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SiN_x Coatings Deposited by Reactive High Power Impulse Magnetron Sputtering:

Process Parameters influencing the Nitrogen Content

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Abstract: Reactive high power impulse magnetron sputtering (rHiPIMS) was used to deposit silicon nitride (SiN_x) coatings for bio-medical applications. The SiN_x growth and plasma characterization were conducted in an industrial coater, using Si targets and N₂ as reactive gas. The effects of different N₂-to-Ar flow ratios between 0 and 0.3, pulse frequencies, target power settings and substrate temperatures on the discharge and the N content of SiN_x coatings were investigated. Plasma ion mass spectrometry shows high amounts of ionized isotopes during the initial part of the pulse for discharges with low N₂-to-Ar flow ratios of < 0.16, while signals from ionized molecules rise with the N₂-to-Ar flow ratio at the pulse end and during pulse-off times. Langmuir probe measurements show electron temperatures between 2 - 3 eV for non-reactive discharges and 5.0 to 6.6 eV for discharges in transition mode. The SiN_x coatings were characterized with respect to their composition, chemical bond structure, density and mechanical properties by X-ray photoelectron spectroscopy, X-ray reflectivity, X-ray diffraction, and nanoindentation, respectively. The SiN_x deposition processes and coating properties are mainly influenced by the N₂-to-Ar flow ratio and thus by the N content in the SiN_x films and to a lower extent by the HiPIMS frequencies and power settings as well as substrate temperatures. Increasing N₂-to-Ar flow ratios lead to decreasing growth rates, while the N contents, coating densities, residual stresses and the hardnesses increase. These experimental findings were corroborated by density functional theory calculations of precursor species present during rHiPIMS.

Keywords: SiN_x, HiPIMS, positive ion plasma mass spectrometry, Langmuir probe measurements, residual film stress, XPS

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1. Introduction

SiN_x is a prospective coating material for metal joint replacements¹⁻⁵; it is a biocompatible compound⁶ with a comparatively high hardness as well as wear resistance. Potential SiN_x wear debris dissolves slowly in aqueous solution⁷⁻⁸. A recent study shows also that the dissolution rate can be tailored with the N content of the SiN_x coating⁹. Additionally, SiN_x coatings can prevent metal ion release from the metal bulk.

Silicon nitride (SiN_x) thin films are commonly deposited by low pressure chemical vapor deposition and plasma enhanced chemical vapor deposition at deposition temperatures above 700 °C and 200 °C, respectively. Both deposition techniques utilize commonly SiH_4/NH_3 , SiH_4/N_2 or $\text{SiCl}_2\text{H}_2/\text{NH}_3$ precursor combinations for the formation of SiN_x ¹⁰⁻¹². Such H-rich precursors, together with comparatively low substrate temperatures, result in H contents as high as 30 at.% in the SiN_x coatings. This leads to a degradation of the favorable mechanical properties¹²⁻¹³. However, the application of SiN_x as protective coating on metal joint replacements requires an excellent wear resistance and comparatively low growth temperatures < 450 °C, since metal replacements degrade potentially under higher temperature loads.

An alternative to above mentioned limitations is the growth of SiN_x by magnetron sputtering as it allows coating deposition without additional substrate heating. Here, SiN_x films can be either deposited from a Si_3N_4 compound target¹⁴, by reactive magnetron sputtering using N_2 as N-source¹⁵⁻¹⁶, or a combination of both¹⁷. One of the major growth parameters for the deposition of SiN_x by reactive magnetron sputtering is the amount of N_2 supplied to the glow discharge as it determines the deposition process characteristics¹⁸ as well as the N content in the SiN_x coatings. In studies^{15-16, 19} SiN_x thin films were deposited by reactive radio frequency magnetron sputtering. Here, the researchers found reduced N contents in the SiN_x films with increasing reactive gas flow. This was attributed to an insufficient activation of N_2 , caused by a decreasing amount of electrons as the N_2 -to-Ar flow ratio ($f_{\text{N}_2/\text{Ar}}$) increased. The lowered N contents resulted also in a decreased hardness and residual stresses.

SiN_x can also be synthesized by reactive high power impulse magnetron sputtering (rHiPIMS) in Ar/ N_2 atmosphere^{3-4, 20}. The inherent, comparatively high plasma densities in HiPIMS^{9, 21-23} should yield sufficient N_2 activation even at elevated N_2 -flows. However, corresponding publications that were issued so far concentrate to our best knowledge mainly on coating properties. Hence, there is a need to investigate HiPIMS deposition parameters for the growth of SiN_x and correlate those to resulting SiN_x properties.

In this study, we report about the influence of rHiPIMS deposition parameters on the N content of SiN_x coatings. Specifically, the $f_{\text{N}_2/\text{Ar}}$, target power settings, and the substrate temperature were considered. Reactive Si/Ar/ N_2 HiPIMS discharges were studied using plasma ion mass spectrometry and Langmuir probe measurements. The effect of above mentioned deposition parameters on the coating composition, density, residual stresses and hardness were investigated by X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), X-ray diffraction (XRD) and nanoindentation, respectively.

