A comparative study of direct current magnetron sputtering and high power impulse magnetron sputtering processes for CNX thin film growth with different inert gases

Susann Schmidt, Zsolt Czigany, Jonas Wissting, Grzegorz Greczynski, Erik Janzén, Jens Jensen, Ivan Gueorguiev Ivanov and Lars Hultman

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Susann Schmidt, Zsolt Czigany, Jonas Wissting, Grzegorz Greczynski, Erik Janzén, Jens Jensen, Ivan Gueorguiev Ivanov and Lars Hultman, A comparative study of direct current magnetron sputtering and high power impulse magnetron sputtering processes for CNX thin film growth with different inert gases, 2016, Diamond and related materials, (64), 13-26.

<http://dx.doi.org/10.1016/j.diamond.2016.01.009>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-128146>

**A Comparative Study of Direct Current Magnetron Sputtering and High Power Impulse
Magnetron Sputtering Processes for CN_x Thin Film Growth with different Inert Gases**

Susann Schmidt^{*,1)}, Zsolt Czigány²⁾, Jonas Wissting¹⁾, Grzegorz Greczynski¹⁾, Erik Janzén³⁾, Jens
Jensen¹⁾, Ivan Gueorguiev Ivanov³⁾, and Lars Hultman¹⁾

¹⁾Thin Film Physics Div., Department of Physics (IFM), Linköping University, SE-58183,
Sweden

²⁾ Institute of Technical Physics and Materials Science, Centre for Energy Research, Hungarian
Academy of Sciences, Konkoly Thege Miklós út 29-33. H-1121 Budapest, Hungary

³⁾Semiconductor Materials Div., Department of Physics (IFM), Linköping University, SE-58183,
Sweden

*Corresponding author: Phone: +46 737 030 433, E-mail: susann.schmidt@liu.se (Susann Schmidt)

ABSTRACT

Reactive direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) discharges of carbon in different inert gas mixtures (N_2/Ne , N_2/Ar , and N_2/Kr) were investigated for the growth of carbon-nitride (CN_x) thin films. Ion mass spectrometry showed that energies of abundant plasma cations are governed by the inert gas and the N_2 -to-inert gas flow ratios. The population of ion species depends on the sputter mode; HiPIMS yields approximately ten times higher flux ratios of ions originating from the target to process gas ions than DCMS. Exceptional are discharges in Ne with N_2 -to-Ne flow ratios $< 20\%$. Here, cation energies and the amount of target ions are highest without influence on the sputter mode. CN_x thin films were deposited in 14% N_2 /inert gas mixtures at substrate temperatures of 110 °C and 430 °C. The film properties show a correlation to the substrate temperature, the applied inert gas and sputter mode. The mechanical performance of the films is mainly governed by their morphology and composition, but not by their microstructure. Amorphous and fullerene-like $\text{CN}_{0.14}$ films exhibiting a hardness of ~15 GPa and an elastic recovery of ~90 % were deposited at 110 °C in reactive Kr atmosphere by DCMS and HiPIMS.

Keywords: Magnetron sputtering; Inert gases; Plasma analysis; Langmuir probe measurement; CN_x film stress; CN_x Hardness

1. INTRODUCTION

The interest in carbon-based thin films is flourishing [1-4]. According to literature, the mechanical properties of fullerene-like carbon nitride (FL-CN_x) render interesting tribological and wear resistant coatings; it is attractive due to a high resiliency (elastic recovery of up to 98 %) as well as low wear and friction [5, 6]. The mechanical properties of FL-CN_x are reported to be determined by their chemical bond structure and microstructure, which in turn, are controlled by the deposition parameters. The key parameters for the reactive magnetron sputter synthesis of FL-CN_x, were defined by Neidhardt et al. [7] and require moderate-to-low particle energies, substrate temperatures above 300 °C, as well as, low N₂/Ar flow ratios. Chemical sputtering (desorption) [8] is understood to be accountable for the distinct FL structure of CN_x films [9-11]. The process of chemical sputtering is described as the dynamic adsorption and desorption of plasma species at the substrate, where dangling C or CN bonds get passivated and structure-defining C_xN_y (x, y ≤ 2) species adsorb, thus contributing to the film growth, additionally volatile C_xN_y (x, y ≤ 2) clusters lift off. Therefore, high deposition rates and particle energies may counteract the formation of a FL structure. Our earlier comparative report [12] on the direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) discharges for the synthesis of CN_x in N₂/Ar revealed that a more pronounced FL structure is obtained by HiPIMS processes, even though higher ion energies were measured for corresponding HiPIMS processes. The study suggested the occurrence of a pulse-assisted chemical sputter process not only at the substrate, but also at the target. HiPIMS processes and film properties for the preparation of CN_x utilizing Ne, Ar, and Kr as inert gases were investigated in [13]. The different inert gases spanned a wide window with regards to the process properties (energy and amount of film forming species) as well as microstructure of the resulting films. The graphite discharge in N₂/Ne resulted in high amounts and

energies of C^+ , C^{2+} , N^+ , and FL structure-defining C_xN_y species. However, the amounts and energies of the species decrease as the inert gas mass rises. Additionally, the reactive process containing N_2 -to-Ne flow ratios of up to 20% was influenced by Penning ionization. A correlation of the plasma species energy to the microstructure could be established; high particle energies destroy a possible FL structure by their impingement on the substrate.

Varying the inert gas implies a high impact on the sputter process, due to differences in sputter yield, electron-impact ionization cross sections (σ_{gas}), inert gas ionization energies (I_p) as well as metastable excitation energies. Table 1 summarizes these process-relevant data. The two major ionization pathways in the PVD plasma - electron impact ionization and Penning ionization (ionization due to metastable inert gas species) - are influenced by those inert gas properties. From table 1 it can be seen that Penning ionization of C is possible for Ne, Ar, and N_2 , but not Kr. The energy and amount of ions in the plasma are additionally influenced by the particles mean free path for collision (cf. table 1) as well as the electron temperature of the discharge. The latter increases with increasing I_p of the process gas. High electron energies contribute to electron impact ionization of all plasma constituents. Moreover, the mechanisms [14] and amount [15] of secondary electron formation are altered. The secondary electron yield is estimated to be approximately three times higher for pure Ne discharges and only 40 % in Kr discharges as compared to the secondary electron yield in Ar discharges. In case pure N_2 is used for the sputter process the secondary electron yield is estimated to 60 % of the Ar discharge.

Table 1: Collection of process-relevant data for C/inert gas/N₂ discharges.

	Inert gases			Reactive gas species		Target material
	Ne	Ar	Kr	N ₂	N	C
1 st Ionization energy [eV], I_P	21.56	15.75	13.99	15.6	14.53	11.26
Total ionization cross section [10 ⁻¹⁷ cm ²], at 25 eV	0.25 [16]	12.5 [16]	17.6 [16]	8.25 [17]	1.17 [18]	14.4 [18]
Metastable excitation energy [eV]	16.62	11.55	9.91	12.08		
	16.71	11.72	9.99	13.03		
	[19]	[19]	[19]	[20] [†]		
Collision mean free path [cm] at 400 mPa [‡] [21]	23.9	7.2	6.0	6.8	14.3	
Secondary electron emission yield	0.218	0.073	0.029	0.069	0.043	
Total sputter yield for C [atoms/ion] at 500 eV [§]	0.165	0.120	0.069	0.193	0.202	0.256
Energy per sputtered atom [eV/atom] at 500 eV [§]	12.7	9.4	7.4	10.6	17.6	21.9

In low-pressure discharges the process gas ionization (Ne, Ar, Kr, N₂) as well as the target material ionization is generally governed by electron impact ionization. However, a special feature of the graphite discharge in Ne/N₂ (N₂ ≤ 50 %) is the creation of a Penning mixture. Here, the addition of small amounts of the reactive gas N₂ to the C/Ne discharge catalyzes the dissociation and ionization of N₂ [13, 22]. This is attributed to metastable states of Ne (Ne*) at 16.62 eV and 16.71 eV that exceed the ionization potential of N₂ ($I_P^{N_2} = 15.6$ eV) and N ($I_P^N = 14.53$ eV).

For each of the sputter modes and inert gases, changes in process- and plasma properties are expected. Their combination opens yet a wider process window for the modification of the CN_x

[†] Reference [20] reports five resonances in the region between 12.59 eV and 13.53 eV. Table 1 cites the resonances of the highest relative intensity 0.8 and 1.0, respectively.

[‡] As calculated using the approach suggested in reference [21]

[§] As obtained by TRIM 2013 simulations (J. F. Ziegler, <http://www.srim.org/>, v SRIM 2013) for ion energies of 500 eV as well as an incidence angle of 0° with respect to the target surface normal,

microstructure and thin film properties. Therefore, in this study we investigate the effect of three different inert gases (Ne, Ar, Kr) in reactive DCMS and HiPIMS processes on the growth, the evolution of residual stresses, the chemical bonding, microstructure and mechanical properties of CN_x thin films. Conclusions on the growth as well as structure-defining mechanisms are drawn from the evaluation of the plasma processes by positive ion mass-spectrometry and related to results from thin film characterization by transmission electron microscopy (TEM) together with selected area diffraction (SAED), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and nanoindentation.

