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Low-temperature growth of low friction wear-resistant amorphous carbon nitride thin films by mid-frequency, high power impulse, and direct current magnetron sputtering

Konstantinos D. Bakoglidis,a) Susann Schmidt, Magnus Garbrecht, Ivan G. Ivanov, Jens Jensen, Grzegorz Grenczynski, and Lars Hultman

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The potential of different magnetron sputtering techniques for the synthesis of low friction and wear resistant amorphous carbon nitride (a-CNₙ) thin films onto temperature-sensitive AISI52100 bearing steel, but also Si(001) substrates was studied. Hence, a substrate temperature of 150 °C was chosen for the film synthesis. The a-CNₙ films were deposited using mid-frequency magnetron sputtering (MFMS) with an MF bias voltage, high power impulse magnetron sputtering (HiPIMS) with a synchronized HiPIMS bias voltage, and direct current magnetron sputtering (DCMS) with a DC bias voltage. The films were deposited using a N₂/Ar flow ratio of 0.16 at the total pressure of 400 mPa. The negative bias voltage, Vₛ, was varied from 20 to 120 V in each of the three deposition modes. All films exhibited compressive residual stress, r, which depends on the growth method; HiPIMS produces the least stressed films with values ranging between −0.4 and −1.2 GPa for all Vₛ, while CNₙ films deposited by MFMS showed residual stresses up to −4.2 GPa. Nanoindentation showed a significant increase in film hardness and reduced elastic modulus with increasing Vₛ for all techniques. The harder films were produced by MFMS with hardness as high as 25 GPa. Low friction coefficients, between 0.05 and 0.06, were recorded for all films. Furthermore, CNₙ films produced by MFMS and DCMS at Vₛ = 100 and 120 V presented a high wear resistance with wear coefficients of k ≤ 2.3 × 10⁻⁵ mm²/Nm. While all CNₙ films exhibit low friction, wear depends strongly on the structural and mechanical characteristics of the films. The MFMS mode is best suited for the production of hard CNₙ films, although high compressive stresses challenge the application on steel substrates. Films grown in HiPIMS mode provide adequate adhesion due to low residual stress values, at the expense of lower film hardness. Thus, a relatively wide mechanical property envelope is presented for CNₙ films, which is relevant for the optimization of CNₙ film properties intended to be applied as low friction and wear resistant coatings. © 2015 American Vacuum Society. [http://dx.doi.org/10.1116/1.4923275]

I. INTRODUCTION

Carbon nitride (CNₙ) compounds are used extensively as protective coatings in disk drives and for biomedical applications.1–3 Their attractive mechanical and tribological properties arise from a structural and bonding complexity induced by the substitution of carbon for nitrogen. CNₙ films may exhibit short-range order (SRO), which is defined by a complex interplay of the sp³, sp², and sp hybridized bonds that carbon and nitrogen can form. Depending on the deposition parameters, a variety of CNₙ microstructures can be formed during thin film synthesis, including amorphous (a-CNₙ),4 graphite-like (g-CNₙ),5 and fullerene-like carbon nitride (FL-CNₙ).6,7 Hard, yet elastic CNₙ films have been reported to form at elevated temperatures (>350 °C), low to medium particle energies, using a wide range of N₂/Ar flow ratios by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS).5,6,9 At such deposition conditions, a distinct FL structural evolution with bent, cross-linked graphene sheets forms with primarily sp² bonding.10,11 Low-density a-CNₙ films are generally produced at low growth temperatures. Depending on process settings other than the substrate temperature, a variety of film morphologies, ranging from columnar with voids to homogeneous close-packed, are observed.8,12 For substrate temperatures <200 °C,
the N fraction in the plasma does not affect the film microstructure, since the chemical sputtering phenomena that have been found to influence the structure of the films\(^8\) are not as distinct. Thus, increasing the substrate temperature yields films that exhibit FL-phase.\(^8\) However, deposition temperatures above 200 °C are intolerable for several important industrial applications employing temperature-sensitive substrates.\(^13\)

A large amount of studies are dedicated to the bonding of N in the C matrix.\(^14\)–\(^16\) The microstructure of a-CNx is a network of \(sp^2\) and \(sp^3\) hybridized states of C and N. Ratios between \(sp^3\) and \(sp^2\) bonding states may vary for a-CNx deposited under different conditions. For instance, different \(sp^3/\sp^2\) ratios were found to determine the mechanical and tribological properties of a-CNx films deposited by radio frequency magnetron sputtering (RFMS) with increasing substrate bias.\(^17\) Moreover, the predominant amount of \(sp^2\) hybridized states of CNx films enhances their elasticity, mechanical resiliency, and wear resistance,\(^12\),\(^18\) which are critical properties for sliding or rolling components.

Several magnetron-sputtering-based techniques have been used to grow a-CNx thin films, among them are DCMS,\(^5\)–\(^12\) RFMS,\(^19\)–\(^21\) and HiPIMS.\(^9\)\(^,\)\(^22\) Depending on the growth conditions, a broad range of hardness and elastic modulus values for CNx films can be found in the literature. Hardness values approaching those of the basically \(sp^2\)-rich tetrahedral amorphous carbon (ta-C) or diamond-like carbon (DLC) films,\(^20\),\(^23\)–\(^26\) were reported. Different deposition techniques also affect the tribological performance of CNx films. Low friction coefficients and low wear rates have been recorded for a-CNx films applying different loads, speeds,\(^25\) and gas environments.\(^27\)

Today, the effects of different growth parameters on CNx properties are relatively understood for DCMS and RFMS processes. The plasma characteristics influencing growth conditions of CNx films deposited by HiPIMS were studied more recently,\(^9\) while knowledge on the influences of some parameters of HiPIMS in the CNx growth remains limited.

