurations. However, Hellgren et al. [31], reinforced by follow-up studies [28], assigned the components for magnetron-sputtered films as follows: Peaks I and II are main components, Peak I is related to two-fold coordinated sp²-hybridized nitrogen (sp² C−N) bonds—attributed to electrons originating from nitrogen atoms having two neighbors; just like in Pyridine. Nitrogen atoms can also be bonded substitutionally for carbon in a graphite ring system. Peak II corresponds to the respective sp² C−N bonds, originating from nitrogen atoms having three neighbors. Peaks III and IV are smaller components, the latter can be assigned to N atoms bonded to sp hybridized C atoms (nitrile C≡N groups), the former is related to a structure similar to peak II. One possibility is that it corresponds to N^+ bonded to three C atoms [31]. The Full Width at Half Maximum (FWHM) for deconvoluted peaks were determined from the fit. There were no obvious changes

for FWHM for each deconvoluted peak as functions of laser fluence or gas pressure. The FWHM corresponding to principal peaks, Peak I and Peak II, are about 1.6 eV and 2.4 eV, respectively. We found good agreement with previous reports [30,32,33]. Conversely, there was no noticeable shift in peak position, nor clear trends in these shifts.

The appearance of the XPS N 1s core level spectra, seen in Fig. 2, is similar to previously reported ones [16,28]. But for the sample grown at 0.13 Pa and a laser fluence of 2 J/cm², all films show double-peak structures. This suggests that N is bonded essentially in the above-mentioned two different bonding configurations. This is most pronounced for films deposited at 10 J/cm²; whereas Peak II is the most intense. According to Neidhardt et al. [28] and Voevodin et al. [17], the ratio of Peaks I and II separated by approximately 2 eV, can be taken as an indicator that the microstructure of the films is fullerene-like, if the ratio of P_{II}/P_I is larger than 1. N atoms in an sp²-rich environment allow for the incorporation of pentagons for the crosslinkage of curved planes leading to the formation of buckled sp²-hybridized planes in the carbon nitride films. For fullerene-like structures with developed basal planes, nitrogen is mostly bonded in an sp²-rich carbon environment [24].

The P_{II}/P_I ratio as a function of gas pressure for films deposited at the two different laser fluences is shown in Fig. 3. At 2 J/cm², the P_{II}/P_I ratio decreases significantly as gas pressure is increased, this trend is less pronounced at 10 J/cm². Here the maximum of 1.27 is observed at 4 Pa (the sample with the highest N content). There is a slight decrease for the P_{II}/P_I ratio with increasing laser fluence, perhaps due to the decrease in N content in a substitutional site (P_{II}) and, in turn, more N atoms are bonded along edges and defects (P_I).

According to Figs. 2 and 3, we can conclude that the incorporation of nitrogen species into the thin films results predominantly in the formation of fullerene-like structures with sp² hybridization of carbon.

Decomposition of C 1s XPS spectra of CN_x films is again, an assignment of bonding by four different peaks as used in the literature [29−36]. Peak I, at the binding energy of (284.5 ± 0.2) eV, represents the C−C bonded phase in an amorphous carbon
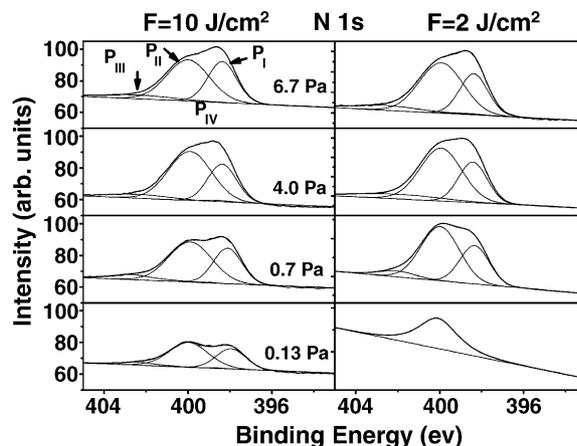

