

# **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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## 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

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## Introduction and Literature Review

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### 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

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## Theoretical Background

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### 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  $10^{10}$ – $10^{12} \text{ A m}^{-2}$ , 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.

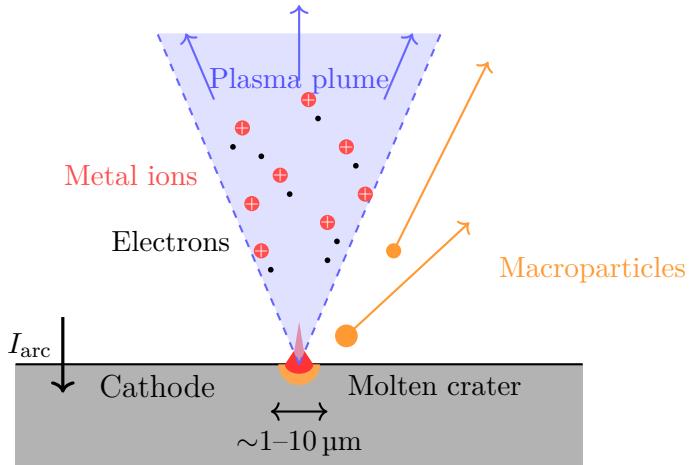


Figure 2.1: Schematic of cathode spot operation. The arc current  $I_{\text{arc}}$  concentrates at a microscopic spot ( $1\text{--}10\ \mu\text{m}$  diameter), creating a molten crater from which a plasma plume of metal ions, electrons and macroparticles expand. Adapted from [10]

### 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  $10^{18} \text{ cm}^{-3}$  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  $I_{\text{arc}}$  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  $90^\circ$  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  $E_{\text{kin}}$  arises from the supersonic expansion of plasma from the cathode spot, while the potential energy  $E_{\text{pot}}$  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	$\langle Q \rangle$	$E_{\text{kin}}$ (eV)	$E_{\text{pot}}$ (eV)	$E_{\text{tot}}$ (eV)
Ti <sup>2+</sup>	2.1	59	21	80
Al <sup>2+</sup>	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  $\Gamma$  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  $J_i$  ( $\text{A cm}^{-2}$ ) relates to  $\Gamma$  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  $\Gamma$  increases approximately linearly with  $I_{\text{arc}}$  [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 N<sub>2</sub> 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 N<sub>2</sub> 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 N<sub>2</sub> 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<sup>+</sup> and N<sub>2</sub><sup>+</sup> ions formed by electron-impact ionization,
- Neutral but excited nitrogen: metastable N<sub>2</sub> 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 N<sub>2</sub> 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  $m_{\text{ion}}$  is the average ion mass,  $\Gamma$  the ion flux,  $S$  the sticking coefficient, and  $\rho_{\text{film}}$  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  $\rho_{\text{film}}$  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].

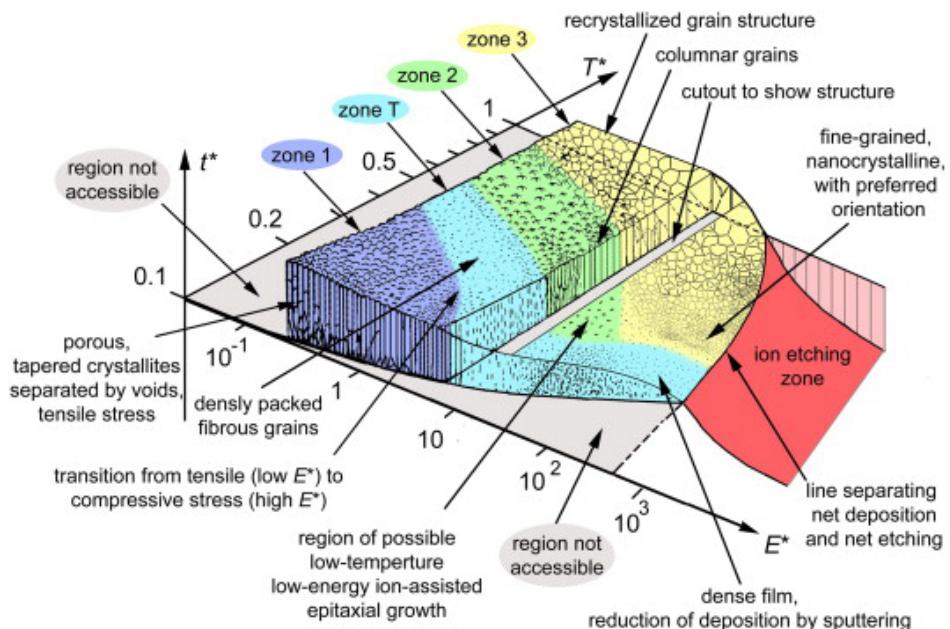


Figure 2.2: Structure-zone diagram for plasma based thin film deposition, showing film microstructure as a function of generalized temperature  $T^*$  and normalized ion energy  $E^*$ . From Anders [12].