2. EXPERIMENTAL DETAILS

Positive ion mass-spectrometry and thin film synthesis were performed in an industrial sputter system (CemeCon AG, Germany) at Linköping University. All investigations employed one rectangular graphite target (88 mm × 500 mm). The target was sputtered in N₂/inert gas mixtures at a constant process pressure of 400 mPa. Ne, Ar, and Kr were chosen as inert gases. For our positive ion mass spectroscopy investigations, the N₂-to-inert gas flow ratio, defined as

$$f_{N_2/g} = \frac{f_{N_2}}{f_{N_2} + f_{inert\ gas}} \cdot 100 \%, \text{ where } f_{N_2} \text{ and } f_{inert\ gas} \text{ are the N}_2 \text{ and corresponding inert}$$

gas flows, respectively, was varied between 0 % and 100 %. CN_x thin films were deposited using a $f_{N_2/g}$ of 14 %. Plasma characterization was performed at a distance of 60 mm perpendicular to the target. During film deposition the same distance between target and substrates was used. All processes were conducted without substrate table rotation. HiPIMS processes were carried out in power-regulated mode applying a pulse frequency of 300 Hz and a pulse width of 200 μs. In order to sustain a stable discharge during ion mass spectrometry measurements in case Ne was used as inert gas, a cathode power of 1800 W was necessary, whereas for processes involving Kr an average power of 1400 W was used. For both power settings (1400 W and 1800W), reference measurements were conducted in Ar-containing atmosphere. In order to provide comparable DCMS processes a cathode power of 1800 W was used for processes in Ne and Ar, while 1400 W were applied for Kr and comparable Ar-based processes.

All thin films were deposited on conventional p-doped Si(001) wafers applying a cathode power of 1400 W. A pulsed bias voltage (V_b) of -100 V, synchronized to the cathode pulses, was applied to the substrate table for thin films deposited in HiPIMS mode. A DC bias voltage of -100 V was used for thin films synthesized in DCMS mode. Substrate temperatures (T_s) of 110 °C (LT

– low temperature) and at 430 °C (HT – high temperature) were used for the deposition of CN_x thin films. CN_x films with thicknesses between 200 nm and 800 nm were deposited. Structural characterization as well as compositional analysis were performed on films with thicknesses ranging between 200 nm and 400 nm, while films with thicknesses between 400 nm and 800 nm were used for mechanical tests. The target current and target voltage were recorded using a Tektronix DPO4054 500 MHz bandwidth digital oscilloscope.

Time averaged positive ion mass spectroscopy measurements were carried out at room temperature. No bias voltage was applied during mass spectrometry investigations. The PSM003 unit from Hiden Analytical, UK was used to record ion energy distribution functions (IEDFs) in time-averaged mode for the most abundant positive charged plasma species, namely C^+ , C_2^+ , N^+ , N_2^+ , Ne^+ , $^{22}Ne^+$, Ne^{2+} , Ar^+ , Ar^{2+} , $^{82}Kr^+$, $^{84}Kr^+$, $^{86}Kr^+$, Kr^{2+} , CN^+ , and $C_2N_2^+$ during HiPIMS and DCMS discharges. In order to allow comparisons, the measurements were conducted with similar global settings (including detector, extractor, and quadrupole voltages and currents) after fine-tuning to mass 12, assigned to C^+ . IEDFs were recorded for an energy range between -0.5 eV – 50 eV using step widths of 0.5 eV. The dwell time was set to 100 ms, implying that each data point for IEDFs recorded in HiPIMS mode contains the information of at least 30 pulses.

Time resolved Langmuir probe measurements were performed using a custom made probe set-up. The Langmuir probe was made out of a W wire with a diameter of 350 μm . The wire was insulated by a ceramic tube, except for 4 mm that were exposed to the plasma. A voltage controlled constant current source was used to drive a current through the probe. The voltage compliance for the current source was -90 V to +30 V. The parasitic output capacitance of the current source was measured to be 200 pF. The current source was controlled via a NI USB-6003 data acquisition card (National Instruments). The data acquisition card together with a source transconductance of 11

mA/V yields a minimum current step size of 3.4 μ A. For each set current, an Agilent DSO-X 2002 oscilloscope was used to measure the voltage on the probe, yielding a resolution of 0.78 V. All oscilloscope measurements were averaged over eight waveforms. For measurements in HiPIMS mode, the electron temperature (T_e) was extracted for pulse times, where the target current reaches its maximum value [13].

Cross-sectional scanning electron microscopy (SEM, LEO 1550 Gemini, Zeiss, Germany) was used to obtain the growth rates (R_d) of the processes and the morphology of the thin films. Images were acquired with an acceleration voltage of 5 kV at a working distance of $\sim$ 3mm. The composition of the deposited films was investigated by time-of-flight elastic recoil detection analysis (ToF-ERDA) applying an 36 MeV $^{127}\text{I}^{9+}$ ion beam with an incidence angle of 22.5° relative to the surface. All ERD data were stored event-by-event and analyzed off-line. Data obtained during the first minutes (yielding sufficient statistics) were used for the evaluation of the composition. The combination of SEM and ERDA allowed the evaluation of the thin film density with a maximum error of 15 %.

The residual film stress was determined by the wafer curvature method assessed by X-ray diffraction (XRD, PANalytical Empyrean) [23]. The diffractometer, equipped with a Cu $K\alpha 1$ source, was operated at 45 kV and 40 mA. The Stoney formula for anisotropic single crystal Si(001) was used for the calculation of the residual film stress. Here, the plane stress in the films was assumed to be uniform [24].

The chemical bonding and elemental composition of the CN_x thin films was investigated by X-ray photoelectron spectroscopy (XPS) with an Axis Ultra DLD instrument from Kratos Analytical, Manchester, UK using monochromatic Al(K_α) radiation ($h\nu = 1486.6$ eV). The base pressure in the analysis chamber during acquisition was $<1 \times 10^{-7}$ Pa. XPS core level spectra of the

C1s, N1s, and O1s regions were recorded on as-deposited samples. Automatic charge compensation was applied throughout the acquisition. CN_x thin films were investigated in detail by the evaluation of the N1s core level spectra. After subtraction of a Shirley-type background, all components of the N1s core level spectra were fitted using a Voigt peak shape with the Lorentzian contribution not exceeding 30 %. The full-width-at-half-maximum (FWHM) of all components was restricted to < 2 eV, and all spectra were referenced to the C-C *sp*²/C-CH signal at 285 eV.

Micro-Raman spectroscopy was used to investigate the bond structure of the CN_x films further. For the measurements a 532 nm single-mode laser, a high-resolution single monochromator (Jobin-Yvon, model HR460) equipped with a CCD camera, and a 600 g/mm grating were used. The resolution of the system was approximately 5 cm⁻¹. An Olympus objective with a magnification of 100X was employed to focus the laser spot to a diameter of approximately 1 μm. In order to avoid thermal damage of the samples, the laser power was kept at 0.5 mW. For accurate evaluation of the contributions of the D and G peaks the Raman spectra were fitted with two Gaussian functions after subtraction of a linear background.

Cross-sectional TEM and SAED were carried out on cleaved samples [25] in a Tecnai G2 TF 20 UT TEM (FEI, The Netherlands). The instrument was operated at an acceleration voltage of 200 kV. After acquisition using a CCD camera, the SAED patterns were processed with diffraction a software [26] in order to evaluate the degree of structural evolution (fullerene-like, graphitic or plain amorphous). The SAED peak intensities (int) of the ~ 3.5 Å and the ~ 2 Å rings were extracted and set into relation (int(3.5Å)/int(2Å)). This ratio presents the degree of structure; the higher the value the higher is the extent of graphitic or FL short-range ordering (SRO) [27].

The mechanical properties of the deposited films were obtained in a setup combining an atomic force microscope (Nanoscope IIIa, Digital instruments) and a nanoindenter (Performech,

Hysitron Inc.). Indentations were carried out with a three-sided Berkovich tip, possessing an apex radius of < 50 nm. All films were tested in load-controlled mode. At first nine indents of decreasing loads between $1500\ \mu\text{N}$ and $100\ \mu\text{N}$ were carried out. Next, at least twenty-five indents utilizing a maximum load of $500\ \mu\text{N}$ were performed. For evaluation, only tests with an indentation depth of 10 % or less of the film thickness were considered. Data were fitted in the range between 95 % and 20 % of the unload curve using the Triboscope (Hysitron Inc.) software.

3. RESULTS AND DISCUSSION

3.1 Effects of inert gases on the positive ion composition and energy of the C/N₂/inert gas DCMS and HiPIMS discharges

Figure 1 a) – 1 k) presents IEDFs of the most abundant species in C/N₂/Ne discharges with different $f_{N_2/Ne}$ in DCMS (1a) – 1e)) and HiPIMS (1f) – 1k)) modes. Considerable are IEDFs from C⁺ and Ne⁺ obtained in both sputter modes (figures 1 a), 1b), 1f), and 1g)) for the metallic plasma (black lines) and the plasma featuring a low $f_{N_2/Ne}$ of 14 % (grey lines). DCMS discharges without N₂ yield well pronounced high-energy tails for C⁺ and Ne⁺ at ~25 eV and ~23 eV, respectively. As 14 % N₂ is added to the discharge those energies are reduced to ~22.5 eV and 17 eV. The energy tails of C⁺ and Ne⁺ in HiPIMS mode appear at slightly higher energies of ~29.5 eV and ~29 eV, respectively, in the pure Ne discharge and show the same trend towards lower energies as 14 % N₂ is added. These comparatively high ion energies are ascribed to:

Figure 1 a)-k) (colour online): Time-averaged IEDFs of the most abundant precursor species recorded a) – e) for DCMS and f) – k) HiPIMS discharges of graphite at $P_{av} = 1800$ W in Ne and Ne/N₂.

- (i) increased target currents, of 3.1 A in Ne vs 2.6 A in N₂ for DCMS discharges as well as high peak target currents of 240 A for the HiPIMS process in Ne vs 170 A of the corresponding

process in N₂ [13, 28], arising mainly due to an increased C sputter yield and secondary electron emission yield.

- (ii) an increased mean free path for collisions of plasma species, of ~ 23.9 cm for the metallic Ne discharge (cf. table 1) and
- (iii) increased electron energies. As a result of the comparatively high ionization energy of Ne ($I_p^{Ne} = 21.56$ eV, cf. table 1) the electron temperature in the plasma increases, contributing significantly to the ionization process of carbon and activation of the sputter gas. As can be seen in figure 2, comparatively high electron temperatures (T_e) of 7.5 eV and 6.7 eV were extracted from the hot electron population for the metallic DCMS and HiPIMS processes, respectively. Corresponding reactive DCMS and HiPIMS discharges using an $f_{N_2/Ne}$ of 14% yielded slightly lower T_e of 6.0 eV and 5.6 eV, respectively. When comparing DCMS and HiPIMS discharges, commonly lower T_e are observed in HiPIMS mode, as the plasma contains an increased percentage of target species, which may be ionized upon electron impact leading to the drop in T_e [29].