2. Materials and Methods

Density functional theory calculations within the synthetic growth concept approach²⁴ were performed to model the most abundant precursor species in Si/N₂ discharges, as corroborated herein by plasma mass spectrometry. The study involved geometry optimizations and cohesive energy calculations of the following neutral species: Si, N, N₂, Si₂, and SiN. The cohesive energy per atom ($E_{coh/at}$) is defined as the required energy for splitting the considered system into isolated atomic species normalized by the total number of atoms, and is calculated according to equation 1:

$$E_{coh/at} = - \frac{E_{system} - N_N \times E_N - N_{Si} \times E_{Si}}{N_N + N_{Si}} \quad (1)$$

, where E_{system} is the total energy of the model system, N_N and N_{Si} are the number of N and Si atoms, and E_N and E_{Si} are the energies of the corresponding free atoms in the ground state, respectively. The calculations were performed at the level of the generalized gradient approximation as implemented in the program Gaussian 09²⁵. The results reported herein were obtained using the PW91²⁶ exchange and correlation functionals with the 6-31G** basis set augmented with polarization functions.

The deposition of SiN_x coatings and plasma characterization were conducted in the industrial coating unit CC800/9 ML (CemeCon AG, Germany) at Linköping University, for which two out of six cathodes can be operated in HiPIMS mode. A base pressure of < 1 mPa was achieved prior to deposition. Si targets with a purity of 99.8 % and N₂-to-Ar flow ratios ($f_{N_2/Ar}$) ranging between 0 and 0.31 were used for the deposition of SiN_x. The $f_{N_2/Ar}$ (Eq. 2) is defined as

$$f_{N_2/Ar} = \frac{f_{N_2}}{f_{Ar}}, \quad (2)$$

where f_{N_2} and f_{Ar} are the N₂ and Ar gas flows, respectively. The deposition pressure was kept constant at 400 mPa. SiN_x films were deposited onto conventional p-doped Si(001) wafers to thicknesses ranging between 1900 nm and 2500 nm. In all HiPIMS processes pulse widths of 200 μs and a pulsed bias voltage (U_B) of -100 V, synchronized to the cathode pulses, were used. The pulse frequency, average target power and the substrate temperature (T_s) were varied between 0.2 kHz and 1 kHz, 600 W and 4000 W, as well as 190 °C and 530°C, respectively.

Time-averaged and time-resolved plasma mass spectrometry were conducted with a Hiden EQP 1000 unit in order to access the composition and temporal evolution of non-reactive and reactive Si discharges. First, the most abundant plasma species were determined with mass scans from 0 to 100 amu at an ion energy of 0.6 eV. Subsequently, the ion energy distribution functions (IEDFs) of the most abundant positive ions were recorded. Time-averaged data were acquired using a distance of 60 mm between the mass spectrometers orifice and the target surface, where the orifice had an opening of 50 μm. For the acquisition of time-resolved data, the orifice faced the target with a distance of 320 mm and had an opening of 300 μm. Here, time-resolved IEDFs of the isotopes ¹⁵N, ²⁹Si, ³⁰Si, and ³⁶Ar were recorded, due to the similarity of the masses and the abundance of Si and N ions. For all measurements, ion energies were recorded between -0.4 eV and 30 eV with a resolution of 0.5 eV and the spectrometer dwell time was set so that the presented data represent an average of at least 30 HiPIMS pulses. Time-

resolved ion mass spectrometry measurements were triggered at pulse onset of the target voltage signal by a Tektronix DPO4054 digital oscilloscope. The delay time for the measurements, relative to the onset of the HiPIMS pulse, ranged from 40 μ s up to 600 μ s with an increment of 20 μ s. For the presented time-resolved data the ion time-of-flight (TOF) within the mass spectrometer was corrected, thus data represent the plasma characteristics at the spectrometer orifice. TOF-correction was applied according to Bohlmark et al.²⁷. A mean particle energy of 2 eV was used for all TOF calculations. The low particle energies are due to the high distance between the target and spectrometer orifice. During ion mass spectrometry measurements the target current and target voltage waveforms were recorded with a Tektronix DPO4054 digital oscilloscope.

A custom-made Langmuir probe set-up was used for time-resolved measurements of the electron temperature (T_e). A tungsten wire with a diameter of 350 μ m was insulated by a ceramic tube, except for 4 mm that were exposed to the plasma. A transconductance amplifier was used to drive a current through the probe. The voltage compliance for the amplifier was -90 V to +30 V and its parasitic output capacitance was measured to be $\sim$ 200 pF. An Agilent DSO-X 2002 oscilloscope was used to measure the voltage on the probe for each set current, yielding a resolution of 0.78 V. The oscilloscope measurements were averaged over 32 waveforms. For the measurements, a substrate temperature of 350 $^{\circ}$ C was used. The electron temperature of HiPIMS processes was extracted for pulse times corresponding to the peak target current.

Cross-sectional scanning electron microscopy (SEM, LEO 1550 Gemini, Zeiss, Germany) was used to determine the SiN_x film thickness and hence the growth rate. The instrument, equipped with an in-lens detector, was operated at an acceleration voltage of 3 kV at a working distance of $\sim$ 3 mm.

