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Ion energy control via the electrical asymmetry effect to tune coating properties in reactive radio frequency sputtering

Stefan Ries\textsuperscript{1,6}, Lars Banko\textsuperscript{2}, Marcus Hans\textsuperscript{3}, Daniel Primetzhof\textsuperscript{4}, Jochen M Schneider\textsuperscript{3}, Alfred Ludwig\textsuperscript{2}, Peter Awakowicz\textsuperscript{1} and Julian Schulze\textsuperscript{1,5}

\textsuperscript{1} Institute of Electrical Engineering and Plasma Technology, Ruhr University Bochum, Universitaetsstra\ss{}e 150, D-44780, Bochum, Germany
\textsuperscript{2} Institute for Materials, Chair for MEMS Materials, Ruhr University Bochum, Universitaetsstra\ss{}e 150, D-44780, Bochum, Germany
\textsuperscript{3} Materials Chemistry, RWTH Aachen University, Kopernikusstra\ss{}e 10, D-52074, Aachen, Germany
\textsuperscript{4} Department of Physics and Astronomy, Uppsala University, Angstr\ö{}mlaboratorium, Box 516 SE-75120, Uppsala, Sweden
\textsuperscript{5} Department of Physics, West Virginia University, 135 Willey St., WV 26506, Morgantown, United States of America

E-mail: ries@aept.ruhr-uni-bochum.de

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Abstract

A knowledge-based understanding of the plasma-surface-interaction with the aim to precisely control (reactive) sputtering processes for the deposition of thin films with tailored and reproducible properties is highly desired for industrial applications. In order to understand the effect of plasma parameter variations on the film properties, a single plasma parameter needs to be varied, while all other process and plasma parameters should remain constant. In this work, we use the Electrical Asymmetry Effect in a multi-frequency capacitively coupled plasma to control the ion energy at the substrate without affecting the ion-to-growth flux ratio by adjusting the relative phase between two consecutive driving harmonics and their voltage amplitudes. Measurements of the ion energy distribution function and ion flux at the substrate by a retarding field energy analyzer combined with the determined deposition rate $R_d$ for a reactive Ar/N$_2$ (8:1) plasma at 0.5 Pa show a possible variation of the mean ion energy at the substrate $E_{\text{mig}}$ within a range of 38 and 81 eV that allows the modification of the film characteristics at the grounded electrode, when changing the relative phase shift $\theta$ between the applied voltage frequencies, while the ion-to-growth flux ratio $\Gamma_{\text{ig}}/\Gamma_{\text{gr}}$ can be kept constant. AlN thin films are deposited and exhibit an increase in compressive film stress from $-5.8$ to $-8.4$ GPa as well as an increase in elastic modulus from 175 to 224 GPa as a function of the mean ion energy. Moreover, a transition from the preferential orientation (002) at low ion energies to the (100), (101) and (110) orientations at higher ion energies is observed. In this way, the effects of the ion energy on the growing film are identified, while other process relevant parameters remain unchanged.

\textsuperscript{6} Author to whom correspondence should be addressed.
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1. Introduction

Thin film deposition on bulk materials has become an important sector of modern industry to improve and control surface properties of various components [1, 2]. There is a broad domain of applications for high quality films with specific properties, e.g. hard coatings or optical filters. In the microelectronic industry, thin films are deployed as insulator, heat sinking or masking material for plasma etching [3–5]. Even for medical applications antibacterial and biocompatible coatings are synthesized and explored [6]. Physical vapor deposition is the most commonly utilized vacuum-based deposition concept for thin film synthesis [7]. In particular, sputter deposition is a generic term for widely used plasma-based sputter deposition processes, using magnetrons and capacitively coupled plasmas (CCP). In sputter deposition systems, low temperature plasmas with tailored ion energy distribution functions (IEDF) for target sputtering and thin film modification are utilized [8–10]. For industrial demands it is highly relevant to precisely control (reactive) sputter processes for the deposition of high-quality, reproducible thin films [11–13]. Hence, it is essential to investigate these processes with experimental diagnostics and simulations to replace the current empirical approach in industry by a knowledge-based approach resting upon a fundamental understanding of the plasma–surface interaction. The insights into these interactions enable reproducible synthesis of coatings with tailored properties [14, 15].

During the deposition process the growing film is exposed to the plasma and a total energy per deposited atom \( E_{\text{pda}} \) is transferred to the film. This parameter is defined as the sum of the energies of all incident particles per deposited atom; i.e. the sublimation energy, kinetic energy of sputtered particles, of bombarding ions, of reflected neutrals, of plasma irradiation, thermal heating, etc [2, 16–18]. Besides external substrate heating, a significant amount of energy incorporation results from ion bombardment. \( E_{\text{pda}} = \Psi_0/\Gamma_{gr} \) describes the energy flux delivered by ions to the film normalized to the growth flux \( \Gamma_{gr} \) [2, 19]. In most investigations global process parameters such as the neutral gas pressure, power input, target-to-substrate distance (TSD), gas mixture ratio, and substrate bias (DC, pulsed DC, or RF) are varied [20, 21]. As a drawback of such strategies a distinct correlation between the plasma and the film growth is very difficult to identify, which leads to the risk of misinterpretations, as several important plasma parameters (e.g. ion energy and flux) are altered in parallel, which has further consequences on both the sputtering process and the film growth.

For a distinct plasma-surface correlation only a single plasma parameter should be varied, while all other parameters should be held constant. Following Petrov et al the ion energy \( E_i \) and the ion-to-growth flux ratio \( \Gamma_i/\Gamma_{gr} \) have to be considered separately since coating properties may vary even for an identical value of \( E_{\text{pda}} \) [19, 22]. Especially, decoupling the ion energy from the ion flux or from the ion-to-growth flux ratio, is highly desired [6]. Adibi et al showed that the deposition of highly dense films without introducing high intrinsic stress [23, 24] requires high ion fluxes exceeding 2 mA cm\(^{-2}\) at ion energies below 100 eV [25]. On the other hand, ion energies above 100 eV allow the improvement of mechanical properties of thin films such as the hardness [26]. The deposition rate determined by the electron density and the ion flux is desired to be above 10 \( \mu \text{m h}^{-1} \) for enhanced processing rates on industrial production time scales [27].

Direct current magnetron sputtering (DCMS) is the most established and explored sputtering method using a strong magnetic electron confinement resulting in high ionization rates in target vicinity and high deposition rates for metallic films with excellent quality [28, 29]. However, reactive DCMS processes struggle with nonlinear hysteresis effects [30–34], deposition rate reduction due to target poisoning, and arcing events causing local target fusing and film defects due to charging of insulating compound layers. Pulsed DCMS stabilizes the reactive deposition process with a reduced sensitivity to undesired arcing events with the advantage to synthesize high quality oxide and nitride films at high rates comparable to metallic films deposited by DCMS [28, 35–37]. High power pulsed magnetron sputtering (HPPMS [37, 38]) is characterized by lower repetition frequencies than pulsed DCMS and exhibits very high plasma densities as well as a high degree of ionized sputtered material of 50%–90% [29]. For example, ionized sputtered metal atoms can be accelerated to moderate kinetic energies for tuning their subplantation depth [39–41] in the surface of metastable transition metal nitride films to control the phase formation [42, 43]. However, HPPMS suffers from the drawback of reduced deposition rates (30%–80% of DCMS deposition rates) caused by self-sputtering, gas rarefaction and a nonlinear dependence of the sputter yield on the target/cathode voltage [44–47]. Classical magnetron systems with static and planar targets have the disadvantage of a low target material utilization, because only the racetrack area below the high density plasma torus is sputtered [48–51]. However, rotating magnetic configurations behind the target were developed [52, 53] and improved with a target utilization up to 77%–86.3% [54, 55]. Another magnetron setup was proposed using cylindrical target tubes rotating around an inner placed static magnetic configurations [56]. In this case, the target tube rotates beneath the stationary plasma volume and is uniformly sputtered across the whole lateral surface with the result of an enhanced target utilization up to 90% [57]. These systems are widely used for industrial coating processes, especially in glass coating processes on large-areas with good homogeneity (up to 20 m\(^2\) [58]).

