

Master's Thesis

Characterization of filtered Cathodic Arc Plasma Processes

Focusing on Mass Spectroscopy and Ion Flux measurements

Investigation of correlation between ion flux and deposition rate
for TiAl and TiAlN thin films

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Contents

1	Introduction and Literature Review	6
1.1	Motivation	6
1.2	State of the Art	7
1.3	Objectives	8
2	Theoretical Background	9
2.1	Plasma Generation and Composition	9
2.1.1	Cathode Spot Plasma Generation	9
2.1.2	Pulsed vs. Continuous Arc Operation	10
2.1.3	Plasma Expansion and Macroparticle Filtering	11
2.2	Ion Energies and Flux in the Substrate Region	11
2.2.1	Ion Energies: Origins and Implications	11
2.2.2	Effect of Distance on Ion Properties	12
2.2.3	Effect of External Magnetic Fields	13
2.2.4	Ion Flux	13
2.3	Reactive Mode and Nitrogen Activation	14
2.3.1	Transition from Metallic to Reactive Mode	14
2.3.2	Activated Nitrogen Species	14
2.4	Plasma–Surface Interactions and Film Growth	15
2.4.1	Energetic Condensation and Subplantation	15
2.4.2	Structure-Zone Models	15
2.4.3	TiAlN Crystal Structures	16
3	Experimental Methodology	18
3.1	Experimental Setup	18
3.1.1	Vacuum & Gas Infrastructure	18

3.1.2	Power Circuits and Arc Operation	19
3.1.3	Diagnostic Positioning and Synchronization	20
3.2	Plasma Diagnostics	21
3.2.1	Ion Current Probe (Langmuir Probe)	21
3.2.2	Quartz Crystal Microbalance	23
3.2.3	Simultaneous Ion Probe and QCM Measurements	24
3.2.4	Energy-Resolving Mass Spectrometer (ERMS)	25
3.2.5	Calculation of Ion Flux and Total Deposited Flux	27
3.3	Ex situ Measurements	28
3.3.1	Profilometry	28
3.3.2	X-ray Diffraction (XRD)	29
3.3.3	X-ray Reflectometry (XRR)	30
3.3.4	Scanning Electron Microscopy (SEM)	31
3.3.5	Energy-dispersive X-ray spectroscopy (EDX)	31
3.4	Data Processing	31
3.5	Error Handling	32
3.5.1	Mass Spectrometry Measurements	32
3.5.2	QCM and Ion Current Probe Measurements	33
3.5.3	Error Propagation Analysis	33
4	Results	35
4.1	Langmuir Probe Bias Voltage Characterization	35
4.1.1	Validation of Langmuir Probe Operation	35
4.1.2	Analysis of the Ion Saturation Curve	36
4.1.3	Selection of Operating Bias Voltage	37
4.1.4	Ion current Variation over different pulses	37
4.2	Quartz crystal Microbalance and Ion current Probe	38
4.2.1	Metallic Case (No Nitrogen)	40
4.2.2	Distance as a variable	41
4.2.3	Magnetic Field as a variable	42
4.2.4	Nitrogen pressure as a variable	43
4.3	Mass spectrometry Results	44
4.4	Ex situ Results	45
4.4.1	Profilometry	45
4.4.2	XRD	46
4.4.3	XRR	46
4.4.4	EDX	46
4.5	Fluxes	46
5	Discussion of Results	47

6 Conclusion	48
7 final words or smt like thanks everyone	49
A Experimental Methods supplementary	50
A.1 Longer QCM depositions	50
B Additional Plots	51
C Python code used	53

Abstract

Pulsed filtered cathodic arc deposition generates highly ionized metal plasmas capable of producing dense, crystalline thin films without substrate heating. However, the process involves multiple coupled parameters: external magnetic fields simultaneously increase both ion charge states (potential energy) and ion flux, while reactive gases alter plasma composition through charge-exchange collisions. This thesis investigates the individual roles of ion flux and ion energy in Ti–Al–N thin film growth by systematically varying magnetic field strength (0–0.25 T), nitrogen pressure (0–0.3 Pa), and spatial position (10–20 cm from the plasma source).

Two diagnostics were operated simultaneously: a Langmuir probe measured ion current density, a quartz crystal microbalance tracked deposited mass. Additionally an energy-resolving mass spectrometer determined charge-state-resolved ion energy distributions. Measurements were performed in both metallic mode (vacuum) and reactive mode (nitrogen background) to characterize the transition between regimes.

The results show that increasing the magnetic field strength can amplify ion flux by up to a factor of eight. In reactive mode, the presence of nitrogen further boosts ion flux, as charge-exchange collisions reduce the number of highly ionized species and increase the proportion of lower-ionization ions. Energy-resolved mass spectrometry shows the charge-state distribution shifts toward lower ionization levels when operating in reactive mode. It also confirms that the total ion energy (kinetic and potential energy) remains within the 30–70 eV range, which is ideal for room-temperature crystallization.

This work extends the energy-flux decoupling framework established for (V,Al)N coatings to the industrially relevant TiAlN system and demonstrates that ion flux control via magnetic field strength provides a viable route to tailoring film microstructure independently of substrate temperature.

CHAPTER 1

Introduction and Literature Review

1.1 Motivation

Titanium aluminum nitride ($\text{Ti}_{1-x}\text{Al}_x\text{N}$) coatings are widely used in cutting tools and wear-resistant applications because of their high hardness (25–35 GPa), thermal stability, and oxidation resistance [1]. These properties depend on maintaining the metastable cubic B1 crystal structure, which provides superior mechanical performance compared to the thermodynamically stable wurtzite phase [2]. Traditional deposition methods require substantial substrate heating to achieve dense, crystalline coatings. Cathodic arc deposition offers a key advantage: highly ionized metal plasmas with intrinsic high ion energies enable room-temperature crystallization through energetic condensation [3].

The challenge is that, cathodic arc processes involve multiple coupled parameters. Ion energy has two components: kinetic energy from plasma expansion and potential energy released upon neutralization. The ion flux determines how rapidly this energy is delivered to the growing film. External magnetic fields can enhance both ion charge states and flux by up to an order of magnitude [4], while adding reactive gases such as nitrogen introduces charge-exchange collisions that alter plasma composition [3]. Understanding how these parameters individually influence film properties remains a fundamental challenge for predictive process control.

1.2 State of the Art

Recent systematic studies have made progress in understanding ion energy effects in cathodic arc deposition. Unutulmazsoy et al. showed that applying an external magnetic field to the cathode increases ion charge states (and thus potential energy), while applying a DC bias to the arc source adjusts kinetic energy [5]. Their work on (V,Al)N films demonstrated that crystalline coatings can be achieved at room temperature through energetic ion bombardment. However, a critical observation was that “application of an external magnetic field also leads to an enhancement of the ion flux and hence the desired complete decoupling of the potential and kinetic energy effects will require further steps” [5]. In their study, the magnetic field not only modified ion charge states but also increased ion flux by up to a factor of 10, making it impossible to isolate the effect of potential energy from that of ion flux intensity.

Kalanov et al. refined this approach using detailed energy-resolved mass spectrometry, taking a step toward decoupling these effects [6]. Their work on (V,Al)N films showed that the enhancement of room-temperature crystallinity correlates primarily with the increase in potential energy input. Notably, applying a DC bias to increase kinetic energy by approximately 30 eV did not produce the same crystallization effect, even though it increased the total ion energy. This demonstrated that potential energy plays a distinct role in promoting film crystallinity. However, even in this refined approach, the magnetic field enhancement of potential energy remained coupled to an increase in ion flux, leaving flux as an additional variable affecting film growth.

Both studies identified ion flux as another parameter requiring systematic investigation. The role of ion flux as an independent variable affecting energy delivery rate and adatom mobility has not been fully isolated. Additionally, these studies explored the effects of activated nitrogen in reactive deposition, which consists of both ionized and neutral (but excited) nitrogen species [3, 7]. The first study [5] focused entirely on reactive deposition with nitrogen, while the second [6] examined both metallic and reactive modes in equal measure. Both works demonstrated that activated nitrogen significantly affects film properties, but a key question remains unanswered: what fraction of the activated nitrogen consists of neutral species versus ionized species? This distinction is crucial for understanding the relative contributions of ions and neutrals to film growth, particularly in reactive mode where both species can participate in nitride formation.

For TiAlN specifically, while comparative studies between cathodic arc and magnetron sputtering have shown that ion energy flux significantly affects texture and me-

chanical properties [8], the flux-energy decoupling framework established for (V,Al)N has not been applied to this industrially important system.

1.3 Objectives

This thesis addresses these gaps by systematically investigating the role of ion flux in Ti–Al–N thin film growth via pulsed filtered cathodic arc deposition. The specific objectives are:

1. Characterize the ion flux and the total deposited flux as functions of external magnetic field strength and distance from the macroparticle filter. Furthermore, analyze the ion energy distributions of individual ion species.
2. Investigate the transition from metallic to reactive mode by varying nitrogen pressure and quantify how this affects the ion-to-neutral arrival ratio and charge-state distributions.
3. Establish quantitative correlations between ion flux and atomic flux across the experimental parameter space of magnetic field, nitrogen pressure, and distance from the macroparticle filter.
4. Characterize the crystal structure, film thickness, film composition, and microstructure of deposited TiAlN films to correlate plasma parameters with film properties.

The experimental approach combines multiple *in situ* plasma diagnostics with *ex situ* film characterization to separate ion flux effects from ion energy effects while extending the Unutulmazsoy/Kalanov framework to both reactive mode operation and the industrially relevant TiAlN system. This multi-diagnostic strategy, applied across a systematic parameter space, enables investigation of two key novel aspects: (1) the application to the TiAlN material system, and (2) the combined measurement of ion flux versus total deposited flux to distinguish the contribution of non-ionized activated nitrogen species and correlate this with film properties.

CHAPTER 2

Theoretical Background

2.1 Plasma Generation and Composition

2.1.1 Cathode Spot Plasma Generation

Cathodic arc plasmas form at microscopic emission centers, known as cathode spots, on an otherwise cold metal electrode under vacuum. Spot ignition occurs when the local cathode surface, through breakdown of adsorbates or field-enhanced thermionic emission, undergoes a rapid, explosive release of electrons and vaporized metal. During a single spot pulse, a few nanograms of the cathode material rapidly heat up, vaporize, and ionize, producing a dense, quasineutral plasma plume composed mostly of metal ions and electrons. The peak spot current densities reach 10^{10} – 10^{12} A m^{-2} , far above steady-state thermionic or field emission limits. These microexplosions, termed ectons (explosive electron emission centers), were first described by Mesyats [9] and produce localized nanosecond-scale plasma bursts. The arc is sustained by repetitive ecton events occurring at or near the same location [3, Chap. 3.3–3.4].

Key Characteristics of Spot-Generated Plasma:

- High degree of ionization: >90 % of the ejected metal atoms emerge as ions, a consequence of the extreme power density in the cathode spot [3, Chap. 3.5].
- Multiply charged ions: the charge state distributions extend to $Q = 3$ – 4 for refractory metals, such as Ti and Al, due to the high electron temperature and density in the spot plasma [3, Chap. 3.5].

Spot ignition and quenching occur on timescales of 10–100 ns, with each pulse ejecting a fully ionized burst of metal vapour. The sustained arc discharge thus consists of continuously overlapping microplasma pulses, producing a metal-rich, high-flux ion

stream well-suited for energetic thin-film deposition.

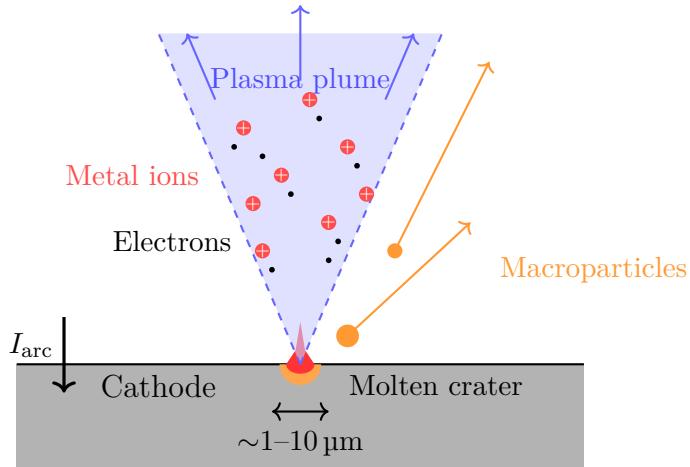


Figure 2.1: Schematic of cathode spot operation. The arc current I_{arc} concentrates at a microscopic spot ($1\text{--}10 \mu\text{m}$ diameter), creating a molten crater from which a plasma plume of metal ions, electrons and macroparticles expand. Adapted from [10]

2.1.2 Pulsed vs. Continuous Arc Operation

Cathodic arcs can operate in either continuous (DC) or pulsed mode, with fundamental differences in plasma generation dynamics. In DC operation, the cathode spot moves continuously across the surface, maintaining a steady-state plasma density determined by the balance between plasma generation at the spot and losses through expansion. The time-averaged plasma properties remain constant, and the ion flux to the substrate is continuous.

In pulsed operation, the arc is periodically initiated and extinguished, creating discrete plasma bursts separated by periods with no plasma generation. During the active phase of each pulse, the instantaneous plasma density can be significantly higher than in DC arcs operating at the same average power, because the energy is concentrated in short time intervals. The peak plasma density scales with the instantaneous arc current, which can reach several hundred amperes during the pulse. Between pulses, the plasma expands and dissipates, allowing the cathode surface to cool. This temporal modulation affects both the spot dynamics and the resulting plasma composition.

The ion charge state distributions in pulsed arcs are typically similar to or slightly enhanced compared to DC arcs, as the higher instantaneous power density can promote additional ionization events in the cathode spot region [3, Chap. 10]. Understanding these temporal plasma dynamics is essential when interpreting flux measurements and correlating them with film growth processes.

2.1.3 Plasma Expansion and Macroparticle Filtering

Following their generation at the cathode spots, the plasma bursts expand into the vacuum chamber. This expansion is supersonic, with ions carrying directed kinetic energy away from the cathode. In many industrial and research systems, the expanding plasma is guided through a magnetic macroparticle filter that removes macroparticles while allowing plasma to pass along curved magnetic field lines.

In the region near the cathode (within a few centimetres of the spot), plasma densities are on the order of 10^{18} cm^{-3} and electron temperatures $T_e \approx 5\text{--}10 \text{ eV}$. As the plume propagates, its density decreases according to

$$n(r) = \frac{C I_{\text{arc}}}{r^2} \quad (2.1)$$

where I_{arc} is the arc current, r the distance, and C a constant related to the ion erosion rate of the cathode material. This $1/r^2$ scaling assumes free expansion, but deviations can occur due to magnetic fields, collisions, or reactive gases, which may alter the plasma trajectory or cause recombination [3, Chap. 4.3, Eq. 4.3, p. 178].

In cathodic arc discharges from titanium cathodes, whether pure Ti or Ti-Al compounds, ions generally carry an average charge state $\langle Q \rangle \approx 2.1\text{--}2.2$ at the source [3, Chap. 4.1, App. B.8]. This high degree of ionization reflects the extreme power density of the spot and follows the cohesive energy rule, which links $\langle Q \rangle$ to the cohesive energy of the cathode material [3, App. B.8].

In the present work, a 90° curved magnetic filter guides the expanding plasma toward the substrate region while removing macroparticles. After passing through the filter, the plasma has evolved from its initial state at the cathode spot, having undergone expansion, potential collisions with background gas, and interaction with guiding magnetic fields. The properties of this filtered plasma in the substrate region determine the energy and flux delivered to the growing film, and are the focus of the following sections.