The chemical composition and bonding states of SiN_x coatings were investigated by XPS (Axis UltraDLD, Kratos Analytical, Manchester, UK) using monochromatic Al(K α) X-ray 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 Si2p, Ar2p, N1s, C1s, and O1s regions were recorded on as-received samples and after sputter cleaning for 120 s with a 2 keV Ar⁺ ion beam, rastered over an area of 3 $\times$ 3 mm² at an incidence angle of 70 $^{\circ}$ with respect to the surface normal. Automatic charge compensation was applied throughout the acquisition, owing to the electrical insulating nature of the SiN_x films as their N content increases. After subtraction of a Shirley-type background from core level spectra obtained after Ar⁺ sputter cleaning, the chemical composition of the SiN_x films was extracted, using elemental cross sections provided by Kratos Analytical. Core level spectra obtained from sputter cleaned samples were also used to study the bond structure of the SiN_x films. Here, a Shirley-type background was subtracted and the core level spectra were referenced to the C-C/C-CH bond at 285 eV²⁸. The spectra were fitted using a Voigt peak shape with a Lorentzian contribution of 30 %. The full width at half maximum (FWHM) of all components was restricted to < 2 eV.

XRD Θ - 2 Θ scans were used to investigate whether the coatings show crystalline phases. The Θ - 2 Θ scans were recorded with a Philips powder diffractometer (PW 1820) equipped with a Cu(K α) radiation source operated at 40 kV and 40 mA.

The residual stresses in the films were determined from the wafer curvature, assessed by XRD (PANalytical Empyrean)²⁹. The diffractometer, equipped with a Cu K α_1 source, was operated at 45 kV and 40 mA. The Stoney formula for anisotropic single crystal Si (001) was used to relate the measured substrate curvature to the residual coating stress, assuming uniform plane stress in the film³⁰. The same instrument was used to investigate the film density by XRR. The density was evaluated using the PANalytical X'Pert reflectivity software. Here, a 3-layer model, resembling the substrate, the SiN_x films and a surface oxide layer was applied.

The hardness and elastic modulus of the SiN_x films were measured in a CSIRO UMIS nanoindenter (Fischer-Cripps Laboratories, New South Wales, Australia) equipped with three-sided Berkovich tip. All films were tested in load-controlled mode. For the tests, 30 indents of increasing loads between 1 mN and 15 mN were performed. The method suggested by Oliver and Pharr³¹ was applied for evaluation.

3. Results and Discussion

3.1 Theoretical calculations

In order to determine the role of the precursor species that are active during the HiPIMS deposition of SiN_x films, the species were evaluated by their stability, and number of dangling bonds. Table 1 shows the $E_{coh/at}$, and bond lengths for the diatomic species, as well as the possible plasma reactions in which they are involved. Our calculations show that the Si/Ar/N₂ plasma is dominated by N₂, N, Si, SiN, and Si₂. These precursor species are created by either dissociation or recombination reactions in the plasma or at the target surface. The values obtained for bond lengths and reaction enthalpies are in agreement with the literature³². The two species with a distinguished role in film formation are the dimers SiN and Si₂, as these form effortlessly, are rather unstable (low $E_{coh/at}$) and are chemically very reactive due to a comparatively high amount of dangling bonds. Regarding the reactive gas molecular nitrogen, its main role is to provide monatomic nitrogen to the sputtering process, but has little impact on the film formation process.

Table 1: $E_{coh/at}$, bond lengths, possible reactions and corresponding calculated reaction enthalpies for the diatomic precursor species: N₂, SiN, and Si₂.

Precursor species	$E_{coh/at}$ (eV/at)	Bond length (Å)	Reactions	ΔH (eV)
N ₂	-5.15	1.12	N ₂ → 2N	10.2
			2N → N ₂	-10.2
SiN	-2.48	1.59	Si + N → SiN	-4.9
Si ₂	-1.68	2.18	2Si → Si ₂	-3.4

3.2 Process Characteristics and Plasma Characterization

The target current and target voltage waveforms as a function of the pulse time for discharges using different $f_{N_2/Ar}$ and pulse energies (E_{pP}) are shown in figures 1a) and b). Current and voltage waveforms were recorded using a pulse frequency of 0.3 kHz and an average target power of 3000 W, 2000 W and 1000 W, corresponding to pulse energies in non-reactive processes of 10 Ws, 6.7 Ws, and 3.4 Ws, respectively. Increasing the E_{pP} results in rising peak target currents and decreasing voltages, and hence in increasingly dynamic discharges. The target current and voltage waveforms are similar for the non-reactive discharges and discharges conducted in $f_{N_2/Ar} = 0.16$. For the discharges using a $f_{N_2/Ar} = 0.30$, a slight increase of the peak target current and target voltage is observed. The target current decreases drastically as $f_{N_2/Ar}$ is further increased to 0.50, while the target voltage increases. The discharge at $f_{N_2/Ar}$ of 0.50 was only possible for a comparatively high pulse energy of 10 Ws.

The target current reflects in first approximation the number of charged species in the vicinity of the target, where the amount of generated ions and the secondary electron emission contribute. The secondary electron emission yield (γ_{SE}) is influenced by the ionization energy of the working gas (I_p) and the work function (ϕ) of the target surface³³. Upon introduction of N₂ to the Si-discharge, the

effective I_p of the process gas does not change considerably owing to similar ionization energies of N_2 ($I_p(N_2) = 15.6$ eV) and N ($I_p(N) = 14.53$ eV) and Ar ($I_p(Ar) = 15.75$ eV). Thus, γ_{SE} is not significantly influenced by I_p of the process gas. Additionally, the target surface chemistry becomes altered by the addition of N_2 and an increase of the target surface work function from 4.83 eV³⁴ for a pure Si surface to ~ 7 eV³⁵ estimated for the N terminated Si target surface leads to decreased γ_{SE} . In consequence, decreasing the peak target currents may be observed. However, this is first observed at a comparatively high $f_{N_2/Ar}$ of 0.50. Therefore, rather than γ_{SE} , the generation of ions in the vicinity of the target and the sputter yield of a compound target surface influence the Si/ N_2 discharge characteristics to a greater extent.