Indeed, ferromagnetic target materials, such as iron, short-circuit the external magnetic field and reset the advantage of a high plasma density zone, which strongly reduces the deposition rate [59]. Axial gradients in electron density from the target towards the substrate lead to a reduced ion flux to the substrate compared to the target bombardment [28]. In order to solve this problem, magnetrons have to be rebuilt with partially ‘opened’
magnetic field lines directed to the substrate (unbalanced MS [28, 60]) to reach a compromise between a good electron confinement and an increased ion flux onto the substrate. Usually, external substrate biasing is applied to compensate the lack of ion flux by enhanced ion energies to reach the required energy incorporation into the film [28].

The decoupling of ion energy and the ion flux or ion-to-growth flux ratio is limited in magnetron sources and only realizable using more complex external magnetic fields to control the ion flux and the external substrate biasing to adjust the ion energy [60–62]. In reactive DCMS an externally applied DC substrate bias is not applicable, as it results in arcing events on the insulating compounds [63]. Pulsed DC or RF substrate biasing in turn influences the plasma density and ion energy again.

By contrast, the separate control of the ion energy and ion-to-growth flux ratio is tunable in ion beam assisted deposition processes (IBAD). In Seitzman et al the ion-to-growth flux ratio was varied at a constant ion energy of 1 keV [64]. Also, stoichiometric thin films can be synthesized controlling the ion-to-growth flux ratio in IBAD systems [65].

CCP driven by a single radio frequency (1fCCP), usually 13.56 MHz, are widely used for a variety of technological applications such as sputter deposition of functional coatings, since they offer a broad variety of advantages over the previously presented types of discharges [6, 66]: CCPs reach a target utilization of almost 100%, allow sputtering of all target materials (even ferromagnetic targets), result in a low thermal load to sensitive surfaces, offer a comparably homogeneous plasma bulk in axial direction with similar ion fluxes to the target and the substrate and there are no arcing events during reactive sputtering. However, CCPs struggle with lower deposition rates compared to magnetrons. If the wavelength of the excitation frequency is smaller or comparable to the range of the chamber dimension, electromagnetic effects lead to spatial inhomogeneities of the plasma density and, therefore, of the deposition rates across large-area surfaces [1, 67–71].

Since the electrical asymmetry effect (EAE) was proposed theoretically [63, 72] and proven experimentally [73–77] a fully separate control of both ion energy and ion flux in dual-frequency CCPs (2fCCP) can be achieved. In order to employ the EAE, a CCP is powered by a fundamental radio frequency (RF) and its second harmonic. By tuning the relative phase angle $\theta$ between the two excitation frequencies the DC self-bias as well as the mean voltage drop across the sheath adjacent to the target and the substrate can be controlled. With the EAE no additional external substrate biasing is needed. Using $\theta$ as control parameter the ion energies at both electrodes can be adjusted independently from the ion flux, while keeping the voltage amplitudes constant. Driving a RF plasma with the superposition of consecutive multiple harmonics of a fundamental frequency and adjusting their amplitudes and phases is generically termed as voltage waveform tailoring (VWT). This technique enables the application of any desired driving voltage waveform to customize fluxes and energy distribution functions of ions at the target and substrate. Also the power absorption of electrons as well as their energy distribution function can be controlled. Several publications demonstrated numerous advantages using VWT to precisely tune plasma processes [78–84].

In this work, a novel large-area multi-frequency CCP (MFCCP) driven by 13.56 and 27.12 MHz is presented and utilized for the synthesis of AlN films. The advantage in this reactive sputter process setup is the application of the EAE in order to decouple the energy and the flux of the ions bombarding the target and the forming film at the substrate, respectively. The separate control of both parameters in this large-area MFCCP is validated by measurements with a retarding field energy analyzer (RFEA, Semion Single Sensor by Impedans Ltd.) at the center of the grounded electrode at different relative phase angles $\theta$. High voltage probe measurements (HVP, Tektronix P6015A) in combination with an EAE model enable the determination of the time-averaged sheath voltage drop in front of the grounded electrode and a comparison with the RFEA results.

Using the example of AlN thin film growth, measurements of the ion flux, ion energy and deposition rate show that the mean ion energy can be varied in a broad range at a constant ion-to-growth flux ratio. Under these conditions and based on several surface diagnostics (ToF-ERDA, XRD, STEM, indentation and stress sensors: section 2.5) the ion energy as the only varied plasma parameter is demonstrated to influence AlN film properties such as the preferential orientation, growth morphology, residual stress, as well as the elastic modulus and hardness. In summary, we demonstrate the ability of multi-frequency CCPs to be a highly flexible coating and sputtering system allowing for a precise control of plasma parameters and the resulting coating properties. This work focuses on the fundamental investigation to control separately important plasma parameters, where the film quality and the absolute deposition rate played a minor role, but will rather be of high relevance in our future work.

The paper is structured in the following way: section 2 introduces the experimental setup, the applied diagnostics and the analytic model to calculate the time-averaged sheath voltages at both electrodes. The results and discussions are presented in section 3 and the decoupling of the mean ion energy from the ion flux as well as the decoupling of the mean ion energy from the ion-to-growth flux ratio are discussed. Further, the influence of the varied mean ion energy on the investigated properties of the deposited AlN films at a constant ion-to-growth flux ratio are addressed. Finally, conclusions are drawn in section 4.

2. Experimental setup, diagnostics and models

2.1. MFCCP setup and conditions

The setup of the MFCCP consists of a stainless steel cubic vacuum chamber with an edge length of 800 mm and a height of 650 mm. The plasma is generated between the upper powered target electrode and the lower grounded substrate electrode. Both electrodes have a diameter of 490 mm each surrounded by a stainless steel grounded shield in 2 mm distance. The electrode gap is 75 mm. The plasma-facing surface of the grounded electrode is also made of stainless steel. The vacuum chamber as well as the electrodes and their
inner structure are custom-designed and built by the company Pfeiffer Vacuum. A grounded cylindrical stainless steel mesh (mesh size 1 mm) surrounds both electrodes and the volume between the electrodes at a radial distance of 15 mm from the grounded electrode shielding. Its purpose is to confine the active plasma volume within the electrode spacing (black dashed line, figure 1).

For the deposition of AlN films a planar circular aluminium target (Al) with a purity of 99.99% is sputtered in an Ar/N₂ (8:1) gas mixture with 11% nitrogen. The target is mounted onto the water-cooled powered stainless-steel electrode. No magnets are placed behind the target in this setup, i.e. the EAE in unmagnetized plasmas is investigated here. A classical magnetron magnetic field topology would cause inhomogeneous sputter rates (racetrack) and a short-circuited magnetic field in front of ferromagnetic targets. The purity of the applied working gases, Ar and N₂, is 99.999%. The gas inlet is realized by 24 holes with a diameter of \(d_h = 1\) mm uniformly distributed across the target for a homogeneous gas distribution within the chamber. Prevention of plasma penetration into these inlets is ensured, if the hole diameter is smaller than two times the plasma sheath thickness \(s_p\) at the target (\(d_h < 2s_p\)). This criterion was previously checked by calculating \(s_p\) for collisionless process conditions (Child-Langmuir Law) with different electron temperatures \(T_e\), electron densities \(n_e\) as well as mean sheath voltages \(\phi_s\). In fact, this criterion is fulfilled and plasma penetration into the gas inlets is not observed under any discharge conditions studied.

All reactive Ar/N₂ plasma processes are operated at a constant total gas flow of \(F_l = 45\) sccm with \(F_{Ar} = 40\) sccm and \(F_{N₂} = 5\) sccm. The total gas pressure is kept constant at \(p_t = 0.5\) Pa. The base pressure of less than \(5 \times 10^{-5}\) Pa within the chamber is sustained by two parallel-connected turbo molecular pumps (Turbovac MAG W 600 iP, Leybold GmbH). The prevacuum is generated by a roots pump (RUVAC WSU 501, Leybold GmbH) and rotary vane pump (Trivac D 65 BCS, Leybold GmbH), which are series-connected with the turbo molecular pumps.

The AlN films are deposited on microcantilever stress sensor chips (6.6 × 7.4 mm²) with a Si₃N₄ surface for residual stress measurements [85] and on thermally oxidized silicon wafers (Si + 1.5 μm SiO₂, 10 × 10 mm²) with a photolithographically applied cross pattern of photo-resist (named as ‘cross wafer’) to create a precise lateral interface between substrate and film for thickness measurements by surface profilometry (XP2, Ambios Technology). Both substrates are positioned besides each other at the center of the grounded electrode.

The grounded electrode and the coated substrates are not heated externally. The substrate temperature is measured by a PT100 thermocouple to be \(T_s \approx 50°\) (see table 1, section 3.2).