2.2 Ion Energies and Flux in the Substrate Region

This section focuses on the properties of ions in the plasma after expansion and filtering, in the region where they reach the substrate and form the growing film.

2.2.1 Ion Energies: Origins and Implications

Ions in cathodic arc plasmas carry both kinetic and potential energy. The kinetic energy E_{kin} arises from the supersonic expansion of plasma from the cathode spot, while the potential energy E_{pot} is released upon neutralization at the substrate surface

and is determined by the ionization states of the ion.

The total energy delivered by an ion to the growing film is

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}}. \quad (2.2)$$

For cathodic arc plasmas, the kinetic energy is closely linked to the arc burning voltage, which remains nearly constant at 20–25 V for most metallic cathodes [3, Chap. 4.2]. This voltage accelerates ions away from the cathode region, giving them characteristic drift velocities. As ions traverse the expanding plasma, they may undergo collisions that modify their energy distribution.

Table 2.1 summarizes characteristic ion properties for Ti and Al cathodic arc plasmas in vacuum, measured near the cathode.

Table 2.1: Characteristic ion properties for Ti and Al cathodic arc plasmas in vacuum, near the cathode [3, App. B, Table B.8].

Species	$\langle Q \rangle$	E_{kin} (eV)	E_{pot} (eV)	E_{tot} (eV)
Ti ²⁺	2.1	59	21	80
Al ²⁺	1.7	28	24	52

These values, measured near the cathode spot, serve as reference for understanding the energy budget of ions. In this work, the plasma is characterized after expansion and filtering, where ion energies may differ from these initial values due to collisions and field effects. Nonetheless, for the materials used in this work, the total ion energies are expected to exceed the approximately 30 eV threshold for subplantation, enabling densification and improved crystallinity in Ti–Al–N films without requiring external substrate heating [3, Chap. 8.1–8.2].

2.2.2 Effect of Distance on Ion Properties

As ions travel from the cathode through the filter and toward the substrate, their properties evolve due to geometric expansion and potential collisions. The ion flux decreases with the square of the distance due to the expanding plasma front. Additionally, collisions with background gas (if present) can reduce ion kinetic energies and alter charge state distributions through charge-exchange reactions.

In vacuum (metallic mode), the ion energy distributions remain relatively narrow and well-defined. At increased distances, the plasma density decreases but the relative composition and charge states are largely preserved. However, the ion flux at the substrate position becomes a critical parameter, as it determines the rate at which energy is delivered to the growing film. Understanding how distance affects the ion

flux therefore provides insight into the spatial uniformity of the deposition process and allows optimization of substrate positioning.

2.2.3 Effect of External Magnetic Fields

Applying an external axial magnetic field at the arc source modifies the plasma properties in several ways. Enhanced magnetic insulation prolongs the interaction time between electrons and ions in the cathode spot region, leading to:

- Increased average ion charge state $\langle Q \rangle$, which increases the ion potential energy,
- Simultaneously increased ion kinetic energy,
- Enhanced ion flux, which can increase by up to an order of magnitude [4].

These effects are inherently coupled: the external magnetic field simultaneously increases both the ion charge states (and thus potential energy) and the total ion flux. This coupling presents a challenge for isolating the individual contributions of ion energy and ion flux to film growth. Decoupling these parameters requires additional experimental approaches, such as varying the source-to-substrate distance to modulate flux while maintaining similar ion energies, or applying bias voltages to shift ion kinetic energies independently [5, 6]. The interplay between magnetic field strength, ion flux, and ion energy forms a central theme of this work.

2.2.4 Ion Flux

The ion flux Γ represents the number of ions arriving per unit area per unit time, expressed in $\text{ions cm}^{-2} \text{s}^{-1}$. In a multiply charged plasma, the total measured ion current density J_i (A cm^{-2}) relates to Γ via

$$\Gamma = \frac{J_i}{e \langle Q \rangle}, \quad (2.3)$$

where e is the elementary charge and $\langle Q \rangle$ the average ion charge state. This relationship is central to correlating time-averaged ion flux with deposited mass.

In vacuum cathodic arcs, the burning voltage remains nearly constant at 20–25 V for arc currents up to 1 kA, so the plasma generation rate and thus Γ increases approximately linearly with I_{arc} [3, Chap. 6.5]. However, the absolute ion flux at the substrate depends not only on the arc current but also on the distance from the source and the presence of magnetic fields or reactive gases. These factors determine the fraction of generated plasma that reaches the substrate and the composition of that plasma. The transition from metallic to reactive operation introduces additional complexity, as discussed in the following section.

2.3 Reactive Mode and Nitrogen Activation

2.3.1 Transition from Metallic to Reactive Mode

Cathodic arc deposition operates in two distinct regimes. In metallic mode, the cathode surface remains uncovered and the plasma consists exclusively of metal ions, characterized by high ionization degrees. In reactive mode, a background gas such as N₂ adsorbs onto the cathode surface, forming a compound layer that poisons the cathode and alters both spot behaviour and plasma composition [3, Chap. 9.2].

When N₂ is introduced, a dynamic equilibrium develops between compound formation (through adsorption and reaction at the cathode surface) and compound removal (via explosive ejection events that eject both metal and nitride fragments) [3, Chap. 9.3]. The equilibrium position depends on gas pressure, arc current, and cathode composition. At low N₂ pressures or high power densities, type-2 (metal-rich) spots prevail, maintaining predominantly metal ion flux. At higher pressures, type-1 (poisoned) spots dominate, producing a mixed plasma of metal and nitrogen ions [3, Chap. 9.4]. This transition affects not only the chemical composition of the deposited film but also the energy distribution and charge state distribution of the plasma, as compound formation at the cathode alters the electron emission and plasma generation mechanisms.

2.3.2 Activated Nitrogen Species

In reactive mode, the plasma contains not only metal ions but also activated nitrogen species. These include:

- Ionized nitrogen: N⁺ and N₂⁺ ions formed by electron-impact ionization,
- Neutral but excited nitrogen: metastable N₂ and atomic N species that carry internal energy but no net charge.

The term “activated nitrogen” encompasses both ionic and neutral excited species that participate in film growth. While ionized species can be detected directly by mass spectrometry, the contribution of neutral activated species is more difficult to quantify. This distinction is important because the total deposited flux includes both ionic and neutral components, whereas ion current measurements detect only the charged fraction.

Charge exchange with N₂ reduces the average charge state of metal ions and introduces gas-ion species, altering the potential energy delivered to the film [3, Chap. 9.4]. Collisions during plasma expansion also reduce ion drift velocities, lowering kinetic energy before substrate impact. These effects collectively modify the energy budget available for film growth in reactive mode compared to metallic mode. The interplay between metal ion flux, activated nitrogen flux, and their respective energies determines the resulting film composition, structure, and properties, as discussed in the following

section.

2.4 Plasma–Surface Interactions and Film Growth

2.4.1 Energetic Condensation and Subplantation

When metal ions with sufficient energy strike the growing film, they penetrate below the surface and deposit energy through a shallow collision cascade. This subplantation process produces two key effects:

- **Localized densification:** Ions with energies above approximately 30 eV implant beneath the surface, occupying interstitial sites and displacing near-surface atoms through knock-on collisions. This reduces porosity and increases film density, which is particularly important for transition-metal nitride coatings such as Ti–Al–N [3, Chap. 8.1].
- **Atomic-scale heating:** The deposition of kinetic energy and release of potential energy (ionization enthalpy) generate localized, nanosecond-scale temperature spikes. These enhance adatom mobility and promote crystallite coalescence without requiring global substrate heating [3, Chap. 8.2].

As the energetic input from ions increases, films transition from porous, amorphous structures to dense, crystalline coatings. This densification introduces compressive stresses of several GPa through atomic peening [3, Chap. 8.1–8.4]. For example, TiN films grown with total ion energies of approximately 60 eV develop a preferred cubic (111) texture and hardness exceeding 30 GPa.

The relationship between ion flux and film growth rate is dependent on

$$R = \frac{m_{\text{ion}} \Gamma S}{\rho_{\text{film}}}, \quad (2.4)$$

where m_{ion} is the average ion mass, Γ the ion flux, S the sticking coefficient, and ρ_{film} the film density. The sticking coefficient S represents the probability that an arriving ion incorporates into the growing film rather than being reflected or resputtered; for metal ions at moderate energies (below the resputter threshold of approximately 100–200 eV), $S \approx 1$. However, the film density ρ_{film} itself depends on the ion energy and flux, as higher energies promote densification through subplantation. This interdependence between flux, energy, and resulting film structure motivates the systematic study of these parameters, which is the focus of this work.

2.4.2 Structure-Zone Models

The microstructure of thin films deposited by physical vapour deposition depends strongly on the energy and flux of incident species. Thornton’s structure-zone model,

originally developed for magnetron sputtering, relates film morphology to the homologous temperature T/T_m (substrate temperature normalized to the melting point) and working gas pressure [11]. At low T/T_m and high pressures, films exhibit porous, columnar structures (Zone 1) due to limited adatom mobility. As T/T_m increases, denser columnar (Zone T) and eventually equiaxed crystalline structures (Zone 2 and Zone 3) develop.

Anders extended this framework to account for the energetic ion bombardment characteristic of cathodic arc deposition [12]. In the revised model, ion energy E^* (normalized to a displacement energy) replaces gas pressure as the second axis, reflecting the dominant role of ion bombardment in densification. High-energy ions can induce subplantation and atomic peening even at low substrate temperatures, enabling dense, crystalline films without external heating, which is a key advantage of cathodic arc processes. However, excessive ion energy leads to lattice damage, defect accumulation, and eventually amorphization or resputtering, defining an optimal energy window for film growth [3, Chap. 8.3].

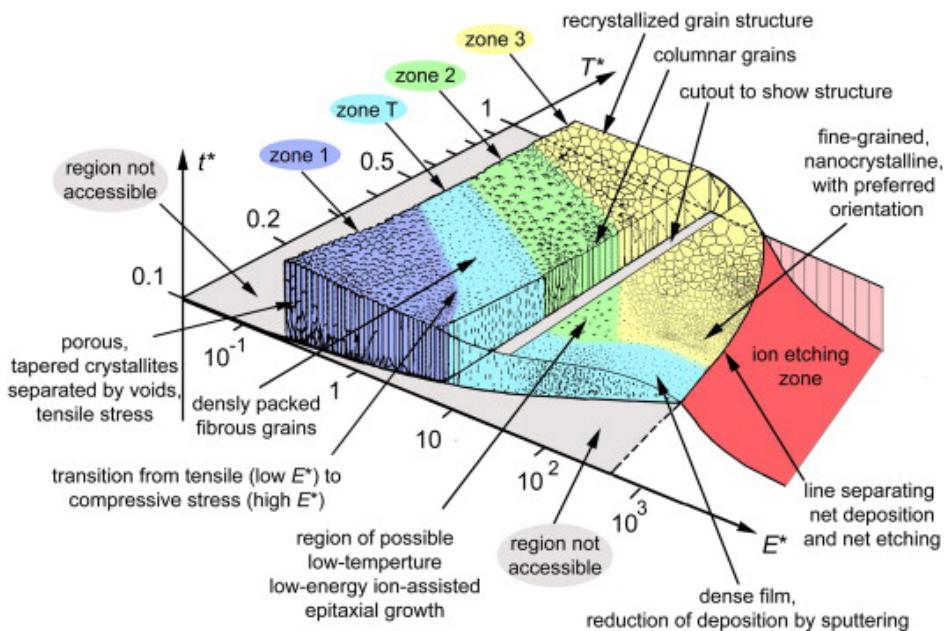


Figure 2.2: Structure-zone diagram for plasma-based thin film deposition, showing film microstructure as a function of generalized temperature T^* and normalized ion energy E^* . From Anders [12].

2.4.3 TiAlN Crystal Structures

Titanium aluminium nitride ($\text{Ti}_{1-x}\text{Al}_x\text{N}$) coatings are widely used for wear protection and cutting tools due to their high hardness, oxidation resistance, and thermal stability. The crystal structure depends primarily on the aluminium content x :

- For $x \lesssim 0.6\text{--}0.7$, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ crystallizes in the metastable cubic B1 structure, where Al atoms substitute for Ti on the metal sublattice. This cubic phase exhibits hardness values of 25–35 GPa and is the preferred structure for most industrial applications [1].
- For $x \gtrsim 0.7$, the thermodynamically stable wurtzite (B4) structure becomes dominant. The wurtzite phase has lower hardness (typically 15–20 GPa) and is generally undesirable for hard coating applications [2].
- At intermediate compositions, mixed cubic-wurtzite structures or nanocomposite arrangements may form, depending on deposition conditions.

The metastable cubic phase is retained at high Al contents through kinetic limitations during low-temperature deposition. Energetic ion bombardment in cathodic arc processes can extend the solubility limit of Al in the cubic phase by providing additional energy for atomic rearrangement without the diffusion lengths associated with thermal equilibration [13].

The cathode composition used in this work (75 wt.% Ti – 25 wt.% Al) is expected to produce cubic-phase $\text{Ti}_{1-x}\text{Al}_x\text{N}$ films under typical cathodic arc conditions.

CHAPTER 3

Experimental Methodology

This chapter describes the experimental apparatus, diagnostic techniques, and data processing methods used to investigate the correlation between ion flux and mass deposition rate in pulsed filtered cathodic arc deposition of Ti–Al–N thin films. The approach combines three complementary diagnostics: a Langmuir probe for ion current measurements, a quartz crystal microbalance (QCM) for real-time mass deposition monitoring, and an energy-resolving mass spectrometer (ERMS) for charge-state-resolved ion energy distributions.

3.1 Experimental Setup

3.1.1 Vacuum & Gas Infrastructure

The vacuum chamber was evacuated using a two-stage pumping system consisting of a dry rotor vacuum pump (Leybold ECODRY+) for roughing and a cryogenic pump (Leybold COOLVAC) for the main pumping line, achieving a base pressure on the order of 1×10^{-5} Pa with the cryopump fully open. To control the working pressure during reactive deposition, the cryopump gate valve was partially closed to position 345 (approximately 34.5% open), which reduced the effective pumping speed and increased the base pressure to approximately 1×10^{-4} Pa. This configuration allowed finer control of the nitrogen partial pressure.

Nitrogen gas (N_2 , 99.999% purity) was introduced via a mass flow controller ([MKS \[MODEL NUMBER\]](#)), with chamber pressures monitored using a [\[GAUGE MODEL\]](#). The nitrogen flow rate of 1 to 12.8 ccms leads to chamber pressure ranges between 0.025 and 0.3 Pa.

Plasma was generated using a water-cooled cylindrical anode and a rod cathode with composition 75 wt.% Ti; 25 wt.% Al (corresponding to 62.8 at.% Ti; 37.2 at.% Al). The cathode had a diameter of 6.35 mm and length of 38.1 mm. The expanding plasma was guided through a 90° curved magnetic macroparticle filter connected in series with the arc power supply, which simultaneously powered both the arc and the filter coils.

3.1.2 Power Circuits and Arc Operation

The arc power supply ([MODEL]) operated in pulsed DC mode, delivering arc currents up to 450 A at pulse frequencies ranging from 0.2 to 5 Hz, with a typical pulse width of 1 ms. The arc current was monitored using a [CURRENT PROBE MODEL] connected to an oscilloscope (Tektronix [MODEL], [sampling rate], [resolution]). The cathode voltage relative to ground and anode voltage relative to ground were measured on additional channels to determine the burning voltage during the pulse.