Figure 2 (colour online): Electron temperatures (T_e) of the hot electron population extracted for DCMS and HiPIMS discharges using pure sputter gases and $f_{N_2/g} = 14\%$. Values shown for HiPIMS discharges were extracted at pulse times corresponding to the peak target current [13].

IEDFs obtained for the metallic plasma and the plasma featuring a low $f_{N_2/Ne}$ of 14 % show additionally only small contributions from thermalized or low energy ions, which is again attributed to the increased mean free path for collisions of plasma species (cf. table 1).

As can be seen in figures 1 a) –1e), the effect of Ne vanishes for all ionized species in

DCMS discharges as soon as the N₂ content in the plasma exceeds 14 %. Here, predominantly

contributions from low energetic ions are observed (~ 2.5 eV) for discharges containing $> 33\%$ N_2 . IEDFs obtained in HiPIMS mode, on the other hand, show gradual changes towards lower energies as the N_2 content in the plasma rises. In both sputter modes, the reduction of the ion energies can be attributed to a decreased mean free path for particle collisions (cf. table 1) as the discharge is carried out using more N_2 . Additionally, Ne is increasingly diluted and the effect induced by Ne - the formation of a Penning mixture - is reduced as the $f_{N_2/Ne}$ in the plasma approaches 33%. In both sputter modes ionized C_xN_y molecules are first observed in significant amounts as 33 % N_2 is added to the discharge (cf. figure 1 e) and k)). This can be attributed to an increased availability of N in the plasma for N_2/Ne flow ratios $> 33\%$ and to reduced ion energies as more N is added to the discharge. Lower species energies contribute to reduced fragmentation of C_xN_y molecular bonds. A low energetic ion flux and the availability of film forming C_xN_y species such as CN were reported to contribute significantly to the structural evolution of a short-range order in the CN_x thin films [30].

Figure 3 a) – 3 k) shows IEDFs of abundant species in DCMS and HiPIMS carbon discharges using N_2/Ar mixtures. Here, IEDFs for the discharges with a cathode power of 1800 W are shown, and data for IEDFs recorded at a cathode power of 1400 W are omitted as the shapes and count rates do not differ significantly for both average target power settings. The increased cathode power results merely in a slight reduction of thermalized C^+ , Ar^+ , and N_2^+ ions.

The most prominent difference comparing IEDFs of DCMS and HiPIMS processes for the carbon discharge in N_2/Ar are the wider energy distributions for all abundant plasma species in HiPIMS discharges. IEDFs recorded in DCMS mode show well pronounced contributions from ions at low energies of ~ 2.5 eV. This is commonly observed when DCMS and HiPIMS discharges are compared [12, 31, 32]. The origin of high energetic ions in HiPIMS processes is a matter of

discussion in literature [33]. However, the here presented results are in agreement with the study performed by Hecimovic et al. [28], attributing the high energetic ions to increased peak target currents.

Figure 3 a)-k) (colour online): Time-averaged IEDFs of the most abundant precursor species recorded a)–e) for DCMS and f)–k) HiPIMS discharges of graphite at $P_{av} = 1800$ W in Ar and Ar/N₂.

Comparing the C⁺ IEDFs recorded in DCMS mode as an increasing amount of N₂ is added to the discharge (cf. figure 3a)), a slight increase in count rate is evident. This can be related to a higher sputter yield (cf. table 1) of C in N₂ and N compared to Ar. IEDFs of the reactive gas ions N⁺ and N₂⁺ as well as for the CN⁺ cluster during DCMS in N₂/Ar discharges also increase in count rate, but hardly in energy as the N₂ content in the plasma is raised. Their increased count rate can be ascribed to an increased availability of N in the plasma. The similarity of ion energies is mainly attributed to comparable target currents in DCMS discharges of ~2.6 A. In contrast to this are IEDFs recorded in HiPIMS mode of all abundant ionized species except Ar⁺; here, slightly wider energy distributions are recorded as the N₂/Ar flow ratio rises. For example, the C⁺ IEDF shows a difference of ~5 eV for 0 % and 100 % N₂ in the plasma. This does not correlate with the corresponding peak target currents of 182 A for the pure Ar discharge and 172 A for the discharge in pure N₂, but may be related to an increased sputter yield [28] of C in N₂ and altered target surface

conditions that contribute to increased sputter yields [12]. As the N_2 content in the plasma increases, C dangling bonds are likely to be terminated by N during the long pulse off times. At the same time the secondary electron emission yield decreases (cf. table 1) [12] and electron quenching by excitation of N_2 reduces the probability of electron impact ionization, leading to lowered peak target currents. This is supported by Langmuir probe measurements, where comparatively high T_e were extracted for reactive Ar and pure N_2 HiPIMS discharges of C (cf. figure 2).

Figure 4 a) – 4 k) presents IEDFs for carbon discharges in N_2 /Kr mixtures of DCMS and HiPIMS processes. Here, IEDFs for the discharges using a cathode power of 1400 W are shown. Especially, C^+ yields higher count rates and energies in HiPIMS discharges, while other abundant species in the plasma show similar or marginally higher count rates and energies compared to their DCMS counterpart. In contrast to IEDFs recorded during HiPIMS discharges, IEDFs obtained from DCMS discharges show high amounts of thermalized ions and low energetic ions at energies between 2.5 eV and 5 eV. However, IEDFs recorded in both sputter modes for increasing N_2 contents of up to 50 % show only a slight increase of ion energies and abundance, while a comparatively steep gain of both, count rate and energy, is observed as C is sputtered in pure N_2 . The C ion count rates are mainly influenced by its sputter yield as well as the probability for electron impact ionization, the working gas and film forming molecules. In C/Kr discharges with up to 50 % N_2 the properties of Kr prevail; due to the high difference in mass of C and Kr, the sputter yield is comparatively low, generating less species that can potentially be ionized. Although, Kr shows a high ionization cross section upon electron impact it also possesses a low ionization potential leading to a low secondary electron yield (cf. table 1) and low electron energies. This results additionally in a reduced generation of electrons, potent to induce further ionization events. Moreover, due to the low excitation energy of metastable Kr species C ionization by

Penning processes is not possible. The reduced generation of charge carriers is also reflected by a low target current of 1.4 A in metallic DCMS mode and a comparatively low peak target current of 58 A in the corresponding HiPIMS process.

The energy of the plasma species originating from the target for reactive Kr discharges in both sputter modes (cf. figure 4 a), d), e) and f), i) k)) is not only determined by the target current but also by their mean free path for collision with other plasma particles. The mean free path was estimated to be approximately 6 cm in pure Kr discharges, corresponding to the target-to-orifice and target-to-substrate distance. Interestingly, for the DCMS discharges in N₂/Kr atmospheres CN⁺ could not be recorded in significant quantities, but low amounts of C₂N₂⁺ were found.

Figure 4 a)-k) (colour online): Time-averaged IEDFs of the most abundant precursor species recorded for a)–e) DCMS and f)–k) HiPIMS discharges of graphite at $P_{av} = 1400$ W in Kr and Kr/N₂.

Considering IEDFs recorded for C⁺ and N⁺ during discharges using either of the different inert gas mixtures in HiPIMS mode, similarities in shape and generally wider energy distributions are observed compared to IEDFs from inert gas ions and N₂⁺. This is reported for reactive metal and C discharges [13, 34, 35]. The similarities indicate that C⁺ and extensive amounts of N⁺ are created by the same source, thus both species originate from the graphite target. This in turn suggests that the graphite target surface chemistry is affected by N in the plasma. Moreover,

dissociative ionization of N_2 upon electron impact may contribute to a lower extent, to the shape of the N^+ IEDFs. IEDFs from inert gas ions and N_2^+ are mainly composed of low energetic and fully thermalized ions. The generally narrow energy distributions for working gas ions are attributed to ionization events during the comparatively long pulse off times that contribute and largely determine the time averaged signal recorded by the mass spectrometer. IEDFs in DCMS mode do not allow an interpretation as for the origin of the species as these are generally determined by the signal arising from thermalized ions and ions possessing low energies up to 5 eV.

Figure 5 a) - d) presents a comparison of the total ion flux of most abundant precursor species for reactive sputter processes using Ne and Ar in DCMS and HiPIMS modes. Here, time-averaged IEDFs were recorded for an average target power of 1800 W and subsequently integrated over their entire energy range (cf. figures 1 and 3). For metallic and reactive discharges using a $f_{N_2/Ne}$ of 14 % in DCMS and HiPIMS modes (figure 5 a) and 5 b)) the relative and total ion fluxes of C^+ and Ne^+ are similar. The comparatively high C^+ ion fluxes for those discharges are attributed to the high C sputter yield and secondary electron emission yield of Ne as well as its ability to ionize C by Penning processes. A remarkable difference between the two deposition modes is noticed as the N_2 content in the plasma approaches 33 %. In DCMS mode the increase of the reactive gas induces a decreased total flux of C^+ , while fluxes of reactive gas ions and Ne^+ increase. Additionally, C^{2+} as well as Ne^{2+} fluxes are not detected anymore, but CN^+ is observed. The ion fluxes extracted for the corresponding HiPIMS discharges show similar values. Compared to DCMS processes high values for C^+ are recorded. The lowered C^+ fluxes in DCMS discharges containing more than 14 % N_2 is typical and ascribed to a lower electron density in the vicinity of the target. This is in agreement with the comparatively high electron temperature extracted for all DCMS processes (cf. figure 2). Another remarkable feature that is evident for DCMS N_2/Ne

discharges with $f_{N_2/Ne} \geq 33 \%$, is the high total ion flux of the process gases, exceeding the corresponding fluxes in HiPIMS mode by approximately one order of magnitude. The increase in working gas ions at this point coincides with the increase in CN^+ and especially a decreased C^+ flux. The fact that the Ne^+ flux increases although less Ne is added to the plasma is explained by a decrease in gas rarefaction; as 33 % of N_2 is added to the plasma the target current drops by $\sim 30 \%$, the Penning mixture disappears, and the amount and energy of C^+ drops abruptly (cf. figure 1a)) [36]. Another cause for the increase in working gas ions is the higher density of species that could potentially be ionized as more N_2 is added to the plasma due to dissociation or dissociative ionization of N_2 into $2N$ leading additionally to a plasma cooling. The effect of gas rarefaction is more pronounced in HiPIMS processes due to the here prevailing elevated peak target power [15] and demonstrated in figure 1f) and 5 b), where the C^+ energy decreases, but not its amount. This, in turn, explains the lower amount of process gas ions (cf. figure 5 b) throughout the range of investigated gas compositions in HiPIMS mode as compared to the DCMS mode.