With a deposition time of \(t_d = 6–9\) h and film thicknesses of 520–630 nm, depending on the process conditions, the deposition rate is relatively low. On the one hand, in reactive sputter processes with an Al target partially covered with an AlN compound the total sputter yield is reduced compared to the sputtering of a pure Al target [86, 87]. On the other hand, a limited ion flux may also limit the sputter flux and finally the deposition rate. In general, the processing rate could be increased using a third higher frequency (generator + impedance matching available: 60 MHz, agilo 6060w MC10, 6 kW, YXLON International). Nevertheless, the main investigations are related to the EAE and its influence on the film properties, while the

![Figure 1. Draft of the experimental setup.](image-url)
magnitude of the deposition rate played a minor role and a third excitation frequency is not used for the presented experiments.

For the application of the EAE the MFCCP is powered by 13.56 MHz and its second harmonic of 27.12 MHz. Both excitation frequencies are generated by individual RF generators (13.56 MHz: cito1356, 2 kW, YXLON International, 27.12 MHz: Cesar VM2715AW 400 V 3P, 1.5 kW, Advanced Energy) and are phase-locked to each other. Each RF generator is connected to the upper electrode via a corresponding impedance matching network for the specific frequency (13.56 MHz: VarioMatch VM5000W, 5 kW, L-type; 27.12 MHz: VarioMatch VM2715AW, 1.5 kW, L-type, Advanced Energy).

An additional bandpass filter (custom-designed by Aurion), which prevents power dissipation in each RF circuit by the other frequency, is located between the matching networks and the electrode (figure 1). The applied voltage waveform is described by

$$\tilde{\phi}(t) = \tilde{\phi}_{13} \cos(2\pi f_1 t + \theta) + \tilde{\phi}_{27} \cos(2\pi f_2 t)$$

with $\tilde{\phi}_{13,27}$ as the applied voltage amplitudes of each frequency with a chosen constant amplitude ratio of $\tilde{\phi}_{13}/\tilde{\phi}_{27} = 2.3$ to optimize the EAE [88]. The relative phase shift $\theta$ between both frequencies is a process control parameter to change the resulting voltage waveform at the electrode. $\theta$ is directly changed using a function generator (Tektronix AFG3202), which triggers both generators. The applied voltage signal is measured by a Tektronix P6015A HVP (see section 2.4). The degree of symmetry of a CCP is described by the symmetry parameter [63]

$$\varepsilon = \left| \frac{\tilde{\phi}_{\text{sg,max}}}{\tilde{\phi}_{\text{sp,max}}} \right| \approx \left( \frac{A_p}{A_g} \right)^{\frac{1}{3}} \frac{\pi_{\text{sg}}}{\pi_{\text{sp}}}$$

with $\tilde{\phi}_{\text{sg,max}}$ and $\tilde{\phi}_{\text{sp,max}}$ as the voltage drop across each sheath during maximum sheath expansion, $A_p$ as the area of the powered electrode and $A_g$ as the area of the grounded surfaces (counter electrode plus mesh). Furthermore, $\varepsilon$ depends on the mean ion densities in each sheath, $\pi_{\text{sp}}$ and $\pi_{\text{sg}}$. A geometrically induced DC self-bias will be generated, if the surface area of the powered electrode is different from that of the total grounded surface. In most cases the powered electrode is smaller than the grounded surface and the symmetry parameter will be below 1 resulting in a large mean voltage drop $[\tilde{\phi}_{\text{sg}}]$ across the plasma sheath in front of the target compared to the sheath voltage drop in front of the grounded electrode $[\tilde{\phi}_{\text{sp}}]$ [89–91]. Following the expression given by [63]

$$\eta = -\frac{\phi_{\text{max}} + \varepsilon \phi_{\text{min}}}{1 + \varepsilon} = \left| [\tilde{\phi}_{\text{sg}}] - [\tilde{\phi}_{\text{sp}}] \right|$$

a negative DC self-bias $\eta$ is generated in this scenario [6, 89]. As a consequence, the target is bombarded by energetic ions of several hundreds of eV, which are required for sputtering or etching. The grounded electrode is exposed to ions of low to intermediate energies of 10–100 eV in an effort to affect structure evolution during thin film growth. Via the EAE the DC self-bias can be controlled electrically tuning $\theta$. By varying this phase shift in equation (1), the resulting voltage signal is tuned from a waveform with equal positive and negative absolute extremes $[\phi_{\text{max}}] = [\phi_{\text{min}}]$ to a waveform with clearly different absolute positive and negative extremes $[\phi_{\text{max}}] = [\phi_{\text{min}}]$ (figure 2). This kind of VWT allows a precise control of the DC self-bias as well as the mean sheath voltages $[\phi_{\text{sg}}]$ and $[\phi_{\text{sp}}]$ [63]. As a consequence, the mean ion energy onto the target, $E_{\text{ip}}$, and substrate, $E_{\text{isp}}$, can be precisely adjusted with this method without any demand of an additional externally applied voltage source. Also the IEDF can be shifted alongside the energy axis and its structure can be tailored for specific applications in material surface processing [8, 79–81, 92]. Finally, via the EAE a fully separate control of the ion energy bombardment from the ion flux impacting the surfaces is possible [63, 72, 93–97].

### 2.2. Model to calculate the time-averaged sheath voltages at both electrodes

For an analysis of the EAE in the MFCCP the time-averaged sheath voltage at the substrate shall be compared with the ion energies at the grounded electrode measured by a RFEA as a function of $\theta$. Primarily, the time-averaged voltage drop across the sheaths has to be computed from absolute HVP measurements (figure 1) using an analytical model applied in several multi-frequency studies as follows [63, 73, 75, 76, 98–100]: first, the voltage drop across the sheath has to be expressed as a function of the net charge in the respective sheath. A central assumption is, that the total net charge in the plasma. $Q_{\text{tot}}$, is completely located in both sheaths with $Q_{\text{tot}} = Q_{\text{sp}}(t) + Q_{\text{sg}}(t) = \text{const}$. The net charges located in the powered and grounded sheath $Q_{\text{sp}}(t)$ and $Q_{\text{sg}}(t)$ are a function of time within the fundamental RF period. Based on the assumption of a quadratic charge voltage relation, it is possible to find an expression for the temporal behaviour of

<table>
<thead>
<tr>
<th>$\phi_{13}$ (V)</th>
<th>$\phi_{27}$ (V)</th>
<th>$\theta$ ($^\circ$)</th>
<th>$p_t$ (Pa)</th>
<th>$T_e$ (°C)</th>
<th>$E_{\text{ip}}^m$ (eV)</th>
<th>$E_{\text{isp}}^m$ (eV)</th>
<th>$E_{\text{isp}}^m$ (eV)</th>
<th>$\eta$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>344</td>
<td>149</td>
<td>0</td>
<td>0.5</td>
<td>—</td>
<td>38</td>
<td>47</td>
<td>358</td>
<td>–312</td>
</tr>
<tr>
<td>348</td>
<td>151</td>
<td>15</td>
<td>0.5</td>
<td>42.2</td>
<td>47</td>
<td>54</td>
<td>349</td>
<td>–295</td>
</tr>
<tr>
<td>372</td>
<td>161</td>
<td>30</td>
<td>0.5</td>
<td>—</td>
<td>53</td>
<td>61</td>
<td>350</td>
<td>–290</td>
</tr>
<tr>
<td>425</td>
<td>184</td>
<td>45</td>
<td>0.5</td>
<td>—</td>
<td>57</td>
<td>64</td>
<td>358</td>
<td>–294</td>
</tr>
<tr>
<td>501</td>
<td>217</td>
<td>60</td>
<td>0.5</td>
<td>59.8</td>
<td>81</td>
<td>96</td>
<td>350</td>
<td>–254</td>
</tr>
</tbody>
</table>
the voltage drop across the sheath at the powered and grounded electrode [100]:

\[
\phi_{sp}(t) = -\phi_{tot} \cdot q_{sp}^2 - \langle \phi_{sp}^B \rangle = -\phi_{tot} \\
\left[ -\varepsilon q_{tot} + \sqrt{\frac{\varepsilon q_{tot}^2 - (1 - \varepsilon)^{\frac{\eta + \dot{\delta}(t)}{\varepsilon}}}{1 - \varepsilon}} \right]^2 - \langle \phi_{sp}^B \rangle
\]

\[
\phi_{sg}(t) = \varepsilon \phi_{tot} \cdot q_{sg} + \langle \phi_{sg}^B \rangle = \varepsilon \phi_{tot} \\
\left[ q_{tot} - \sqrt{\frac{\varepsilon q_{tot}^2 - (1 - \varepsilon)^{\frac{\eta + \dot{\delta}(t)}{\varepsilon}}}{1 - \varepsilon}} \right]^2 + \langle \phi_{sg}^B \rangle
\]