The slightly higher peak target currents obtained at $f_{N_2/Ar}$ of 0.30 are attributed to the dissociation of N_2 . Here, the target surface chemistry may on average not be significantly affected; Upon N_2 incorporation, dangling Si bonds at the target surface get terminated by N_2 or N during comparatively long pulse-off times. This leads to a partially developed SiN layer at the target surface, which is sputtered away during pulse-on times and the target is operated in transition mode. At a deposition pressure of 400 mPa the transition mode is observed at a $f_{N_2/Ar}$ of 0.30. As $f_{N_2/Ar}$ is increased to 0.50, the target current and voltage waveforms suggest that a permanent SiN compound layer is formed at the target surface and is not sputtered away during pulse-on times. Here, the discharge is operated in poisoned mode. The reduction of the peak target current is mainly caused by a reduced sputter yield of the SiN target surface compound, and to minor extents by a lowered γ_{SE} .

The voltage waveforms diverge increasingly as the $f_{N_2/Ar}$ increase and the pulse energies are decreased. At a low E_{pP} of 3.4 Ws, rising $f_{N_2/Ar}$ result in the largest drop of the target voltage. This is attributed to a decreased sputter yield of the target material at comparatively low target voltages. Hence, the N removal from the target surface is less efficient. Comparing the bond strength of Si-Si and Si-N of ~ 2.30 eV and ~ 3.68 eV, respectively, it is apparent that approximately 40 % more energy needs to be invested in the reactive sputter process to initiate knock out events at the target surface. Thus, increasing the average discharge power or E_{pP} delays the onset of target poisoning. This is illustrated in figure 1 b), where the target voltage waveform does not show significant changes with increasing $f_{N_2/Ar}$ at $E_{pP} = 10$ Ws. It is also in agreement with the fact that the discharge in poisoned mode using $f_{N_2/Ar} = 0.50$ was only possible for a comparatively high pulse energy of 10 Ws. Finally, the results from current and voltage waveforms are in agreement with findings reported by Depla et al.³⁶.

Figure 1 a) and b): Target current a), and target voltage b) over the pulse time recorded for processes using a pulse frequency of 0.3 kHz and an average target power of 3000 W, 2000 W and 1000 W corresponding to pulse energies in non-reactive processes of 10 Ws, 6.7 Ws, and 3.4 Ws, respectively and different N_2 -to-Ar flow ratios ($f_{N_2/Ar}$). The discharge using $f_{N_2/Ar} = 0.50$ was only feasible at 10 Ws.

Figure 2 a) - c) shows IEDFs recorded for most prevalent plasma species of discharges with different $f_{N_2/Ar}$ using a pulse frequency of 0.3 kHz and an average target power of 1000 W, corresponding to an E_{pp} of 3.4 Ws. As shown in figure 2 a) - c), the addition of N_2 to the sputter gas results in a strong reduction of the ion flux and energy for all precursor fragments. Reduced ion energies and fluxes are already recorded at $f_{N_2/Ar} = 0.16$ (cf. figure 2 b)). The shape of the IEDF assigned to Si^+ or N_2^+ in figure 2 b) resembles the shape of Si^+ recorded for the non-reactive discharge, but shows a reduced count rate for ions with energies ranging between 15 and 22 eV. Moreover, low energy ions that were recorded between 5 eV and 10 eV in the non-reactive discharge shift towards lower energies by approximately 5 eV. The variations observed in the corresponding Si^+ / N_2^+ IEDF are ascribed to be mainly due to the combination of IEDFs arising from N_2^+ and Si^+ . Thus, the Si^+ / N_2^+ IEDF is a combination of IEDFs from ions originating from the target (Si^+) and from the plasma (N_2^+). In a similar experimental set-up and for C discharges, N_2^+ was shown to originate in the plasma bulk rather than from the target³⁷. In³⁷ the corresponding N_2^+ IEDFs were mainly composed of low energetic and thermalized ions and did not resemble the shape of ions originating from the target, while IEDFs from N^+ resembled the shape of the target ions. Hence, it was concluded that N^+ is originating from the target. The latter is to some extend also observed for the here investigated discharges as the IEDF assigned to N^+ (and Si^{2+}) in figure 2 b) shows a comparatively high count rate for ions with energies ranging between 15 eV and 20 eV. However, this IEDF shows also high amounts of thermalized ions, which may arise from the plasma.