The reactive graphite DCMS discharges in Ar (figure 5 c)) show distinct differences in C^+ and sputter gas ion fluxes over the entire range of applied N_2/Ar mixtures. The DCMS discharges are dominated by N_2^+ , N^+ , and Ar^+ , while contributions from C^+ , Ar^{2+} , and CN^+ fluxes are up to two orders of magnitude lower. The corresponding HiPIMS discharges (figure 5 d)) are dominated by equal parts of N_2^+ , N^+ , Ar^+ , and C^+ . Minor fluxes were extracted for C_2^+ , Ar^{2+} , and CN^+ . The rather constant course of fluxes from most abundant ionized species in HiPIMS mode can be ascribed to comparable ionization potentials, although the sputter yields of Ar and N_2 change considerably (cf. table1). As in the cases of the Ne/N_2 discharges, increased ion fluxes from the

target in HiPIMS mode cause gas rarefaction and thus reduced working gas ions as compared to Ar/N₂ DCMS discharges.

Figure 5 a)-d) (colour online): Ion fluxes in dependence of the N₂ content in the process gas as graphite is sputtered in Ne and Ne/N₂ mixtures extracted for a) DCMS and b) HiPIMS processes as well as the comparison to discharges in Ar and Ar/N₂ for c) DCMS and d) HiPIMS processes.

Figure 6 a)–d) shows the total ion flux of the most abundant positive plasma species for reactive Kr (figure 6 a) and 6 b)) and corresponding Ar (figure 6 c) and 6 d)) discharges in DCMS and HiPIMS modes. The processes were carried out at an average target power of 1400 W. The comparison of DCMS and HiPIMS discharges in Kr (cf. figure 6 a) and 6 b)) indicates especially for the C⁺ ion flux distinct differences. The DCMS discharge in metallic mode is dominated by Kr⁺ and Kr²⁺, whereas the C⁺ flux is two orders of magnitude lower. The high amount of Kr²⁺ is ascribed to be due to a combination of the relatively high cathode voltage (with peak values of up to 920 V in HiPIMS mode and 635 V in DCMS mode) that is necessary to sustain the discharge, the comparatively low Kr ionization potential and the absence of gas rarefaction. The latter is indicated by the low discharge current along with the low sputter yield for C in Kr (cf. table 1) [36], [37]. The metallic HiPIMS discharge shows high signals for Kr⁺ followed by C⁺. Kr²⁺ is also found, although to a considerable lower extent compared to the corresponding DCMS discharge. As soon

as N_2 is introduced to the DCMS discharge, the N_2^+ flux exceeds the Kr^+ flux, as the latter drops. With a further increase of N_2 , the total fluxes of N^+ , C^+ , C_2^+ , and $C_2N_2^+$ increase, while Kr^+ and Kr^{2+} fluxes remain unaffected by the increasing N_2 flow. The reactive HiPIMS discharges show a slight but steady increase of the total fluxes of C^+ , reactive gas ions, and CN^+ as more N_2 is added. Increasing ion fluxes originating from the target are ascribed to the increased C sputter yield and secondary electron emission yield induced by N and N_2 . Apart from the high Kr^{2+} signal in the metallic DCMS discharge, the observations for Ar and Kr-containing DCMS and HiPIMS discharges are qualitatively comparable.

Figure 6 a)-d) (colour online): Extracted ion fluxes in dependence of the N_2 content in the process gas as graphite is sputtered in Kr and Kr/ N_2 mixtures for a) DCMS and b) HiPIMS processes as well as the comparison to discharges in Ar and Ar/ N_2 for c) DCMS, and d) HiPIMS processes.

This is also mirrored in Figure 7, where the sum of the total ion flux from species that obviously originate from the target (namely C^+ , C_2^+ , CN^+ , and $C_2N_2^+$) is set into relation to the sum of process gas ion species (single and double charged inert gas ions, N_2^+ , and N^+). The figure shows the relative significances of the sputter gas and the sputter mode with regards to plasma ionization. In case Ne or N_2/Ne mixtures with $f_{N_2/Ne} < 20\%$ are used, the sputter mode possesses little

Figure 7 (colour online): Sum of the total ion flux of species originating from the target in relation to the sum of process gas ion species over the amount of N₂ in the inert gas for DCMS and HiPIMS discharges.

influence on the ionization of the target material. In other inert gas/N₂ atmospheres the sputter mode gains major significance regarding the ionization of carbon.

3.2 Impact of inert gases on CN_x film growth, microstructure and Hardness

As demonstrated by ion mass spectrometry, the 14 % N_2 containing DCMS and HiPIMS discharges for graphite differ when Ar or Kr are used as inert gases. In the case the DCMS and HiPIMS processes are carried out in 14% N_2/Ne , comparable plasma chemistries and ion energies are observed. Moreover, the amount of so-called structure-defining $C_xN_y^+$ species varies to a great extent in these discharges. Therefore, this section addresses the effects of the above presented process characteristics on the film growth and the microstructure of CN_x thin films grown in 14 % N_2 /inert gas atmosphere.

Figure 8 shows the growth rates (R_d) and density of CN_x thin films deposited by reactive DCMS and HiPIMS at substrate temperatures of 110 °C (LT) as well as R_d and 430 °C (HT) in inert gas mixtures with 14 % N_2 . At low substrate temperatures, the DCMS growth rates decrease with increasing inert gas mass. This agrees with the C sputter yield values (cf. table 2) that take the actual cathode voltage for the corresponding processes into account; the reactive DCMS process in Ne yields a comparatively high growth rate of ~26 nm/min, while the reactive DCMS processes in Ar and Kr show growth rates of ~16 nm/min and ~12 nm/min, respectively. Nevertheless, the growth rate using the reactive Ne gas mixture in DCMS discharges at 110 °C appears to be comparatively high, thus the film density of $1.48 \text{ g/cm}^3 \pm 0.15 \text{ g/cm}^3$ needs to be taken into account. Using Ne gas mixtures, both sputter modes yield film densities that are comparatively low as a density of $1.67 \text{ g/cm}^3 \pm 0.15 \text{ g/cm}^3$ for the corresponding reactive HiPIMS process was extracted. Hence, we speculate that the high cation energies of all abundant plasma species (at a bias voltage of -100 V) together with the comparatively high momentum transfer by Ne promote re-sputtering of the deposited film. This is confirmed by TRIM simulations (see table 2), where the three different inert gases with an ion energy of 100 eV (corresponding to the bias voltage) were

considered. In case the reactive Ne process is carried out in DCMS mode, a re-deposition of re-sputtered species may be possible, since a constant bias voltage is fed and a continuous particle flux towards the substrate takes place. As the pulsed bias voltage in HiPIMS processes operates with a duty cycle of 6 %, less re-sputtered particles may be re-deposited, resulting in higher film densities and lowered growth rates. CN_x thin films prepared in reactive Ar and Kr mixtures of $f_{N_2/g} = 14\%$ show higher and comparable densities of 2.30 and $2.17 \text{ g/cm}^3 \pm 0.15 \text{ g/cm}^3$, respectively. These film densities do not significantly differ for films deposited in DCMS and HiPIMS modes. Moreover, the film density of CN_x deposited at 110°C is higher than for films sputtered at 430°C , which showed values of $\sim 2.0 \text{ g/cm}^3$ [12].

Figure 8 (colour online): Film growth rates (R_d , filled symbols) and density (open symbols) of CN_x thin films deposited at a substrate temperature of 110°C (LT, black squares) and 430°C (HT, red circles) in different 14% N_2 /inert gas mixtures using DCMS and HiPIMS.

Considering the sputter yield of the different inert gases for carbon together with the actual target voltage during HiPIMS processes using a $f_{N_2/g}$ of 14% (cf. table 2), a slightly higher growth rate is expected as processes are conducted in reactive Ar mixtures compared to processes using reactive Ne mixtures, while the growth rate for the Kr gas mixture is expected to be significantly lower. This is mainly caused by

i) the comparatively low cathode voltage for HiPIMS processes using Ne gas mixtures, but at the same time a high momentum transfer of Ne and ii) the comparatively low momentum transfer by Kr, even though high cathode voltages in Kr based HiPIMS processes were observed. In figure 8, the growth rates of reactive HiPIMS processes at a substrate temperature of 110°C (LT) reflect

sputter yield data (cf. table 2) very well. An insignificantly higher CN_x growth rate of 16.4 ± 0.9 nm/min is observed as carbon is sputtered in $f_{N_2/Ar}$ of 14% compared to the growth rate of 15.6 ± 0.8 nm/min using the Ne based process, while the corresponding process in Kr yields 13.3 ± 0.8 nm/min.

