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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

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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 $CN_{0.14}$ 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.

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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 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 N_2/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 ($x, y \leq 2$) species adsorb, thus contributing to the film growth, additionally volatile C_xN_y ($x, y \leq 2$) 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 N_2/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 N_2/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

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Table 1
Collection of process-relevant data for C/inert gas/N_2 discharges.

	Inert gases			Reactive gas species		Target material
	Ne	Ar	Kr	N_2	N	C
1st 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 [19]	11.72 [19]	9.99 [19]	13.03 [20][a]		
Collision mean free path [cm] at 400 mPa[b] [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[c]	0.165	0.120	0.069	0.193	0.202	0.256
Energy per sputtered atom [eV/atom] at 500 eV[c]	12.7	9.4	7.4	10.6	17.6	21.9

[a] 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.
[b] As calculated using the approach suggested in reference [21].
[c] 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.

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.

In low-pressure discharges the process gas ionization (Ne, Ar, Kr, N_2) as well as the target material ionization is generally governed by electron impact ionization. However, a special feature of the graphite discharge in Ne/N_2 (N_2 ≤ 50%) is the creation of a Penning mixture. Here, the addition of small amounts of the reactive gas N_2 to the C/Ne discharge catalyzes the dissociation and ionization of N_2 [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 N_2 ($I_P^{N_2} = 15.6$ 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 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 N_2/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 N_2-to-inert gas flow ratio, defined as $f_{N_2/g} = \frac{f_{N_2}}{f_{N_2} + f_{inert\ gas}} \cdot 100\%$, where f_{N_2} and $f_{inert\ gas}$ are the N_2 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 1800 W), 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

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