The contribution of Si^{2+} to this IEDF is expected to be negligible, due to the fact that no Si^{2+} was found in the corresponding non-reactive discharges and the comparatively high second ionization energy of Si ($I_p^{\text{Si}^{2+}} = 16.35$ eV). As in the case of the discharge in pure Ar, the reactive discharge contains high amounts of Ar^{2+} , which even exceeds that of Ar^+ at a $f_{\text{N}_2/\text{Ar}} = 0.16$. As more N_2 is added to the working gas, all IEDFs show reduced count rates and energies. This is attributed to a N-terminated target surface and a lowered sputter yield of the Si-N compound (cf. $E_{\text{coh/at}}$ in table 1, and figure 1) as well as to the ability of N_2 to cool the plasma efficiently. The results from time averaged ion mass spectrometry are in agreement with results and conclusions drawn from current and voltage waveforms and reflect our theoretical calculations (cf. 3.1 Theoretical calculations).

Figure 2 a)-c): IEDFs of Si/Ar/ N_2 discharges using a deposition pressure of 400 mPa, a pulse frequency of 0.3 kHz and an average target power of 1000 W; a) in pure Ar, b) $f_{\text{N}_2/\text{Ar}} = 0.16$, and c) $f_{\text{N}_2/\text{Ar}} = 0.50$.

Langmuir probe measurements were carried out for discharges using 0.3 kHz in pure Ar, as well as in gas mixtures with $f_{N_2/Ar}$ of 0.16 and 0.28. The electron temperature, shown in figure 3, was extracted at a pulse time of 60 μ s, representing the point at which the target current reaches its maximum value (cf. figure 1 a)). Figure 3 shows that the electron temperature decreases with increasing discharge power for processes carried out in pure argon. This is in agreement with results from ³⁸ and attributed to an increased amount of sputtered species that are ionized upon electron impact resulting in decreased T_{es} . As the N_2 content in the process gas is raised to 0.16 the T_{es} show similar values of $1.8 \text{ eV} \pm 0.1 \text{ eV}$ for all applied average target powers, suggesting that the addition of low amounts of N_2 to discharges conducted at average target powers up to 2400 W contributes to increased plasma densities. This may be due to the ionization according to (3) with an onset for appearance at 15.58 eV as well as dissociative ionization according to (4) at 24.34 eV ³⁹⁻⁴².

The mere dissociation (5) at 9.75 eV or excitation (6) of the N_2 molecule according to

do not contribute to an increased plasma density, since these reactions do not provide additional charge carriers. The results shown in figure 3 obtained at a $f_{N_2/Ar}$ of 0.16 up to an average target power of 1200 W suggest that the ionization according to (3) may be most probable as it requires the least energy. As the target power is raised to 1800 W and 2400 W an additional excitation or dissociation of N_2 is likely, since T_e remains at 1.8 eV. As the discharge is carried out at a $f_{N_2/Ar}$ of 0.28 the electron temperature is generally high and increases steadily as the average target power increase. The high electron temperatures agree with results from ion mass spectrometry showing reduced amounts of ionized species. The elevated electron temperatures indicate low plasma densities caused by the temporary change of the target surface chemistry, which in turn causes lowered sputter yields and secondary electron emission yields. As the target power increases the increasing T_{es} suggest that the N_2 molecule may also be activated according to (5) or (6), where dissociation or excitation (electron quenching) prevails ^{15, 39-41, 43-44}. Additionally, recombination reactions ⁴⁵ like

may account for lowered plasma densities at $f_{N_2/Ar}$ of 0.28 as the target power increases. An increasing electron temperature with increasing discharge power was also reported in references ⁴⁶⁻⁴⁷.

Figure 3: Electron temperature (T_e) over the N_2 -to-Ar flow ratio ($f_{(N_2/Ar)}$) for Si/Ar and Si/Ar/ N_2 discharges conducted at $T_s = 350$ °C, a process pressure of 400 mPa and a pulse frequency of 0.3 kHz with increasing average target powers.

Time-resolved plasma mass spectrometry was used to access the temporal evolution of the plasmas species in the Si/ N_2 /Ar plasma. Due to the similarity of the masses and the abundance of ions in the chosen experimental set-up, the IEDFs of isotopes ^{15}N , ^{29}Si , ^{30}Si , and ^{36}Ar were recorded. Additionally, the IEDFs for mass 56 accounting for SiN_2^+ or Si_2^+ were measured. Time-resolved data are shown in figure 4 a) - c) as the discharges are operated at a process pressure of 400 mPa for two different N_2 /Ar flow ratios and the case when Si is sputtered in pure Ar. Comparing the different discharges shown in figure 4 a) - c) it can be extracted that most prevalent precursor species in the plasma during the pulse on-time are Si^+ , Si^{2+} and/or N^+ . Larger ionized plasma species like ^{36}Ar , the Ar cluster $2Ar$ and SiN or Si_2 increase in intensity during the second part of the pulse on-time and reach their maximum intensity during pulse off times. This discrimination can mainly be attributed to the mass and dimension of these ionized species, their origin and the effect of gas rarefaction. The mass and dimension of the species determines its time of flight through the plasma as well as its probability for collision, which in turn will affect the corresponding delay time. The origin of the species affects the recorded delay time as ions originating from the target exhibit higher kinetic energies compared to species that are formed by recombination or fragmentation in the plasma^{37, 48}. Gas rarefaction affects the temporal evolution of intensities of the sputter gases, since the gas depletes temporally in front of the target when energetic, sputtered particles cause gas heating. The onset of gas depletion is usually observed as the target current peaks and many energetic species are sputtered. In this study, the effect is observed for discharges in pure Ar and for a low N_2 /Ar flow ratio of 0.16 (cf. figure 1, and figure 4 a), b)). In the discharge containing an $f_{N_2/Ar}$ of 0.30, the signal of $^{36}Ar^+$ is completely absent during pulse-on times. The absence of $^{36}Ar^+$ is attributed to the fact that the overall amount of ionized Ar is lowered and further due to the limited natural abundance of 0.3336 % of $^{36}Ar^+$, thus the effect of gas rarefaction may be concealed.