Table 2: Sputter yield for C in different inert gases considering the actual target voltages during reactive processes using $f_{N_2/g} = 14\%$ in DCMS and HiPIMS modes as well as at an incident ion energy of 100 eV. Respective HiPIMS target voltages were extracted from voltage wave forms at pulse times corresponding to the peak target current.

	Ne	Ar	Kr
Total sputter yield for C [atoms/ion] at DCMS cathode potential in 14 % N_2 /inert gas **	0.176 at 510 V	0.120 at 500 V	0.097 at 600 V
Total sputter yield for C [atoms/ion] at HiPIMS cathode potential in 14 % N_2 /inert gas **	0.178 at 567 V	0.185 at 650 V	0.156 at 868 V
Total sputter yield for C [atoms/ion] at 100 eV ††	0.023	0.002	-

The growth rates for CN_x films synthesized at 430 °C become additionally influenced by chemical desorption processes at the substrate and an increased ad-atom mobility. Both processes occur at the growing film surface and have a reverse influence on the growth rates; while the desorption (chemical sputtering) of predominantly N-rich species will decrease the growth rate, an increased ad-atom mobility will promote a columnar morphology (cf. figure 9) and hence an increasing growth rate is obtained. This is usually observed in both sputter modes for substrate temperature > 300 °C and N_2 contents lower than 50 % in the plasma. Moreover, the formation of a columnar morphology may also be assisted by chemical sputtering. The reactive DCMS and HiPIMS processes conducted in all three inert gases show a similar trend; generally higher growth rates are

** As obtained by TRIM 2013 (J. F. Ziegler, <http://www.srim.org/>, v SRIM 2013) simulations for stated cathode potential and an incidence angle of 0° with respect to the target surface normal

†† As obtained by TRIM 2013 (J. F. Ziegler, <http://www.srim.org/>, v SRIM 2013) simulations for ion energies of 100 eV and an incidence angle of 0° with respect to the target surface normal

observed for HiPIMS processes, which are ascribed to less re-sputtering due to the low bias duty cycle. Moreover, in HiPIMS-mode the corresponding CN_x growth rates decrease with increasing inert gas mass. This is in accordance with the corresponding inert gas sputter yields of C. The CN_x films sputtered in DCMS modes show a maximum growth rate of ~ 16 nm/min for the process in 14 % N_2/Ar , while the processes conducted in 14 % N_2/Ne and 14 % N_2/Kr at 430 °C yield growth rates ~ 9 nm/min and ~ 12 nm/min, respectively. Although both sputter modes show similar ion energies and fluxes for processes conducted in 14 % N_2/Ne , the growth rate drops to approximately half of the value of the corresponding HiPIMS process. We attribute this loss in growth rate to an increased gas rarefaction in the vicinity of the target induced by a) the high degree of ionization of the plasma, b) the increased gas temperatures and velocities especially at 430 °C, and c) the constant gas depletion due to the continuous power supply, in contrast to the HiPIMS mode, where the gas can sufficiently refill during the long pulse-off times. All scenarios lead to a lowered amount of gas particles present in the vicinity of the target during high temperature DCMS processes using Ne. Moreover, pronounced re-sputtering due to the continuous power supply at the substrate table may contribute to a lowered growth rate.

Figure 9 presents the morphology of CN_x thin films deposited in HiPIMS mode using a) 14% N_2/Ne at 110 °C (LT), b) 14% N_2/Ne at 430 °C (HT), c) 14% N_2/Ar at 110 °C (LT), d) 14% N_2/Ar at 430 °C (HT), e) 14% N_2/Kr at 110 °C (LT), and f) 14% N_2/Kr at 430 °C (HT). SEM cross-sections of films deposited in DCMS mode show the same qualitative information, hence the corresponding images are omitted. As can be seen in figure 9, the film morphology is mainly influenced by the substrate temperature and only to a small extent by the choice of the inert gas. At a substrate temperature of 110 °C all film appear glassy, and rather featureless. At $T_s = 430$ °C, the deposition processes yield a film morphology which can be described as granular, rather than columnar. The qualitative information obtained from SEM images is not only consistent with the growth rates but also with the residual film stresses (cf. figure 10) and the composition of the CN_x films, especially their oxygen concentration (cf. figure 11).

Figure 9 a) - f): SEM cross-sections of CN_x thin films deposited by HiPIMS in a) 14% N_2/Ne at 110 °C (LT), b) 14% N_2/Ne at 430 °C (HT), c) 14% N_2/Ar at 110 °C (LT), d) 14% N_2/Ar at 430 °C (HT), e) 14% N_2/Kr at 110 °C (LT), and f) 14% N_2/Kr at 430 °C (HT).

Figure 10 shows the residual stresses of the CN_x films. The deposition in HiPIMS mode yields lower compressive film stresses compared to the synthesis in DCMS mode. In HiPIMS, the intermittent energetic particle bombardment offers means for the growing material to relax, while the constant particle bombardment in case DCMS is used results in increasing compressive film stresses. This was also observed in [38]. Correspondingly, the relatively low stress values for films deposited in HiPIMS mode at 110 °C appear not significantly affected by the different inert gases.

Figure 10: Residual stress of CN_x thin films deposited in DCMS and HiPIMS mode at LT ($T_s = 110$ °C) and HT (430 °C) in 14 %N₂/inert gas atmosphere.

Since mass spectrometry data of Ne discharges revealed comparatively high amounts and energies of ions, higher compressive film stresses could have been expected for the resulting CN_x films [39, 40].

However, the low film densities may facilitate stress relief. Hence, it can be concluded that re-sputtering of FL-structure forming

precursors, rather than forward sputtering due to ion-bombardment occurs. As the CN_x deposition is carried out in DCMS mode using Ar at 110 °C the highest compressive film stress of 2.8 GPa is measured, while the corresponding process in reactive Kr atmosphere yields 1.3 GPa. The Ar containing DCMS discharge comprised additionally to increased monatomic ion count rates and moderately increased ion energies also a higher amount of the ionized molecules $C_2N_2^+$ and CN^+ . Such complex molecules were supposed to contribute to increased film stresses [40], due to their constrained mobility at the growing film surface. It should be added that CN_x films deposited in Ar and Kr containing DCMS discharges showed low and similar contents of incorporated inert gas of 0.5 at% and 0.4 at%, respectively. The corresponding film deposited in reactive Ne atmosphere did not contain Ne. Hence, inert gas incorporation cannot account for the evolution of the residual

film stresses. As the substrate temperature is raised to 430 °C the compressive stress of CN_x films deposited in reactive Ne discharges increases and is higher compared to films deposited in Ar and Kr containing process gases. Here, the residual stresses show an expected dependency on the recorded ion energies and the extent of ion bombardment for the different inert gases and sputter modes, respectively. Furthermore, a relief of the compressive stress is observed for films sputtered in reactive Ar and Kr mixtures at 430 °C. The observation can be attributed to the pronounced granular appearance of the films.

Figure 11 shows the composition of the CN_x thin films as obtained from XPS measurements after a sputter cleaning step of 120 s was carried out using a 500 V Ar^+ ion beam. The results show the composition obtained from the evaluation of the C1s, N1s, and O1s core level regions of CN_x thin films deposited in either DCMS or HiPIMS mode at $T_s = 110$ °C (LT) and 430 °C (HT) in

Figure 11 (colour online): Carbon ([C]), nitrogen ([N]), and oxygen ([O]) contents of CN_x thin films as obtained by XPS measurements. CN_x thin films were deposited in either DCMS or HiPIMS mode at $T_s = 110$ °C (filled symbols) and 430 °C (open symbols) in 14 % N_2 /inert gas atmosphere.

$f_{N_2/g} = 14\%$. Obvious is the comparatively high N content of 21.5 at% and 22.2 at.% of CN_x thin films deposited by DCMS and HiPIMS, respectively, in N_2/Ne gas mixtures at $T_s = 110$ °C. This is mainly attributed to the high energy of N^+ and to a lower extent its abundance in the corresponding discharges (cf. figure 1c) and h)). Energetic N^+ ions will increase the probability for N intercalations in the carbon matrix, while its high abundance promotes reactions of N at the target surface and the substrate. The N content in CN_x films

produced by DCMS and HiPIMS decreases and diverges increasingly as the processes are carried out in Ar and Kr-containing sputter gas mixtures. Here, the lower N contents are attributed to a reduced excitation, ionization and dissociation of the N_2 molecule. Hence, comparatively low energies and amounts of reactive gas ions are present in the sputter plasma. In DCMS and HiPIMS mode, the N^+ -to- N_2^+ ratio drops to 30% and ~39% as well as 9% and 24% for reactive processes conducted in N_2/Ar and N_2/Kr , respectively, when compared to the corresponding Ne discharges. Oxygen concentrations of CN_x films deposited at 110 °C in DCMS mode are generally low and show a minimum of 0.3 at% as CN_x is deposited in N_2/Ar , while reactive Ne and Kr discharges yield 0.5 at% and 0.4 at%, respectively. Corresponding HiPIMS processes result in CN_x films with slightly higher oxygen contents of 0.6 at%, 0.6 at%, and 0.5at% for reactive Ne, Ar, and Kr discharges, respectively. As the substrate temperature increases to 430 °C the oxygen contents rise as well. Under such conditions, the N_2/Ar discharge in DCMS mode produce again CN_x films with the lowest O content of 0.7 at%. The corresponding films deposited in Ne and Kr gas mixtures show oxygen concentrations of 1.1 at% and 2.3 at%. These elevated O concentrations can be attributed to lowered CN_x growth rates in both processes. However, the high ion energies in Ne containing processes may lead to re-sputtering of surface O during growth and thus to a lower O content compared to CN_x sputtered in Kr mixtures. In HiPIMS mode, all CN_x films show higher oxygen concentrations of 2.4 at%, 4.4 at%, and 3.7 at% when deposited in reactive Ne, Ar, and Kr mixtures, respectively. The elevated oxygen contents found for both sputter modes at 430 °C are attributed to the distinct granular and columnar morphology of the films (cf. figure 9 b), d), and f); upon exposure to ambient conditions, more oxygen will attach to the CN_x surface as the granular and columnar morphology possesses a higher surface area. The comparatively high O contents of CN_x films deposited in HiPIMS mode can moreover be ascribed to long pulse-off times, in which

no ion bombardment takes place. Here, the growing film surface is susceptible to remaining residual oxygen in the chamber.