(4)

(5)

with the sum of the applied voltage amplitudes \( \phi_{tot} \). The charges in the grounded and powered electrode sheath \( q_{sg} = Q_{sg}/Q_0 \) and \( q_{sp} = Q_{sp}/Q_0 \) as well as the total net charge \( q_{tot} = Q_{tot}/Q_0 = \sqrt{(\hat{\phi}_{max} - \hat{\phi}_{min})/\varepsilon} \) are normalized to \( Q_0 = A_p \sqrt{2e\varepsilon_0 \pi \rho_{sp} Q_0} \). The constant floating potential \( \langle \phi_{sg}^B \rangle \) can be found from the balance of the ion flux and the electron flux to the grounded electrode on time average \( \langle \Gamma_{sg} \rangle = \langle \Gamma_{eg} \rangle \): \n
\[
\langle \phi_{sg}^B \rangle = \frac{k_B T_e}{e} \ln \left[ T_{if} \frac{m_i}{2\pi m_e} \int_0^{T_{if}} \exp \left( -\frac{-e\phi_{sg}(t)}{k_B T_e} \right) dt \right] \quad \langle \phi_{sp}^B \rangle
\]

\( \hat{\phi}_{max} \) depends on the electron temperature \( T_e \). For the calculation of the floating potential the electron temperature is assumed to be constant: based on the uniform density discharge model by Lieberman [6], \( T_e \) is determined by the particle balance equation and dependent on the gas density and TSD. The latter is held constant at 75 mm for all conditions as well as the total gas pressure at 0.5 Pa, which determines the gas density. At the same time, \( T_e \) is independent of the electron density in the discharge center, while the latter one is dependent on the power balance equation. Therefore, no variation of \( T_e \) is expected during changing the relative phase shift \( \theta \) or an increased power input. The absolute value of \( T_e \approx \) 3 eV is chosen according to measurement results at similar conditions in previous experiments [101]. The time-averaged voltage drop across the grounded sheath is

\[
\langle \phi_{sg}^B \rangle = f_{13} \cdot \int_0^{T_{13}} \phi_{sg}^B(t) \, dt.
\]

The floating potential \( \langle \phi_{sp}^B \rangle \) at the powered electrode is negligible compared to the magnitude of the time averaged value of \( \phi_{sp}(t) \) as most of the total voltage drops across the powered sheath in asymmetric CCPs. The temporal evolution and the time-average of both sheath voltage drops can, thus, be obtained from \( \eta, \hat{\phi}_{max}, \hat{\phi}_{min}, \hat{\phi}_{13}, \hat{\phi}_{27} \), which are known from absolute voltage measurements with a HVP. While \( \langle \phi_{sg}^B \rangle \) is compared to RFEA measurements at the grounded electrode (section 3.1), \( \langle \phi_{sp}^B \rangle \) cannot be directly compared to RFEA measurements at the powered electrode as parts of the RFEA...
setup would cover the gas inlets in the target. Nevertheless, the analytical model of the EAE, which is used here, has been validated in other publications and was proven to be able to predict the sheath voltage waveforms at both electrodes correctly [77, 100].

2.3. Retarding field energy analyzer

IEFDs, \( f(E_{ig}) \), are measured at the grounded electrode by a RFEA [102–104] Semion™ single sensor from Impedans [105–108]. The ion flux, \( \Gamma_{ig} \), and the mean ion energy, \( E_{ig}^m \), at the center of the grounded electrode are calculated from the IEDF via:

\[
\Gamma_{ig} = \int_0^{E_{\text{max}}} f(E_{ig}) \, dE_{ig} \tag{8}
\]

\[
E_{ig}^m = \frac{1}{\Gamma_{ig}} \int_0^{E_{\text{max}}} f(E_{ig}) \cdot E_{ig} \, dE_{ig}. \tag{9}
\]

The energy resolution of the RFEA is \( \pm 1 \) eV. In order to validate the influence of the varied sheath voltage on the ion bombardment using the EAE, a characteristic ion energy is associated with the time-averaged sheath voltage drop \( e \langle \phi_{ig}^\text{fl} \rangle \) [107, 109]. If a single peak IEDF is measured, the ion energy at the maximum of \( f(E_{ig}) \), \( E_{ig}^\text{fl} \), is \( e \langle \phi_{ig}^\text{fl} \rangle \). For a bimodal structure the intermediate energy value of the two peak energies is compared with \( e \langle \phi_{ig}^\text{fl} \rangle \).

2.4. Calibration procedure for absolute voltage measurements

The applied voltage waveform is important for the electrical characterization and the reproducible adjustability of the plasma process. It is measured by a Tektronix P6015A HVP. The driving voltage amplitudes, \( \hat{\phi}_{13} \) and \( \hat{\phi}_{27} \), and the phase shift between the two harmonics, \( \theta \), are determined by a Fourier analysis of the measured superposition. The direct access to the powered electrode during the plasma process is prohibited and the voltage is measured at the electrode backside (figure 1). Due to interference on the cable connected to the powered electrode [73], \( \hat{\phi}_{13} \), \( \hat{\phi}_{27} \), and \( \theta \) are different at the center of the powered electrode and at the backside position. Therefore, \( \hat{\phi}_{13} \), \( \hat{\phi}_{27} \), and \( \theta \) have to be calibrated in the following way: a plasma is operated at the same pressure (0.5 Pa) and gas mixture (Ar:N2 = 8:1) as it is used for the actual deposition conditions, but is only powered by 13.56 MHz. The driving voltage amplitude, \( \hat{\phi}_{13} \), one of the input parameters for the EAE model, is varied as fitting parameter until the time-averaged sheath voltage drop at the grounded electrode, \( e \langle \phi_{ig}^\text{fl} \rangle \), which is calculated using the equations (5) and (7) from the EAE model (section 2.2), equals the measured peak ion energy, \( E_{ig}^\text{fl} \). Then, the calibration factor is the ratio of the fitted driving voltage amplitude at the center of the plasma-facing powered electrode to the non-calibrated one measured at the backside. This procedure is also done for \( \hat{\phi}_{27} \) at 27.12 MHz. The phase shift correction is found for the dual-frequency condition. \( \theta \) is varied at constant \( \hat{\phi}_{13} \) and \( \hat{\phi}_{27} \), until the measured dc self-bias reaches its minimum. In this case, the voltage waveform at the center of the powered electrode has a phase shift of 0°, which is compared to the phase shift of the measured signal at the electrode backside. The reliability of this method is shown in section 3.

2.5. Characterization of AlN thin films

The chemical composition of deposited AlN films is investigated by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) using a primary beam of 36 MeV \( {\beta}^+ \) ions at the tandem accelerator laboratory of Uppsala University, Sweden. The angle between the detector telescope and the primary beam is 45°, with both incidence and exit angle of the beam and the detected species at 22.5° with respect to the sample surface. Time-energy coincidence spectra are obtained by a combination of a thin carbon foil time-of-flight setup and a gas ionization detection system [110]. The obtained spectra are evaluated using the CONTES code [111]. Systematic uncertainties are on the order of \( \pm 10\% \) (relative deviation), while statistic uncertainties are on the order of \( \pm 1\%–2\% \) (relative deviation) for the major constituents Al and N. A detailed analysis can be found in Baben et al and its supplements [112].

The morphology as well as the thickness of AlN thin films are examined by scanning transmission electron microscopy (STEM). Thin lamellae are prepared by focused ion beam techniques utilizing Ga ions within a FEI Helios Nanolab 660 dual-beam microscope. For each film, the region of interest is protected against Ga contamination by application of a Pt protection layer with length, width and height of 10, 1.5 and 1 μm, respectively. Lamella preparation includes lift-out of the region of interest employing an EasyLift manipulation needle, mounting on an Omniprobe 5-post Cu grid and thinning of the lamella to a final thickness <100 nm. A STEM III detector is used to obtain bright-field cross-section micrographs of the AlN lamellae at an acceleration voltage and current of 30 kV and 50 pA, respectively. The uncertainty of the measured thickness values is \( \pm 20 \) nm.