To the best of our knowledge, growth of CNx films using mid-frequency magnetron sputtering (MFMS) has not been reported yet, although MFMS can be used to investigate a further customization of the structural and mechanical properties of CNx films. Thus, it is timely to make a comparative study of the structural and mechanical properties of CNx films, grown by various sputtering methods, applied under similar growth conditions at low substrate temperature.

In this study, properties of low temperature CNx films grown in one industrial deposition system using MFMS, HiPIMS, or DCMS are compared. Growth conditions, specifically gas composition, total gas pressure, substrate temperature, and average cathode power were kept constant for all depositions, facilitating a direct comparison of results. For each of the methods, a series of films are grown as a function of the negative substrate bias, \(V_s\). Bonding type and composition of the CNx films, as well as the amount and role of incorporated impurities, such as Ar and O, are discussed. Furthermore, we compare the nanomechanical properties and the nanotribological performance of the films and relate these properties to their structural characteristics and to the corresponding deposition conditions.

**II. EXPERIMENT**

Si(001) and steel substrates (grade AISI52100) were used for the deposition of CNx thin films. The steel grade AISI52100 is commonly used in bearing applications. The choice of steel substrates permits investigations as for the applicability of the CNx films on rolling and sliding components. Si(001) substrates, on the other hand, were selected as these suit a wide variety of characterization techniques. The cleaning of the steel substrates prior to the depositions was a three-step procedure: (1) a decon-90 (Decon Laboratories Limited, England) ultrasonic bath, (2) a 10 min acetone (Merck KGaA, Germany) ultrasonic bath, and (3) an isopropanol rinse (Merck KGaA, Germany). The substrates were subsequently dried in N2. The cleaning of the conventional boron doped Si(001) substrates included only steps (2) and (3).

An industrial deposition chamber (CC800/9 ML, CemeCon AG, Germany) was used to grow CNx thin films on the aforementioned Si and steel substrates. A schematic of the deposition chamber configuration is presented in Fig. 1. A hollow cathode etching step of 25 min was performed in order to clean the substrates prior to CNx deposition. Here, a Kr/Ar gas mixture with a Kr/Ar flow ratio of 0.76, at a total pressure of 600 mPa, a temperature of 150 °C, and negative substrate bias of 200 V was applied. For the CNx depositions, two rectangular graphite targets with a size of 8.8 × 50 cm\(^2\) were mounted on planar cathodes. The substrates were one-fold rotated, with a rotation speed of 1 rpm. The depositions were conducted with a N/Ar flow ratio of 0.16 and a total pressure of 400 mPa. The substrate temperature was kept at ~150 °C throughout the deposition. CNx films were deposited by MFMS, HiPIMS, and DCMS with an average target power of 1200 W.

In MFMS configuration, one target operates as cathode while the other works as an anode, changing their polarity every half a cycle. In this case, the targets were operated at frequency \(f = 50\) kHz, with a pulse length (pulse-on time) of \(t_{\text{on}}^{\text{MFMS}} = 10\) μs and a pulse-off time of \(t_{\text{off}}^{\text{MFMS}} = 10\) μs. The

![Fig. 1. Schematic top view of the industrial deposition chamber CC800/9 ML from CemeCon AG.](image-url)
average target current during the MFMS process was $I_{\text{MF ave}}$ $\sim$ 2.65 A, and the target voltage averaged $V_{\text{MF ave}}$ $\sim$ 452 V. During DCMS processes, the average target current was $I_{\text{ave}}$ $\sim$ 2.5 A and the average target voltage $V_{\text{ave}}$ $\sim$ 480 V. The HiPIMS processes featured a pulse frequency of 300 Hz, pulse lengths of $t_{\text{HiP on}}$ $\sim$ 200 $\mu$s, with $t_{\text{HiP off}}$ $\sim$ 3.1 ms, resulting in a pulse energy of $E_p$ $\sim$ 4 J, with peak target current $I_{\text{HiP max}}$ $\sim$ 80 A and peak target voltage $V_{\text{HiP max}}$ $\sim$ 700 V. During HiPIMS processes, the average target current was $I_{\text{ave}}$ $\sim$ 2 A with an average target voltage of $V_{\text{HiP}}$ $\sim$ 600 V.

Negative substrate bias voltages, $V_s$, with amplitudes of 20, 60, 100, and 120 V were applied during films growth. For MFMS depositions, $V_s$ was pulsed and not synchronized to the cathode operation using $t_{\text{on}}^{\text{HiP max}}$ $\sim$ 2.2 $\mu$s and $t_{\text{off}}^{\text{HiP max}}$ $\sim$ 2.8 $\mu$s. During HiPIMS processes, the bias voltage supply was pulsed and synchronized to the cathode pulses, with $t_{\text{HiP on}}^{\text{max}}$ $\sim$ 200 $\mu$s and $t_{\text{HiP off}}^{\text{max}}$ $\sim$ 3.1 ms. DC bias voltages were applied during DCMS. Hence, the substrate bias duty cycles, D, were 44%, 6%, and 100% for MFMS, HiPIMS, and DCMS, respectively. The deposition times were adjusted to result in CN$_x$ film thickness of 1 $\pm$ 0.2 $\mu$m.