Fig. 2. XPS N 1s core level spectra of CN_x thin films deposited by PLD of graphite at the indicated pressures and fluences.
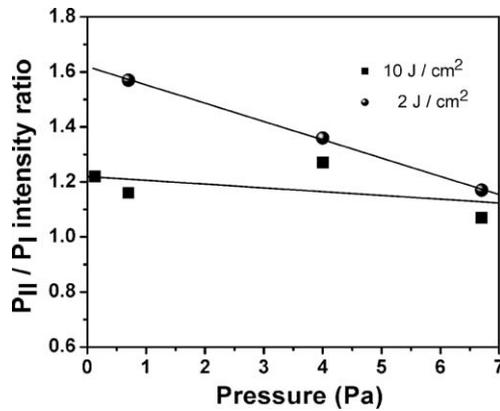
Fig. 3. Variation of the intensity ratio P_{II}/P_I as a function of gas pressure, for two different laser fluences: 2 and 10 J/cm^2, where peaks I (398 eV) and II (400 eV) are the main components of N 1s core level spectra.

Fig. 5. XPS N 1s/C 1s peak area ratio, qualitatively indicating the N concentration, as a function of nitrogen gas pressure for CN$_x$ thin films deposited by PLD of graphite at 10 and 2 J/cm^2.

structure and C–H bonding. Peak II and Peak III, at higher binding energies, were related to the phases containing carbon and nitrogen atoms. The higher binding energy of these phases is probably given by the charge transfer resulting from the incorporation of nitrogen, which is more electronegative than carbon. Peak II, at (285.3 ± 0.3) eV, was assigned to the sp^2 trigonal C–N bonding. Peak III, at (286.6 ± 0.4) eV, corresponds to the sp^3 C–N bonding. While Peak IV, at (288.8 ± 0.7) eV, was attributed to the C–O bonding phase [21].

The C 1s XPS spectra from the present films, shown in Fig. 4, reveal that the C 1s spectrum shape changes when gas pressure increases, having a more symmetric shape at low pressures and indicating that carbon nitride films have other bonding configurations when gas pressure increases. No significant shifts in the binding energy of the peaks were observed. However, it should be noted that the P_{II} intensity decreases with gas pressure and laser fluence increase, suggesting increasing sp^2 bonding. Hence, we find that low gas pressure and high laser fluence present suitable growth conditions for the fullerene-like structure of CN$_x$ films.

In addition to nitrogen and carbon, oxygen was detected by XPS within the samples as a contaminant; the presence of oxygen can be partly explained due to the prolonged exposure of the samples to the laboratory atmosphere. A qualitative
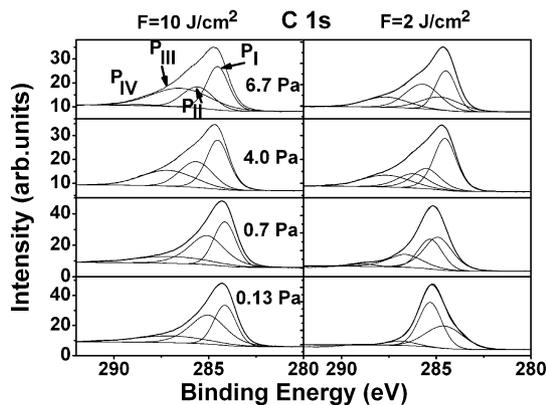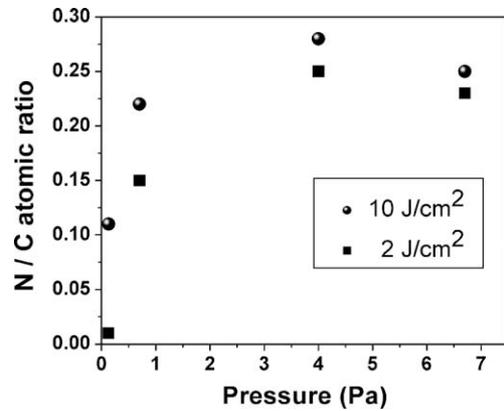
analysis of the N/C ratio of the deposited thin films was obtained by integrating the XPS N 1s and C 1s peaks. Fig. 5 shows the N/C peak area ratio in the CN$_x$ films as a function of gas pressure and laser fluence. As gas pressure was increased, the N/C peak area ratio and, thus, N/C ratio first sharply increased to a maximum at a gas pressure of approximately 4 Pa, and then decreased slightly as gas pressure increases further. The dependence of the N/C atomic ratio on the incident laser fluence is also shown. The N/C atomic ratio seems to increase when the laser fluence increases. During film deposition, a significant sputtering effect given high ion energy, can be expected [37]; therefore, the ratio of carbon to nitrogen species impacting on the substrate surface determines the final N/C atomic ratio in the carbon nitride films. Additionally, the possible effect of laser fluence upon the plasma dimension and distribution cannot be excluded, possibly influencing the final N/C atomic ratio in the films.