### 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

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## Experimental Methodology

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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  $1 \times 10^{-5}$  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  $1 \times 10^{-4}$  Pa. This configuration allowed finer control of the nitrogen partial pressure.

Nitrogen gas ( $\text{N}_2$ , 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 a Tektronix MSO64 oscilloscope. 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  $\mu$ 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  $\mu$ 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 C.1.

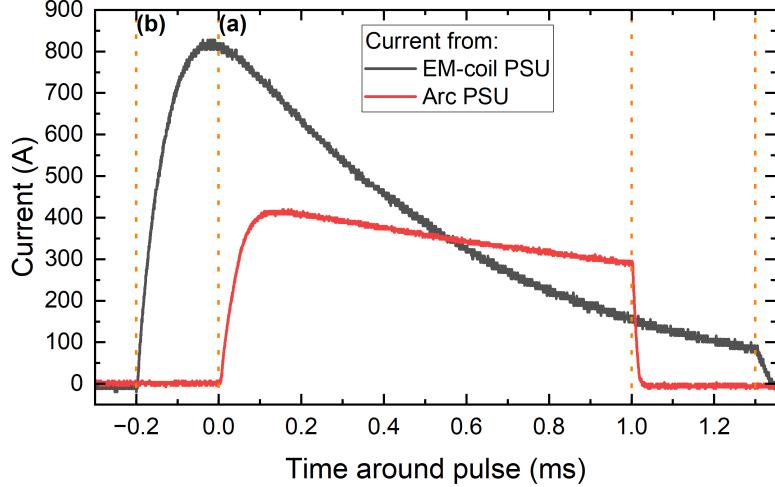


Figure 3.1: Example pulse waveforms showing the arc current (red) and EM-coil current (black) as functions of time. The orange dashed lines indicate the trigger timing: (a) EM-coil trigger at  $t = -0.2$  ms, (b) arc trigger at  $t = 0$  ms. The waveforms shown are pulses at 250 V EM-coil input voltage.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