Cross-sectional high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were acquired with a double corrected and monochromated FEI Titan$^\text{3}$ 60–300 TEM, equipped with a high-brilliance extreme field emission gun source. The energy of the electron beam for the TEM imaging and SAED acquisition was set to 300 keV, for optimum image contrast. The TEM cross sections of the thin films were prepared with the lift-out technique using a dual-beam focused ion beam (FIB-SEM 1540 ESB, Zeiss, Germany) with a Ga ion source.$^{28}$ A Pt layer was deposited prior to the milling in order to protect the CN$_x$ films from the Ga beam. The cross sections were prepared using an ion energy of 30 kV. Currents of 2 nA, 1 nA, 500 pA, 200 pA, 100 pA, and 20 pA were sequentially used for the preparation of the TEM lamella. For the final polishing of the lamella, a Ga ion energy of 5 kV at 100 pA was applied to minimize surface amorphization of the CN$_x$ films and to decrease the probability of Ga implantation.

In order to investigate the CN$_x$ film compositions and assign the bonding states, X-ray photoelectron spectroscopy (XPS) was carried out using an Axis Ultra DLD (Kratos Analytical, UK) instrument equipped with a monochromatic Al K$_\alpha$ source ($\hbar\nu$ $=$ 1486.69 eV) operating at a base pressure of $1.5 \times 10^{-7}$Pa. C1s, N1s, O1s, and Ar2p core level spectra were acquired, on as-deposited samples and after 300 s of sputter cleaning using a 500 eV Ar$^+$ ion beam with an incident angle of 70° from the surface normal. A Shirley type background and Voigt peak shape, with the Lorentzian contribution restricted to 20% were used to create peak fit models for the evaluation of the CN$_x$ bonding states. Here, the C1s and N1s core level spectra obtained from as-deposited samples were considered. The full-width-at-half-maximum (FWHM) of contributions in the peak fit models was constraint to 2 eV. The quantification of the CN$_x$ film composition, based on the C1s, N1s, and O1s core level spectra, was performed on sputter-cleaned samples using CASAXPS software (version 2.3.16) together with sensitivity factors supplied by Kratos Analytical, Ltd.

Micro-Raman spectroscopy was performed using a 532 nm single-mode laser for excitation and a high-resolution single monochromator (Jobin-Yvon, model HR4600) equipped with a CCD camera. The resolution of the system equipped with a 600 g/mm grating was $\sim$ 2 cm$^{-1}$. The laser power was kept at $\sim$0.5 mW in order to avoid thermal damage of the samples. The laser spot on the sample was $\sim$1 $\mu$m in diameter using an objective with numerical aperture 0.95 and magnification 100. The acquisition time for all presented spectra was 30 s. A Gaussian function was used for the deconvolution of the D and G bands in order to extract the FWHM and I(D)/I(G) peak area ratio.

Elemental depth profiles of the deposited films were obtained by time-of-flight ERDA (ToF-ERDA). The measurements were performed with a 36 MeV $^{127}$I$^{6+}$ primary ion beam incident at 67.5° relative to the surface normal and a recoil angle of 45°. All recoil ToF-ERDA spectra were analyzed using the CONTES code, where the measured recoil energy spectrum of each element was converted to relative atomic concentration profiles.

Cross-sectional scanning electron microscopy (SEM, LEO 1550 Gemini, Zeiss, Germany) was used to determine the thickness and study the morphology of the CN$_x$ films.

X-ray reflectivity (XRR) was performed to determine the density of the films using an Empyrean MRD x-ray diffractometer (PANalytical, Holland), equipped with a Cu K$_\alpha$ radiation (1.54 Å) source, a hybrid Ge(220) monochromator, and a parallel plate collimator at the 3D PIXcel detector. x$^\text{pert}$ reflectivity software and a generic algorithm were chosen for the fitting of the reflectivity spectra. Three layers were used for the fitting model, representing the Si substrate with a thickness of 525 $\mu$m, the native silicone oxide layer (with 2 nm thickness) at the (Si substrate)/(CN$_x$ film) interface and a CN$_x$, layer of 1 $\mu$m thickness.

In order to assess the residual film stresses, measurements on samples with a size of 3 $\times$ 2 cm were performed with a Dektak 6M stylus surface profilometer (Veeco, USA). Data were acquired electromechanically with a diamond stylus coupled to a Linear Variable Differential Transformer. The radius of curvature was extracted and the modified Stoney’s formula, Eq. (1), for thin films was used to calculate the residual film stress, $\sigma_{\text{CN}_x}$,

$$\sigma_{\text{CN}_x} = \frac{Y_d d_{\text{Si}}^2}{6R(1-\nu_{\text{Si}})}d_{\text{CN}_x},$$  

where $d_{\text{Si}}$, $\nu_{\text{Si}}$, and $Y_{\text{Si}}$ are the thickness, the Poisson’s ratio, and the Young’s modulus of the Si substrate, respectively [$d_{\text{Si}}$ $=$ 525 $\mu$m, $\nu_{\text{Si}}$ $=$ 0.36, and $Y_{\text{Si}}$ $=$ 169 GPa (Ref. 32)], $d_{\text{CN}_x}$ is the thickness of the CN$_x$ film as measured by SEM cross sections, and $R$ is the radius of curvature of each individual sample.$^{33}$ $R$ was corrected with the radius of curvature obtained from an uncoated Si substrate.