FTIR spectra of CN$_x$ thin films deposited at different nitrogen gas pressures within the 0.13–6.7 Pa range and at a fluence of 10 J/cm^2 is presented in Fig. 6. The spectra show, at 1640 cm^{-1} and 1545 cm^{-1}, peaks associated with the C=C (1640–1667 cm^{-1}) and C=N (1471–1689 cm^{-1}), stretching

Fig. 4. XPS C 1s core level spectra of CN$_x$ thin films deposited by PLD of graphite at the indicated pressures and fluences.
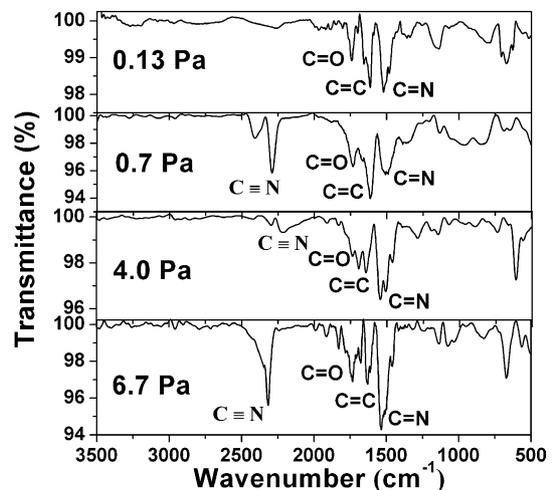

Fig. 6. FTIR analyses of CN$_x$ thin films deposited by PLD of graphite at 300 °C, 10 J/cm^2, and at the indicated nitrogen pressures.

Table 1
Summary of the N and C bonding present in the carbon nitride film and associated features detected by XPS [29,34–36] and FTIR

C								N			
Coordination	C–C	C=C	sp^2 C–N	C–N	C=N	C–O	C=O	N–2C	N–3C	N^+–3C	C≡N
XPS (eV)	284.5		285.3	286.6	–	288.8	–	398.3	400.0	402.6	398.6
FTIR (cm^{-1})	–	1640	–	–	1545	–	1730	–	–	–	2270

vibrations of non-conjugated alkenes and azometinic groups, respectively [37]. These peaks were improperly claimed [35] to be associated to specific C–H, C–N, N–H, and N–N vibrations. The peak at 1730 cm^{-1} is well established with the C=O, carbonyls groups [38]. Conversely, films deposited at different pressures reveal the presence of the 2270 cm^{-1} stretching peak related to CN triple bonds (C≡N) of nitriles [38]. Fig. 6 shows that C=C, C=N, and C=O peaks are observed at different pressures, while the CN peak associated to triple bonds (C≡N) is smaller than these peaks and not present at low nitrogen pressures (0.13 Pa). The C≡N peak in the samples grown at a low laser fluence of 2 J/cm^2 does not appear, and only shows C=C and C=N peaks. According to Ferrari et al. [35] in amorphous carbon nitrides, it is possible to classify the bonding in carbon nitride films into four types, based on the bonding in the corresponding N-free film: (a) the mainly sp^2 bonded amorphous carbon nitrides (a-C:N), (b) the mainly sp^3 bonded tetrahedral carbon nitrides (ta-C:N), (c) a-C:H:N with moderate sp^3 content, and (d) ta-C:H:N, with a higher sp^3 content and lower hydrogen content. The IR spectra of H-free films show only a single broad band with two modulations at ~1300 and ~1550 cm^{-1}, with slightly different intensity ratios. In contrast, films with hydrogen (such as a-C:H:N and (t)a-C:H:N) show increasingly well-defined peaks at 1550–1600 cm^{-1} [34]. As evident from Fig. 6, our IR spectra at different nitrogen pressures, present a well-defined peak at 1500–1600 cm^{-1} associated to the C=N stretching vibrations (sp^2 bond) and a peak at ~2270 cm^{-1} associated with the C≡N stretching peak (sp bond), smaller than C=N peak and suggesting that our growth conditions allow for the deposition of films with the mainly sp^2-bonded amorphous carbon nitrides. These IR results agree with the XPS results discussed above. We do not discard the presence of H.