A coil wound around the cylindrical anode (EM-coil) was used to enhance the ion charge states leaving the source through magnetic confinement. This coil was connected to a separate pulsing unit ([MODEL]) capable of delivering currents up to 850 A. The EM-coil was triggered 200 μ s before arc ignition to ensure the magnetic field reached steady-state conditions before plasma generation. The coil current was monitored using a [CURRENT PROBE MODEL], and the pulse duration was offset with 200 μ s to stabilize the magnetic field before and during the arc pulse.

The magnetic field strength within the EM-coil solenoid was estimated using:

$$B = \frac{\mu_0 N I}{L} \quad (3.1)$$

where $L = 0.02$ m is the solenoid length, $N = 5$ is the number of turns, $\mu_0 = 1.256 \times 10^{-6}$ T m A $^{-1}$ is the vacuum permeability, and I is the peak coil current. The peak current was determined from oscilloscope measurements at the beginning of the pulse, as this represents the maximum field strength before resistive losses cause the current to decay. The current waveform drops within a pulse due to the design of the pulsing unit in the power supplies. Figure 3.1 shows example current waveforms for both the arc and EM-coil for a 250 V input to the coil power supply. An additional example for 100 V input is provided in Appendix B.1.

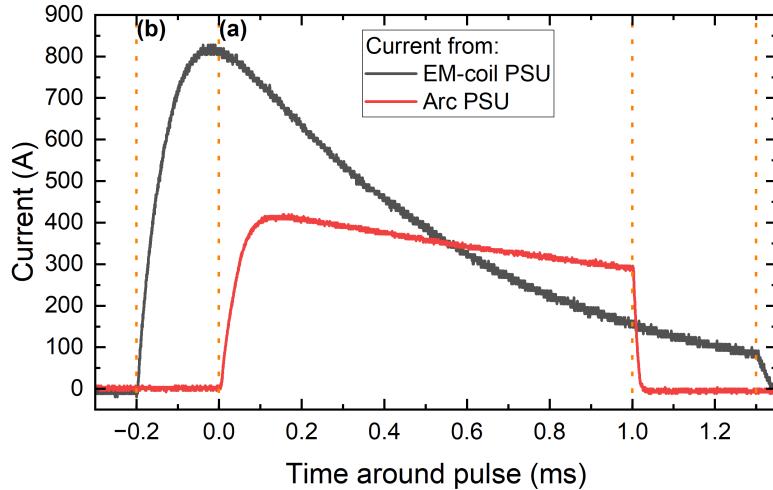


Figure 3.1: Example pulse waveforms showing the arc current (red) and EM-coil current (black) as functions of time. The orange dashed lines indicate the trigger timing: (a) EM-coil trigger at $t = -0.2$ ms, (b) arc trigger at $t = 0$ ms. The waveforms shown are pulses at 250 V EM-coil input voltage. Distance: 10 cm, pressure: 0 Pa, magnetic field: 0.25 T.

3.1.3 Diagnostic Positioning and Synchronization

A delay generator (Stanford Research Systems DG645) served as the master clock for the experimental system, providing precisely timed trigger signals to:

- the arc power supply (channel **a**),
- the EM-coil power supply (channel **b**),
- the energy-resolving mass spectrometer (channel **c**).

The oscilloscope was triggered on the *is it actually* falling edge of the cathode voltage (channel 1), which marks the onset of the arc pulse. Channels 1 and 2 of the oscilloscope measured the cathode-to-ground voltage and anode-to-ground voltage, respectively. Channels 3 and 4 recorded the arc current and EM-coil current via current probes. The ion current was recorded separately, more on that in Section 3.2.1.

The ion current probe and quartz crystal microbalance (QCM) were not triggered by the delay generator. The ion probe signal was recorded directly by the oscilloscope (triggered on the cathode voltage), automatically synchronizing ion current measurements with the arc pulses. The QCM operated continuously, with frequency measurements recorded before and after each deposition run to determine the accumulated mass change over a fixed number of pulses.

For in situ plasma diagnostics, the Langmuir probe and QCM were mounted on a custom movable assembly positioned at distances ranging from 10 to 20 cm from the macroparticle filter exit. The energy-resolving mass spectrometer (ERMS) was

mounted on a separate linear feedthrough, allowing independent adjustment of its axial position (distance from the filter exit) for spatial characterization of the plasma. Film depositions were performed using silicon substrates (Si (100)) mounted on a third movable holder, also positioned at controlled distances from the filter exit.

The vacuum chamber setup for cathodic arc plasma diagnostics and thin film deposition is shown in Figure 3.2. The green arrow illustrates the trajectory of the plasma plume as it expands from the cathode, passes through the 90° macroparticle filter, and reaches the diagnostics and substrate region. This experimental configuration enabled systematic investigation of plasma properties and film growth as functions of distance, magnetic field strength, and nitrogen pressure, as detailed in the following sections.

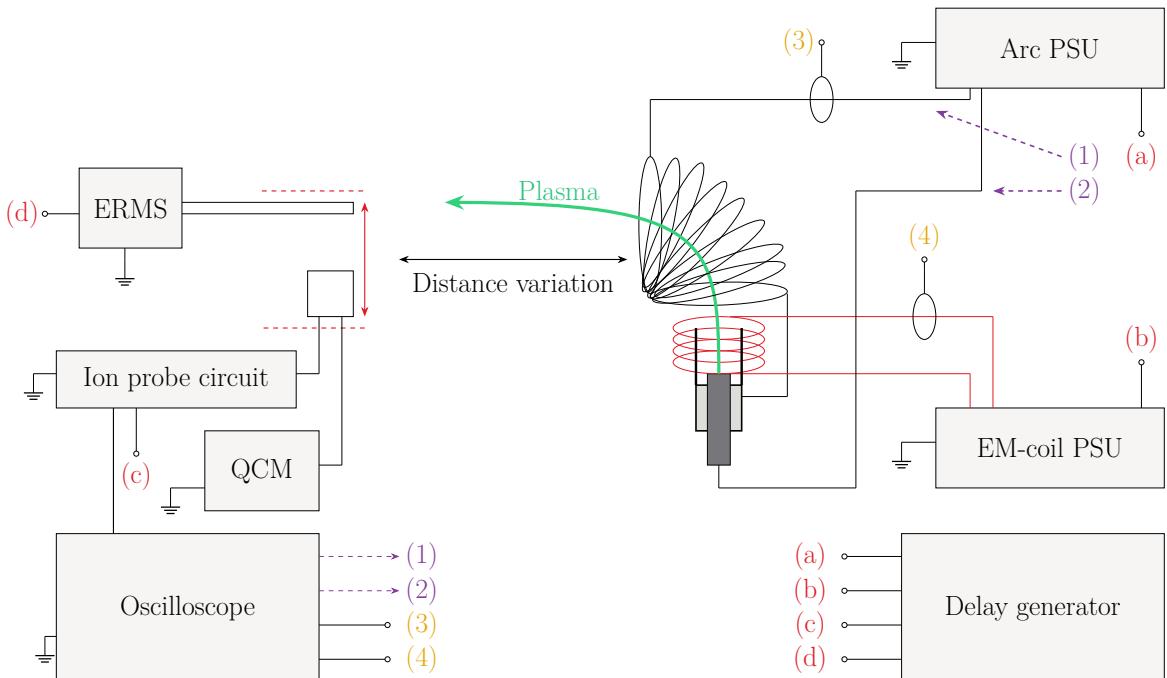


Figure 3.2: Schematic of the vacuum chamber setup for cathodic arc plasma diagnostics and thin film deposition. (a) Arc power supply, (b) EM-coil power supply, (c) Langmuir probe and QCM, (d) energy-resolving mass spectrometer (ERMS). The delay generator (a-d) synchronizes the arc power supply, EM-coil activation, and diagnostic tools.

3.2 Plasma Diagnostics

3.2.1 Ion Current Probe (Langmuir Probe)

An in-house-built ion collector probe was designed to measure the ion current density in ion saturation mode. The probe consisted of a 5 mm diameter copper rod machined to form a cylindrical collection surface with a nail-head geometry. This design ensured a well-defined collection area while minimizing perturbation of the plasma flow. The

probe body was wrapped in Kapton tape for electrical insulation from the electrically grounded surrounding aluminum mounting assembly (Figure 3.6).

To ensure full ion collection and suppress electron current, the probe was negatively biased at $V_b = -80$ V, as determined through bias voltage characterization measurements (Section 4.1.1). The bias voltage was supplied through a protection circuit consisting of a 22 nF capacitor and 1 k Ω resistor, which acted as a low-pass filter to smooth the bias voltage and minimize high-frequency ripple. Two Zener diodes (1 k Ω and 10 k Ω) provided overvoltage protection for the 80 V bias supply against transient voltage spikes during arc ignition.



Figure 3.3: In-house built ion collector probe wrapped in Kapton tape for electrical insulation from the aluminum assembly holder. The probe includes an attachment point for a screw terminal connector, enabling connection to the ion probe circuit.

The probe circuit (Figure 3.4) converts the collected ion current to a voltage signal suitable for oscilloscope measurement. The ion current flows through a 400 Ω measurement resistor, producing a voltage drop V_{measured} that is directly proportional to the ion current. A 0.5 μF capacitor in series with the measurement resistor acts as a high-pass filter with a cutoff frequency of:

$$f_c = \frac{1}{2\pi RC} = \frac{1}{2\pi \cdot 400 \Omega \cdot 0.5 \times 10^{-6} \text{ F}} \approx 795 \text{ Hz} \quad (3.2)$$

This filter blocks DC offsets and low-frequency noise while passing the plasma fluctuations associated with the 1 ms arc pulses (equivalent to 1 kHz). The RC time constant of this circuit is:

$$\tau = RC = 400 \Omega \cdot 0.5 \times 10^{-6} \text{ F} = 200 \mu\text{s} \quad (3.3)$$

This time constant is significantly shorter than the pulse period (200 ms to 2 s), ensuring that the capacitor fully discharges between consecutive pulses.

The processed voltage signal was recorded using a 20 MHz bandwidth oscilloscope ([Tektronix \[MODEL\]](#), [\[sampling rate\]](#), [\[resolution\]](#)). Figure ?? shows an example ion current waveform averaged over [NUMBER] pulses at a repetition rate of [X] Hz. The time-averaged ion current during the pulse (0 to 1 ms) was calculated by integrating the voltage signal and dividing by the pulse duration.

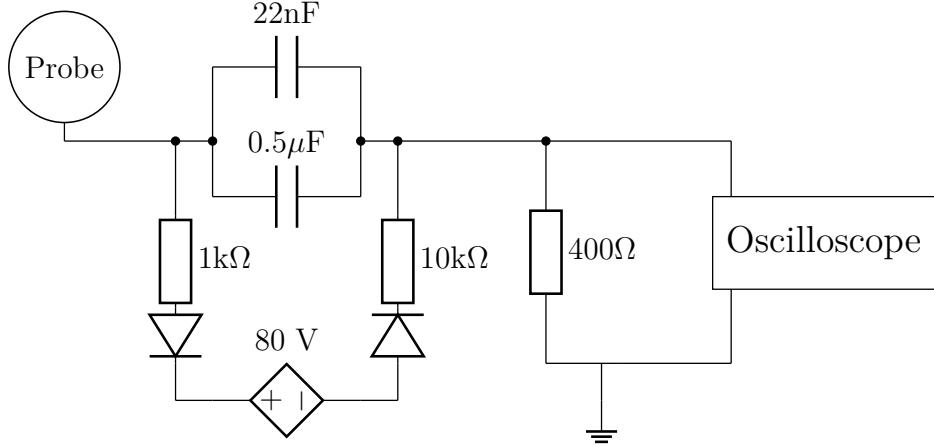


Figure 3.4: Schematic of the ion-flux probe circuit. The 400Ω resistor converts ion current to voltage, while the $0.5\mu F$ capacitor and 400Ω resistor form a high-pass filter with a 795 Hz cutoff.

The ion current density J_i (A cm^{-2}) is calculated from the measured voltage as:

$$J_i = \frac{V_{\text{measured}}}{AR} \quad (3.4)$$

where $A = 0.1963 \text{ cm}^2$ is the probe collection area (5 mm diameter) and $R = 400 \Omega$. The ion flux Γ_i (ions $\text{cm}^{-2} \text{s}^{-1}$) is then determined by accounting for the average ion charge state $\langle Q \rangle$:

$$\Gamma_i = \frac{J_i}{e\langle Q \rangle} = \frac{V_{\text{measured}}}{e\langle Q \rangle AR} \quad (3.5)$$

where $e = 1.602 \times 10^{-19} \text{ C}$ is the elementary charge. The average charge state $\langle Q \rangle$ was determined from energy-resolved mass spectrometry measurements (Section 3.2.4) for each experimental configuration.

The circuit incorporates a $0.5\mu F$ capacitor in series with the 400Ω resistor, forming a high-pass filter with a cutoff frequency of 795 Hz. This configuration effectively blocks DC and low-frequency noise, ensuring that only plasma fluctuations above 795 Hz are recorded. The high-pass characteristic is essential for isolating the dynamic ion current signal from any static offsets or drift.

3.2.2 Quartz Crystal Microbalance

A quartz crystal microbalance (QCM) was used to measure the deposited mass during pulsed cathodic arc deposition. The system consisted of an INFICON Cool Drawer™ with a single sensor in standard orientation, water-cooled to ensure thermal stability. A 14 mm diameter, 6 MHz AT-cut quartz crystal was operated with an SQM-160

controller for electronic readout.

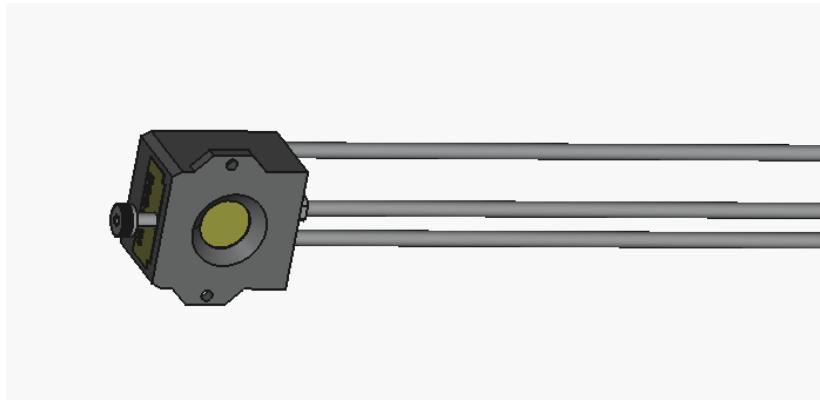


Figure 3.5: Sensor head of the INFICON Cool Drawer™ Quartz Crystal Microbalance (QCM) used for in-situ mass deposition monitoring during cathodic arc sputtering. The assembly includes a water-cooled housing, a 14 mm diameter AT-cut quartz crystal (6 MHz), and electrode leads for connection to the SQM-160 controller. (Schematic adapted from INFICON STP file, available at <https://www.inficon.com/en/products/thin-film-technology/cool-drawer-single-sensor>).

The measurement principle follows the Sauerbrey equation [14], which relates the change in resonance frequency of the quartz crystal to the deposited mass:

$$\Delta m = \frac{N_{\text{AT}} \rho_q \pi r^2}{F_q^2} \Delta F = 18.8146023 \times 10^{-9} \frac{\text{g}}{\text{Hz}} \cdot \Delta F \quad (3.6)$$

Here $\rho_q = 2.649 \text{ g cm}^{-3}$ is the quartz density, $r = 0.7 \text{ cm}$ is the radius of the exposed crystal area, $N_{\text{AT}} = 166\,100 \text{ Hz cm}$ is the frequency constant of the AT-cut quartz, $F_q = 6 \text{ MHz}$ is the uncoated resonance frequency, and ΔF is the measured frequency shift.