The chemical bonding and structural evolution of CN_x thin films were investigated by XPS. The C1s core level spectra obtained from the CN_x thin films are rather broad and without apparent features, while N1s core level regions show two distinct components (N1, N2, cf. figure 12 a) - f)). Figure 12 a) - f) shows the N1s core level spectra of CN_x films deposited at $T_s = 110^\circ\text{C}$ (LT) and $T_s = 430^\circ\text{C}$ (HT) in DCMS and HiPIMS modes using a $f_{\text{N}_2/g}$ of 14% in Ne, Ar, and Kr. As indicated in Figure 12, a maximum of five peaks were used for deconvolution of the N1s core level spectra. The main contributions, N1 (at $389.8\text{ eV} \pm 0.1\text{ eV}$) and N2 (at $\sim 400.9\text{ eV} \pm 0.3\text{ eV}$) are assigned to sp^2 -hybridized nitrogen (pyridine-like) and substitutional bonded nitrogen in a 3-fold coordinated C network (e.g., N bonded into a sp^2 -coordinated carbon plane), respectively [41, 42]. A minor, but broad component appearing at $402.8\text{ eV} \pm 0.2\text{ eV}$ is often ascribed to N-O bonds [42]. However, our results do not suggest the exclusive assignment of this component to N-O bonds, as there is no correlation with either film O contents or appearance of extracted components of the O1s core level region. The component at $\sim 402.8\text{ eV}$ increases in at% as the inert gas mass during film deposition decreases. Keeping the high N^+ ion energies that were found for the corresponding Ne processes in mind, an assignment to trapped, charged N or N_2 [43] is reasonable. Both the component at $\sim 402.8\text{ eV}$ and the one arising at $\sim 404.5\text{ eV} \pm 0.3\text{ eV}$, may also contain contributions from the $\pi\text{-}\pi^*$ shake-up satellite [44]. Another contribution arising at $399.8\text{ eV} \pm 0.1\text{ eV}$ has previously been ascribed to nitrile groups ($\text{N}\equiv\text{C}$) by Hellgren et al. [45]. This component is most pronounced for films deposited at 430°C and increases in at% from 1.1 and 0.6 for films sputtered in reactive Kr atmosphere, to 1.3 and 1.1 for films sputtered in N_2/Ar , as well as 2.7 and 3.9 for CN_x deposited in N_2/Ne by DCMS and HiPIMS, respectively.

Figure 12 a)-f) (colour online): XPS N1s spectra of CN_x thin films deposited using reactive a)-c) DCMS and d)-f) HiPIMS processes at substrate temperatures of 110 °C (LT) and 430 °C (HT) in Ne, Ar, and Kr atmospheres containing 14 % N_2 . The different deposition parameters, the peak deconvolution and the N2/N1 ratios are indicated.

The bonding configuration associated with N1 arises next to defects or at the periphery of the graphene-sheets, breaking their continuity and provoking a higher degree of disorder. Therefore, increased N2/N1 ratios, but also a pronounced N2 and N1 separation were found to be

indicative for a distinct evolution of the CN_x SRO towards a graphitic or FL-like microstructure. Comparing N1s core level spectra of CN_x thin films deposited by DCMS and HiPIMS in either Kr or Ar-containing atmosphere at 430 °C, the N2/N1 ratios are > 1.3 and additionally N1 and N2 are well separated indicating that those CN_x films exhibit a FL-structure. This is in agreement with above discussed results from positive ion mass spectroscopy as the corresponding processes showed moderate-to-low ion energies preserving structure defining C_xN_y -species ($x, y \leq 2$) in the plasma, which in turn promote the chemical desorption processes at the substrate [30]. The deposition of CN_x thin films in DCMS and HiPIMS modes using reactive Ne-gas mixtures yield a N2/N1 ratio of ~ 0.9 and 1.1 , respectively, indicating an amorphous structure with short, frequently disrupted graphene sheets. This correlates with IEDFs recorded for the DCMS and HiPIMS carbon discharges in $f_{\text{N}_2/\text{Ne}} = 14\%$, consisting mainly of ions exhibiting high energies, which in turn are likely to break up structure defining C_xN_y species adsorbing at the substrate surface. However, as CN_x is deposited at 430 °C in $f_{\text{N}_2/\text{Ne}} = 14\%$ by DCMS (cf. figure 12 a)), N2 and N1 appear well separated by ~ 2.5 eV. This is usually observed for CN_x thin films exhibiting a FL or graphitic SRO.

The CN_x bond configuration was further studied by Raman spectroscopy. In figure 13 Raman spectra of the same CN_x films as studied by XPS are presented. The D and G band region of all spectra were fitted using all four possible combinations of Lorentzian and Gaussian line shapes. It was found that in all cases the best fit is provided using Gaussian line shape for both D and G peaks. The results from the fit suggest that the samples can be divided in two groups; samples grown at a substrate temperature of 110 °C (LT) and 430 °C (HT). The groups show mainly differences in the G peak position, its linewidth, and the ratio between the amplitudes of D and G (I_D/I_G). The G peak of the LT samples is found at lower energies ($1556 - 1569 \text{ cm}^{-1}$) compared to

the G peak position of the HT group (1575 – 1586 cm^{-1}). The HT group exhibits also reduced linewidths of the G peak with FWHM ranging between 124 cm^{-1} and 149 cm^{-1} , compared to the FWHM of samples grown at 110 °C between 162 cm^{-1} and 173 cm^{-1} . Furthermore, the I_D/I_G of LT samples ranges between 1.28 and 1.60, except for the CN_x film sputtered in reactive Ar atmosphere using DCMS, for which a higher I_D/I_G of 1.77 was extracted. An increased I_D/I_G between 1.94 and 2.05 is found for HT samples, but for one exception; the film deposited in reactive Kr atmosphere in HiPIMS mode shows an I_D/I_G of 1.71. In the latter CN_x thin film, the D and G peaks are better resolved (cf. figure 13). This is mainly caused by a narrower G line (also the D line has the smallest linewidth of all spectra according to the fit), whereas both D and G peak positions are essentially the same as for the rest of the films grown at 430 °C. The decreased linewidths suggest a lowered degree of disorder, where variations in bond lengths and cluster size are more confined. Such interpretation agrees well with XPS N1s core level spectra of the same sample. Here, a high N2/N1 ratio of 1.4 was extracted, which suggests likewise a higher degree of order. Since I_D/I_G of the LT samples is lower than the corresponding value for the HT samples, due to diminished D peak contributions in the spectra, it may be concluded that the CN_x matrix is largely composed of C-C chains and N induces comparatively high amounts of sp^3 -hybridized C. As the substrate temperature increases to 430 °C, increased D peak contributions suggest an increased amount of sp^2 -hybridized C that is bond in rings rather than chains. At the same time, the G peak positions shift from ~1560 cm^{-1} to ~1580 cm^{-1} . The D-peak positions and line widths do not show any correlation to the substrate temperature and range between 1376 – 1390 cm^{-1} and 359 – 377 cm^{-1} , respectively.

Figure 13 (colour online): Raman spectra obtained for CN_x thin films deposited by DCMS and HiPIMS at 110 °C (LT) and 430 °C (HT) in Ne, Ar, and Kr atmospheres containing 14 % N_2 . Note the scale changes in the region of the N-C vibrational mode.

The Raman spectra of all samples show also a weak mode at $\sim 2220 \text{ cm}^{-1}$ that was previously associated with N–C vibrations [46]. This mode is present in all samples (cf. figure 13) and manifests the presence of N in the films. The absolute intensity of the N–C mode is highest in the two samples with highest N-content, specifically the CN_x films sputtered in Ne at 110 °C using HiPIMS and DCMS (cf. figure 11). The absolute intensity of the N–C mode for the rest of the samples does not seem to be well correlated with the

corresponding N-contents presented in figure 11. Nevertheless, the presence of the N–C mode in the Raman spectra provides useful confirmation of the incorporation of N in the carbon network.

In order to verify the conclusions drawn from XPS and Raman spectroscopy, CN_x thin films deposited by DCMS and HiPIMS in reactive Ne, Ar, and Kr atmospheres using a $f_{\text{N}_2/g}$ of 14% were investigated by TEM in combination with SAED. Figure 14 a) - d) presents HRTEM images with corresponding SAED pattern from samples deposited in reactive Ne atmosphere by DCMS (figure 14 a) and c)) and HiPIMS (figure 14 b) and d)) at $T_s = 110 \text{ °C}$ (LT, figure 14 a) and b)) as well as $T_s = 430 \text{ °C}$ (HT, figure 14 c) and d)). The SAED pattern shown in c) indicates three features. These features were evaluated closer for all samples by integration of the individual first and second SAED peaks (at $\sim 3.5 \text{ Å}$ and $\sim 2 \text{ Å}$), as suggested by Czigany *et al.* [27]. The extracted peak intensity ratio R ($R = I_{3.5\text{Å}}/I_{2\text{Å}}$) results in a quantitative parameter, allowing to categorize the

Figure 14 a)–d): Cross-sectional HRTEM images with corresponding SAED patterns of CN_x thin films deposited in $\text{Ne}/14\% \text{N}_2$ by a) DCMS at $T_s = 110\text{ °C}$, b) HiPIMS at $T_s = 110\text{ °C}$, c) DCMS at $T_s = 430\text{ °C}$, and d) HiPIMS at $T_s = 430\text{ °C}$. Labels in the SAED pattern in panel c) mark the positions of $\sim 1.15\text{ Å}$ and $\sim 2.05\text{ Å}$ diffuse rings as well as $\sim 3.5\text{ Å}$ ring section. The growth direction in the HR images and SAED shows upwards.

degree of the CN_x short-range ordered microstructure. The evaluation of the TEM images and SAED pattern shown in figure 14 a), b), d) revealed an amorphous microstructure for thin films deposited in reactive Ne atmosphere by DCMS at $T_s = 110\text{ °C}$ as well as for CN_x deposited by HiPIMS at $T_s = 110\text{ °C}$ and $T_s = 430\text{ °C}$. The SAED pattern acquired from the CN_x thin film deposited at $T_s = 430\text{ °C}$ in DCMS mode (cf. figure 14 c)) shows a dot/ring segment at $\sim 3.5\text{ Å}$, which corresponds to a graphitic microstructure [3]. This observation is in

agreement with XPS data of the same thin film (cf. figure 12 a)) showing well separated main contributions by 2.5 eV.