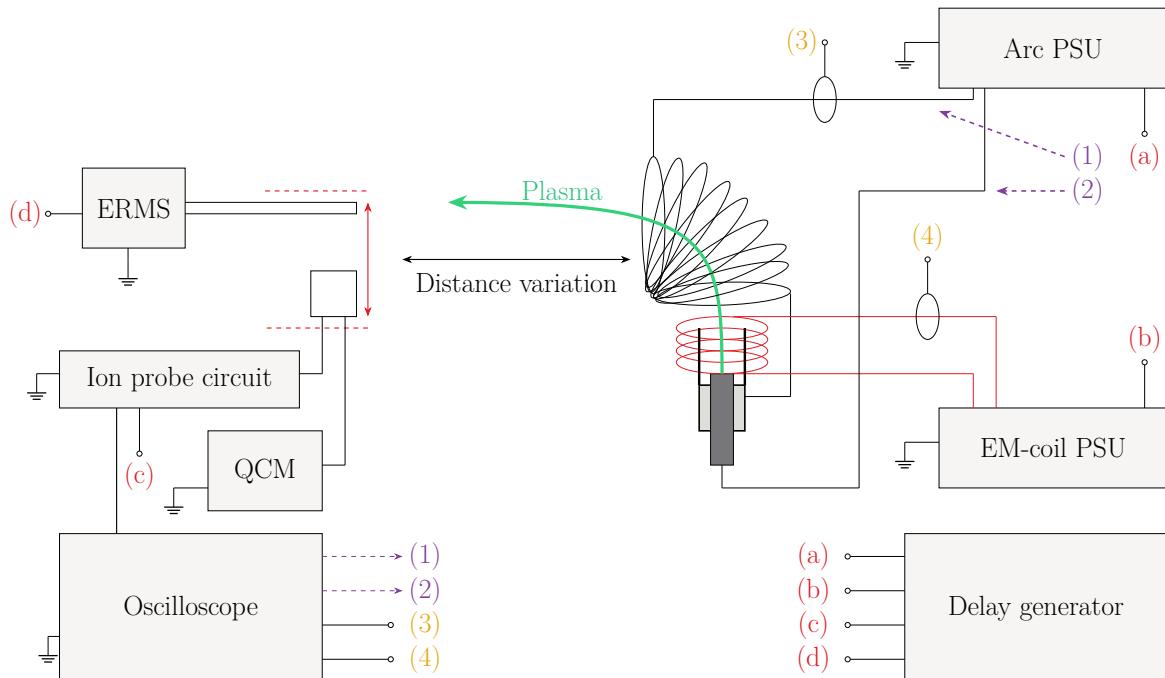


Figure 3.2: Schematic of the vacuum chamber setup for cathodic arc plasma diagnostics and thin film deposition. (a) Arc power supply, (b) EM-coil power supply, (c) Langmuir probe and QCM, (d) energy-resolving mass spectrometer (ERMS). The delay generator (a-d) synchronizes the arc power supply, EM-coil 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 prevented short circuits between the probe and the grounded mount due to metallic

deposition. The probe body was wrapped in Kapton tape for electrical insulation from the aluminum mounting assembly (Figure A.1).



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.

To ensure full ion collection and suppress electron current, the probe was negatively biased at  $V_b = -80$  V to operate in the ion saturation regime [14], as determined through bias voltage characterization measurements (Section B).

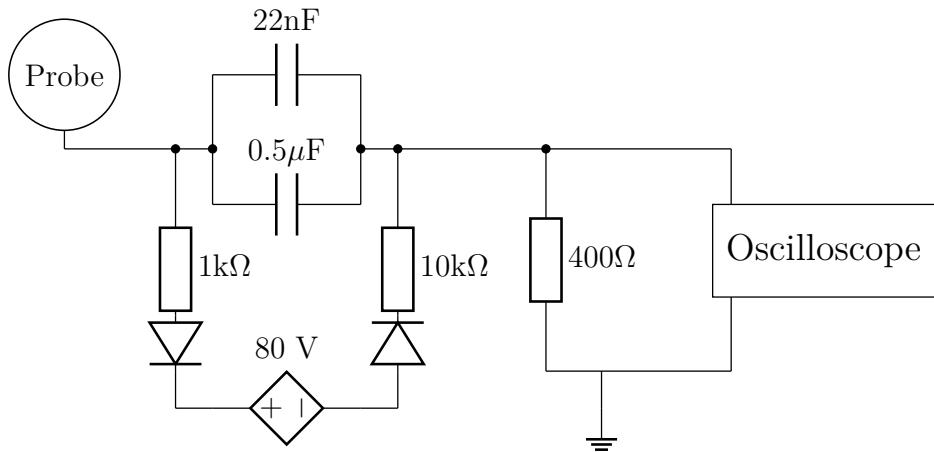


Figure 3.4: Schematic of the ion-flux probe circuit. The  $400\Omega$  resistor converts ion current to voltage, while the  $0.5\mu\text{F}$  capacitor and  $400\Omega$  resistor form a high-pass filter with a 795 Hz cutoff.

The probe circuit (Figure 3.4) converts the collected ion current to a voltage signal. The ion current passes through a  $0.5\mu\text{F}$  coupling capacitor and develops a voltage across the  $400\Omega$  measurement resistor. This RC configuration forms a high-pass filter with cutoff frequency:

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

The high-pass filter blocks DC offsets while passing the pulsed ion current signal. The RC time constant  $\tau = 200\mu\text{s}$  is much shorter than the 2 s interval between pulses, ensuring complete capacitor discharge between measurements. The bias supply line incorporates a  $22\text{nF}$  capacitor and  $1\text{k}\Omega$  resistor as a low-pass filter to smooth the

–80 V bias voltage.