The Sauerbrey relation is accurate as long as $\Delta F \lesssim 0.05 F_q$ (approximately 0.3 MHz for a 6 MHz crystal), for more details on the correction above this limit look in Appendix A.1. In the present experiments, the observed frequency shifts ranged from approximately 1 Hz to 50 Hz over 64 pulses. These shifts are well above the SQM-160 resolution of approximately 0.03 Hz at 6 MHz, yet orders of magnitude below the Sauerbrey breakdown limit. The Sauerbrey approximation was therefore fully sufficient for all measurements in this work.

3.2.3 Simultaneous Ion Probe and QCM Measurements

To enable direct comparison between ion current and deposited mass, the Langmuir probe and QCM were mounted on the same movable aluminum assembly (Figure 3.6).

The probe was positioned through a precision-milled pass-through hole, while the QCM was secured in a dedicated cutout and fixed via screws. This configuration ensured rigid mechanical alignment between the two diagnostics throughout all measurements.

The probe collection area ($A_{\text{probe}} = 0.196 \text{ cm}^2$, diameter 5 mm) was smaller than but contained within the QCM active area ($A_{\text{QCM}} = 0.5027 \text{ cm}^2$, diameter 8 mm). Both diagnostics were positioned as close as possible to each other to minimize spatial gradients between measurement locations. However, this design does not completely eliminate the effect of radial plasma density gradients, which are inherent to expanding cathodic arc plasmas [3, Chap. 6.2]. The close proximity brings the measured flux and plasma conditions as close as possible, though small differences due to the radial gradient remained and were evident in the experimental results.

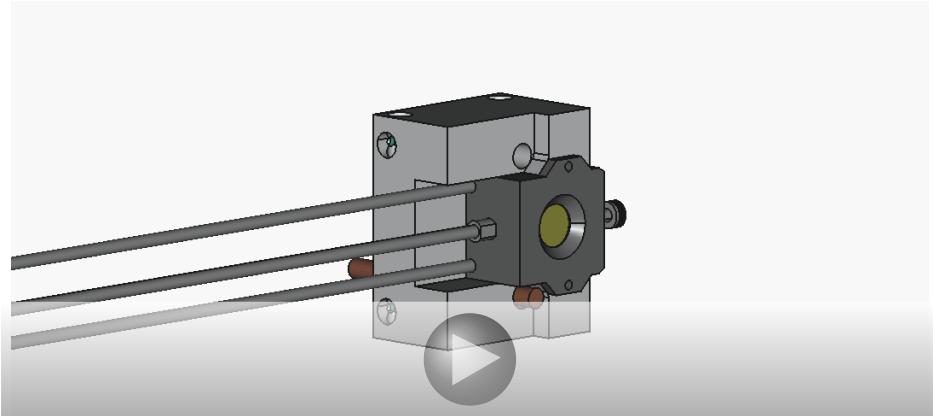


Figure 3.6: Holder Assembly for In-Situ Plasma Diagnostics: Integrated QCMs and Langmuir Ion Collector Probe (interactive 3D model; static preview shown in non-Adobe viewers).

3.2.4 Energy-Resolving Mass Spectrometer (ERMS)

An energy-resolving mass spectrometer (ERMS, Hiden EQP 1000) was used to measure ion energy distribution functions (IEDFs) and charge-state-resolved fluxes of plasma species. The system combines an electrostatic energy analyzer with a quadrupole mass filter to measure distributions of energy-to-charge ratios (E/Q) at fixed mass-to-charge ratios (M/Q), and vice versa.

Ions enter the ERMS through a $50 \mu\text{m}$ sampling orifice and are transported to the energy analyzer, where their kinetic energy E_i is selected according to:

$$E_i = \left(V_{\text{ENERGY}} + \frac{R}{d} V_{\text{PLATES}} - V_{\text{AXIS}} \right) Q \cdot e \quad (3.7)$$

Here, V_{ENERGY} and V_{AXIS} are opposing potentials applied to the analyzer, R is the mean radius of the cylindrical sector, d is the plate separation, V_{PLATES} is the potential difference across the sector plates, Q is the ion charge state, and e is the elementary charge [15].

The energy-selected ions are then injected into the quadrupole mass filter, where a combination of AC and DC electric fields creates a stability region dependent on M/Q , described by the Mathieu equations [16]. The potential in the quadrupole is:

$$V(x, y, t) = \frac{U_0 \cos(\omega t)}{r_0^2} (x^2 - y^2) \quad (3.8)$$

where U_0 is the amplitude of the AC voltage, ω is the angular frequency, and r_0 is the field radius. The stability of ion motion is determined by the dimensionless parameters:

$$a = \frac{8eU_{\text{DC}}}{Mr_0^2\omega^2}, \quad q = \frac{4eU_0}{Mr_0^2\omega^2} \quad (3.9)$$

with U_{DC} as the superimposed DC voltage and M the ion mass. For a given M/Q , stable transmission occurs only within specific (a, q) regions, enabling mass separation [16, 17]. Only ions with trajectories stable in both radial and axial directions reach the detector.

To reduce interference from the arc's magnetic field, the ERMS was equipped with a grounded mu-metal shield [4]. IEDFs were measured using a double-trigger acquisition scheme synchronized with the arc pulses (1 ms duration, 5 Hz repetition rate). For each M/Q value, two 20 ms acquisition windows were recorded, activated 10 ms before the onset of the pulse. The combined 40 ms of data for each point were averaged to obtain the final IEDF.

Molar mass over charge ratio of:				
Ionization	Al	Ti	N	N_2
1+	27	47.867	14	28
2+	13.5	23.933	-	-
3+	9	15.955	-	-
4+	-	11.966	-	-

To obtain the ion energy distribution functions (IEDFs), the energy-to-charge (E/Q) distributions were measured for different mass-to-charge ratios (M/Q). The energy distributions for ions of different charge states were derived by multiplying the E/Q values by the corresponding charge state number Q . This correction accounts for the charge-dependent scaling of ion energies.

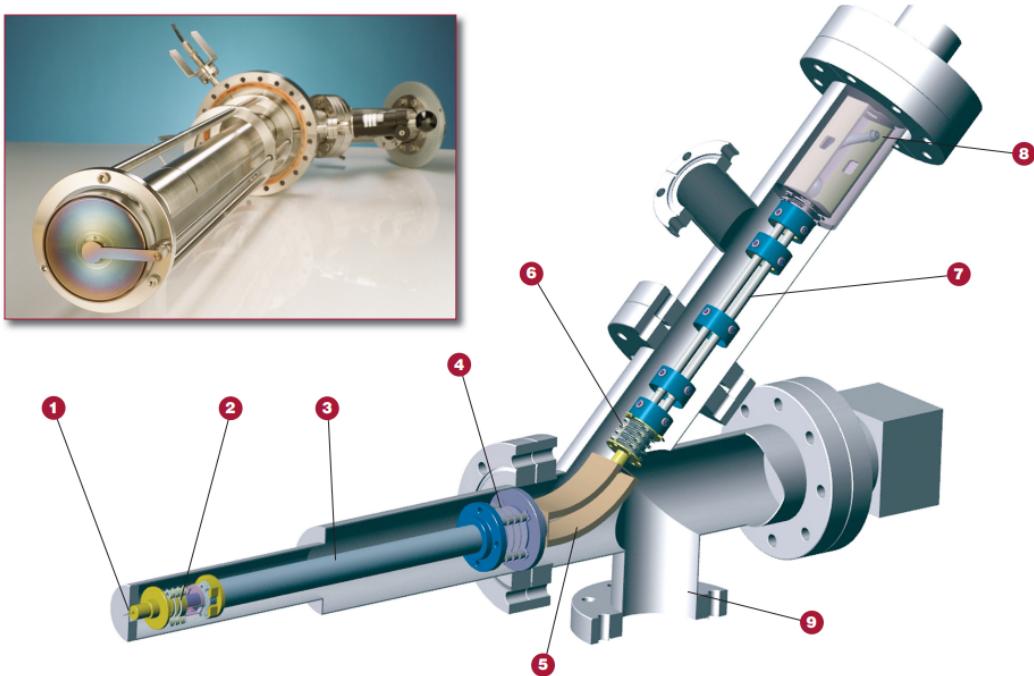


Figure 3.7: ERMS, Hiden EQP HE 1000: (1) Sampling Orifice, (2) Electron Impact Ion Source, (3) Transfer Ion Optics, (4) Quadrupole Lens, (5) Energy Filter, (6) Decelerating Lens, (7) Quadrupole Mass Filter, (8) Detector, (9) Differential Pump Port [18]

IEDFs were measured using a double trigger acquisition scheme synchronized with the arc pulses, which had a 1 ms duration and a 5 Hz repetition rate. For each m/q value, two 20 ms acquisition windows were recorded, activated 10 ms before the onset of the pulse. The combined 40 ms of data for each point were averaged to obtain the final IEDF. Measurements were performed for charge states 1^+ , 2^+ , and 3^+ of aluminum ions, and for charge states 1^+ , 2^+ , 3^+ , and 4^+ of titanium ions. For nitrogen ion species (N and N_2), only the 1^+ ionization level was measured. This was achieved by scanning V_{ENERGY} while fixing the quadrupole mass filter to the corresponding m/q values.

3.2.5 Calculation of Ion Flux and Total Deposited Flux

The ion flux and total deposited flux are key parameters for understanding the correlation between plasma properties and film growth. These quantities are derived from the combined measurements of the Langmuir probe, QCM, ERMS and film composition.

Ion Flux from Probe and ERMS Measurements

The ion flux Γ_{ion} ($\text{ions cm}^{-2} \text{s}^{-1}$) is calculated from the ion current density measured by the Langmuir probe:

$$\Gamma_{\text{ion}} = \frac{J_i}{e\langle Q \rangle} = \frac{V_{\text{measured}}}{e\langle Q \rangle A_{\text{probe}} R} \quad (3.10)$$

where $\langle Q \rangle$ is the average charge state determined from ERMS measurements. This combination of probe and mass spectrometer data accounts for the multiply charged nature of the cathodic arc plasma and enables accurate determination of the particle flux from the electrical current measurement.

Total Deposited Flux from QCM and Film Characterization

The total deposited flux Φ_{total} ($\text{atoms cm}^{-2} \text{pulse}^{-1}$) includes contributions from both ions and neutrals (in reactive mode). This quantity is derived from the QCM mass deposition rate:

$$\Phi_{\text{total}} = \frac{\Phi_{\text{mass}} N_A}{M_{\text{eff}}} = \frac{\Delta m \cdot N_A}{A_{\text{QCM}} \cdot N_{\text{pulses}} \cdot M_{\text{eff}}} \quad (3.11)$$

where $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ is Avogadro's constant and M_{eff} is the effective molar mass of the deposited material.

The effective molar mass depends on the film composition, which was determined by energy-dispersive X-ray spectroscopy (EDX, Section 3.3.5). M_{eff} reflects the TiAlN stoichiometry determined by EDX analysis of the deposited films. The film density ρ_{film} required to relate mass deposition rate to film thickness was determined by X-ray reflectometry (XRR, Section 3.3.3).

The ratio $\Phi_{\text{total}}/\Gamma_{\text{ion}}$ provides insight into the fraction of deposited material arriving as ions versus neutrals, which is particularly important for understanding reactive mode deposition where activated nitrogen species contribute significantly to film growth.

3.3 Ex situ Measurements

3.3.1 Profilometry

Stylus profilometry was used to measure film thickness by mechanically tracing the surface topography using a diamond-tipped stylus. The technique provides direct measurement of step heights between masked and deposited regions, making it particularly useful for verifying film thickness values obtained by QCM [19].

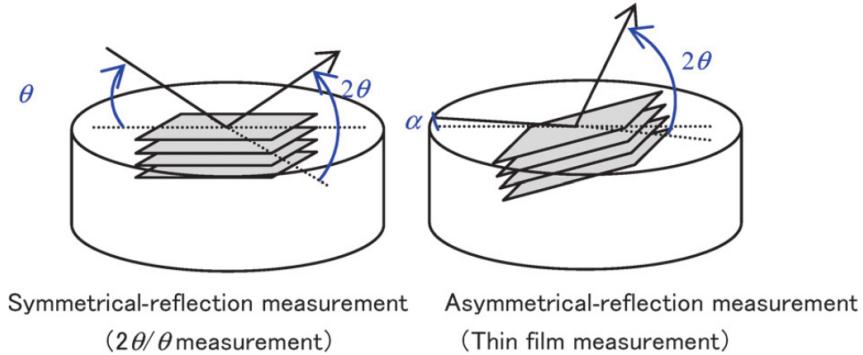


Figure 3.8: Schematic of out-of-plane diffraction geometries: symmetrical reflection (left) and asymmetrical reflection (right) for thin film analysis. Taken from [20].

In profilometry, a stylus with a small tip radius is dragged across the sample surface with a controlled force of 3 mg while its vertical displacement is monitored electromagnetically. The resulting trace provides a profile of the surface from which the step height (film thickness) with vertical resolution down to ~ 1 nm can be extracted.

3.3.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) was employed to analyze the crystallographic structure of the thin films deposited during the experiments. XRD is a non-destructive technique that provides detailed information about the crystalline phases present in the material, as well as their lattice parameters, crystallite size, and strain.

Due to the small film thickness, out-of-plane diffraction techniques were used to enhance the film signal relative to the substrate. Two measurement geometries are employed [20]:

- **Symmetrical reflection ($2\theta/\theta$ scan):** Both incident and diffracted beams make equal angles with the sample surface. This geometry probes lattice planes parallel to the substrate and is suitable for textured films, but substrate peaks can obscure weak film signals.
- **Asymmetrical reflection (thin-film method):** The incident beam is fixed at a small grazing angle α , while the detector scans in 2θ . This reduces the X-ray penetration depth from tens of micrometers to a few micrometers, greatly enhancing sensitivity to thin films [20].

The XRD measurements were performed using a model name of xrd machine diffractometer equipped with non monochromatic Cu_α source with smt smt wavelength- The

asymmetrical reflection scans were performed with an add incidence angle and speed and step size used

The crystallographic structure was determined by analyzing the diffraction patterns. The Bragg equation was used to identify the crystalline phases:

$$2d \sin(\theta) = n\lambda, \quad (3.12)$$

where d is the spacing between atomic planes, θ is the diffraction angle, n is an integer, and λ is the X-ray wavelength.

3.3.3 X-ray Reflectometry (XRR)

X-ray reflectometry (XRR) is a non-destructive technique used to determine film thickness, density, and surface or interface roughness by measuring the intensity of X-rays reflected at grazing incidence angles (0.01–5°) [21].

When X-rays strike a flat surface at shallow angles below the critical angle θ_c , total external reflection occurs. The critical angle is related to the electron density of the material through:

$$\theta_c = \sqrt{2\delta}, \quad (3.13)$$

where δ depends on the material density and composition [21]. Above θ_c , X-rays penetrate the film and reflect from interfaces, creating interference patterns known as Kiessig fringes. The period of these oscillations is directly related to film thickness [22]:

$$d \approx \frac{\lambda}{2\Delta\theta}, \quad (3.14)$$

where λ is the X-ray wavelength and $\Delta\theta$ is the angular spacing between fringes.

The XRR technique provides three key parameters [21]:

- **Film thickness:** Determined from the oscillation period, with accuracy of 0.1–0.2 nm for films in the 1–150 nm range.
- **Density:** Extracted from the critical angle position and oscillation amplitude. Larger density contrast between film and substrate produces higher amplitude oscillations.
- **Surface and interface roughness:** Surface roughness causes faster decay of reflectivity at higher angles, while interface roughness reduces oscillation amplitude.