As was shown in our former report [12] comparing the CN_x growth in Ar/N_2 mixtures by DCMS and HiPIMS, the CN_x films deposited by in either mode at $T_s = 430\text{ °C}$ yielded $R > 1$, corresponding to the evolution of a FL microstructure. However, in case the CN_x thin films were deposited in HiPIMS mode, the FL microstructure was more pronounced. A deposition temperature of 110 °C in Ar/N_2 mixtures resulted in amorphous thin films for both sputter modes (cf. figure 9 a)-d) in reference [12]).

The reactive discharges in Kr (figure 15 a)-d)) yield comparable results to those in reactive Ar discharges [12], but for one exception; the SAED pattern obtained from the CN_x film deposited

Figure 15 a)–d): Cross-sectional HRTEM images with corresponding SAED patterns of CN_x thin films deposited in Kr/14% N_2 by a) DCMS at $T_s = 110^\circ\text{C}$, b) HiPIMS at $T_s = 110^\circ\text{C}$, c) DCMS at $T_s = 430^\circ\text{C}$, and d) HiPIMS, $T_s = 430^\circ\text{C}$. Labels in the SAED pattern in panel c) mark the positions of $\sim 1.15\text{ \AA}$ and $\sim 2.0\text{ \AA}$ diffuse rings as well as $\sim 3.5\text{ \AA}$ ring. The growth direction in the HR images and SAED shows upwards.

at 110°C in HiPIMS mode shows a $\sim 3.5\text{ \AA}$ ring ($R=1$), and thus a weakly pronounced FL structure. This agrees with results obtained by the evaluation of the XPS N1s core level spectra ($\text{N2/N1} = 1.3$). In this context the combination of low ion energies and an enhanced probability of cluster sputtering by the comparatively bulky Kr from the N-terminated C target (leading to an increased relative flux of CN^+ in the 14% N_2 /Kr HiPIMS discharge) should be considered to account for the structural evolution at a substrate temperature of 110°C .

Nanoindentation was performed on CN_x films prepared at substrate temperatures of 110°C and 430°C in $f_{\text{N}_2/g} = 14\%$ atmosphere. In table 3, the hardness values, H/E ratios (H/E), and elastic recovery (ER) are collected. CN_x films deposited at low substrate temperatures in DCMS mode show an increasing hardness with increasing inert gas atomic mass, and decreasing N-incorporation. Here, the $\text{CN}_{0.14}$ film sputtered in reactive Kr atmosphere shows the highest hardness and elastic recovery of $\sim 15\text{ GPa}$ and 88% , respectively. CN_x deposited in the reactive Ar gas mixture shows comparable results to the film sputtered in the Kr mixture, while the corresponding film sputtered in Ne yields a Hardness of 10.5 GPa and an elastic recovery of 84% . The improved hardness of 15 GPa measured for the film sputtered in Kr-based atmosphere at a substrate

temperature of 110 °C is explained by the comparatively low N-content together with the comparatively high film density. This correlation of an enhanced hardness to the N content and density of films sputtered at low substrate temperatures was also observed by Neidhardt et al. [5]. However, in reference [5] the authors ascribe the higher hardness to the formation of a FL-microstructure, which cannot be claimed for the corresponding film in this study (cf. figures 12 c), 13, and 15 a)). Moreover, the mechanical properties for the corresponding CN_x film sputtered in HiPIMS mode are comparable to those found for the film sputtered in DCMS mode, although the film sputtered in HiPIMS mode shows a weakly pronounced microstructural SRO (cf. figures 12 f), 13, and 15 b)). Hence, the mechanical properties appear to be independent of the microstructural SRO, and are rather determined by deposition conditions, that influence the density, N content and morphology of the deposited films. Similar observations were made by Tucker et al. [3]. However, only a weak correlation of the hardness of CN_x films sputtered in DCMS and HiPIMS modes to residual stress values is observed.

At a substrate temperature of 430 °C the hardness of all investigated films decreases rapidly to approximately half of the value extracted for films deposited at 110 °C. This is mainly ascribed to the above discussed, under-dense morphology (cf. figure 9 b), d), and f)) and is generally observed as the substrate temperature exceeds 300 °C. Substrate temperatures > 300 °C promote chemical sputtering of N-rich plasma species at the substrate surface and an increased ad-atom mobility. Both mechanisms are accountable for an under-dense morphology, while the process of chemical sputtering leads also to decreased N contents. As discussed above, the N contents in the CN_x films are moreover influenced by the deposition mode and the inert gas. However, the mechanical properties show only minor dependencies on those deposition parameters. The films sputtered in reactive Ne or Kr atmosphere and in DCMS mode yield slightly higher hardness

values, than those sputtered in HiPIMS mode. This is attributed to the bias voltage settings; the constant bias voltage in DCMS mode is assumed to provoke a constant re-sputtering of less strongly bond species, while re-sputtering in HiPIMS mode will extend only through the on-time of the bias pulse for 6% of the time.

Table 3: Hardness, H/E ratio (H/E), and elastic recovery (ER) for CN_x thin films deposited by DCMS and HiPIMS in 14% N₂/Ne, 14% N₂/Ar, and 14% N₂/Kr atmosphere at substrate temperatures of 110 °C (LT) and 430 °C (HT)

	Hardness [GPa] H/E ER [%]			
	LT		HT	
	DCMS	HiPIMS	DCMS	HiPIMS
14% N ₂ /Ne	10.5 ± 0.3 0.10 84	11.9 ± 0.6 0.10 90	5.8 ± 0.7 0.08 81	3.2 ± 0.9 0.07 82
14% N ₂ /Ar	13.4 ± 0.6 0.10 88	10.7 ± 0.5 0.09 84	6.7 ± 0.5 0.10 88	6.4 ± 0.6 0.09 90
14% N ₂ /Kr	15.0 ± 1.9 0.10 88	15.7 ± 0.8 0.11 87	8.8 ± 0.4 0.09 84	4.1 ± 0.4 0.09 83

4. CONCLUSIONS

Reactive DCMS and HiPIMS discharges of C in N₂/Ne, N₂/Ar, and N₂/Kr were investigated by positive ion mass spectrometry. The cation energies are found to depend on the type of inert gas and the amount of N₂ in the sputter gas mixture. The sputter mode gains major significance with regards to the ionization of species originating from the target relative to the ionization of the sputter gases. HiPIMS processes yield approximately a ten times higher flux ratio of ions originating from the target compared to those originating from the process gas. For the case when graphite is sputtered in N₂/Ne mixtures containing $f_{N_2/Ne}$ up to ~ 20 %, the influence of the sputter mode on cation energies and degree of ionization was insignificant.

It is shown that reactive DCMS and HiPIMS discharges using a $f_{N_2/g}$ of 14 % at a substrate temperature of 430 °C produce graphitic or FL CN_x thin films, but for one exception; the reactive HiPIMS discharge in Ne yields an amorphous structure. At a low substrate temperature of 110 °C the synthesized films are amorphous, only the CN_x film deposited by HiPIMS in reactive Kr atmosphere shows a weak graphitic short ranged ordered microstructure. The structural evolution of CN_x thin films sputtered in HiPIMS mode was more pronounced, which is attributed to pulse assisted chemical sputtering. The microstructural results suggest that two different mechanisms may be determining for the evolution of a short range order in CN_x thin films; one related to a high ad-atom mobility and chemical sputtering and another where cluster deposition in combination with chemical sputtering prevails.

Films deposited in HiPIMS mode show elevated O concentrations, lower compressive stresses and slightly lower hardness values compared to films deposited by DCMS. This is attributed to the inherently different bias voltage settings, i.e. pulsed with a duty cycle of 6% vs continuous using HiPIMS and DCMS modes, respectively. The CN_x film hardness is moreover

influenced by the applied inert gas as this influences the film density and N content. Contrary to previous reports, the hardness and the elastic recovery of the films show no dependency on the microstructural short range order, but are strongly related to the film morphology, which in turn is determined by the deposition temperature.

ACKNOWLEDGEMENTS

The VINN Excellence Center *Functional Nanoscale Materials (FunMat)* is acknowledged. With regards to ERDA measurements we are thankful for the access to the Tandem Laboratory, Uppsala University. Zsolt Czigány acknowledges the Bolyai Scholarship of the Hungarian Academy of Sciences. S.Sch. acknowledges the support by the Carl Tryggers Foundation for Scientific Research.