The mechanical properties of the CN$_x$ films were investigated by nanoindentation using a Triboindenter TI 950 (Hysitron, USA) and a Berkovich tip with an apex radius of $\sim$100 nm. The mechanical response of the CN$_x$ thin films

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was recorded for 20 nanoindents per sample and evaluated based on the approach by Oliver and Pharr. The maximum load was constrained to 1500 μN, corresponding to a penetration depth ranging between 100 and 45 nm. The elastic recovery (ER) of the films was calculated using following equation:

$$\frac{(L_{\text{max}} - L_{\text{res}})}{L_{\text{max}}} \times 100\%,$$

where $L_{\text{max}}$ is the indentation depth at maximum load, and $L_{\text{res}}$ is the residual depth after unloading. The tribological response of the CN$_x$ films was studied with reciprocal wear tests in air using a Triboindenter TI 950 (Hysitron, USA), equipped with a conical tip with an apex radius of $\sim$5 μm. A load of 5 mN, resulting in a contact pressure of $\sim$8.5 GPa, was used for the measurements. The track length was set to 5 μm. Each test comprised 31 cycles, where one cycle is considered to be one sweep forward and one backward. The coefficient of friction, $\mu$, and the profile of the worn film surface were recorded consecutively. After the first 6 cycles, the average steady-state coefficient of friction was extracted and wear was calculated after 31 cycles. During the wear tests, the ambient temperature was held at $\sim$22 °C and the relative humidity was $\sim$30%–40%.

III. RESULTS AND DISCUSSION

A. Thin film structure, composition, and bonding

Figure 2 shows cross-sectional SEM images of the CN$_x$ thin films deposited at $V_s = 20, 60,$ and $120$ V under MFMS [Figs. 2(a)–2(c)], HiPIMS [Figs. 2(d)–2(f)], and DCMS [Figs. 2(g)–2(i)] conditions. The films deposited at $V_s = 100$ V are omitted, since the morphology of the films grown in HiPIMS and DCMS modes at 100 V is similar to those grown at 60 V in the corresponding sputter mode, while the morphology of the film deposited by MFMS at $V_s = 100$ V resembles by the morphology of the film deposited at $V_s = 120$ V.

At $V_s = 20$ V, all three deposition techniques produced films with apparent columns. MFMS [Figs. 2(a)–2(c)] effectively decreases the porosity of the films at $V_s \geq 60$ V, while HiPIMS [Figs. 2(d)–2(f)] produces columnar structured films. Only at $V_s = 120$ V, the columnar structure is significantly attenuated in HiPIMS mode. Films produced by DCMS [Figs. 2(g)–2(i)] show a decreased porosity at $V_s \geq 100$ V. The differences in film morphology comparing the different deposition techniques are caused by the different ion irradiation conditions that are specific for each method. Not only the ion density is expected to vary, but also the bias duty cycle is different for each of the techniques tested. In the case of films deposited by HiPIMS, the bias pulse length of 200 μs effectively limits the influence of low-energy Ar$^+$ ion irradiation that arrives at the growing film surface at $t > 200 \mu$s, i.e., when the substrate is at the floating potential. This is in contrast to films grown by the two other techniques (MFMS or DCMS), in which case the substrate bias duty cycle is significantly higher, 44% and 100%, respectively, resulting in more severe Ar$^+$ ion bombardment, leading to an increased extent of forward sputtering, and thus higher densification for a given $V_s$ (ion energy) as compared to HiPIMS.

In addition, MFMS plasmas are expected to contain higher amounts of ions due to their special cathode–anode configuration, where cathodes operate against each other, confining the ions in the working region and allowing densification at lower $V_s$. Moreover, a considerable amount of Ar$^+$ ions (that was $\sim$7 times higher than in HiPIMS processes and $\sim$100 times higher than in DCMS processes) was observed in a similar experimental MFMS process set up using a Si/Ar/16%N$_2$ discharge. As $V_s$ increases, the energy of the incident ions rises. This induces forward sputtering and renucleation at the film surface resulting in a densified morphology, where the films appear increasingly homogeneous and the columnar morphology is replaced by fine, more equiaxed grains.

Low substrate temperatures ($\lesssim$300 °C) in physical vapor deposition tend to yield low density C films. The density of our films, $\rho_c$, corrected for the presence of Ar, is plotted in Fig. 3(a) as a function of $V_s$. Index c indicates the corrected values of density, $\rho_c$. The values of $\rho_c$ of CN$_x$ films deposited with each technique are also collected in Table I. For all three techniques, $\rho_c$ increases with increasing $V_s$. At a low $V_s$ of 20 V, all films showed a $\rho_c \leq 1.85 \pm 0.02$ g/cm$^3$, which is less than the density of sputtered C and CN$_x$ (2.2 g/cm$^3$) and in agreement with the SEM images in Fig. 2, which show open columnar structures. At $V_s = 120$ V, the density increases to $\sim$2.3 $\pm$ 0.03 g/cm$^3$ for HiPIMS and MFMS and is thus comparable to that of graphite. As elaborated above, densification is a result of increased ion energy as $V_s$ increases and is consistent with a porous-free, columnar morphology observed by SEM.