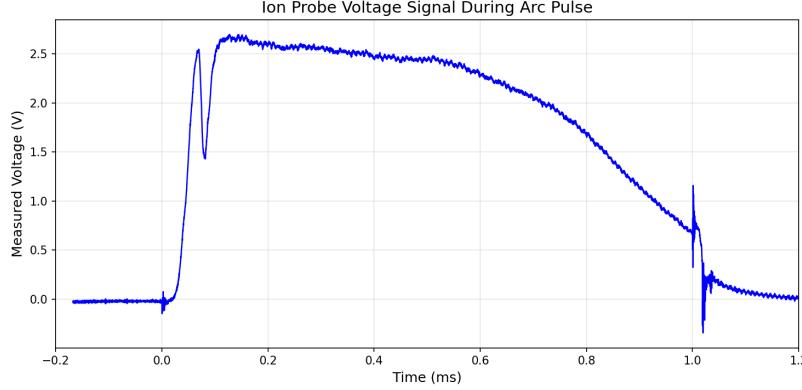


Figure 3.5: Example voltage waveform measured across the  $400 \Omega$  resistor during a single arc pulse. The signal shows transients at pulse ignition (0 ms) and termination (1 ms), with gradual decay during the pulse due to the high-pass filter characteristics.

The ion current is calculated from the measured voltage as:

$$I_{\text{ion}} = \frac{V_{\text{measured}}}{400 \Omega} \quad (3.3)$$

The voltage signal was recorded using a Tektronix MSO64 oscilloscope. Figure 3.5 shows an example waveform of 64 pulses averaged. The ion current density  $J_i$  is calculated as:

$$J_i = \frac{V_{\text{measured}}}{A \cdot R} \quad (3.4)$$

where  $A = 0.1963 \text{ cm}^2$  is the probe collection area and  $R = 400 \Omega$ .

### 3.2.2 Quartz Crystal Microbalance

A quartz crystal microbalance (QCM) was used to measure the deposited mass during pulsed cathodic arc operation. 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.

The measurement principle follows the Sauerbrey equation [15], which relates the change in resonance frequency of the quartz crystal to the deposited mass:

$$\Delta m = \frac{N_{\text{AT}} \rho_q \pi r^2}{F_q^2} \Delta F = 18.8146023 \times 10^{-9} \frac{\text{g}}{\text{Hz}} \cdot \Delta F \quad (3.5)$$

Here  $\rho_q = 2.649 \text{ g cm}^{-3}$  is the quartz density,  $r = 0.375 \text{ cm}$  is the radius of the exposed crystal area,  $N_{\text{AT}} = 166\,100 \text{ Hz cm}$  is the frequency constant of the AT-cut

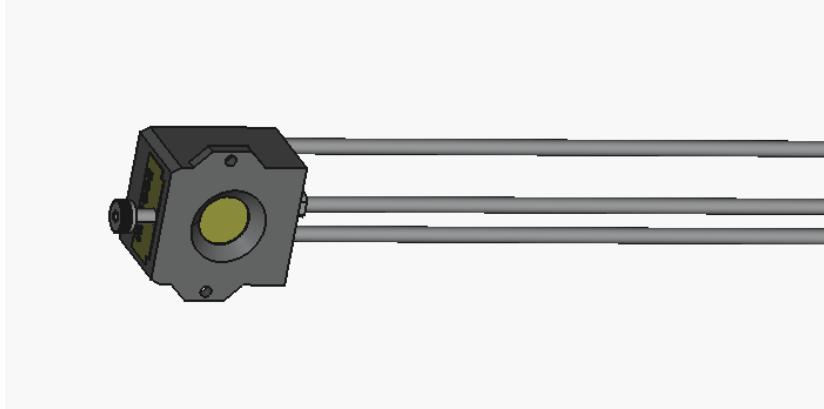


Figure 3.6: Sensor head of the INFICON Cool Drawer™ Quartz Crystal Microbalance (QCM) used for in-situ mass operation monitoring during cathodic arc sputtering. The assembly includes a water-cooled housing, a 14 mm diameter AT-cut quartz crystal (6 MHz), and electrode leads for connection to the SQM-160 controller. (Schematic adapted from INFICON STP file, available at <https://www.inficon.com/en/products/thin-film-technology/cool-drawer-single-sensor>).

quartz,  $F_q = 6$  MHz is the uncoated resonance frequency, and  $\Delta F$  is the measured frequency shift.

The Sauerbrey relation is accurate as long as  $\Delta F \lesssim 0.05F_q$  (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. The probe was positioned through a precision-milled pass-through hole, while the QCM was secured in a dedicated cutout and fixed via screws (see Appendix A.2 for assembly details). 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 ( $A_{\text{QCM}} = 0.442 \text{ cm}^2$ , diameter 7.5 mm). Both diagnostics were positioned as close as possible to each other to minimize spatial gradients between measurement locations. This design is meant to mitigate radial

plasma density gradients inherent to expanding cathodic arc plasmas [3, Chap. 6.2], though even with close proximity, gradients cannot be completely eliminated and remained evident in the experimental results.