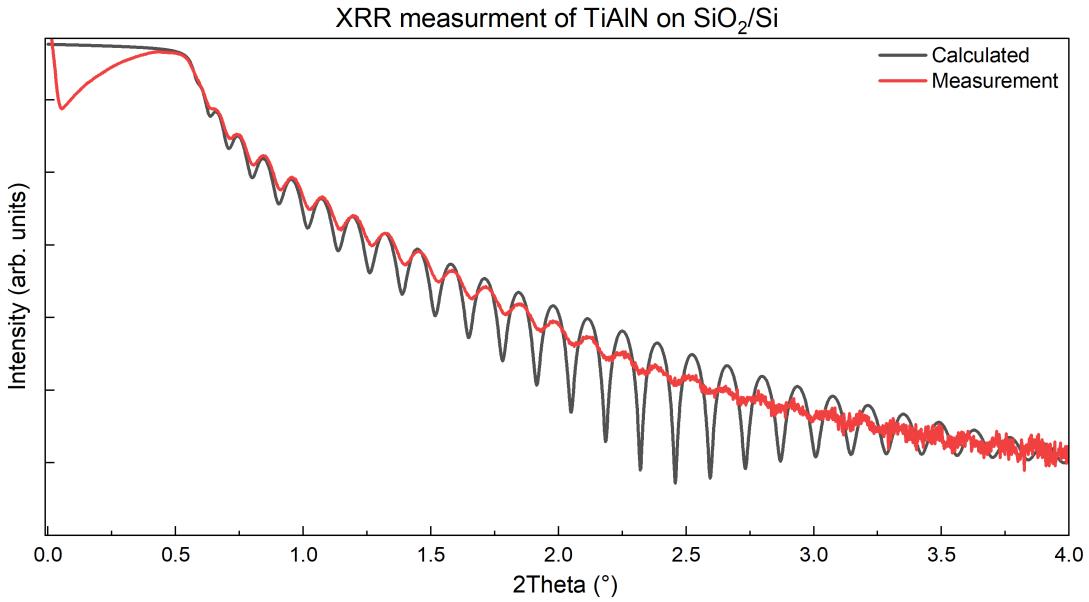


Figure 3.9: Example XRR measurement and fit for a TiAlN thin film deposited on Si substrate. The oscillations (Kiessig fringes) arise from interference between reflections from the film surface and the film-substrate interface.

The measured reflectivity curves were analyzed using the Parratt recursive formalism [23], which accounts for multiple reflections at each interface. Film thickness, density, and roughness parameters were refined by fitting the calculated reflectivity curve to the experimental data. Initial thickness estimates from Profilometry measurements (Section 4.4.1) were used as starting values for the fitting procedure. XRR is particularly suited for verifying thicknesses and characterizing film density and surface quality for the deposited TiAl/TiAlN films.

3.3.4 Scanning Electron Microscopy (SEM)

need to look into before writing about it, more precisely about the specs of the device

3.3.5 Energy-dispersive X-ray spectroscopy (EDX)

need to look into before writing about it, more precisely about the specs of the device

3.4 Data Processing

Experimental data were processed using custom Python scripts to ensure consistency and reproducibility. A central Excel logbook served as the reference for all measurements, each identified by a unique suffix and linked to its corresponding data files. The logbook recorded experimental parameters such as date, distance, pressures, MFC flow

rate, cryopump position, power supply settings, and pulse characteristics, as well as initial and final QCM frequencies for deposited mass determination. Associated oscilloscope waveforms were stored as CSV files for ion current analysis.

A Python script automated data handling by matching logbook entries to raw data, averaging ion current waveforms over multiple pulses to reduce noise when possible, and compiling all parameters into a unified dataset. This ensured uniform processing and efficient preparation for subsequent analysis.

QMS data were evaluated with a separate Python script that integrated raw spectra, applied mass transmission corrections to account for detection biases, and extracted parameters such as mean ion energy, charge state distribution, and potential and kinetic energy components for each species (different ionization levels of the four atoms measured). The processed results were visualized and exported into a structured CSV file for detailed examination of the ion energy distributions.

3.5 Error Handling

3.5.1 Mass Spectrometry Measurements

In mass spectrometry measurements, particularly in the context of cathodic arc processes, the standard deviation is crucial for characterizing data variability. The non-stationary nature of cathode spots in cathodic arcs leads to significant fluctuations in ion flux and charge composition from pulse to pulse [3]. Calibrating mass spectrometry measurements can be challenging due to these fluctuations, as random errors at each standard point used to determine the calibration curve can lead to a distribution of values for the same observed response for the unknown [24]. As a result, achieving optimal calibration in such conditions may not be straightforward, and the accuracy of the calibration could be affected.

In this study, while efforts were made to calibrate the mass spectrometer accurately, the inherent difficulties associated with the calibration process in cathodic arc environments suggest that the calibration might not have been optimal. To account for this potential source of error, the impact of truncating the measurement artifact (e.g., signal noise or background interference) at different points was evaluated, and its effect on the data was analyzed in detail. This analysis will be further discussed in Section ??.

As detailed in Appendix C, the standard deviation of energy measurements is calculated using the `calculate_energy_stats` function, providing both average energy and standard deviation. This statistical approach offers a visual representation of

measurement variability through error bars. The use of standard deviation in mass spectrometry is well-documented in scientific literature. For instance, standard deviation is commonly used to represent uncertainties in measurements and to describe the scatter among measured data points [25]. This statistical approach is crucial for characterizing data variability and ensuring the accuracy of the measurements.

3.5.2 QCM and Ion Current Probe Measurements

For the ion current probe measurements, the standard deviation of the averaged measurements is calculated to characterize the variability in the data. This variability within a pulse can be attributed to several factors: the fluctuations in the plasma potential at the beginning of the pulse, charge exchange reactions between ions and neutrals and variations in the arc current and pulse parameters. These factors can cause fluctuations in the ion current during the pulse, leading to the observed variability [26]. This kind of instability within the pulse will be henceforth shown with the help of error bars.

However, certain sources of error specific to the ion probe must be considered. The design of the ion probe can influence the measurements due to sheath effects, where the sheath around the probe can expand based on the probe's size and the biasing applied [3, Appendix A.2]. Additionally, secondary electron emissions from the probe surface can affect the ion current measurements [3, Chap. 8.2]. These emissions can be caused by interactions between the ions and the probe surface leading to inaccuracies in the measurements. As stated before, each pulse varies in terms of energies and amount of particles; these variations are investigated briefly in Sec. 4.1.4, but cannot be considered for every data point.

The QCM measurements are subject to inaccuracies in terms of the error in the resonance frequency measurements, which is based on the manufacturer's specifications. The given measurement inaccuracy is $\Delta f = 0.03$ Hz, which will be taken for error propagation [27]. Additionally, the relative position of the QCM sensor with respect to the ion flux affects the accuracy of the measurements especially at close distances.

3.5.3 Error Propagation Analysis

To properly characterize the uncertainties in the derived quantities, a comprehensive error propagation analysis was performed. The primary measured quantities with associated uncertainties are: the ion current I_{ion} with standard deviation σ_I , the deposited mass m measured by QCM with uncertainty σ_m , and the mean charge state \bar{Q} with standard deviation σ_Q determined from mass spectrometry measurements. These independent measurements are combined to calculate particle fluxes, necessitating careful propagation of uncertainties through the calculation chain.

Ion Flux from Current Measurements

The ion flux in mass units Φ_{ion} (in $\mu\text{g}/\text{cm}^2/\text{s}$) is calculated from the measured ion current according to:

$$\Phi_{\text{ion}} = \frac{I_{\text{ion}}}{A \cdot \bar{Q} \cdot e} \quad (3.15)$$

where e is the elementary charge, A is the collection area of the ion probe and \bar{Q} is the mean charge state.

For error propagation, considering the independent uncertainties in I_{ion} , \bar{Q} , the standard Gaussian error propagation formula gives [28]:

$$\left(\frac{\sigma_{\Phi_{\text{ion}}}}{\Phi_{\text{ion}}} \right)^2 = \left(\frac{\sigma_I}{I_{\text{ion}}} \right)^2 + \left(\frac{\sigma_Q}{\bar{Q}} \right)^2 \quad (3.16)$$

This shows that the relative uncertainties add in quadrature, which is typical for multiplicative error propagation.

Atomic Flux from QCM Measurements

The atomic flux Φ_{atom} (in atoms/ cm^2/s) is determined from the mass flux measured by the QCM:

$$\Phi_{\text{atom}} = \frac{\Phi_{\text{mass}} \cdot N_A}{M_{\text{eff}}} \quad (3.17)$$

where $\Phi_{\text{mass}} = m/(A_{\text{QCM}} \cdot t)$ is the mass flux and $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ is Avogadro's constant. Following the same approach: **this depends what kind of data i get from EDX, else just standard error**

$$\left(\frac{\sigma_{\Phi_{\text{atom}}}}{\Phi_{\text{atom}}} \right)^2 = \left(\frac{\sigma_m}{m} \right)^2 + \left(\frac{\sigma_{M_{\text{eff}}}}{M_{\text{eff}}} \right)^2 \quad (3.18)$$

The QCM mass uncertainty σ_m is calculated from the frequency measurement uncertainty $\Delta f = 0.03 \text{ Hz}$ using the Sauerbrey relation.

CHAPTER 4

Results

4.1 Langmuir Probe Bias Voltage Characterization

4.1.1 Validation of Langmuir Probe Operation

Before plasma diagnostics were performed, the functionality of the custom-built Langmuir probe was verified by checking the characteristic voltage current curve (I-V curve) and fitting it against the theoretical relationship 4.1. Additionally the appropriate negative bias voltage for ion saturation measurements was determined . The aim of this test was to ensure that the probe operates in a regime where the collected current is dominated by ions, excluding contributions from electrons.

The bias voltage tests were performed without nitrogen in the chamber, at a fixed distance of 10 cm from the macroparticle filter, and with an EM coil strength of 0.25 T. Figure 4.1 displays the measured ion current as a function of bias voltage. The blue data points are the experimental results, with the green line shows the exponential saturation fit.

The relationship between the collected current I and the bias voltage V was analyzed using the modified Langmuir equation [29]:

$$I = I_{\text{sat}} \left(1 - e^{\frac{-V}{V_0}} \right) + m \cdot V \quad (4.1)$$

where I_{sat} is the saturation current and V_0 is a characteristic voltage. The term k

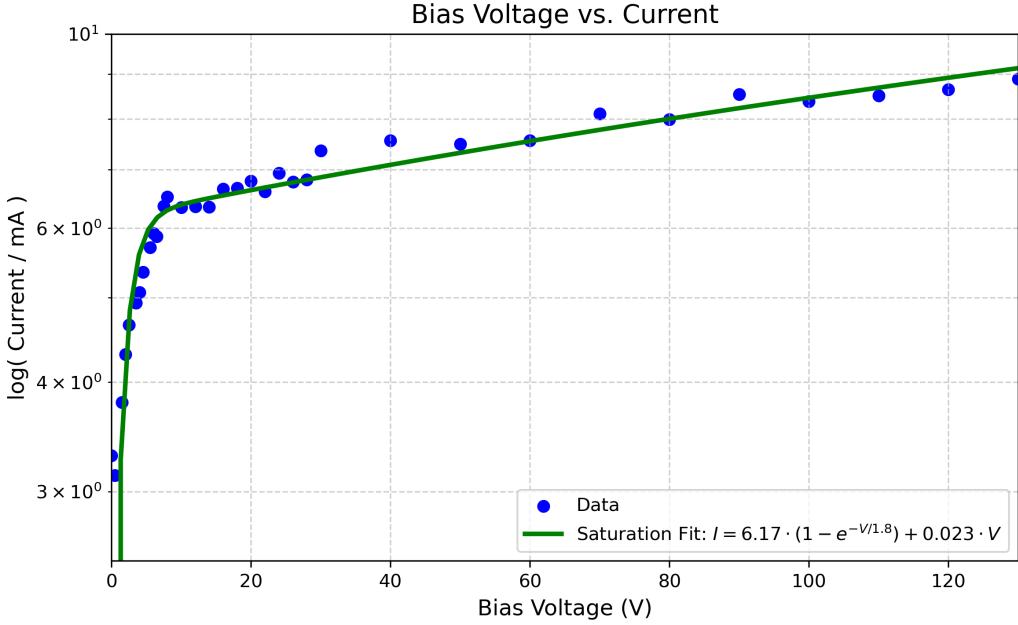


Figure 4.1: Measured ion current vs. bias voltage for the Langmuir probe, showing exponential saturation fit $I = 6.17 \cdot (1 - e^{-V/1.8}) + 0.023 \cdot V$. Conditions: no nitrogen, 10 cm from the macroparticle filter, 0.25 T EM-coil strength.

in the equation accounts for plasma sheath expansion and collisional effects at higher bias voltages.

4.1.2 Analysis of the Ion Saturation Curve

As the bias voltage increases, the sheath around the probe grows, which can lead to a non-saturating component in the collected current, this is a common effect seen in small probes. Additionally, collisions within the sheath or presheath region can modify the ion trajectory, resulting in a small linear increase in the collected current with voltage. This correction ensures the model accurately describes the probe's behavior across the full range of applied voltages [29, Chap. 7].

The experimental data were fitted to this equation using a nonlinear least-squares method in Python, yielding the following parameters:

$$I_{sat} = 6.17 \text{ mA}, \quad V_0 = 1.8 \text{ V}, \quad k = 0.023.$$

The bias voltage test results (Figure 4.1) show two distinct regimes:

1. Transition Regime (0 – 40 V):

At low bias voltages the probe collects both ions and electrons. As the negative bias increases, more electrons are repelled, reducing their contribution to the

measured current. This results in a rapid rise in net current as the ion flux begins to dominate. The transition regime is characterized by the decreasing electron flux and the increasing ion flux.

2. Saturation Regime (40 – 130V):

Beyond approximately 40V, the current plateaus, indicating that the probe has entered the ion saturation regime. At this point, the negative bias effectively repels all electrons, and the collected current is dominated by ions. However, the current increases slightly with voltage, which is captured by the linear correction term $k = 0.023$ in the modified Langmuir equation.

4.1.3 Selection of Operating Bias Voltage

A bias voltage of -80 V was selected for subsequent measurements to ensure the probe operates well within the ion saturation regime. While the curve begins to saturate around 40 V, choosing a higher voltage provides confidence that the probe is fully repelling electrons and measuring ion flux reliably.

4.1.4 Ion current Variation over different pulses

To analyze the pulse-to-pulse variation, approximately 30 single pulses were recorded for each magnetic field strength. The average ion current of each pulse was calculated over the 0–1 ms pulse interval. The final mean and standard deviation were then determined by combining these averages, allowing for an assessment of the differences between pulses. Notably, the 0.05 T data point in Fig. 4.2 includes a significant outlier, with a recorded ion current of approximately 4.8 mA, as detailed in Table 4.1.