The O content of the films as presented in Fig. 3(b) was obtained from XPS measurements after Ar$^+$ sputter cleaning. Comparable contents were also obtained from ERDA measurements. The O uptake results primarily from exposure of the films to atmosphere subsequent to the depositions. Thus, the film porosity determines the measured O content to a high extent. Generally, the O content decreases with increasing $V_s$, corroborating an increasing film density, which is consistent with above presented SEM and XRR results. The highest O concentrations are obtained from films deposited at $V_s = 20$ V, with values ranging between 1.2 and 1.5 at. %. The lowest values of 0.2 ± 0.1 at. % are observed for films deposited by MFMS and DCMS using a $V_s$ of 120 V, while the O content of CN$_x$ films deposited by HiPIMS at $V_s = 120$ V (0.3 ± 0.1 at. %) was slightly, but not significantly higher. In the case of CN$_x$ films grown by HiPIMS, the O content is comparatively high, even for $V_s = 100$ V, indicating an elevated degree of porosity. This was also observed in corresponding SEM cross sections [Figs. 2(d) and 2(e)]. Eventually, the intercolumnar voids close at $V_s = 120$ V and the O content decreases to very low levels [Fig. 3(b)]. For films deposited by MFMS and DCMS, this is observed at $V_s = 60$ V and $V_s = 100$ V, respectively.

In Fig. 3(c), the Ar content in the CN$_x$ films as obtained by ERDA measurements is plotted as a function of $V_s$ for the three deposition methods. For all investigated $V_s$, the Ar content is lowest in films grown by HiPIMS. Here, the Ar
FIG. 2. SEM cross sections from the CN₅ films deposited under (a)–(c) MFMS, (d)–(f) HiPIMS, and (g)–(i) DCMS conditions at different $V_s$. 

Fig. 2. SEM cross sections from the CN₅ films deposited under (a)–(c) MFMS, (d)–(f) HiPIMS, and (g)–(i) DCMS conditions at different $V_s$. 

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The highest amount of Ar (0.8 ± 0.2 at. %) was found in films grown by MFMS at $V_s = 120$ V. The different Ar uptake for each technique is ascribed to a combination of the significantly different bias duty cycles and the different Ar ion densities. As described above, lower bias duty cycles and lower amounts of single and double charged Ar ions in the plasma yield less Ar ion irradiation of the growing film and thus, reduced Ar incorporation. Furthermore, mass spectrometry studies have shown a significant difference between HiPIMS and DCMS plasmas, regarding the amount of specific ion species. The amount of Ar$^+$, N$^+$, and N$_2^+$ ions in films grown by MFMS and DCMS plasmas, though HiPIMS plasmas contain additionally molecular CN$^+$ and C$_2$N$^+$ as well as C$^+$ species.9 Due to the continuous biasing in DCMS processes, a comparatively high amount of ions is attracted and impinges on the substrates, resulting in a higher Ar incorporation. In HiPIMS processes, on the other hand, ions are only attracted during the short bias pulses, resulting in lower Ar contents in the CN$_x$ coatings. Figure 4(a) shows the N/C ratio as a function of $V_s$ as obtained from XPS analysis subsequently to Ar$^+$ sputter cleaning. The N/C ratio of the CN$_x$ films deposited by MFMS decreases linearly with increasing $V_s$. For films deposited by DCMS and HiPIMS, the N/C ratio shows a maximum at $V_s = 60$ V. The N content of films deposited by MFMS and DCMS is higher than in case HiPIMS is used.

The lower N/C ratio extracted for films deposited at higher $V_s$ can be attributed to higher respattering rates of N-containing species from the film surface.19,38 This is confirmed by the density and the deposited mass per area and time, $m_d$, of the CN$_x$ films, as demonstrated in Figs. 3(a) and 3(b), respectively. The $m_d$ was determined from the deposition rate and density of the CN$_x$ films, using SEM cross sections and XRR measurements, respectively. For all investigated films, $m_d$ shows a decreasing trend with increasing $V_s$ and is not significantly affected by the deposition mode. For films deposited by MFMS up to $V_s = 100$ V, the decreased $m_d$ in combination with the decreased N/C ratios indicates that progressively N-rich species are resputtered from the growing CN$_x$ film surface. An increase of $m_d$ at 120 V implies that resputtering slightly decreases, whereas even more N is removed from the film surface. For films grown by HiPIMS, the rather constant $m_d$ and N/C ratios indicate a process without or less resputtering. For films deposited by DCMS, $m_d$ decreases linearly with increasing $V_s$. This indicates that resputtering also takes place in DCMS mode. However, the corresponding N/C ratios suggest that the resputtering rate of N-rich species picks up as $V_s$ approaches 100 and 120 V, where reduced N concentrations are observed.

XPS was used to determine C and N bonding configurations for all CN$_x$ films. Figures 5(a)–5(c) show the normalized C1s core level spectra and Figs. 5(d)–5(f) the corresponding normalized N1s core level spectra for films deposited by the three deposition techniques and the chosen $V_s$. The presented core level spectra were obtained from as-deposited samples in order to show unaffected (i.e., from

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<th>$V_s$ (V)</th>
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<th>$E_r$ (GPa)</th>
<th>ER (%)</th>
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<td>137.9</td>
<td>74.4</td>
<td>2.3</td>
</tr>
<tr>
<td>DCMS</td>
<td>20</td>
<td>7.3</td>
<td>71.5</td>
<td>77.2</td>
<td>1.76</td>
</tr>
<tr>
<td>DCMS</td>
<td>60</td>
<td>11.1</td>
<td>180.6</td>
<td>73.8</td>
<td>2</td>
</tr>
<tr>
<td>DCMS</td>
<td>100</td>
<td>15.2</td>
<td>119.6</td>
<td>82.8</td>
<td>2.29</td>
</tr>
<tr>
<td>DCMS</td>
<td>120</td>
<td>18.4</td>
<td>172.2</td>
<td>83.4</td>
<td>2.18</td>
</tr>
</tbody>
</table>