As indicated above, the temporal evolution of the ionized plasma species for the three different gas compositions (cf. figure 4 a) - c)) suggest a dependency on the $f_{N_2/Ar}$. In figure 4 c) the plasma containing a $f_{N_2/Ar}$ of 0.30 shows a very distinct temporal discrimination of charged species with regards

to their mass and dimension. This effect becomes less pronounced with decreasing N_2 content in the plasma, which is ascribed to increasing particle energies as the N_2 content in the plasma decreases (cf figure 2 a), b)). Furthermore, the time-resolved measurements show that, similarly to time averaged measurements, the overall ion intensity decreases as more N is added to the plasma and is also confirmed by Langmuir probe measurements (cf. figure 3).

Figure 4 a) – c): Time-resolved positive ion mass spectrometry measurements integrated over the ion energy and corrected by the time-of-flight within the mass spectrometer of Si/Ar/ N_2 discharges using a pulse frequency of 0.3 kHz, an average target power of 1000 W and a deposition pressure of 400 mPa; a) pure Ar, b) $f_{N_2/Ar} = 0.16$ and c) $f_{N_2/Ar} = 0.30$.

3.3. Deposition parameters influencing the N content of SiN_x coatings and impact of the film N contents on SiN_x properties

3.3.1 N₂-to-Ar flow ratio

As discussed above, the SiN_x deposition process characteristics and stability are controlled to a high extent by the $f_{N_2/Ar}$ and this is also reflected in the properties of SiN_x. In figure 5, the growth rate (R_G) and the N content of SiN_x films deposited at a pulse energy of 6 Ws using different $f_{N_2/Ar}$ between 0 and 0.30 are shown. As expected, increasing $f_{N_2/Ar}$ lead to increasing N contents in the SiN_x films and to decreasing deposition rates. This is in agreement with conclusions drawn from the current waveforms (cf. figure 1a)), the lowered negative cathode potential as $f_{N_2/Ar}$ increases (cf. figure 1 b)), and the results from plasma mass spectrometry (cf. figure 2 and 4). The latter shows decreased abundance of all cations in the plasma as $f_{N_2/Ar}$ increases, leading – in a first approximation – to the conclusion that the sputter yield and hence, the growth rate (R_G) decreases as the target is operated in transition or poisoned mode. This is commonly observed for reactive magnetron sputtering discharges^{15, 49}.

Figure 5: Growth rate (R_G , black squares) and N contents (grey circles) in SiN_x films as a function of the N₂-to-Ar flow ratio ($f_{N_2/Ar}$) obtained from films deposited at a substrate temperature of 350 °C using a pulse energy of 6 Ws, and a process pressure of 400 mPa.

Figure 6 a) - d) presents the influence of increasing N contents on the Si bond structure. As the N content in the Si-matrix increases, the signals of Si2p_{3/2} and Si2p_{1/2} at binding energies of 99.0 eV and 99.7 eV, respectively, decrease, while different Si-N bond types at 100.3 eV, 101.4eV, and 102 eV increase⁵⁰. The different binding energies of the Si-N bonds indicated in figure 6 originate due to the different tetrahedral bond regimes of SiN_x, i.e. Si-Si-N, Si-N-N, and to a smaller extent the presence of nearest-neighbor effects (secondary chemical shifts). Here, the Si2p binding energy is affected by the bond type of the neighboring Si atoms. Moreover, the spectra components are broadened as more N is incorporated in the Si matrix. The FWHM of the Si2p_{3/2} component in the spectrum obtained from pure Si is 0.7 eV (cf. figure 6 a)), while the FWHM of the contribution assigned to Si-N-(-N) bonds of the sample containing 49 at. % N (cf. figure 6 d)) amounts to 1.7 eV. Since Θ -2 Θ XRD scans showed that the here investigated SiN_x coatings are X-ray amorphous (cf. supporting information), the broadening of the XPS core level components is mainly attributed to the stochastic nature of the bond formation process, where

repeating unit cells, and thus well-defined binding energies associated with a given bond type are lacking⁵⁰. Ar⁺ sputter cleaning increased the FWHM of the components by a maximum of 0.2 eV.

At a N content of 49 at.%, the Si2p core level comprises merely one component arising from Si-N bonds and Si-Si bonds are absent (cf. figure 6 d)). Moreover, as the N content in the coatings increases and approaches 49 at.%, the Ar content decreases from ~2 at.% to 0 at.%, while a slight increase of oxygen from ~2 at.% to ~4 at.% was recorded. The incorporation of carbon was < 1at.% and appeared unaffected by the N content of the coatings.

Figure 6 a) – d): XPS core level spectra of the Si2p region for a) pure Si, b) SiN_x containing 23 at.% N, c) SiN_x containing 39 at.% N, and d) SiN_x containing 49 at.% N. The spectra were acquired after Ar⁺ sputter cleaning.