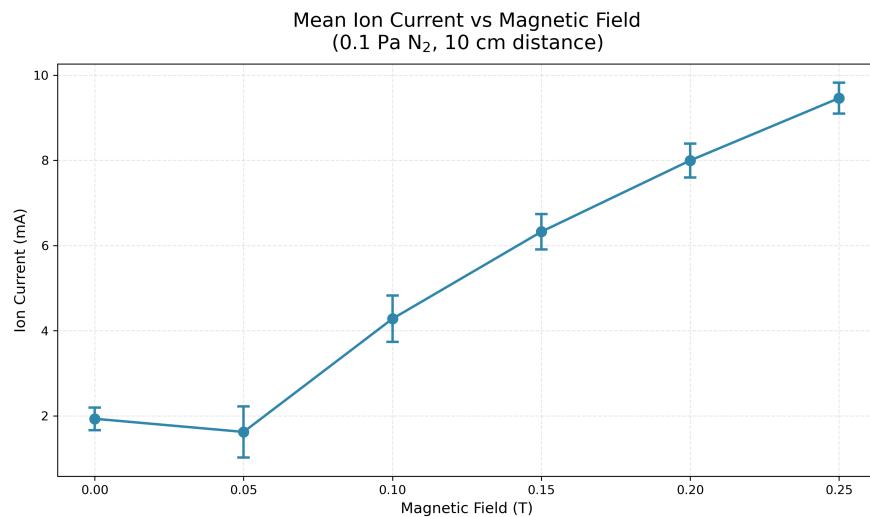


Figure 4.2: Pulse-to-Pulse Variation in Mean Ion Current at Varying Magnetic Fields (0.1 Pa N₂, 10 cm distance)

EM-coil field (T)	Mean I_{ion} (mA)	Std (mA)	Std (%)	Range (mA)	# Pulses
0.00	1.931	0.266	13.8	[1.13, 2.26]	30
0.05	1.622	0.602	37.1	[1.16, 4.85]	32
0.10	4.279	0.542	12.7	[2.72, 4.88]	31
0.15	6.323	0.414	6.6	[4.99, 6.92]	27
0.20	7.996	0.399	5.0	[7.26, 8.78]	22
0.25	9.460	0.363	3.8	[8.61, 10.02]	30

Table 4.1: Summary of pulse measurement statistics for varying magnetic field strengths.

In all other measurements, the oscilloscope averaged the voltage drop of the ion current over multiple pulses to produce smoother curves. Therefore, the error reported in subsequent sections primarily reflects variations in ion current within individual pulses, rather than differences between distinct pulses, as previously discussed in Section 3.5.2.

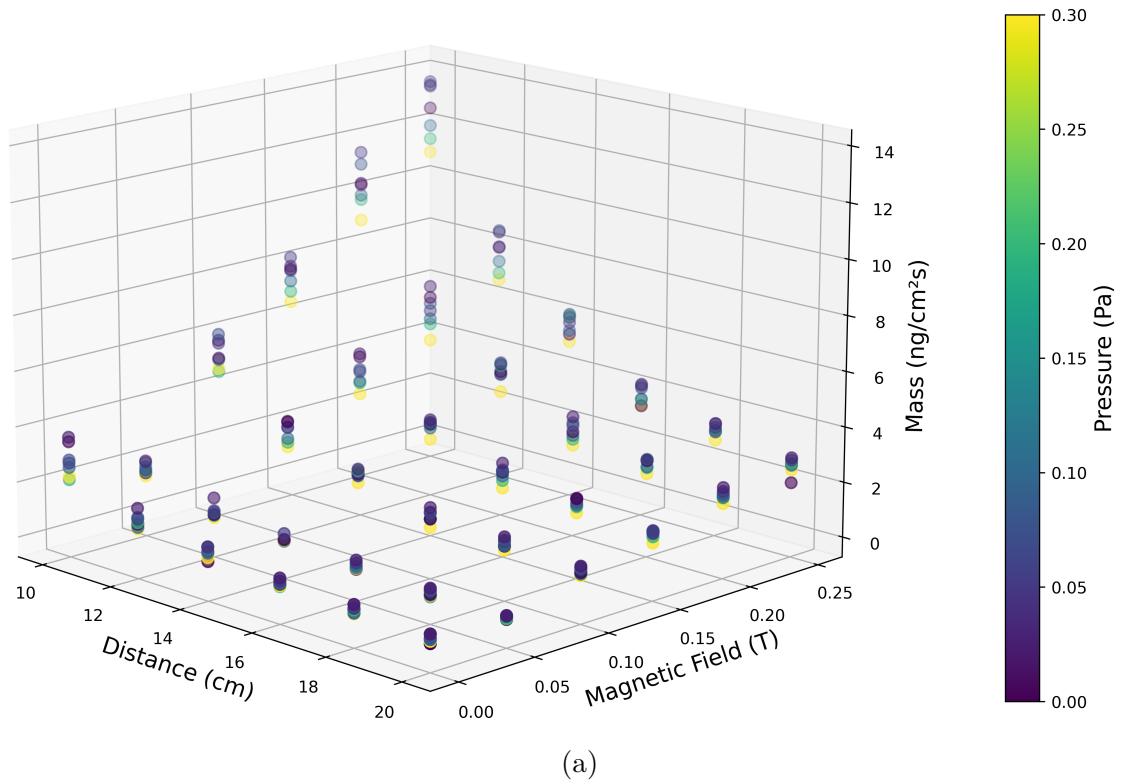
4.2 Quartz crystal Microbalance and Ion current Probe

To systematically characterize the plasma dynamics and deposition behavior, measurements were conducted using both a quartz crystal microbalance (QCM) for mass deposition and a biased ion collector probe for ion current density.

The experimental parameter space spanned three variables: distance from the macroparticle filter (10–20 cm), applied magnetic field strength (0–0.25 T), and nitrogen background pressure (0–0.3 Pa), with all permutations measured as listed in Table C.1. At this stage, the raw quantities (mass flux in nanograms/cm²s and ion current in milliamperes) are not directly comparable and only trends will be observed. Their relationship will be established through flux calculations in Section 4.5.

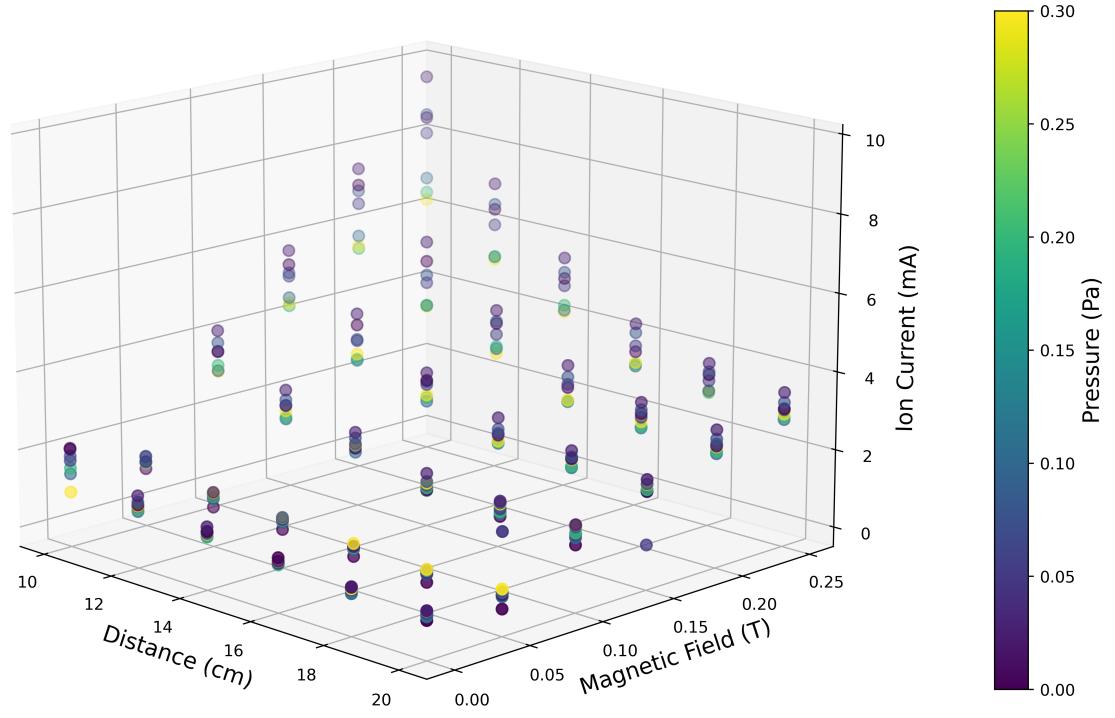
Figure 4.3 provides a three-dimensional visualization of the complete dataset, illustrating how the mass flux and ion current vary simultaneously with all three control parameters. Several global trends are immediately apparent: both quantities decrease with increasing distance due to plasma expansion, increase with applied magnetic field due to enhanced plasma confinement and ionization, and exhibit complex pressure dependence that warrants detailed investigation.

Mass ($\text{ng}/\text{cm}^2\text{s}$) vs. Distance (cm), Magnetic Field (T) and Pressure (Pa)



(a)

Ion Current (mA) vs. Distance (cm), Magnetic Field (T) and Pressure (Pa)



(b)

Figure 4.3: Three-dimensional visualization of (a) mass flux and (b) pulse-averaged ion current as functions of distance (10–20 cm), magnetic field strength (0–0.25 T), and nitrogen pressure (0–0.3 Pa).

To systematically dissect these multidimensional trends, the following subsections examine cross-sections through the parameter space in order of increasing complexity. We begin with the metallic case (vacuum conditions, no reactive gas) to establish baseline behavior as functions of distance and magnetic field. Subsequently, we introduce nitrogen pressure as an additional variable and examine its interplay with geometry and magnetic confinement. The parameter combinations analyzed in detail: distances of 10, 14, and 20 cm; magnetic fields of 0, 0.15, and 0.25 T; and pressures of 0.1 and 0.3 Pa. These parameters were selected because they correspond to the conditions used for energy-resolved mass spectrometry (ERMS) measurements and thin film deposition, enabling an introduction.

4.2.1 Metallic Case (No Nitrogen)

In the absence of reactive gas, the plasma expansion and deposition dynamics are governed solely by geometric dilution and magnetic confinement. Figure 4.4 presents mass flux and ion current as functions of magnetic field strength for three representative distances.

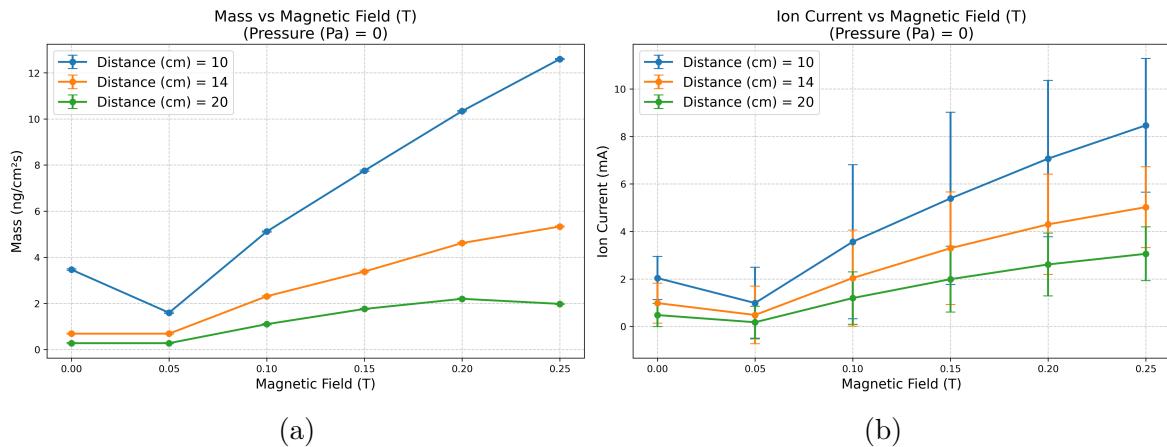


Figure 4.4: Metallic case measurements showing (a) mass flux and (b) the ion current, each plotted as a function of magnetic field strength. Data selected for three distances (10, 14, 20 cm), with error bars representing variation within pulses.

As shown in Figure 4.4, both the mass and the ion current increase with applied magnetic field. The enhancement is most pronounced at the shortest distance (10 cm), where the magnetic field can effectively guide ions before significant radial expansion occurs. At 20 cm, the plasma has already expanded substantially, reducing the relative impact of magnetic confinement on the collected flux.

A notable anomaly appears at 0.05 T, where both quantities drop below their zero-field values. This counterintuitive behavior is attributed to a magnetic mirror effect at the entrance of the EM coil. When plasma transitions from the weak fringing field

(~ 0.01 T) into the stronger coil field (0.05 T), conservation of the magnetic moment causes electrons with significant perpendicular velocity components to be reflected [30, 3]. This creates a localized space-charge layer that retards ion flow, temporarily reducing both the ion flux and deposition rate. At higher fields (0.1 T and above), the beneficial effects of plasma compression and enhanced ionization [6] overcome this mirror loss. Similar behavior is observed across all experimental conditions involving increasing magnetic field.

4.2.2 Distance as a variable

Figure 4.5 examines the effect of source-to-substrate distance under fixed magnetic confinement (0.25 T) for both metallic and reactive conditions. Four nitrogen pressures are compared: 0 Pa (metallic), 0.1 Pa, 0.2 Pa, and 0.3 Pa.

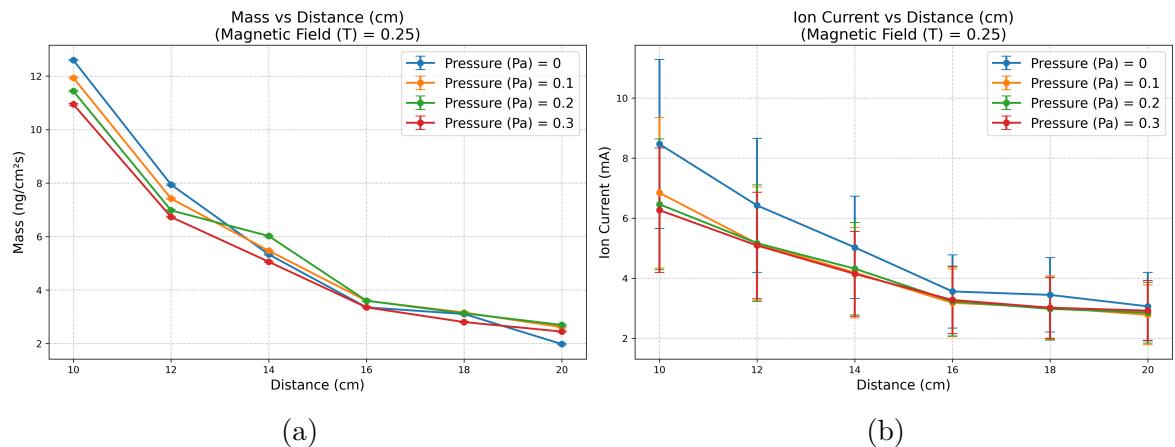


Figure 4.5: QCM and Ion Probe measurements showing (a) mass flux and (b) the ion current, each plotted as a function of distance. Data shown for representative pressures, with error bars representing variation within pulses.

Both mass flux and ion current decrease with distance, reflecting the natural expansion and dilution of the plasma plume. In the case for the mass, this decay is relatively gradual and follows an approximate $1/r^2$ dependence expected for free expansion [3, Chap. 4.3].

In contrast, the ion current exhibits a far more dramatic pressure dependence. The steep drop in measured current when nitrogen is introduced primarily reflects charge-exchange collisions, in which fast metal ions transfer charge to slow nitrogen molecules, producing fast neutral metal atoms and slow N^+ / N_2^+ ions [3, Chap. 9.4]. The resulting neutral flux is invisible to the biased probe, leading to an apparent reduction in "ion" current even though the total metal flux (ions plus neutrals) may remain comparable. Additionally, nitrogen ions contribute less to the measured current due to their lower

charge states ($Q \approx 1$) compared to multiply charged metal ions ($Q \approx 2$) [7].

The contrast between mass with a moderate pressure effect and current with a noticeably stronger pressure effect confirms that charge-exchange neutralization, rather than simple scattering loss, is the dominant process at short distances in reactive mode. This interpretation will be further validated through ERMS charge-state measurements in Section ??.

To isolate the effect of magnetic confinement in reactive mode, we next examine field strength as an independent variable.