The different Ar$^+$ uptake for each technique is ascribed to a combination of the significantly different bias duty cycles and the different Ar ion densities. As described above, lower bias duty cycles and lower amounts of single and double charged Ar ions in the plasma yield less Ar ion irradiation of the growing film and thus, reduced Ar incorporation. Furthermore, mass spectrometry studies have shown a significant difference between HiPIMS and DCMS plasmas, regarding the amount of specific ion species. The amount of Ar$^+$, N$^+$, and N$_2^+$ ions in films grown by MFMS and DCMS plasmas, though HiPIMS plasmas contain additionally molecular CN$^+$ and C$_2$N$^+$ as well as C$^+$ species.9 Due to the continuous biasing in DCMS processes, a comparatively high amount of ions is attracted and impinges on the substrates, resulting in a higher Ar incorporation. In HiPIMS processes, on the other hand, ions are only attracted during the short bias pulses, resulting in lower Ar contents in the CN$_x$ coatings. Figure 4(a) shows the N/C ratio as a function of $V_s$, as obtained from XPS analysis subsequently to Ar$^+$ sputter cleaning. The N/C ratio of the CN$_x$ films deposited by MFMS decreases linearly with increasing $V_s$. For films deposited by DCMS and HiPIMS, the N/C ratio shows a maximum at $V_s = 60$ V. The N content of films deposited by MFMS and DCMS is higher than in case HiPIMS is used.

The lower N/C ratio extracted for films deposited at higher $V_s$ can be attributed to higher respattering rates of N-containing species from the film surface.19,38 This is confirmed by the density and the deposited mass per area and time, $m_d$, of the CN$_x$ films, as demonstrated in Figs. 3(a) and 3(b), respectively. The $m_d$ was determined from the deposition rate and density of the CN$_x$ films, using SEM cross sections and XRR measurements, respectively. For all investigated films, $m_d$ shows a decreasing trend with increasing $V_s$ and is not significantly affected by the deposition mode. For films deposited by MFMS up to $V_s = 100$ V, the decreased $m_d$ in combination with the decreased N/C ratios indicates that progressively N-rich species are resputtered from the growing CN$_x$ film surface. An increase of $m_d$ at 120 V implies that resputtering slightly decreases, whereas even more N is removed from the film surface. For films grown by HiPIMS, the rather constant $m_d$ and N/C ratios indicate a process without or less resputtering. For films deposited by DCMS, $m_d$ decreases linearly with increasing $V_s$. This indicates that resputtering also takes place in DCMS mode. However, the corresponding N/C ratios suggest that the resputtering rate of N-rich species picks up as $V_s$ approaches 100 and 120 V, where reduced N concentrations are observed.

XPS was used to determine C and N bonding configurations for all CN$_x$ films. Figures 5(a)–5(c) show the normalized C1s core level spectra and Figs. 5(d)–5(f) the corresponding normalized N1s core level spectra for films deposited by the three deposition techniques and the chosen $V_s$. The presented core level spectra were obtained from as-deposited samples in order to show unaffected (i.e., from

Fig. 3. (Color online) (a) Density, (b) O content, and (c) Ar content of the CN$_x$ films deposited by MFMS, HiPIMS, and DCMS as a function of $V_s$. O contents were obtained from XPS measurements after sputter cleaning with Ar$^+$ ions. Ar contents were obtained from ERDA measurements.

Table I. Hardness (H), reduced elastic modulus ($E_r$), elastic recovery (ER), and density $\rho_c$ of CN$_x$ deposited in MFMS, HiPIMS, and DCMS mode.

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sputter-cleaning) C and N bonding configurations in the films. The C1s core level spectra can be satisfactorily fitted with five components; C1 assigned to sp^2-hybridized C–C bonds (∼284.8 ± 0.2 eV), C2 assigned to sp^3-hybridized C bonds (∼286 ± 0.2 eV), C3 resembling sp^2 or sp^3-hybridized C–N bonds (∼287.6 ± 0.2 eV), as well as C4 (289.1 ± 0.2 eV) and C5 (290 ± 0.2 eV) resembling C–O and C=O bonds, respectively.39,40 For all films, the C1s core level spectra are broadened as Vs increases, suggesting elevated amounts of sp^2-hybridized C. The width of the C1s core level spectra scales not only with Vs but also with the Ar content in the films. Considering the highest Vs, the broadening of the C1s spectra is most pronounced for CN_x films deposited by HiPIMS and DCMS as a function of Vs, while the C1s component for films deposited in HiPIMS mode hardly changes. For films deposited by MFMS, an increase of sp^2-hybridized C from 26.6 at. % at Vs = 20 V to 34.5 at. % at Vs = 120 V was extracted from C1. The C sp^2 content of films deposited by HiPIMS shows the lowest variation with values of 28.8 at. % at Vs = 20 V to 33.2 at. % at Vs = 120 V. Films grown by DCMS present sp^2 contents ranging between 27.5 at. % for Vs = 20 V and 33.2 at. % for Vs = 120 V. Consequently, the sp^2/sp^3 ratio, extracted only from C1 and C2 components, appears to increase distinctly with increasing Vs in the case MFMS and DCMS processes are used for the deposition of CN_x, while the sp^2/sp^3 ratio in films grown by HiPIMS presents only small changes. The N1s core level spectra can be satisfactorily fitted with three components; N1 (∼398.6 ± 0.2 eV) attributed to N bond in two-fold coordination at the periphery of graphene sheets in a C matrix (pyridine-like structure), N2 (∼400.6 ± 0.1 eV) is commonly attributed to sp^2-hybridized N bond to three C atoms in a graphitic network, and N3 (∼402.7 ± 0.1 eV) arises due to N=O bonds.12,16,41