Figure 7 a) and b) present the impact of an increased N content in the coatings on the compressive residual stress and the density as well as the hardness (H) and the Young's modulus, respectively. As demonstrated in figure 7 a), increasing N contents in the SiN_x matrix result in increasing film densities

up to 2.98 g/cm^3 , approaching the density of Si_3N_4 of 3.2 g/cm^3 . The evolution of the coating density agrees well with the tabulated bond length of Si-N of $\sim 170 \text{ pm}$ compared to the bond length of Si-Si of 233 pm . At the same time the residual compressive stresses increase up to -1.5 GPa . High compressive stresses in the GPa range were also observed by Burkhardt and Marvel⁵¹, where the coefficient of thermal expansion of sputtered SiN_x (CTE_{SiN}) at 350°C was estimated to $3.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and that of Si (CTE_{Si}) to $3.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The observed increase of the residual compressive stress with increasing N content of the SiN_x films may result from a combination of the differences in CTE of the film and substrate material, the reduced bond Si-N bond lengths and the related increased SiN_x densities as well as an increasing number of polyatomic film forming species in the plasma as the $f_{\text{N}_2/\text{Ar}}$ is raised up to ~ 0.30 . An elevated amount of complex molecules in the sputter plasma was proposed by Nir et al.⁵² to contribute to higher film stresses, due to their constrained mobility at the growing film surface. In this study the relative amount of ionized molecules increased as the $f_{\text{N}_2/\text{Ar}}$ increases up to 0.30 (cf. figure 4 c)).

The hardness and elastic modulus extracted for the SiN_x coatings with increasing N contents show a similar trend as the coating density. The linear dependence of the hardness on the SiN_x coating density is shown in the inset in figure 7 b). Hence, the increase of the hardness can be attributed to an increased SiN_x density as the N content of the material increases. Similar observations are also reported in references^{17, 53-54}.

Figure 7 a) and b): a) Residual stress (black squares) and density (grey circles) as well as b) Hardness (black squares) and Young's modulus (grey circles) for films with increasing N contents deposited at a substrate temperature of 350°C using a pulse energy of 6 Ws, and a process pressure of 400 mPa. In b) the hardness (black rectangle) and Young's modulus (grey rectangle) from a Si_3N_4 reference³ are shown.

3.3.2 HiPIMS power settings

The N content in the SiN_x coatings is also influenced by the applied energy per pulse (E_{pp}) as SiN_x coatings are deposited at N₂ deficiency, accounting for $f_{N_2/Ar} < 0.28$ (at a deposition pressure of 400 mPa and $T_s = 350$ °C) in the plasma. In such N-depleted Si/N₂/Ar discharges, the ratio of sputtered Si to the availability of dissociated or ionized N₂ is inversely proportional to the N content in the SiN_x coating. This is exemplified in figure 8 a), where the Si/N ratios of SiN_x coatings deposited at $f_{N_2/Ar}$ of 0.16 and 0.28 are shown over the applied average target power. Additionally, the growth rates of the corresponding coatings are shown in figure 8 b). The coatings were deposited using either a constant E_{pp} (implying proportionally increasing pulse frequencies as the average target power increases) or a constant pulse frequency (implying that the E_{pp} increases as the average target power is increased). Obvious are increasing Si/N ratios with increasing average target power of films deposited at $f_{N_2/Ar} = 0.16$ with a pulse frequency of 0.3 kHz and increasing E_{pp} (cf. figure 8 a) grey circles). Hence, the N content in the coating decreases as the E_{pp} is raised. For SiN_x coatings deposited at an E_{pp} of 3 Ws (corresponding to increasing pulse frequencies as the average target power is raised), the obtained Si/N ratios are comparable over the range of applied average target powers (cf. figure 8 a) black squares). This can be explained on the basis of the Si-sputter yield and growth rates (cf. figure 8 b)); increasing pulse frequencies influence the sputter yield to a lower extent, while increasing average target powers have the strongest effect, since the sputter yield increases with the average target voltage (cf. figure 3). The average target voltage varied between 500 V and 600 V for the investigated processes, applying the lowest E_{pp} of 1.5 Ws and the highest E_{pp} of 7.5 Ws, respectively. According to TRIM simulations⁵⁵ the Si sputter yield in Ar is 0.38 at/ion at an average target voltage of 500 V and 0.46 at/ion at 600 V.

As the SiN_x coatings are deposited in transition mode, accounting for $f_{N_2/Ar}$ ranging between 0.28 and 0.31 (at a deposition pressure of 400 mPa and $T_s = 350$ °C), the Si/N ratios decrease and are only slightly influenced by the HiPIMS power settings, since an adequate amount of activated N species is existent. These N species contribute to the formation of a N-rich compound layer at the target surface during pulse-off times. As can be drawn from figure 8, a slight trend towards higher Si/N ratios is also observed as SiN_x coatings are deposited with increasing E_{pp} in transition mode. This is again attributed to increasing Si-sputter yields and the fact that operating at an $f_{N_2/Ar}$ of 0.28 renders the lower region of the transition mode. From figure 8 as well as figures 1 and 2, it is evident that the extent of compound layer formation increases not only with the $f_{N_2/Ar}$, but also with decreasing average target power, while the sputter rate of metallic particles is inversely proportional to both.