4.2.3 Magnetic Field as a variable

Figure 4.6 presents mass flux and ion current as functions of magnetic field strength at a fixed intermediate distance (14 cm) for the same set of pressures.

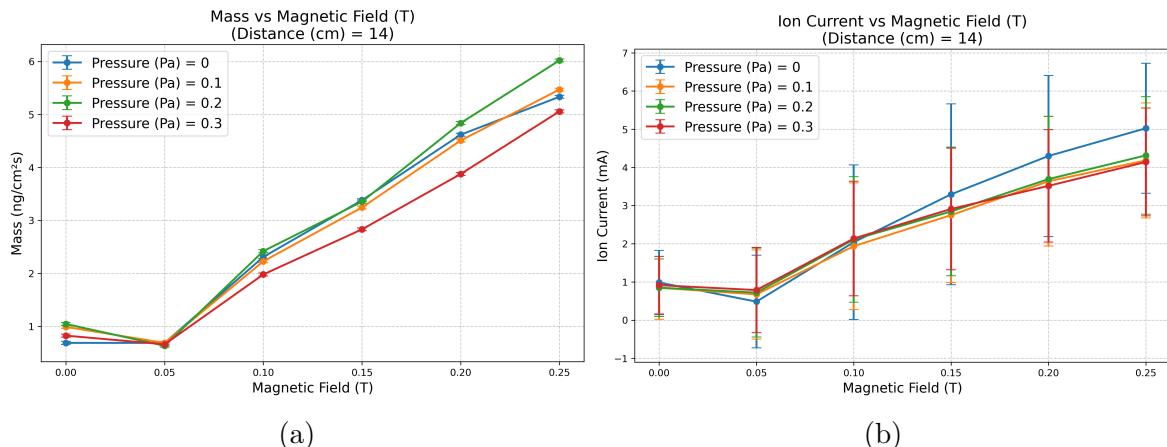


Figure 4.6: QCM and Ion Probe measurements showing (a) mass flux and (b) the ion current, each plotted as a function of Magnetic Field. Data shown for representative pressures, with error bars representing variation within pulses.

The magnetic mirror anomaly at 0.05 T, clearly visible in the 10 cm metallic data (Figure 4.4), is significantly attenuated at 14 cm. Both mass and current remain approximately constant between 0 and 0.05 T, suggesting that the adverse mirror effect is either weaker after 4 cm of additional expansion or is masked by increased statistical noise at this intermediate distance.

Above 0.1 T the trends shows a clear constant increase in both quantities, confirming that magnetic confinement enhances plasma density and ion flux at the substrate. In the case of the ion current, there exists a pronounced divergence between metallic and reactive conditions at high fields. This behavior is consistent with enhanced charge-exchange rates under strong confinement: tighter magnetic focusing increases

the ion path length through the background gas, providing more opportunities for neutralization before reaching the substrate [3, Chap. 9.4]. The result is that, although the magnetic field successfully generates more plasma at the source, a larger fraction arrives as less ionized ions or neutrals in reactive mode.

These observations demonstrate that background gas pressure has a relatively minor influence on total mass flux compared to distance or magnetic field, but significantly affects the charge-state composition of the arriving flux. This distinction motivates the final cross-section through the parameter space: examining pressure as the primary variable.

4.2.4 Nitrogen pressure as a variable

Figure 4.7 presents mass flux and ion current as functions of nitrogen pressure at maximum magnetic confinement (0.25 T) for three distances (10, 14, and 20 cm).

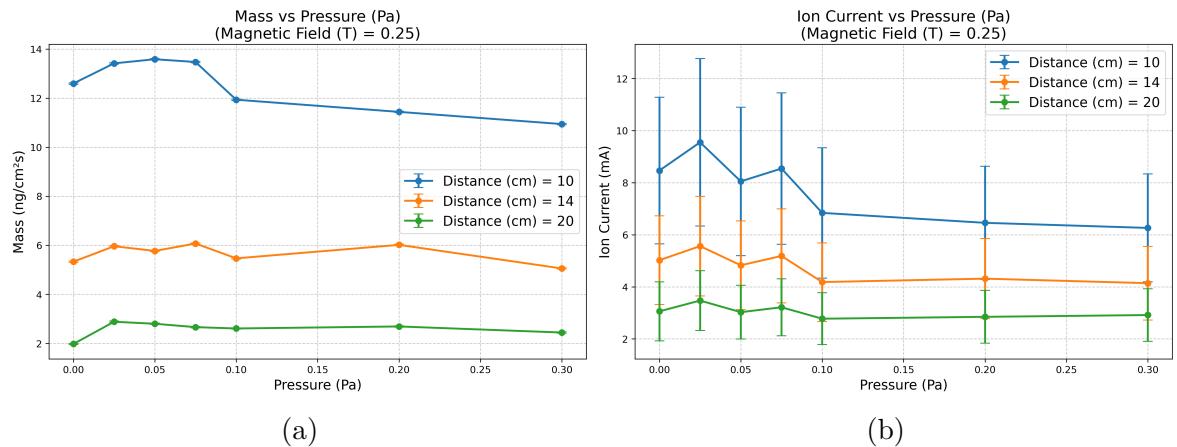


Figure 4.7: QCM and Ion Probe measurements showing (a) mass flux and (b) the ion current, each plotted as a function of Pressure. Data shown for representative pressures, with error bars representing variation within pulses.

At 10 cm, both mass and ion current exhibit complex, pressure dependence with substantial variability. This behavior reflects collisional deflection of the plasma plume: nitrogen molecules scatter metal ions through momentum transfer broadening the spatial distribution [31, 32].

At 14 cm and 20 cm, the pressure dependence becomes negligible. Both mass and ion current remain essentially constant across the entire pressure range. After sufficient expansion, the plasma has already undergone extensive collisional scattering regardless of absolute pressure, resulting in a broad, diffuse distribution.

The non-monotonic behavior observed at 10 cm, particularly the apparent increase in both quantities at low pressures (0.025–0.075 Pa), suggests complex interactions between unequal plasma expansion dynamics and collisional deflection at short standoff distances. The mechanisms underlying this local maximum warrant further investigation but remain beyond the scope of the present work.

4.3 Mass spectrometry Results

- shortly about mean charge state and energies not a focus tho
- maybe a table and a picture

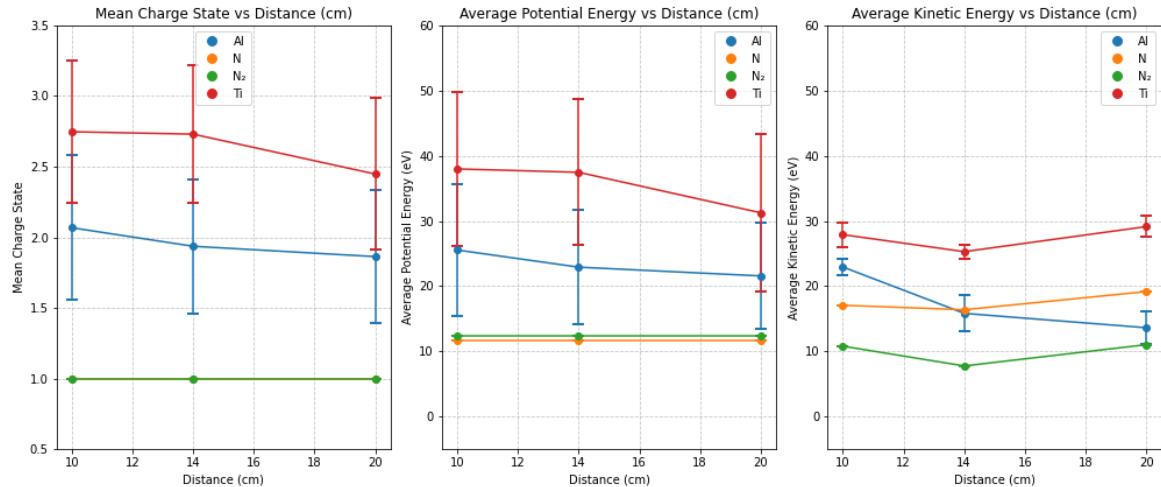


Figure 4.8: 0Pa 0.25T

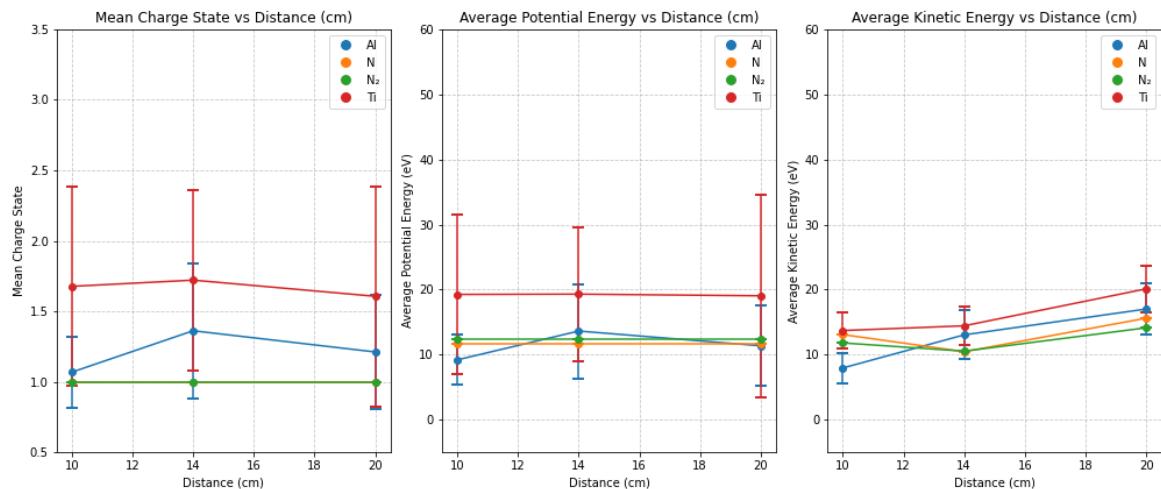


Figure 4.9: 0.3Pa 0.25T

Missing 14cm 0.25T

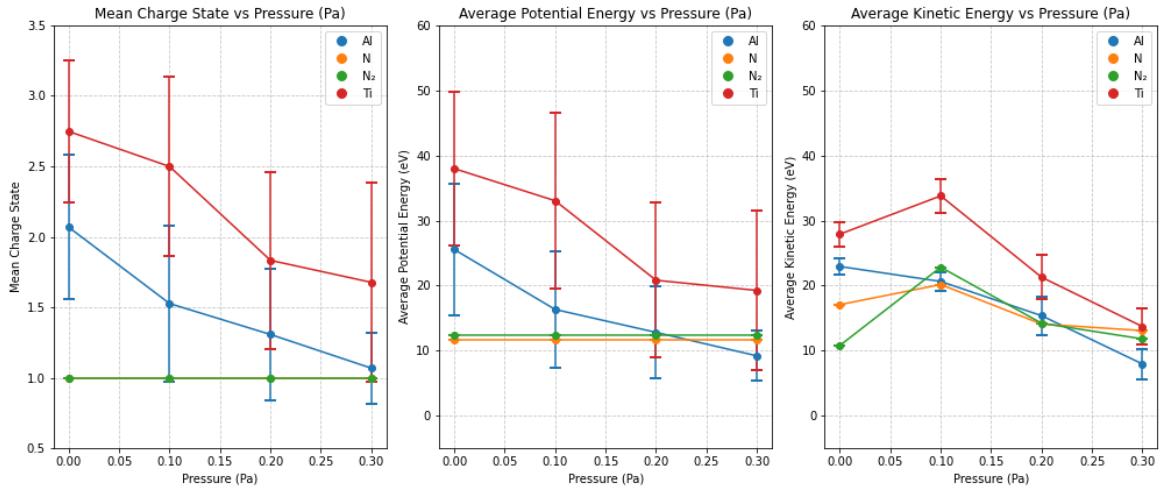


Figure 4.10: 10cm 0.25T

4.4 Ex situ Results

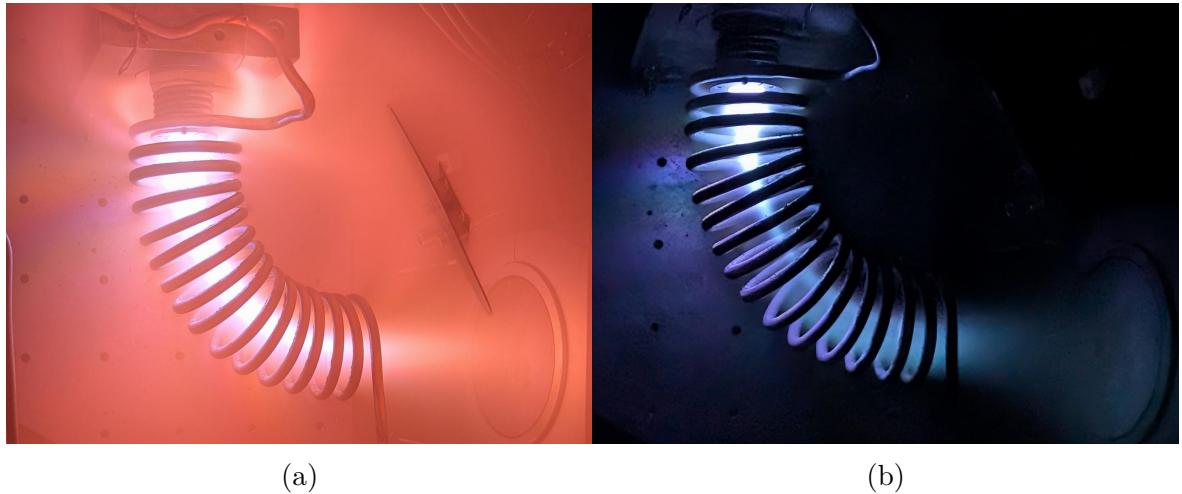


Figure 4.11: to be written picture taken with phone a) with nitrogen and b) metallic... colors are wrong need to change it haha

A total of [insert number of films once i've done all of them, probably like 6-8] were taking into account for further measurements and looked at in the following sections. Blablabla

4.4.1 Profilometry

Samples were prepared by placing a straight marker line near the edge of each substrate prior to deposition. This marker could be cleanly removed by ultrasonic washing after film growth, revealing the deposition step for thickness analysis. Profilometry measurements were performed at three positions on each sample, one near the center and one near each edge. The three measurements were averaged to obtain the mean

film thickness. All resulting values are summarized in Table 4.2.

Table 4.2: Profilometry thickness measurements for the deposited films

4.4.2 XRD

4.4.3 XRR

4.4.4 EDX

4.5 Fluxes

CHAPTER 5

Discussion of Results

Direct comparison between ion current and deposited mass at close distances is complicated due the plasma density gradient

CHAPTER 6

Conclusion

CHAPTER 7

final words or smt like thanks everyone

APPENDIX A

Experimental Methods supplementary

A.1 Longer QCM depositions

For larger mass loadings of the QCM, the linear approximation fails and the Z-match™ technique is used. This method, introduced by Lu and Lewis in 1972 on the basis of Miller and Bolef's theoretical treatment [33, 34], incorporates the acoustic properties of both the quartz and the deposited film via the acoustic impedance ratio

$$Z = \left(\frac{d_q \mu_q}{d_f \mu_f} \right)^{1/2}, \quad (\text{A.1})$$

with d and μ denoting the density and shear modulus of quartz (q) and film (f), respectively [27]. In practice, the controller applies a correction function $f(Z)$ to the Sauerbrey relation,

$$m_f = \frac{N_{\text{AT}} d_q \pi r^2}{F_q^2} \cdot \Delta F \cdot f(Z), \quad (\text{A.2})$$

which compensates for the acoustic mismatch and extends the validity of thickness determination up to $\sim 0.4F_q$.