The positions of N1 and N2 peaks as well as the N2/N1 peak area ratio indicate the degree of SRO of the C network. Fullerene-like microstructures are usually observed for N2/N1 ratios higher than one and for a N1–N2 peak separation of ∼2 eV.12,42 The here investigated films show a N2/N1 ratio < 1 and the separation of the peaks is lower than 2 eV, indicating that all films have an amorphous microstructure without apparent SRO.12 This is in agreement with results from HRTEM imaging and SAED, as shown in Fig. 6. The TEM micrograph together with the corresponding SAED pattern is representative for all investigated films. Both indicate an amorphous film microstructure with scattering distances at ∼2.1 Å and ∼1.1 Å, being typical for amorphous CN_x films.9 The ∼2 nm interfacial layer between the CN_x film and the Si substrate is ascribed to the formation of SiO_2 at the surface of the substrates, due to the exposure to atmosphere prior to depositions.

Raman spectra recorded for all CN_x films are shown in Figs. 7(a)–7(c). The spectra exhibit one dominant and one weaker band (denoted CN). The most prominent band is dominated by two contributions at ∼1380 and ∼1560 cm⁻¹ corresponding to the disordered (D) and graphitic (G) mode, respectively. The individual positions and linewidths of the D and G contributions have been obtained by fitting the band using Gaussian peak shapes for both D and G. The D and G bands are observed at similar positions as in pure carbon films, and both have been associated with sp^2 C sites.15 According to Ferrari et al.,15 the G band arises due to the C–C stretching vibrations of sp^2 bonds, while the D band is due to the bond breathing modes in both sp^2 rings and chains. For all deposition techniques, the D and G bands are better resolved for
CN$_x$ films deposited at $V_s = 20$ V (cf. black curves in Fig. 7) than for the films deposited at higher $V_s$. For CN$_x$ films grown at higher $V_s$, this distinction is less apparent as the G band shifts toward lower wavenumbers and the D band becomes broader. The shift of the G bands is not significant enough to justify conclusions with regards to changes in the C–C stretching modes. However, the broadening of the D band with increasing $V_s$ is well pronounced for each technique and implies changes in the breathing modes of the C$_{sp^2}$ sites in rings. This correlates well with the results by XPS from the deconvolution of the C1s core level spectra; here, an increased amount of $sp^2$-hybridized C was extracted from the C1 components with increasing $V_s$. The $I(D)/I(G)$ ratio is associated with the number of graphitic ($sp^2$) domains or the degree of $sp^2$ clustering in pure carbon films, where $I(D)$ and $I(G)$ are the peak intensities of the D and G bands, respectively. In all cases, the deconvolution of the compound band by Gaussian peak shapes shows a broad

Fig. 5. (Color online) (a)-(c) Normalized C1s core level spectra for films deposited with (a) MFMS, (b) HiPIMS, and (c) DCMS and (d)-(f) normalized N1s core level spectra for films produced by (d) MFMS, (e) HiPIMS, and (f) DCMS. Films deposited at $V_s = 20, 60, 100, 120$ V are presented. All core level spectra were acquired from as-deposited samples.
D band that is higher in intensity than the G band. Hence, in this work, the obtained I(D)/I(G) ratios range between \(1.54 < \frac{I(D)}{I(G)} < 1.76\) for all films. However, this ratio does not show particular dependency on \(V_s\). This may be ascribed to rather small changes in the bond configuration, which are further disguised by errors introduced by the peak fit model.

**B. Mechanical and tribological film properties**

Figure 8 shows the residual stress, \(\sigma\), for all CN\(_x\) films as a function of \(V_s\). All films exhibit compressive residual stresses, which increase with increasing \(V_s\). For films grown with MFMS, \(\sigma\) increases linearly from \(-0.3\) GPa for \(V_s = 20\) V to \(-4.2\) GPa for \(V_s = 120\) V. The residual stresses are lowest in films grown by HiPIMS. In this case, only a small increase of \(\sigma\) from \(-0.4\) GPa for \(V_s = 20\) V to \(-1.2\) GPa for \(V_s = 120\) V is observed. The films deposited in DCMS mode constitute the intermediate case, where \(\sigma\) increases to \(-2.1\) GPa for \(V_s = 120\) V. The residual stress levels are covarying with the Ar concentration in the CN\(_x\) films [see Figs. 3(c) and 8]; all deposition techniques yield an increase of the Ar content in the films corresponding to an increase in \(\sigma\). Thus, we reason that Ar intercalation in the films adds to compressive stresses. However, the higher \(\sigma\) values encountered at higher \(V_s\) are primarily ascribed to a decreased void formation and suppressed columnar growth,\(^{44}\) due to an increased energy of the incident ions, resulting in forward sputtering.\(^{44}\) The \(\sigma\) induced by the different deposition techniques is primarily related to the amount and charge of the generated ions in the corresponding plasmas together with the different bias duty cycles.

The hardness, \(H\), and reduced elastic modulus, \(E_r\), of the CN\(_x\) films as a function of \(V_s\) are shown in Figs. 9(a) and 9(b), respectively, and listed in Table I. \(H\) and \(E_r\) increase linearly with increasing \(V_s\) and depend on the deposition mode. Films deposited by MFMS show the strongest dependency on \(V_s\), and additionally the highest values of \(H\) (24.6 GPa) and \(E_r\) (191.9 GPa) at a substrate bias of 120 V. Moreover, these films exhibit higher \(H\) and \(E_r\) at each \(V_s\) than films deposited by DCMS and HiPIMS.