The residual stress is determined using microcantilever sensors [85]. Initially, the flat cantilevers obtain no residual stress. After the deposition the degree of curvature caused by the grown film is analyzed \textit{ex situ} using digital holographic microscopy [85].

The intrinsic film stress is calculated using the Stoney-equation [113]. Phase formation and preferential AlN orientations are investigated by x-ray diffraction (XRD) using a Bruker D8 Discover diffractometer with an x-ray source (50 W, \( \lambda \)S microfocus) with Cu–Kα radiation and a 2D-detector (VANTEC 500). 2D-frames are measured to cover a 2θ range from 25° to 70°. The incident angle is set to fulfill the Bragg–Brentano geometry.

Elastic modulus as well as hardness are measured by nanoindentation utilizing a Hysitron TI-900 TribolIndenter. A diamond Berkovich tip with 100 nm radius is used with a maximum load of 2 mN, resulting in maximum contact depth values of 33 ± 3 nm. 30 individual load-displacement curves are obtained per sample. Indentation moduli are determined from the unloading part of load-displacement curves.
according to the method of Oliver and Pharr [114]. The elastic modulus is calculated from the measured indentation modulus with the Poisson’s ratio of $\nu = 0.179$ [115].

3. Results and discussion

3.1. Control of the energy flux bombardment

3.1.1. Decoupling of ion energy and ion flux. In order to verify the ability of the EAE to decouple the ion energy and flux at the grounded electrode in the large-area MFCCCP, an Ar/N$_2$ (8:1) plasma at 0.5 Pa is investigated. The relative phase shift $\theta$ is varied from 0° to +90° at constant voltage amplitudes of $\phi_{13} = 344$ V and $\phi_{27} = 149$ V with a ratio of 2.3. The resulting voltage drop across each sheath is calculated as a function of time within the fundamental RF period from the measured voltage signals using the model introduced in section 2.2 (equations (4) and (5)) and is depicted in figure 3 (the floating potential is not included). The sheath at the grounded electrode starts with its maximum voltage drop at $t = 0$ ns and fully collapses after a quarter of the RF period of the lowest excitation frequency. For $\theta = 0°$ the grounded sheath exhibits a weakly pronounced local maximum of a few volts at $t = 37$ ns (not visible in figure 3), because $\phi_{sp}(t)$ locally decreases. After three quarters of the RF period of the lowest frequency, the sheath expands again to full width at $t = 74$ ns. If $\theta$ is increased, the temporal dynamics of $\phi_{sp}(t)$ is continuously modified from a single voltage maximum at $\theta = 0°$ to a double peak structure for $\theta = 90°$ within one fundamental RF period. This sheath is collapsed only for about a quarter of a fundamental RF period at $\theta = 90°$. The temporal dynamics of $\phi_{sp}(t)$ is contrary to the sheath at the grounded electrode. Also, the voltage drop magnitude across the powered sheath is much higher than $\phi_{sp}(t)$, since the system is always geometrically asymmetric.

Apparently, with the EAE a direct control of the voltage drop across both sheaths is possible. In figure 4, the influence of the varied voltage drop across the sheath at the grounded electrode on the measured IEDF can be observed directly. The IEDF is shifted to higher energies due to the increased local sheath voltage, which is adjusted by the phase shift.

Another feature is the modification of the IEDF shape: the single peak IEDF at $\theta = 0°$ slightly turns into a bimodally structured IEDF as $\theta$ is increased to 90°. Single peak IEDFs will be obtained, if the transit time of the ions crossing the sheath is much larger than the RF-period of the lowest applied frequency ($\tau_i \gg T_{RF}$). Then the ions experience an acceleration by the time-averaged electric field in the sheath [107, 109, 116, 117]. Bimodal IEDFs will develop, if $\tau_i$ is on the order or shorter than the RF period ($\tau_i \leq T_{RF}$). During this shorter transit the ions react to the time dependent electric field and the IEDF forms a more complex shape with several energy peaks. In the simplest case a low and a high energy peak are obtained. Therefore, the ion transit time seems to be reduced with increasing phase shift as the ion acceleration is enhanced.

In figure 5 the calculated time-averaged sheath voltage drop $\langle \phi_{sp} \rangle$, the mean ion energy $E_{ig}^{\text{m}}$ and the peak ion energy $E_{ig}^{\text{p}}$ at the grounded electrode are plotted for various $\theta$ between −105° and +105° at the same process conditions.

The mean ion energy $E_{ig}^{\text{m}}$ and the peak ion energy $E_{ig}^{\text{p}}$ can be controlled in a broad range between 38 eV (47 eV) at $\theta = 0°$ up to 87 eV (104 eV) at $\theta = 90°$. Therefore, the ion energy can be more than doubled. The calculated sheath voltage drop matches the measured peak ion energy for different $\theta$ with high accuracy. For higher relative phases the discrepancy between both parameters is within the range of about 5% especially for $\theta = \pm 90°$. In figure 4, each IEDF exhibits a slight low energetic tail below the peak structure, which can be attributed to charge exchange collisions between ions and atoms within the sheath causing a redistribution of energetic ions to lower energy regimes [100, 107]. The sheath width increases with increasing $\theta$ and more collisions might take place with a higher effect on $E_{ig}^{\text{p}}$. Also, broadening effects by the RFEA apparatus, for instance.

![Figure 3](image-url) Temporal dynamics of the voltage drop across the powered sheath $\phi_{sp}(t)$ and grounded sheath $\phi_{sg}(t)$ for different $\theta$ ($\phi_{13} = 344$ V: 149 V = 2.3 $\pm$ $\theta$; 0.5 Pa Ar/N$_2$ (8:1)). The floating potential is excluded.

![Figure 4](image-url) Measured IEDF at the center of the grounded electrode $f(E_{ig})$ for different $\theta$ ($\phi_{13} = 344$ V: 149 V = 2.3 $\pm$ $\theta$; 0.5 Pa Ar/N$_2$ (8:1)).
energy dependent grid transparency, might affect the distribution function and, therefore, the energy peak values [107].

Both, the measured ion energy and the calculated mean sheath voltage exhibit slightly, but consistently different values for phase shifts from $+15^\circ$ to $+90^\circ$ compared to the values measured for the range of $-15^\circ$ to $-90^\circ$. When the relative phase shift is changed, the impedance matching of both excitation frequencies also slightly changes. This behaviour is compensated by small iterative adjustments of the phase shift and both driving voltage amplitudes ($\hat{\phi}_{13}, \hat{\phi}_{27} = 2.3$). This procedure can cause slight distortions of the voltage waveform at the electrode, which, in turn, can lead to the observed effect on the ion energy. Despite all simplifications made in the EAE model to calculate the sheath voltages and the uncertainties of the RFEA measurements, $e(\hat{\phi}_{ig})$ matches the measured peak ion energy well and allows a prediction of expectable ion energies for the MFCCP by only measuring the total voltage signal.

Finally, in figure 6 the ion flux measured by the RFEA at the grounded electrode center is plotted for the same variation of $\theta$ and exhibits a nearly constant behaviour with only 4% alteration.

In general, the reproducibility of the measured ion flux is about ±4%, if the chamber is not vented between two measurement days. If the chamber is vented between two measurement days, the ion flux reproducibility is about ±9% under the same discharge conditions. The reproducibility of the measured ion energies is about ±4%, if the chamber is not vented between two measurement days and ±12% if the chamber is vented between two measurement days. Summarizing, the nearly constant ion flux together with the large range of ion energy variation demonstrates the possibility to fully decouple both plasma parameters from each other using the EAE in this large-area MFCCP.

3.1.2. Decoupling of ion energy and ion-to-growth flux ratio.

A full decoupling of the ion energy $E_{ig}$ and the ion-to-growth flux ratio $\Gamma_{ig}/\Gamma_{gr}$ is highly desired to control the plasma process and the resulting coating properties. These two parameters describe the contribution of the incorporated amount of energy delivered by ions per deposited atom

$$E_{pda,i} = E_{ig} \cdot \frac{\Gamma_{ig}}{\Gamma_{gr}}.$$

In order to clarify how these two plasma parameters influence the film properties, one of them has to be kept constant [118].