### 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:

$$E_i = \left( V_{\text{ENERGY}} + \frac{R}{d} V_{\text{PLATES}} - V_{\text{AXIS}} \right) Q \cdot e \quad (3.6)$$

Here,  $V_{\text{ENERGY}}$  and  $V_{\text{AXIS}}$  are opposing potentials applied to the analyzer,  $R$  is the mean radius of the cylindrical sector,  $d$  is the plate separation,  $V_{\text{PLATES}}$  is the potential difference across the sector plates,  $Q$  is the ion charge state, and  $e$  is the elementary charge [16].

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 [17]. The potential in the quadrupole is:

$$V(x, y, t) = \frac{U_0 \cos(\omega t)}{r_0^2} (x^2 - y^2) \quad (3.7)$$

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

$$a = \frac{8eU_{\text{DC}}}{Mr_0^2\omega^2}, \quad q = \frac{4eU_0}{Mr_0^2\omega^2} \quad (3.8)$$

with  $U_{\text{DC}}$  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 [17, 18]. 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].

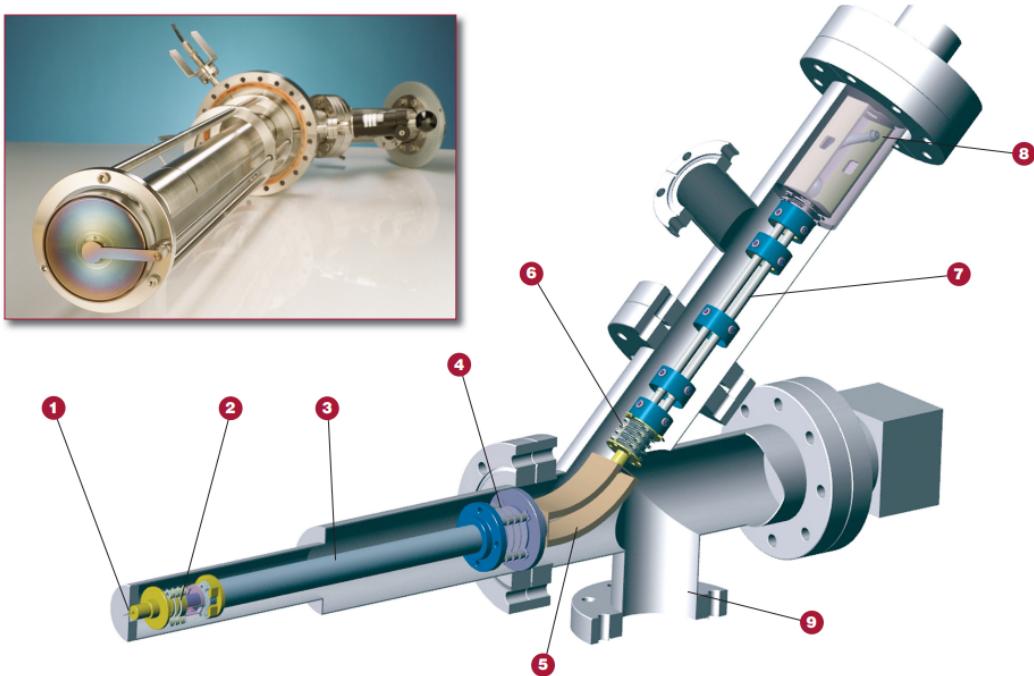


Figure 3.7: ERMS, Hiden EQP HE 1000: (1) Sampling Orifice, (2) Electron Impact Ion Source, (3) Transfer Ion Optics, (4) Quadrupole Lens, (5) Energy Filter, (6) Decelerating Lens, (7) Quadrupole Mass Filter, (8) Detector, (9) Differential Pump Port [19]

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. 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 ( $\text{N}$  and  $\text{N}_2$ ), only the  $1^+$  ionization level was measured. This was achieved by scanning  $V_{\text{ENERGY}}$  while fixing the quadrupole mass filter to the corresponding  $M/Q$  values (Table 3.1).

Table 3.1: Mass-to-charge ratios measured for each ion species and charge state.