Figure 8 a) and b): a) Si/N ratios as obtained by XPS measurements and b) the corresponding growth rates (R_G) over the applied average target power. SiN_x coatings were deposited using a total process pressure of 400 mPa and a substrate temperature of 350 °C. Applied process settings such as the N_2/Ar flow ratio ($f_{N_2/Ar}$), the energy per pulse (E_{pP}) and the pulse frequency (f_p) are indicated. Errors as for the Si/N ratio are estimated to be ± 0.03 and for $R_G \pm 3$ nm/min.

3.3.2 Substrate temperature

Figure 9 presents cross-sectional SEM images of SiN_x coatings deposited at a substrate temperature of a) 190 °C, b) 350 °C, c) 420 °C, and d) 510 °C. As can be seen in figure 9, the dense, featureless morphology of the SiN_x coatings does not change significantly as the substrate temperature is increased. Facets in figure 9 c) and d) are mainly attributed to the sample preparation by wafer cleavage. Owing to the insulating nature of the presented coatings, the microscope brightness and contrast settings were chosen as to emphasize the coating morphology rather than the $SiN_x/Si(001)$ interface. However, the $SiN_x/Si(001)$ interfaces were identified during imaging at intensified contrast and brightness settings and are indicated in figure 9.

The N content in the SiN_x coatings decreases slightly with increasing substrate temperatures. From figure 10 it is evident that the N contents decrease from 53.7 at.% to 50.5 at.% as the substrate temperature increases from 190 °C to 510 °C. A similar observation was reported in reference ¹⁷. The

growth rate appears not significantly influenced by the substrate temperature. These observations are attributed to an increased ad-atom mobility, which leads to

- i) an increased probability of N-N recombination (based on our theoretical results)
- ii) an increased probability of chemical sputtering (desorption) of N-containing film forming species⁵⁶⁻⁵⁷ at the substrate surface especially with the presence of background gas
- iii) the effect that film forming species can select more energetically favorable bonding sites.

As the substrate temperature increases, amounts of O, C, and Ar in the coatings increase from 0.9 at.% to 4.2 at.%, 0.2 at.% to 1.3 at.% and 0 at.% to 0.2 at.%, respectively. At the same time a trend towards lower densities is recorded, which decrease from 2.9 g/cm³ at 190 °C to 2.6 g/cm³ at 520 °C. Both, the increased amount of contaminants and lowered coating densities at 520°C may result due to elevated desorption of contaminants from the chamber walls. Although cross-sectional SEM micrographs do not show significant changes of the coating morphology as the substrate temperature increases (cf. figure 9) the reduced film density at elevated substrate temperatures indicates that the SiN_x coatings become increasingly porous. This, in turn, leads to an amplified O and C uptake of the films upon exposure to air. Consequently, optimal substrate temperatures for the deposition of SiN_x using rHiPIMS are above 150 °C and below 400 °C.

Figure 9: Cross-sectional SEM images of SiN_x coatings deposited at a substrate temperature of a) 190 °C, b) 350 °C, c) 420 °C, and d) 510 °C. The magnification was set to the same value during acquisition. The $\text{SiN}_x/\text{Si}(001)$ interface was observed during acquisition at intensified contrast and brightness settings.

Figure 10: N content as obtained by XPS and growth rate of SiN_x coatings deposited at 190 °C, 350 °C, 420 °C, and 510 °C. The standard deviation for the presented N contents is < 0.3 at.%.

4. Summary and Conclusions

Growth conditions for rHiPIMS processes, influencing the N content of SiN_x coatings were investigated. The Si magnetron sputter discharge and the SiN_x coating properties are heavily influenced by the amount of N_2 in the plasma. Moreover, the applied target power as well as the substrate temperature were found to influence the N contents in SiN_x coatings and thus the coating properties - although to a much lower extent. While increasing N_2 -to-Ar ratios in the sputter plasma yield rapidly increasing N contents up to

~50 at.%, an increasing target power and substrate temperatures above 350 °C result in up to 6 at.% and 4 at.% lower N contents in the coatings, respectively. The target surface condition determines to which extent the applied average target power influence the N contents in SiN_x coatings. Under metallic target surface conditions, accounting for N₂-to-Ar flow ratios below 28 %, increasing target powers, yield significantly higher Si/N ratios. The Si/N ratios are hardly affected by an increase of the average target power as the target is operated in transition mode corresponding to N₂-to-Ar flow ratio between 0.28 and 0.31.

Langmuir probe and ion mass spectrometry measurements in Si/Ar/N₂ discharges showed that low N₂-to-Ar flow ratios of ~ 0.16 induce an increased plasma density due to the dissociation and ionization of N₂. As the N₂-to-Ar flow ratio increases to 0.28 reduced plasma densities and ion count rates were observed and ascribed to a temporally poisoned target surface and an altered activation path of N₂. At the same time the SiN_x growth rates decrease and the coating density, residual compressive stress, hardness as well as the Young's modulus increase. SiN_x coatings containing ~50 at.% N show a bond configuration where Si-N bonds prevail and Si-Si bonds are absent. Such coatings were grown in discharges using N₂-to-Ar flow ratios between 0.28 and 0.31. These coatings show a comparatively high density of 2.98 g/cm³ and hardness and of up to ~27.5 GPa and are suited for the further evaluation for bio-medical applications.

Supporting Information

XRD Θ - 2Θ scans of a sputter deposited Si coating and representative SiN_x coatings

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