In the present work, the ion impact energy onto the growing film is varied using the EAE. Therefore, $\Gamma_{ig}/\Gamma_{gr}$ has to be kept constant as a function of $\theta$. However, it will be shown, that only the variation of $\theta$ will not be sufficient to keep $\Gamma_{ig}/\Gamma_{gr}$ constant, because the growth flux, $\Gamma_{gr}$, at the grounded electrode depends on the ion flux, $\Gamma_{ip}$, and the ion energy, $E_{ip}$, onto the target, since these parameters determine the sputter rate. The film forming growth flux $\Gamma_{gr}$ is a function of the deposition rate:

$$\Gamma_{gr} = \frac{\rho_{AlN} N_{N}}{M_{AlN}} \cdot R_{d}$$

with the Avogadro constant $N_A$, the film density $\rho_{AlN}$ and the molar mass $M_{AlN}$ of the film [119, 120]. The deposition rate $R_{d} = d_{th} / t_{th}$ scales with the measured film thickness, $d_{th}$, and the deposition time, $t_{th}$. Following the approaches of the Berg model for reactive sputtering processes [30, 31], the film forming growth flux $\Gamma_{gr}$ consists of the flux of deposited Al, $\Gamma_{Al}^{N}$, and the total flux of adsorbed nitrogen, $\Gamma_{gr}^{N}$, contributing to the film growth. The latter consists of sputtered N atoms from the target, $\Gamma_{gr}^{N,s}$, chemisorbed nitrogen from the surrounding gas,
The contribution of each partial flux from different N sources plays a minor role here, as the synthesized films are adjusted to be nearly stoichiometric, which will be shown in section 3.2 later. For a stoichiometric AlN film, the flux of deposited Al at the substrate equals approximately the total flux of adsorbed nitrogen contributing to the film. In addition, \( \Gamma_{\text{Al}}^{\text{fl}} \) corresponds to the Al sputter flux \( \Gamma_{\text{Al}}^{\text{s}} \) originating from the target and mainly directed towards the substrate, which is weighted with the effective transport coefficient \( c_{\text{Al}} \) considering the amount of sputtered Al actually reaching the substrate. \( c_{\text{Al}} \) can be assumed to be independent of the phase shift, \( \theta \), because it stems from the pure collisional interaction between the sputtered material and the background gas at the constant pressure of 0.5 Pa. The particle transport from the target to the substrate was discussed by Trieschmann et al. for a pure Al deposition process using the MFCCP [121].

The total Al sputter flux is the sum of the partial Al sputter fluxes, \( \Gamma_{\text{Al}}^{\text{fl}} \), \( \Gamma_{\text{N}_{2}}^{\text{fl}} \), and \( \Gamma_{\text{N}^{+}}^{\text{fl}} \), resulting from the sputtering processes by different ion species (equation (12)). Each partial sputter flux of Al can be described by the product of the ion flux times the partial Al sputter yield for the respective ion species:

\[
\Gamma_{\text{Al}}^{\text{fl}} = \Gamma_{\text{Al}}^{\text{ip}} Y_{\text{Al},\text{ip}} (E_{\text{ip}}, \Theta_{\text{ip}}) = \Gamma_{\text{Al}}^{\text{ip}} \left[ Y_{\text{Al}}^{\text{i}} (E_{\text{ip}}) \cdot (1 - \Theta_{\text{ip}}) + Y_{\text{Al},\text{ip}} (E_{\text{ip}}) \cdot \Theta_{\text{ip}} \right] \tag{13}
\]

\[
\Gamma_{\text{Al}}^{\text{N}_{2}}^{\text{fl}} = \Gamma_{\text{Al}}^{\text{N}_{2}}^{\text{N}_{2}} Y_{\text{Al},\text{ip}} (E_{\text{ip}}, \Theta_{\text{ip}}) = \Gamma_{\text{Al}}^{\text{N}_{2}} \left[ Y_{\text{Al}}^{\text{i}} (E_{\text{ip}}) \cdot (1 - \Theta_{\text{ip}}) + Y_{\text{Al},\text{ip}} (E_{\text{ip}}) \cdot \Theta_{\text{ip}} \right] \tag{14}
\]

\[
\Gamma_{\text{Al}}^{\text{N}^{+}}^{\text{fl}} = \Gamma_{\text{Al}}^{\text{N}^{+}} Y_{\text{Al},\text{ip}} (E_{\text{ip}}, \Theta_{\text{ip}}) = \Gamma_{\text{Al}}^{\text{N}^{+}} \left[ Y_{\text{Al}}^{\text{i}} (E_{\text{ip}}) \cdot (1 - \Theta_{\text{ip}}) + Y_{\text{Al},\text{ip}} (E_{\text{ip}}) \cdot \Theta_{\text{ip}} \right] \tag{15}
\]

The partial sputter yields describing the sputter efficiency at the target areas with pure Al and target areas covered with AlN are weighted by the degree of target poisoning, \( \Theta_{\text{ip}} \). Furthermore, each partial sputter yield scales predominantly with the energy, \( E_{\text{ip}} \), of the impacting ions. Additional dependencies of the sputter yields are linked to the characteristic surface binding energies of Al–Al and Al–N bonds at the target [122, 123] and the mass ratio between projectile and target species [124], which are constant for the presented conditions.

The ion flux onto the target consists of argon ions, \( \text{Ar}^{+} \), ionized nitrogen molecules and atoms, \( \text{N}_{2}^{+} \) and \( \text{N}^{+} \). With an admixture of 89% argon and 11% nitrogen gas, the total ion flux onto the target and substrate consists predominantly of argon ions and with a minor part of nitrogen ions. Concerning this, the amount of \( \text{N}_{2}^{+} \) in relation to \( \text{Ar}^{+} \) is estimated to be only 7% by a calculation of the ionization rate coefficients for \( \text{Ar}^{+} \) and \( \text{N}_{2}^{+} \) using the fit formulas provided by Gudmundsson [125, 126] assuming \( T_{\text{e}} \approx 3 \text{ eV} \) in combination with the ratio of the applied gas admixture. Ulrich et al. estimated the relation of \( \text{N}_{2}^{+} : \text{N}^{+} \) to be \( \approx 9 : 1 \) and concluded that this amount of \( \text{N}^{+} \) is characteristic for \( \text{N}_{2} \) containing plasma processes [120]. Even with the estimated low \( \text{N}_{2}^{+} \) content the amount of \( \text{N}^{+} \) would be less than 1% than the neutral gas density. A more detailed analysis of the amount of nitrogen ions in an argon discharge is given by Kimura et al. [127]. They estimated the amount of \( \text{N}_{2}^{+} \) to be \( \approx 10\% \) of the amount of \( \text{Ar}^{+} \) and also \( \text{N}^{+} \) scales below 1% (13.56 MHz, Inductively Coupled Plasma (ICP)) \( \text{Ar:} \text{N}_{2} = 10:1 \) at 0.4 Pa). Therefore, it is justified to neglect the \( \text{N}^{+} \) flux onto the target and the generated partial sputter flux \( \Gamma_{\text{Al}}^{\text{N}^{+}} \) in equation (15) can be neglected. Therefore, the ion flux simplifies to \( \Gamma_{\text{ip}} \approx \Gamma_{\text{Ar}}^{\text{ip}} + \Gamma_{\text{N}^{+}}^{\text{ip}} \approx 1.07 \Gamma_{\text{Ar}}^{\text{ip}} \).

While the mean sputter yield drop at the grounded electrode is increased as a function of \( \theta \) following a parabolic-like behaviour with a maximum at \( \theta = 90^\circ \), a reduction of the mean sputter yield drop at the powered target electrode, \( \langle \phi_{\text{sp}} \rangle \), is the consequence, which is shown in figure 7 for five different driving voltage amplitude pairs \( (\hat{\phi}_{13}, \hat{\phi}_{27}) \) at a constant amplitude ratio of 2.3. The ions directed towards the target impact with a strongly reduced ion energy, if higher values of \( \theta \) are chosen. The ion energy at the target for \( \hat{\phi}_{13} = 344 \text{ V} \) and \( \hat{\phi}_{27} = 149 \text{ V} \) is only 153 eV at 90° compared to 352 eV at 0°. This means, that the total sputter yield will strongly decrease and will reduce the sputter flux and finally the resulting growth flux, while the total ion flux stays constant i.e. the ion-to-growth flux ratio \( \Gamma_{\text{ip}} / \Gamma_{\text{gr}} \) is not constant as a function of \( \theta \). Figure 8 depicts the evolution of the measured deposition rate (red dashed line) of the AlN coating at the center of the grounded electrode for 0°, 45° and 90°.
To address this issue, the ion energy $E_{ip}$ at the target has to be kept constant during the increase of the phase shift $\theta$. In this case, the total sputter yield will also be constant. The idea is not only to vary the relative phase shift $\theta$, but to adjust each driving voltage amplitude, $\hat{\phi}_{13}$ and $\hat{\phi}_{27}$, in parallel, while keeping a constant amplitude ratio of 2.3 to keep the time averaged sheath voltage drop, $\langle \phi_{sp} \rangle$, and therefore, the ion energy onto the target, $E_{ip}$, constant. Of course with an increase of the driving voltage amplitudes the ion flux onto the target and substrate will increase, but if the sputter yield is kept constant, the sputter flux and, therefore, the growth flux will increase identically so that the flux ratio will be held constant. The ion flux onto the target is assumed to be the same as the ion flux onto the grounded electrode with