Ionization	Molar mass over charge ratio of:			
	Al	Ti	N	$\text{N}_2$
$1^+$	27	47.867	14	28
$2^+$	13.5	23.933	-	-
$3^+$	9	15.955	-	-
$4^+$	-	11.966	-	-

To derive ion energy distributions for different charge states, the measured  $E/Q$  distributions were multiplied by the corresponding charge state number  $Q$ . This approach accounts for the charge-dependent scaling of ion energies and enables calculation of mean charge states  $\langle Q \rangle$  and the energies for each species, as detailed in Section ??.

### 3.3 Thin Film Deposition and Characterization

Thin films were deposited on silicon substrates mounted on a movable substrate holder positioned at controlled distances from the macroparticle filter exit. Prior to deposition, the 2x2 substrates were cut into four pieces and cleaned with compressed nitrogen gas. For thickness measurements, a masking technique was employed: a marker line was drawn near the edge of each substrate before deposition, creating a well-defined step edge. After deposition, this marker was removed by ultrasonic cleaning in isopropanol, leaving a sharp boundary between the coated and uncoated regions for profilometry analysis.

The deposition parameters (distance, magnetic field strength, nitrogen pressure) were selected to match a subset of the plasma diagnostic measurements, enabling direct correlation between plasma properties and film characteristics. All depositions were performed with 6000–8000 pulses at 5 Hz repetition rate (1 ms pulse duration) to ensure sufficient film thickness for ex situ characterization. The substrate holder was not heated, allowing the investigation of room-temperature film growth under energetic ion bombardment conditions characteristic of cathodic arc deposition.

#### 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 [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  $\sim 1$  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

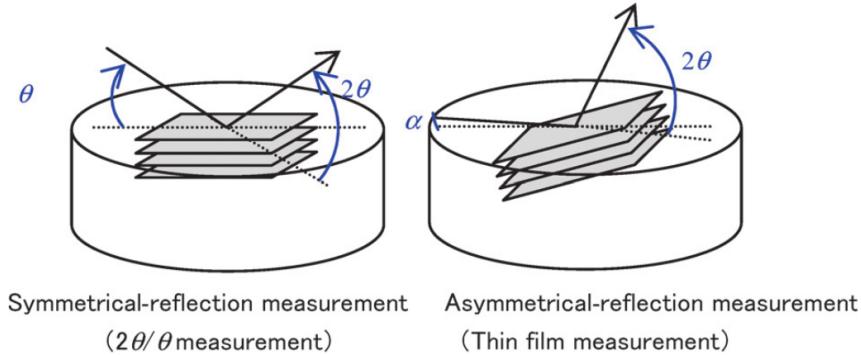


Figure 3.8: Schematic of out-of-plane diffraction geometries: symmetrical reflection (left) and asymmetrical reflection (right) for thin film analysis. Taken from [21].

enhance the film signal relative to the substrate. Two measurement geometries are employed [21]:

- **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  $\alpha$ , while the detector scans in  $2\theta$ . This reduces the X-ray penetration depth from tens of micrometers to a few micrometers, greatly enhancing sensitivity to thin films [21].

The XRD measurements were performed using a Rigaku Ultima IV system equipped with a non monochromatic  $Cu_\alpha$  source. The crystallographic structure was determined by analyzing the diffraction patterns. The Bragg equation was used to identify the crystalline phases:

$$2d \sin(\theta) = n\lambda, \quad (3.9)$$

where  $d$  is the spacing between atomic planes,  $\theta$  is the diffraction angle,  $n$  is an integer, and  $\lambda$  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 ( $0.01\text{--}5^\circ$ ) [22].

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

material through:

$$\theta_c = \sqrt{2\delta}, \quad (3.10)$$

where  $\delta$  depends on the material density and composition [22]. Above  $\theta_c$ , 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 [23]:

$$d \approx \frac{\lambda}{2\Delta\theta}, \quad (3.11)$$

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

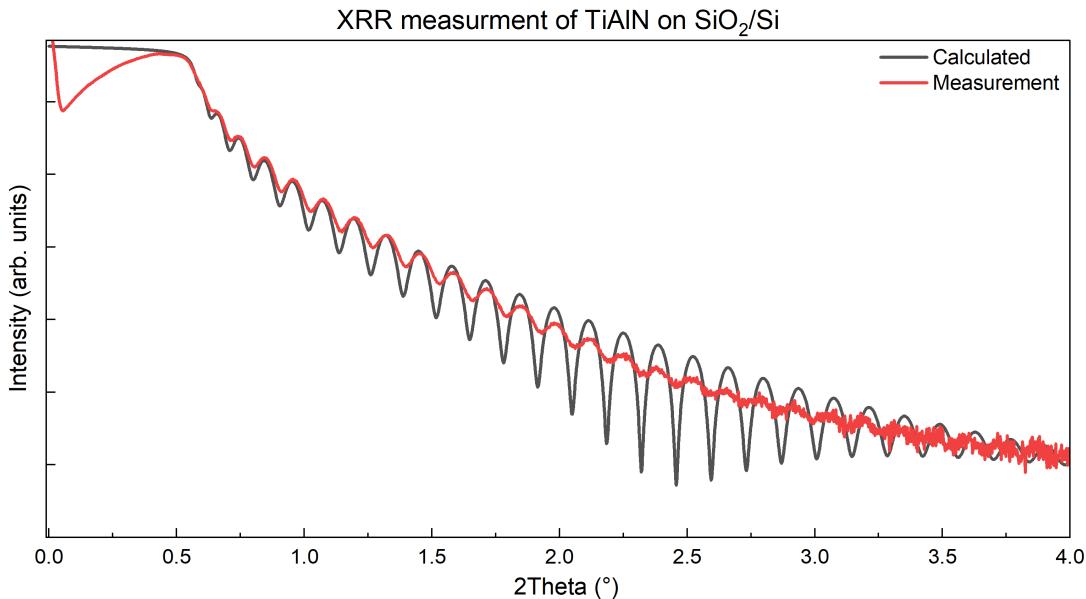


Figure 3.9: Example XRR measurement and fit for a TiAlN thin film deposited on Si substrate. The oscillations (Kiessig fringes) arise from interference between reflections from the film surface and the film-substrate interface.

The XRR technique provides three key parameters [22]:

- **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.

The measured reflectivity curves were analyzed using the Parratt recursive formalism [24], 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 4.3.1) 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)

Scanning electron microscopy (SEM) was employed to characterize the surface morphology and microstructure of the deposited films. SEM uses a focused electron beam to scan the sample surface, generating secondary electrons (SE) and backscattered electrons (BSE) that provide information about surface topography and compositional contrast, respectively [25, 26].

SEM imaging was performed using a [MODEL - Zeiss Gemini/Sigma] field emission scanning electron microscope equipped with an in-lens detector for high-resolution secondary electron imaging. Samples were imaged at an accelerating voltage of 15 kV with magnifications ranging from  $30,000\times$  to  $100,000\times$ . The conductive TiAlN films required no additional coating preparation.

The primary objectives of SEM characterization were to:

- Examine surface morphology and the presence of any macroparticles typical of cathodic arc deposition
- Assess film uniformity across the substrate
- Identify microstructural features resulting from different deposition conditions

Representative SEM micrographs and analysis of surface features are presented in Section ??.

### 3.3.5 Energy-Dispersive X-ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) relies on the ionization of inner-shell electrons by the incident electron beam. When an inner-shell electron is ejected, an electron from a higher energy level fills the vacancy, releasing energy in the form of a characteristic X-ray. The energy of this X-ray is unique to each element, allowing identification and quantification of the sample composition. The intensity of the characteristic X-ray peaks is proportional to the concentration of each element, enabling quantitative analysis through comparison with standards or standardless quantification algorithms

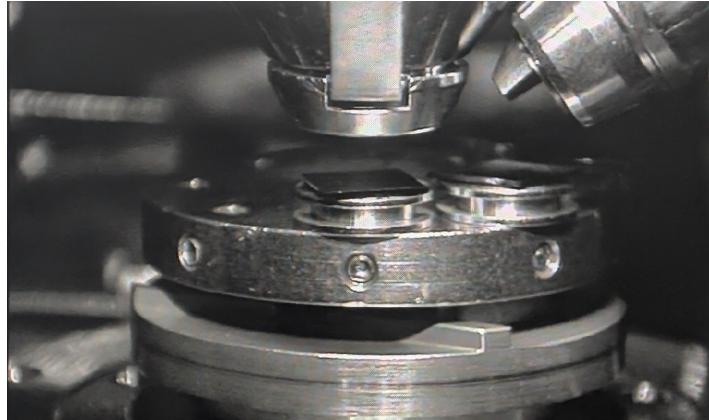


Figure 3.10: Interior view of the SEM sample chamber showing the sample holder stage and detector configuration used for imaging and EDX analysis.