The mechanical resiliency of the films, extracted as \(H/E_r\) ratio, expresses the plastic and elastic behavior of materials. Figure 9(c) shows that films deposited in MFMS and DCMS mode at higher \(V_s\) exhibit a \(H/E_r\) ratio equal or higher than magnetron sputtered DLC films,\(^{17}\) where DLC is considered to belong to the category of very resilient materials. The reduction in porosity (Fig. 2) combined with an increased density [Fig. 3(a)] of the CN\(_x\) films grown by MFMS produces harder films than DCMS and HiPIMS. The ER of the films (Table I) ranges between 73.5\% and 90.7\% and generally increases with increasing \(V_s\). The films deposited in...
MFMS and DCMS mode show medium to high ER (see also Ref. 12 for comparison). The highest ER of 90.7% was extracted for a CNx film deposited by MFMS at $V_s = 120$ V and is thus within the ER ranges of FL-CNx films. The ER of films deposited in HiPIMS mode shows no dependency on $V_s$. The increased ER of the films deposited in MFMS and DCMS modes at higher $V_s$ is ascribed to increased amount of $sp^2$-hybridized configurations (cf. Fig. 5).

The tribological performance of the films is presented in Fig. 10. In Fig. 10(a), the average steady-state friction coefficient, $\mu$, of the films as a function of $V_s$, is shown. The data were extracted after the 6th cycle when the surface was stabilized and most asperities have been smoothened. For all films, the steady-state friction ranges between 0.053 ($\pm 0.001$) $\leq \mu \leq 0.065$ ($\pm 0.001$) (the errors refer to the dispersion of the values from the 6th to 31st cycle of the same wear test for each film). The friction does not show a dependency on $V_s$ or the sputter mode. The dispersion of the extracted friction coefficient values is influenced by the surface roughness of the films, the variation between consecutive tests of the same film, possible contamination of the tip or the film surface, and the tip shape, as well as embedded particles. These parameters may affect the values of the tangential frictional force and consequently the values of the friction coefficient. The thin error bars in Fig. 10(a) indicate the dispersion of the friction coefficient that has been extracted from different wear tests on the same film. The relatively high dispersion between the wear tests of the same films indicates that the characteristics of the chosen area for the wear test influence the friction. Figure 10(b) shows the wear coefficient, $k$, derived from the last cycle of each measurement as a function of the $V_s$. The wear coefficient decreases with increasing $V_s$ for all deposition techniques. The films deposited by MFMS show generally lower $k$ than films grown by HiPIMS and DCMS. Specifically, the film deposited by MFMS at $V_s = 120$ V shows no wear. Films deposited by HiPIMS show higher wear than MFMS and DCMS. For the CNx films deposited by HiPIMS, the lowest value of $7.46 \times 10^{-6}$ mm$^3$/Nm was achieved at $V_s = 120$ V. Films deposited in DCMS mode show the lowest wear of $2.4 \times 10^{-6}$ mm$^3$/Nm also at $V_s = 120$ V. The wear correlates with the hardness of the films. This agrees with Archard’s observations for wear and the formula stated by Holmberg et al., where the volume of the worn material is inversely proportional with the hardness of the material,

$$V = \frac{k}{H} L F_n$$

Here, $L$ is the sliding distance, $F_n$ is the applied normal force, and $k$ is the wear coefficient. Moreover, high elastic recovery and thus high amounts of $sp^2$-hybridized states in the CNx films as observed for CNx films grown by MFMS at $V_s = 100$ and 120 V appears to contribute to low wear. Therefore, the wear rate of the CNx films seems to depend
on a combination of high hardness and high elastic recovery. This combination of film properties is likely to advance an abrasive wear mechanism for these films. Adhesive wear was not observed for the relatively high contact pressure of 8.5 GPa that has been applied.

IV. SUMMARY AND CONCLUSIONS

Amorphous C_N thin films of high mechanical resiliency can be deposited at a low substrate temperature of 150°C using MFMS, HiPIMS, and DCMS techniques, provided that a substrate bias is applied to obtain nonporous materials. For MFMS, the bias can be as low as 60 V, whereas for HiPIMS and DCMS, a bias of 120 and 100 V is required, respectively. DCMS was confirmed to be a technique to produce C_N films of high hardness,[12] while HiPIMS yields the least stressed films and a moderate hardness ≤14 GPa. C-based films and especially C_N films with low stresses are desirable for applications where adhesion is essential, such as steel sliding or rolling components. The C_N films grown by MFMS are characterized by high hardness (~25 GPa) and compressive stresses up to ~4.2 GPa. The corresponding elastic recovery of the films reaches 90%, resembling the elastic recovery of fullerene-like C_N films.[23] Low friction coefficients between 0.053 and 0.065 were recorded for all studied C_N films. Thus, the different deposition techniques and conditions are not detrimental for the C_N friction coefficient. On the other hand, high wear resistance can be directly related to homogeneous, dense, and hard C_N films with high elastic recovery. The high elasticity of these films is promoted by sp²-hybridized C bonds that increase in abundance as V_s increases. These resilient a-C_N thin films pose the advantages of both hard and soft films and can potentially be used in application requiring low friction and very good wear resistance.

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