N and C bonding types in the CN$_x$ film identified by these techniques are summarized in Table 1, along with the experimental evidence observed by the techniques employed in this study.

The hardness and Young's modulus measurements of the sample deposited at 10 J/cm^2 and 0.13 Pa pressure were 13±1 and 75±2 GPa, respectively. These values demonstrate that the CN$_x$ film material exhibits a rather low resistance to penetration. However, no plastic deformation was observed for the load–displacement curves, indicating the extreme elasticity of the films. This super-elastic behavior is also indicated by the large H/M ratio of approximately 0.17. The high compliance is inherent to CN$_x$ material having a fullerene-like microstructure as investigated in Refs. [18–20] on magnetron-sputtered films.

According to Voevodin et al. [4], the fullerene-like CN$_x$ films can be synthesized by (UV)PLD when the deposition is performed at 300 °C and at N$_2$ pressures of 1.3 to 3.9 Pa. It was also shown that a high concentration of CN radicals having high vibrational temperature in the ablation plume are necessary for the production of fullerene-like structures. It is clear, however, that such concentration of CN radicals depend on the wavelength of the laser. In the literature, it is well established [17,39] that longer wavelength lasers generate larger quantities of C$_2$ radical groups and shorter wavelength lasers generate larger quantities of single atoms and ions. On other hand, background pressure is another parameter studied for CN$_x$ films growth. Detection of C$_2$ molecules was related to plume thermalization caused by collisions with background nitrogen molecules, promoting recombination of C to form C$_2$ [39]. Fullerene-like CN$_x$ films have predominantly graphite-like structure and require sp^2 electron hybridization. Plume thermalization and a greater availability of C$_2$ species provide a larger fraction of sp^2 hybridization as opposed to sp^3 hybridization, which is observed in high-quality DLC films produced through laser plumes without a C$_2$ component [39,40]. One can therefore suggest that with IR lasers a smaller background pressure may be needed to generate similar amounts of C$_2$ and CN in comparison to UV lasers. In fact, the higher wavelength (1064 nm) of the Nd:YAG laser used during this study leads, therefore, to different optimum conditions for the formation of fullerene-like films, namely 0.13 Pa N$_2$ as compared to 1.3–3.9 Pa. Further investigation is needed to clarify the influence of the wavelength upon the plasma conditions and number and energy of film-forming species, which in turn define the structure and mechanical properties of the resulting PLD CN$_x$ films.

4. Conclusions

The complex structure of carbon nitride thin films was investigated via a combination of TEM, XPS, and FTIR techniques. Based on the XPS analysis, we can conclude that the laser fluence not only affects the total nitrogen content of the carbon nitride films, but also has a significant effect upon the bonding between carbon and nitrogen atoms. A higher laser fluence and, hence, higher energetic growth conditions promotes the formation of CN$_x$ films consisting of nitrogen containing graphene fragments similar to fullerene-like structures. Indeed, hardness and Young's modulus measurements demonstrate that the PLD-grown CN$_x$ films exhibit very high elastic recovery, comparable to that of fullerene-like CN$_x$ made by other physical vapor deposition techniques; in particular, reactive magnetron sputtering.

Acknowledgements

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