$$\Gamma_{ip} = \Gamma_{ig}. \quad (16)$$

The electron density alongside the circular electrode axis within the plasma gap was measured using optical emission spectroscopy in a previous work for similar process conditions [101]. In that work, the plasma emission was observed with an optical fibre connected to an Echelle spectrometer ESA 3000 (200–800 nm, LLA Instruments GmbH). The spectrometer collected photons through a window port across the whole plasma volume with the line of sight at different vertical positions between the electrodes. As a result, it was found that line-integrated electron density and temperature in axial direction are approximately constant, which supports the assumption of similar ion fluxes onto the target and the substrate.

Based on these assumptions an expression for the energy per deposited atom can be found, which is only dependent on the ion energy onto the substrate, $E_{ig}$, and the partial Al sputter yields by $Ar^+$ and $N_2^+$:

$$E_{pda,i} = E_{ig} \cdot \frac{1.07}{2t_{ir} \left[ Y_{i,Ar}^Al (E_{ip}, \Theta_t) + 0.07 Y_{i,N_2}^Al (E_{ip}, \Theta_t) \right]}.$$  

(17)

The ion-to-growth flux ratio can be kept constant, if the driving voltage amplitudes of the excitation frequencies are adjusted in parallel to changing the phase shift in a way, that ensures that the ion energy $E_{ip}$ onto the target and, therefore, the partial sputter yields remain constant. At this point, it has to be mentioned, that the real target condition is unknown. Although the measured total ion flux will increase due to the change of $\hat{\phi}_{13}$ and $\hat{\phi}_{27}$ (as it is shown later in figure 10), it is assumed that the degree of target poisoning, $\Theta_t$, will not be affected.

In table 1, the chosen voltage amplitudes are listed for the phase shifts 0, 15, 30, 45 and 60°, for which the ion energy onto the target is kept constant. Also, in figure 7 the variation of the powered sheath voltage drop for different relative phase shifts $\theta$ and the adjusted voltage amplitude pairs of $\hat{\phi}_{13}/\hat{\phi}_{27} = 2.3$ are shown. The horizontal dashed line at 352 V marks the target value of $e^\langle \phi_{sp} \rangle$, which is held constant. The ion energy is calculated using $E_{ip}^p \approx e^\langle \phi_{ip} \rangle = e^\langle \phi_{sp}^{\ast} \rangle - \eta$ with $\eta < 0$. This procedure of changing the voltage amplitudes and $\theta$ yields...
a variation of the mean ion energy at the substrate from 38 eV up to 81 eV. In figure 10, this is depicted together with the peak ion energy (grey dashed line). The total ion flux onto the grounded electrode increases as a function of $\theta$ with the highest value at $\theta = 45^\circ$ and slightly decreases for $60^\circ$ (figure 10). At the same time, the deposition rate $R_d$ (figure 8) reveals a similar behaviour like the ion flux as a function of $\theta$, while adjusting $\phi_{13,27}$. Here, $R_d$ is determined by the film thickness $d_f$ analyzed by surface profilometry and STEM (figure 15). Both methods exhibit similar values for the deposition rate at each condition with an average relative deviation of 8% to each other (figure 8). Also, the qualitative agreement is shown by both analyzing methods. It can be clearly seen, that the target bombarding ion flux determines the growth flux, $\Gamma_{13}/\Gamma_{gr}$ is plotted in (figure 9) using the same ion flux, but with the evaluated deposition rates determined from profilometry and STEM. Both datasets for $\Gamma_{13}/\Gamma_{gr}$ result in a nearly constant ion-to-growth flux ratio for all phases $\theta$ with adjusted voltage amplitudes (figure 9). On average, $\Gamma_{13}/\Gamma_{gr}$ turns out to be $\approx 4.3 \pm 0.2 (\pm 5\%)$.

As a first conclusion, using the EAE supported by adjusted voltage amplitudes at higher relative phase angles, $\theta$, is an appropriate method for the presented conditions, which provides the opportunity to vary only the ion energy onto the growing film in a broad range, while the ion-to-growth flux ratio can be kept constant. It also shows, that the simple conditions. In

Figure 10. Measured mean and peak ion energy as well as the ion flux at the grounded electrode for five different relative phase shifts while adjusting the driving voltage amplitudes in parallel to keep the ion energy onto the target constant ($\phi_{13}/\phi_{27} = 2.3 \mp \theta$ at 0.5 Pa Ar/N$_2$ (8:1)). The driving voltage amplitudes at each phase are listed in table 1.

3.2. Influence of ion energy variation on AlN thin film properties

Utilizing the possibility of decoupling the ion energy from the ion-to-growth flux ratio, AlN thin films are deposited at the center of the grounded electrode for each choice of $\theta$ and its respective driving voltage amplitude pair ($\phi_{13}^*, \phi_{27}^*$) to investigate the influence of the varied mean ion energy (table 1) on the film characteristics.

3.2.1. Chemical composition. The chemical composition of the AlN thin films is determined by ERDA (see section 2.5).

In figure 12 the average concentrations averaged across the film thickness excluding the surface-near region are plotted. The variation in mean ion energy does not influence the chemical composition significantly regarding the concentrations of Al and N. All thin films are nearly stoichiometric with $c_{\text{Al}} = 49.1 \pm 0.7 \text{ at.\%}$ and $c_{\text{N}} = 47.0 \pm 0.6 \text{ at.\%}$ and a N/Al ratio of 0.95. Within the vicinity of the surface, the oxygen concentration for all analyzed AlN films is relatively high (6–7 at.\%), but decays to an average level of 1.6 $\pm 0.4 \text{ at.\%}$ several nanometers below the surface. The

Figure 11. Measured IEDF at the center of the grounded electrode $f(E_f)$ for different $\theta$ while adjusting the driving voltage amplitudes ($\phi_{13}^*/\phi_{27}^* = 2.3 \mp \theta$ at 0.5 Pa Ar/N$_2$ (8:1)).

Figure 12. Average chemical composition of each AlN film deposited at different mean ion energies controlled via the EAE ($\phi_{13}/\phi_{27} = 2.3 \mp \theta$, $\Gamma_{13}/\Gamma_{gr} = 4.3 = \text{const.}$ at 0.5 Pa Ar/N$_2$ (8:1)).
surface-near amount of O can result from the oxidation process after the deposition process upon exposure of the film to atmospheric oxygen and/or during the process by reactions with residual gas in the chamber [128]. The O within the deeper layers most likely originates from the residual gas. In combination with low deposition rates it can be adsorbed at the film surface and incorporated into the coating. A very low resputtering at the respective incident ion energies cannot effectively remove the adsorbed O [119]. The Ar concentration inside the film is 2.5 ± 0.1 at.% at 47 and 53 eV ion energy and 0.51 ± 0.03 at.% at 57 and 81 eV. Fe is also detected with a low amount of 0.33 ± 0.06 at.% and might originate from the plasma surrounding metal grid or the ground shields of the electrodes both made of stainless steel.

3.2.2. Phase formation, preferential orientation and growth morphology. In figure 13 the diffractograms of AlN films obtained from Bragg–Brentano configuration are shown for the different mean ion energy conditions at the substrate (table 1). All thin films exhibit a single hexagonal wurtzite-type structure (space group P63). In figure 13 a change in the peak intensities at different angles with increasing ion energy can be observed clearly. Also, the (100) peak appears to gradually shift the position with increasing ion energy. Simultaneously, the (002) peak appears to broaden significantly.