REFERENCES

- [1] Dai HY, Cheng XR, Wang CF, Xue YC, Chen ZP. Structural, optical and electrical properties of amorphous carbon films deposited by pulsed unbalanced magnetron sputtering. *Optik - International Journal for Light and Electron Optics*. 2015;126(7–8):861-4.
- [2] Wang C, Ling X, Shi J, Xia R. Structure evolution of hydrogenated carbon films from amorphous carbon to fullerene-like nanostructure. *Surf Interface Anal*. 2014;46(8):550-5.
- [3] Tucker MD, Czigány Z, Broitman E, Näslund L-Å, Hultman L, Rosen J. Filtered pulsed cathodic arc deposition of fullerene-like carbon and carbon nitride films. *J Appl Phys*. 2014;115(14):144312.
- [4] Lourcing S, Madsen ND, Berthelsen AN, Christensen BH, Almqvist KP, Nielsen LP, et al. Turbostratic-like carbon nitride coatings deposited by industrial-scale direct current magnetron sputtering. *Thin Solid Films*. 2013;536:25-31.
- [5] Neidhardt J, Hultman L, Broitman E, Scharf TW, Singer IL. Structural, mechanical and tribological behavior of fullerene-like and amorphous carbon nitride coatings. *Diam Relat Mat*. 2004;13(10):1882-8.
- [6] Hultman L, Neidhardt J, Hellgren N, Sjöström H, Sundgren JE. Fullerene-like carbon nitride: A resilient coating material. *MRS Bull*. 2003;28(3):194-202.
- [7] Neidhardt J, Czigany Z, Brunell IF, Hultman L. Growth of fullerene-like carbon nitride thin solid films by reactive magnetron sputtering; role of low-energy ion irradiation in determining microstructure and mechanical properties. *J Appl Phys*. 2003;93(5):3002-15.
- [8] Schlüter M, Hopf C, Jacob W. Chemical sputtering of carbon by combined exposure to nitrogen ions and atomic hydrogen. *New J Phys*. 2008; 10: 053037.
- [9] Hellgren N, Johansson MP, Hjørvarsson B, Broitman E, Ostblom M, Liedberg B, et al. Growth, structure, and mechanical properties of CN_xH_y films deposited by dc magnetron sputtering in N₂/Ar/H₂ discharges. *Journal of Vacuum Science & Technology A - Vacuum Surfaces and Films*. 2000;18(5):2349-58.
- [10] Hellgren N, Johansson MP, Broitman E, Sandström P, Hultman L, Sundgren JE. Effect of chemical sputtering on the growth and structural evolution of magnetron sputtered CN(x) thin films. *Thin Solid Films*. 2001;382(1-2):146-52.
- [11] Neidhardt J, Hogberg H, Hultman L. Cryogenic deposition of carbon nitride thin solid films by reactive magnetron sputtering; suppression of the chemical desorption processes. *Thin Solid Films*. 2005;478(1-2):34-41.
- [12] Schmidt S, Czigany Z, Greczynski G, Jensen J, Hultman L. Ion mass spectrometry investigations of the discharge during reactive high power pulsed and direct current magnetron sputtering of carbon in Ar and Ar/N₂. *J Appl Phys*. 2012;112(1):013305-11.
- [13] Schmidt S, Czigany Z, Greczynski G, Jensen J, Hultman L. Influence of inert gases on the reactive high power pulsed magnetron sputtering process of carbon-nitride thin films. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 2013;31(1):011503.
- [14] Ohya K. Comparative study of target atomic number dependence of ion induced and electron induced secondary electron emission. *Nucl Instrum Methods Phys Res Sect B-Beam Interact Mater Atoms*. 2003;206:52-6.
- [15] Anders A. Discharge physics of high power impulse magnetron sputtering. *Surf Coat Technol*. 2011;205:S1-S9.
- [16] Rejoub R, Lindsay BG, Stebbings RF. Determination of the absolute partial and total cross sections for electron-impact ionization of the rare gases. *Phys Rev A*. 2002;65(4):042713.

- [17] physics.nist.gov/cgi-bin/Ionization/table.pl?ionization=N2. March, 2013 [cited; Available from:]
- [18] Kim Y-K, Desclaux J-P. Ionization of carbon, nitrogen, and oxygen by electron impact. *Phys Rev A*. 2002;66(1):012708.
- [19] Mattox DM. Handbook of Physical Vapor Deposition (PVD) Processing Park Ridge, New Jersey, USA: Noyes Publications 1998.
- [20] Lawton SA, Pichanick FMJ. Resonances in the Metastable Excitation of Molecular Nitrogen. *Phys Rev A*. 1973;7(3):1004-7
- [21] Depla D, Mahieu S. Reactive Sputter Deposition: Springer Verlag Berlin Heidelberg; 2010: 210-211.
- [22] Avelar-Batista JC, Wilson AD, Davison A, Leyland A, Matthews A, Fancey KS. A study of neon-nitrogen interactions in d.c. glow discharges by optical emission spectroscopy. *Thin Solid Films*. 2001;398-399(0):507-12.
- [23] Rosakis AJ, Singh RP, Tsuji Y, Kolawa E, Moore Jr NR. Full field measurements of curvature using coherent gradient sensing: application to thin film characterization. *Thin Solid Films*. 1998;325(1-2):42-54.
- [24] Janssen G, Abdalla MM, van Keulen F, Pujada BR, van Venrooy B. Celebrating the 100th anniversary of the Stoney equation for film stress: Developments from polycrystalline steel strips to single crystal silicon wafers. *Thin Solid Films*. 2009;517(6):1858-67.
- [25] McCaffrey JP. Improved tem samples of semiconductors prepared by a small-angle cleavage technique. *Microsc Res Tech*. 1993;24(2):180-4.
- [26] Labar JL. Electron Diffraction Based Analysis of Phase Fractions and Texture in Nanocrystalline Thin Films, Part II: Implementation. *Microsc microanal*. 2009;15(1):20-9.
- [27] Czigany Z, Hultman L. Interpretation of electron diffraction patterns from amorphous and fullerene-like carbon allotropes. *Ultramicroscopy*. 2010;110(7):815-9.
- [28] Hecimovic A, Burcalova K, Ehasarian AP. Origins of ion energy distribution function (IEDF) in high power impulse magnetron sputtering (HIPIMS) plasma discharge. *Journal of Physics D - Applied Physics*. 2008;41(9):10.
- [29] Gudmundsson JT, Sigurjonsson P, Larsson P, Lundin D, Helmersson U. On the electron energy in the high power impulse magnetron sputtering discharge. *J Appl Phys*. 2009;105(12):123302.
- [30] Neidhardt J, Hultman L, Abendroth B, Gago R, Moller W. Diagnostics of a N-2/Ar direct current magnetron discharge for reactive sputter deposition of fullerene-like carbon nitride thin films. *J Appl Phys*. 2003;94(11):7059-66.
- [31] Bohlmark J, Lattemann M, Gudmundsson JT, Ehasarian AP, Aranda Gonzalvo Y, Brenning N, et al. The ion energy distributions and ion flux composition from a high power impulse magnetron sputtering discharge. *Thin Solid Films*. 2006;515(4):1522-6.
- [32] Ferrec A, Keraudy J, Jacq S, Schuster F, Jouan PY, Djouadi MA. Correlation between mass-spectrometer measurements and thin film characteristics using dcMS and HiPIMS discharges. *Surface and Coatings Technology*. 2014;250:52-6.
- [33] Maszl C, Breilmann W, Benedikt J, Keudell Av. Origin of the energetic ions at the substrate generated during high power pulsed magnetron sputtering of titanium. *Journal of Physics D: Applied Physics*. 2014;47(22):224002.
- [34] Jouan PY, Le Brizoual L, Ganciu M, Cardinaud C, Tricot S, Djouadi M. HiPIMS Ion Energy Distribution Measurements in Reactive Mode. *Plasma Science, IEEE Transactions on*. 2010;38(11):3089-94.

- [35] Greczynski G, Hultman L. Time and energy resolved ion mass spectroscopy studies of the ion flux during high power pulsed magnetron sputtering of Cr in Ar and Ar/N₂ atmospheres. *Vacuum*. 2010;84(9):1159-70.
- [36] Rossnagel SM. Gas-density reduction in magnetrons. *Journal of Vacuum Science & Technology A - Vacuum Surfaces and Films*. 1988;6(1):19-24.
- [37] Olthoff JK, Vanbrunt RJ, Radovanov SB, Rees JA, Surowiec R. Kinetic-energy distributions of ions sampled from argon plasmas in a parallel-plate, radiofrequency reference cell. *J Appl Phys*. 1994;75(1):115-25.
- [38] Bakoglidis KD, Schmidt S, Garbrecht M, Ivanov IG, Jensen J, Greczynski G, et al. Low-temperature growth of low friction wear-resistant amorphous carbon nitride thin films by mid-frequency, high power impulse, and direct current magnetron sputtering. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films*. 2015;33(5).
- [39] Windischmann H. Intrinsic stress in sputter deposited thin-films. *Crit Rev Solid State Mat Sci*. 1992;17(6):547-96.
- [40] Nir D. Intrinsic stress in diamond-like carbon films and its dependence on deposition parameters. *Thin Solid Films*. 1987;146(1):27-43.
- [41] Neidhardt J, Hultman L, Czigany Z. Correlated high resolution transmission electron microscopy and X-ray photoelectron spectroscopy studies of structured CN_x (0 < x < 0.25) thin solid films. *Carbon*. 2004;42(12-13):2729-34.
- [42] Rodil SE, Muhl S. Bonding in amorphous carbon nitride. *Diam Relat Mat*. 2004;13(4-8):1521-31.
- [43] Kusunoki I, Sakai M, Igari Y, Ishidzuka S, Takami T, Takaoka T, et al. XPS study of nitridation of diamond and graphite with a nitrogen ion beam. *Surf Sci*. 2001;492(3):315-28.
- [44] Soto G, Samano EC, Machorro R, Farias MH, Cota-Araiza L. Study of composition and bonding character of CN(x) films. *Appl Surf Sci*. 2001;183(3-4):246-58.
- [45] Hellgren N, Guo JH, Luo Y, Sathe C, Agui A, Kashtanov S, et al. Electronic structure of carbon nitride thin films studied by X-ray spectroscopy techniques. *Thin Solid Films*. 2005;471(1-2):19-34.
- [46] Ferrari AC, Rodil SE, Robertson J. Interpretation of infrared and Raman spectra of amorphous carbon nitrides. *Phys Rev B*. 2003;67(15):155306.