APPENDIX B

Additional Plots

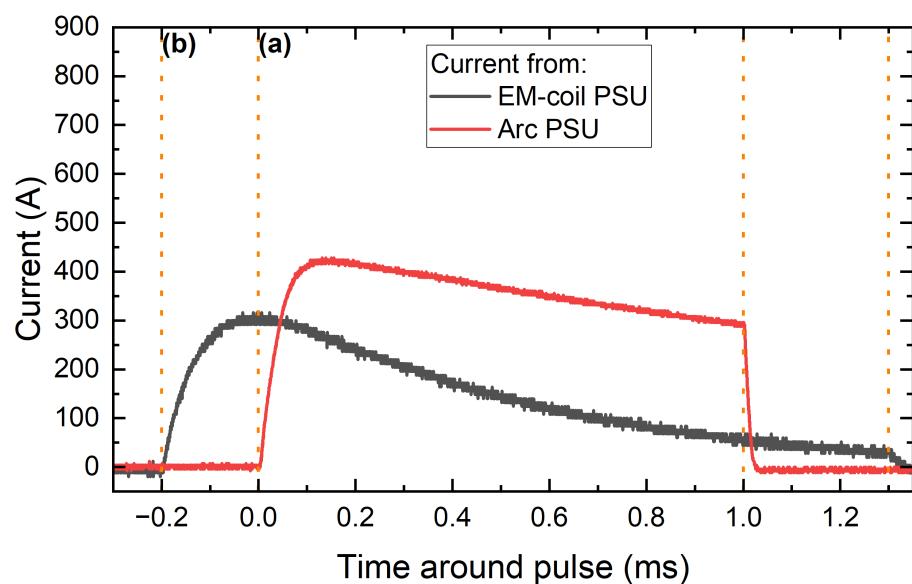
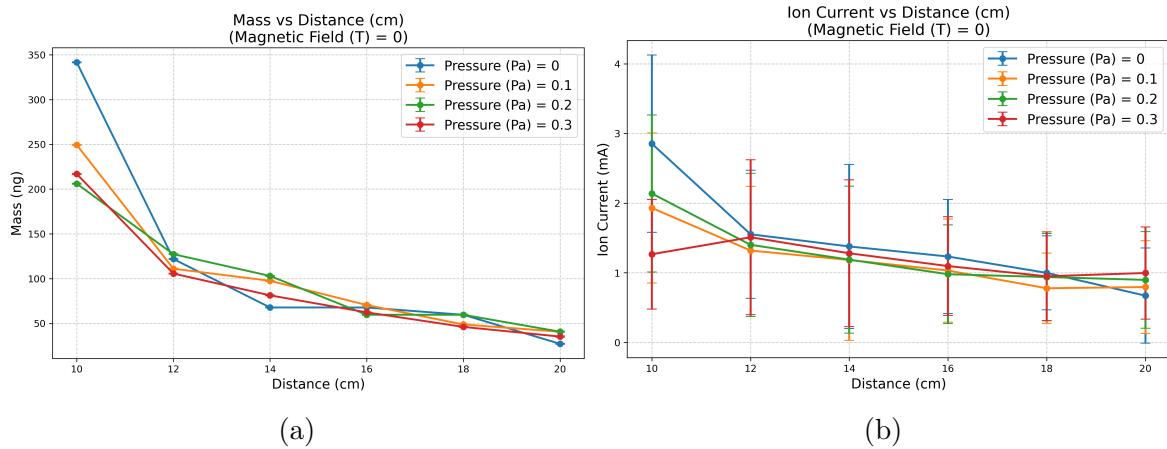


Figure B.1: Additional Pulse waveform with the triggering timings (a) and (b) for the Arc-PSU and the EM-coil PSU marked with the orange dashed line for 100V input



(a)

(b)

Figure B.2: Additional plot for Section 4.2.2. QCM and Ion Probe measurements showing (a) the deposited mass after 64 pulses and (b) the ion current averaged over a single pulse, each plotted as a function of distance. Data shown for representative pressures, with error bars representing variation within pulses.

APPENDIX C

Python code used

Table C.1: Complete overview of experimental measurements. All distance/field/pressure combinations not explicitly listed were measured with ion current probe and QCM only. In total: 252 Ion+QCM measurements, 17 ERMS measurements, 6 deposited films

Distance (cm)	Magnetic Field (T)	Pressure (Pa)	Measurements Performed			Film ID
			Ion/QCM	Mass Spec	Ex-situ	
Systematic parameter scan:						
12, 16, 18	0, 0.05, 0.1, 0.15, 0.2, 0.25	0, 0.025, 0.05, 0.075, 0.1, 0.2, 0.3	✓	—	—	—
Distance 10 cm — standard conditions:						
10	0.05, 0.1, 0.2	all pressures [†]	✓	—	—	—
10	0	0.025, 0.05, 0.075, 0.2	✓	—	—	—
10	0.15	0.025, 0.05, 0.075, 0.2	✓	—	—	—
10	0.25	0.025, 0.05, 0.075	✓	—	—	—
Distance 10 cm — with mass spectrometry:						
10	0, 0.15	0, 0.1, 0.3	✓	✓	—	—
10	0.25	0	✓	✓	✓	003
10	0.25	0.1	✓	✓	✓	004
10	0.25	0.2	✓	✓	—	—
10	0.25	0.3	✓	✓	✓	002
Distance 14 cm — standard conditions:						
14	0, 0.05, 0.1, 0.2	all pressures [†]	✓	—	—	—
14	0.15	0, 0.025, 0.05, 0.075, 0.2, 0.3	✓	—	—	—
14	0.25	0.025, 0.05, 0.075, 0.2	✓	—	—	—
Distance 14 cm — with mass spectrometry:						
14	0.15	0.1	✓	✓	—	—
14	0.25	0	✓	✓	✓	008
14	0.25	0.1	✓	(✓)	(✓)	—
14	0.25	0.2	✓	(✓)	(✓)	—
14	0.25	0.3	✓	✓	✓	009
Distance 20 cm — standard conditions:						
20	0, 0.05, 0.1, 0.15, 0.2	all pressures [†]	✓	—	—	—
20	0.25	0.025, 0.05, 0.075, 0.1, 0.2	✓	—	—	—
Distance 20 cm — with mass spectrometry:						
20	0.25	0, 0.3	✓	✓	—	—

[†]all pressures = 0, 0.025, 0.05, 0.075, 0.1, 0.2, 0.3 Pa

Ion/QCM: Ion current probe and quartz crystal microbalance measured at the same time (in situ)

Mass Spec: Energy-resolved mass spectrometry (ERMS)

Ex-situ: XRD, SEM, profilometry characterization of deposited films

Bibliography

- [1] S. Paldey and S. C. Deevi. “Single layer and multilayer wear resistant coatings of (Ti,Al)N: a review”. In: *Materials Science and Engineering: A* 342.1–2 (2003), pp. 58–79. DOI: [10.1016/S0921-5093\(02\)00259-9](https://doi.org/10.1016/S0921-5093(02)00259-9).
- [2] P. H. Mayrhofer, D. Music, and J. M. Schneider. “Ab initio calculated binodal and spinodal of cubic $Ti_{1-x}Al_xN$ ”. In: *Applied Physics Letters* 88.7 (2006), p. 071922. DOI: [10.1063/1.2177360](https://doi.org/10.1063/1.2177360).
- [3] André Anders. *Cathodic arcs: from fractal spots to energetic condensation*. Vol. 50. Springer, 2008.
- [4] André Anders and George Yu Yushkov. “Ion flux from vacuum arc cathode spots in the absence and presence of a magnetic field”. In: *Journal of Applied Physics* 91.8 (2002), pp. 4824–4832. ISSN: 0021-8979.
- [5] Yeliz Unutulmazsoy et al. “Toward decoupling the effects of kinetic and potential ion energies: Ion flux dependent structural properties of thin (V,Al)N films deposited by pulsed filtered cathodic arc”. In: *Journal of Vacuum Science & Technology A* 41.6 (2023). ISSN: 0734-2101. DOI: [10.1116/6.0002927](https://doi.org/10.1116/6.0002927). URL: <https://doi.org/10.1116/6.0002927>.
- [6] Dmitry Kalanov et al. “Decoupling the effects of potential energy, kinetic energy, and ion flux on crystallinity of V-Al and V-Al-N thin films in pulsed filtered cathodic arc deposition”. In: *Surface and Coatings Technology* 497 (2025). ISSN: 02578972. DOI: [10.1016/j.surfcoat.2024.131720](https://doi.org/10.1016/j.surfcoat.2024.131720).
- [7] J. Benedikt and A. Kersten H. and Henning. “Quadrupole mass spectrometry of reactive plasmas”. In: *Journal of Physics D: Applied Physics* 40.20 (2007), pp. 6300–6316. DOI: [10.1088/0022-3727/40/20/S13](https://doi.org/10.1088/0022-3727/40/20/S13).

- [8] Soheil Karimi Aghda et al. “Ion kinetic energy- and ion flux-dependent mechanical properties and thermal stability of (Ti,Al)N thin films”. In: *Acta Materialia* 251 (2023), p. 118897. DOI: [10.1016/j.actamat.2023.118897](https://doi.org/10.1016/j.actamat.2023.118897).
- [9] G. A. Mesyats. “Ecton mechanism of the vacuum arc cathode spot”. In: *IEEE Transactions on Plasma Science* 23.6 (1995), pp. 879–883. DOI: [10.1109/27.476469](https://doi.org/10.1109/27.476469).
- [10] Burkhard Jüttner. “Cathode spots of electric arcs”. In: *Journal of Physics D: Applied Physics* 34.17 (2001), R103–R123. DOI: [10.1088/0022-3727/34/17/202](https://doi.org/10.1088/0022-3727/34/17/202).
- [11] John A. Thornton. “High rate thick film growth”. In: *Annual Review of Materials Science* 7 (1977), pp. 239–260. DOI: [10.1146/annurev.ms.07.080177.001323](https://doi.org/10.1146/annurev.ms.07.080177.001323).
- [12] André Anders. “A structure zone diagram including plasma-based deposition and ion etching”. In: *Thin Solid Films* 518.15 (2010), pp. 4087–4090. DOI: [10.1016/j.tsf.2009.10.145](https://doi.org/10.1016/j.tsf.2009.10.145).
- [13] R. Rachbauer et al. “Decomposition pathways in age hardening of Ti-Al-N films”. In: *Journal of Applied Physics* 110.2 (2011), p. 023515. DOI: [10.1063/1.3610451](https://doi.org/10.1063/1.3610451).
- [14] Günter Sauerbrey. “Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung”. In: *Zeitschrift für Physik* 155.2 (Apr. 1959), pp. 206–222. DOI: [10.1007/bf01337937](https://doi.org/10.1007/bf01337937).
- [15] *EQP Technical Manual: Energy-Resolving Quadrupole Mass Spectrometer*. Hiden Analytical. Warrington, UK, 2024. URL: <https://www.hidenanalytical.com>.
- [16] P. H. Dawson. *Quadrupole Mass Spectrometry and Its Applications*. Chichester, UK: IM Publications, 1997. ISBN: 978-1-901019-01-4.
- [17] R. E. March and R. J. Hughes. *Quadrupole Storage Mass Spectrometry*. Wiley, 1989. ISBN: 978-0-471-85841-0.
- [18] Hiden Analytical. *EQP: Mass and Energy Analyser for plasma diagnostics*. https://www.hidenanalytical.com/wp-content/uploads/2016/08/EQP-poster_A1_print.pdf. [Accessed 18-11-2025]. 2016.
- [19] C. Y. Poon and B. Bhushan. *Comparison of surface roughness measurements by stylus profiler, AFM and non-contact optical profiler*. Vol. 190. 1. 1995, pp. 76–88. DOI: [10.1016/0043-1648\(95\)06697-7](https://doi.org/10.1016/0043-1648(95)06697-7).
- [20] Toru Mitsunaga. “X-ray thin-film measurement techniques II. Out-of-plane diffraction measurements”. In: *The Rigaku Journal* 25.1 (2009), pp. 7–12.
- [21] Miho Yasaka. “X-ray thin-film measurement techniques: V. X-ray reflectivity measurement”. In: *The Rigaku Journal* 26.2 (2010), pp. 1–9.
- [22] H. Kiessig. “Interferenz von Röntgenstrahlen an dünnen Schichten”. In: *Annalen der Physik* 402.7 (1931), pp. 769–788. DOI: [10.1002/andp.19314020702](https://doi.org/10.1002/andp.19314020702).

- [23] L. G. Parratt. “Surface Studies of Solids by Total Reflection of X-Rays”. In: *Physical Review* 95.2 (1954), pp. 359–369. DOI: [10.1103/PhysRev.95.359](https://doi.org/10.1103/PhysRev.95.359).
- [24] A. Hubaux and G. Vos. “Quantitative Mass Spectrometry: Part II”. In: *Anal. Chem.* 42.8 (1970), p. 849. URL: <https://www.spectroscopyonline.com/view/quantitative-mass-spectrometry-part-ii>.
- [25] R. L. Boxman, S. Goldsmith, and D. M. Sanders. “Cathodic arc plasmas and their applications”. In: *IEEE Transactions on Plasma Science* 23.6 (1995). Includes quantitative plasma diagnostics where standard deviation is used to characterize measurement scatter and reproducibility of arc plasma parameters., pp. 939–956. DOI: [10.1109/27.475210](https://doi.org/10.1109/27.475210). URL: <https://doi.org/10.1109/27.475210>.
- [26] André Anders. “The evolution of ion charge states in cathodic vacuum arc plasmas: a review”. In: *Plasma Sources Science and Technology* (2012). A review article that discusses various factors influencing ion charge states in cathodic vacuum arc plasmas.
- [27] *SQM-160 Multi-Film Rate/Thickness Monitor Operating Manual*. PN 074-511-P1E. INFICON. Bad Ragaz, Switzerland, 2015. URL: <https://www.inficon.com>.
- [28] John R. Taylor. *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*. 2nd. Sausalito, CA: University Science Books, 1997.
- [29] Francis F. Chen. *Introduction to Plasma Physics and Controlled Fusion*. Vol. 1. New York: Springer, 1984. ISBN: 978-0-306-41332-2.
- [30] Luis Fernández et al. “Charged particle reflection in a magnetic mirror”. In: *Revista Mexicana de Física E* 21 (July 2024). DOI: [10.31349/RevMexFisE.21.020211](https://doi.org/10.31349/RevMexFisE.21.020211).
- [31] André Anders. “Cathodic arcs: a fractal approach”. In: *IEEE Transactions on Plasma Science* 33.5 (2005), pp. 1456–1464. DOI: [10.1109/TPS.2005.856488](https://doi.org/10.1109/TPS.2005.856488).
- [32] R. L. Boxman, S. Goldsmith, and D. M. Sanders. “Cathodic arc plasmas and their applications”. In: *IEEE Transactions on Plasma Science* 23.6 (1995), pp. 939–956. DOI: [10.1109/27.475210](https://doi.org/10.1109/27.475210).
- [33] R. E. Miller and D. I. Bolef. “Shear modulus and internal friction in single-crystal quartz at low temperatures”. In: *Journal of Applied Physics* 39.11 (1968), pp. 5815–5821. DOI: [10.1063/1.1656042](https://doi.org/10.1063/1.1656042).
- [34] C. Lu and O. Lewis. “Investigation of film-thickness determination by oscillating quartz resonators with large mass load”. In: *Journal of Applied Physics* 43.11 (1972), pp. 4385–4390. DOI: [10.1063/1.1660985](https://doi.org/10.1063/1.1660985).