For a better evaluation, the peak intensity of each orientation from the XRD pattern is normalized by the sum of all intensities, I_{tot}, and is plotted in figure 14 as the degree of film orientation versus the mean ion energy. For the orientations (100), (002) and (110) a clear trend with the varied ion energy is found. While the (002) orientation dominates the diffractograms at low ion energies (≈80%) and nearly vanishes for high energies (≈4%), the peak intensity of the (100) and (110) planes exhibit a clear rising trend as a function of the ion bombardment energy and dominate the crystal orientation at the highest ion energy with 46% and 33%. In contrast to this, there seems to be an energy regime for the (101) plane, where the intensity maximum is reached at 57%. Below and above this value the degree of this orientation scales between 12% and 17%. The (103) orientation is very weakly pronounced in the range of only 0.5%–7%. It is evident that the AlN thin film, deposited at the highest mean ion energy exhibits significant contributions of (100) and (110) orientations.

Summarizing, a correlation of the grown preferential orientation with the varied mean ion energy is found. The preferential orientation can be adjusted in a narrow energy regime between 53 and 57 eV for the preferential (002) orientation and switches to a coexistence of the upcoming (100), (101) and (110) oriented grains. At this point, a detailed understanding of the change in preferential film orientation with increasing ion energy bombardment requires further investigations of the atomic processes at the film surface during film growth, which are beyond the scope of this work. We find that a distinct modification of the texture can be reached by well-defined deposition conditions especially by a precise control of the ion bombardment energy, while the ion-to-growth flux ratio is kept constant.

In figure 15 the cross-sectional morphology of the AlN films determined by STEM is depicted for different mean ion energies. The homologous film temperature $T_h$ is obtained from the measured substrate temperature of $T_s$ and normalized by the melting temperature. For the increased relative phase shift $\theta$ in combination with the adjusted driving voltage amplitudes to keep the ion-to-growth flux ratio constant, it is expected, that the ion energy and ion flux will increase, as it is shown in figure 10. Also, it is assumed, that the ion
bombardment of the substrate is the main energy supplier to the growing film. Therefore, $T_s$ is measured for the case with the lowest and the highest expected ion energy flux ($\dot{N}_{ig} = \dot{E}_{ig} \cdot \Gamma_{ig}$ [2, 19]), as the highest substrate temperature is expected for the latter case (81 eV, table 1). While the substrate temperature only varies about 20 °C (20 K) between these two cases, the measurement of $T_s$ for the conditions with intermediate ion energy fluxes (53–57 eV) is left out, as no drastic temperature rise is expected for these conditions. The homologous temperature of $T_s/T_m = 0.13$ is obtained with $T_s \approx 50$ °C. The morphology of the deposited films for the ion energies at 47, 53 and 57 eV exhibits a growth of V-shaped columnar grains, which evolve after the first 200 nm. This micro-structural evolution with increasing film thickness is typical for the well-known Zone T of the structure zone diagram by Thornton [129]. In contrast, the deposited film at an ion energy of 81 eV exhibits a finer fibrous/columnar micro-structure. Finally, an impression of the surface roughness, which is representative for the entire film in each case, is visible in the cross-sectional morphology for all four AlN films in figure 15. If the ion energy is increased from 57 to 81 eV a change in surface roughness can be observed as the film with the highest ion energy seems to be more smooth compared to the film surfaces synthesized at the lower ion energies. However, a direct measurement of the surface roughness is beyond the scope of this work.

3.2.3. Residual stress. The residual stress versus the mean ion energy is depicted in figure 16. All films exhibit a high compressive stress: starting with $-5.8$ GPa at 47 eV the stress increases monotonously to $-8.4$ GPa at 81 eV. Therefore, a qualitative trend between the compressive stress and the increased ion energy is found. This kind of correlation has already been described and discussed in the literature [130]. In a certain energy regime an enhanced surface mobility, film relaxation and recrystallisation leading to film densification and healing of lattice defects reduces the stress. Beyond this regime an excessive energetic bombardment is able to elevate the compressive stress by direct implantation and/or knock-on subplantation of ions, neutrals and gas impurities causing

![Figure 15. Morphology of AlN coatings deposited at different ion energies imaged by STEM ($\dot{N}_{11}/\dot{N}_{27} = 2.3 \forall \theta, \Gamma_{1g}/\Gamma_{2g} = 4.3 = const.$ at 0.5 Pa Ar/N$_2$ (8:1)).](image1)

![Figure 16. Residual compressive stress as a function of the mean ion energy at the substrate ($\dot{N}_{11}/\dot{N}_{27} = 2.3 \forall \theta, \Gamma_{1g}/\Gamma_{2g} = 4.3 = const.$ at 0.5 Pa Ar/N$_2$ (8:1)).](image2)
lattice distortion and crystal defects. The measured stress magnitude is comparable to AlN films of other works found in the literature, which were coated at similar process conditions in magnetron plasmas \[23, 131–133\]. In general, the low amount of nitrogen, here 11%, might contribute to an increased stress for all films, because the energy transfer to the growing film is more efficient for the dominant argon ions than for the nitrogen species as it was observed in \[132\].

3.2.4. Mechanical properties. In figure 17(a) the elastic modulus and the hardness of the AlN thin films are plotted as a function of the mean ion energy at the substrate. The deposited films show an increase of the film hardness from approximately 16 ± 1.6 GPa to 25.6 ± 0.8 GPa. This range of hardness values is similar to AlN films synthesized with dc and RF magnetrons \[134–136\]. Absolute elastic modulus values range from 174.6 ± 10.3 to 224.0 ± 4.0 GPa and are significantly lower than published elastic moduli, which are in the range of 294–392 GPa (\[115\] and references therein). It should be noticed that the AlN films within this work exhibit thickness values of only 570 nm on average. Hence, the elastic modulus values may be underestimated due to a substrate effect induced by elastic strain fields, which are larger than the film thickness \[137\]. However, qualitatively an increasing elastic modulus with increasing mean ion energy is observed.

In figure 17(b) the elastic modulus and hardness are presented as a function of the residual stress of each film. Recently, in \[138\] density functional theory calculations as well as experiments were performed correlatively for CrAlN and it was shown that a high compressive stress can be generated due to the formation of Frenkel pairs. Such defects are induced by energetic particle bombardment and result in an increase of the elastic modulus compared to stress-free films \[138\]. Hans et al investigated the stress-elasticity correlation on arc evaporated TiAlN coatings and demonstrated that underdense film regions can induce an elastic modulus reduction \[139\]. In the present work, a correlation between elasticity and stress is indicated.

4. Conclusions

In this work, a large-area multi-frequency capacitively coupled reactive sputtering system is presented. This system employs the EAE and, therefore, has the advantage to fully decouple the ion energy from the ion flux. By tuning the relative phase shift, \(\theta\), between the two excitation frequencies as an additional process parameter it is possible to adjust the mean ion energy at both electrodes, target and substrate, with a precision of ±1 eV, while the ion flux is nearly constant with only 4% alteration. Additionally, it is possible to vary the ion energy, while the ion-to-growth flux ratio is kept constant within a range of 5% alteration, if the phase control is combined with an adjustment of the driving voltage amplitudes. Therefore, it is possible to isolate one plasma parameter, here \(E_{ig}\), from the others to study its effects on film characteristics. Referring to this, AlN films are deposited and exhibit an increase in compressive film stress from \(-5.8\) to \(-8.4\) GPa as well as an increase in elastic modulus from \(175\) to \(224\) GPa as a function of the mean ion energy at the substrate. Hence, the identified correlations emphasize that utilization of the electrical asymmetry effect enables tailoring of
thin film properties. Also, existing CCPs can be retrofitted with the respective technology to employ the EAE. While the presented results are obtained by investigations at the center of the grounded electrode, the spatial distribution (degree of uniformity) of the ion flux, ion energy, deposition rates, ion-to-growth flux ratio as well as the AIM film properties across the large area of the grounded electrode will be the scope of future work. In addition, it will be of high relevance to investigate, if the decoupling of the ion energy and the ion-to-growth flux ratio is still valid across the whole grounded electrode surface. Also, a future topic will be the increase of the deposition rate using higher excitation frequencies.

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ORCID iDs

Stefan Ries https://orcid.org/0000-0001-5291-8276
Alfred Ludwig https://orcid.org/0000-0003-2802-6774
Julian Schulze https://orcid.org/0000-0001-7929-5734

References

[21] Igual A and Mohd-Yasif F 2018 Sensors 18 1797
[28] Kelly P and Arnell R 2000 Vacuum 56 159
[34] Smith D L 1995 Thin-Film Deposition: Principles and Practice (New York: McGraw-Hill)
[40] Robertson J 1994 Diamond Relat. Mater. 3 361


[137] Bull S 2014 Phil. Mag. 95 1907