[25].

EDX measurements were performed using a silicon drift detector (SDD) integrated with the SEM system, operating at an accelerating voltage of 10 kV. To minimize substrate contribution from the thin films, samples were tilted to 55° relative to the electron beam increasing the effective path length by  $\approx 1.74$ .

Prior to analysis, samples were cleaned ultrasonically in isopropanol to remove loose particles. However, organic solvent residues and hydrocarbon contamination from the vacuum system can lead to carbon deposition under electron beam irradiation [25, 26]. A small carbon peak was therefore typically observed in EDX spectra and was excluded from compositional quantification of the TiAlN films. Multiple area measurements were taken on each sample to verify that all surface features, including any macroparticles or morphological structures, had the same metal-nitride composition as the underlying thin film and to identify potential impurities beyond the surface carbon layer.

The primary elements analyzed were titanium (Ti), aluminum (Al), and nitrogen (N). Oxygen (O) and silicon (Si) were also monitored to assess surface oxidation and to detect any contribution from the Si substrate. The measured film compositions are used to calculate the effective molar mass  $M_{\text{eff}}$  required for determining total deposited flux from QCM measurements (Section 3.2.4). Compositional results and representative EDX spectra are presented in Section ??.

### 3.4 Calculation of Ion Flux and Total Deposited Flux

The plasma diagnostic measurements described in Section 3.2.1–3.2.4 provide electrical currents, deposited masses, and ion energy distributions. To quantify the actual

particle arrival rates and relate these to film growth, these raw measurements must be converted to particle fluxes. This section describes the calculation procedures that combine multiple diagnostic techniques to derive ion flux and total deposited flux.

### 3.4.1 Ion Flux from Probe and ERMS Measurements

The ion flux  $\Gamma_{\text{ion}}$  ( $\text{ions cm}^{-2} \text{s}^{-1}$ ) represents the number of charged metal ions arriving per unit area per unit time. It is calculated from the ion current measured by the Langmuir probe (Section 3.2.1) combined with the mean charge state determined from ERMS measurements (Section 3.2.4):

$$\Gamma_{\text{ion}} = \frac{I_{\text{ion}}}{e\langle Q \rangle A_{\text{probe}}} \quad (3.12)$$

where  $\langle Q \rangle$  is the average charge state determined from ERMS measurements (Section 3.2.4),  $e = 1.602 \times 10^{-19} \text{ C}$  is the elementary charge,  $A_{\text{probe}} = 0.196 \text{ cm}^2$  is the probe collection area, and  $R = 400 \Omega$  is the measurement resistor. 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.

### 3.4.2 Total Deposited Flux from QCM and Film Characterization

The total deposited flux  $\Phi_{\text{total}}$  ( $\text{atoms cm}^{-2} \text{s}^{-1}$ ) quantifies the arrival rate of all species contributing to film growth, including both ions and neutrals. It is calculated from QCM mass measurements (Section 3.2.2) combined with film composition from EDX (Section 3.3.5):

$$\Phi_{\text{total}} = \frac{\Delta m \cdot N_A}{A_{\text{QCM}} \cdot \Delta t \cdot M_{\text{eff}}} \quad (3.13)$$

where  $\Delta m$  is the mass change measured by QCM over time interval  $\Delta t$ ,  $A_{\text{QCM}} = 0.5027 \text{ cm}^2$  is the active crystal area (8 mm diameter),  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$  is Avogadro's constant, and  $M_{\text{eff}}$  is the effective molar mass calculated from film composition:

$$M_{\text{eff}} = \sum_i x_i M_i = x_{\text{Ti}} \cdot 47.867 + x_{\text{Al}} \cdot 26.982 + x_{\text{N}} \cdot 14.007 \quad (3.14)$$

where  $x_i$  are the atomic fractions from EDX measurements (Table 4.2) and  $M_i$  are the atomic masses.

The effective molar mass varies significantly between metallic and reactive mode:  $M_{\text{eff}} \approx 43.5 \text{ g}\cdot\text{mol}^{-1}$  for Ti-Al films versus  $M_{\text{eff}} \approx 31.8\text{--}33.2 \text{ g}\cdot\text{mol}^{-1}$  for TiAlN films.

This 25% reduction reflects the incorporation of light nitrogen atoms (14.0 g·mol<sup>-1</sup>) displacing heavier metal atoms.

# CHAPTER 4

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## Results

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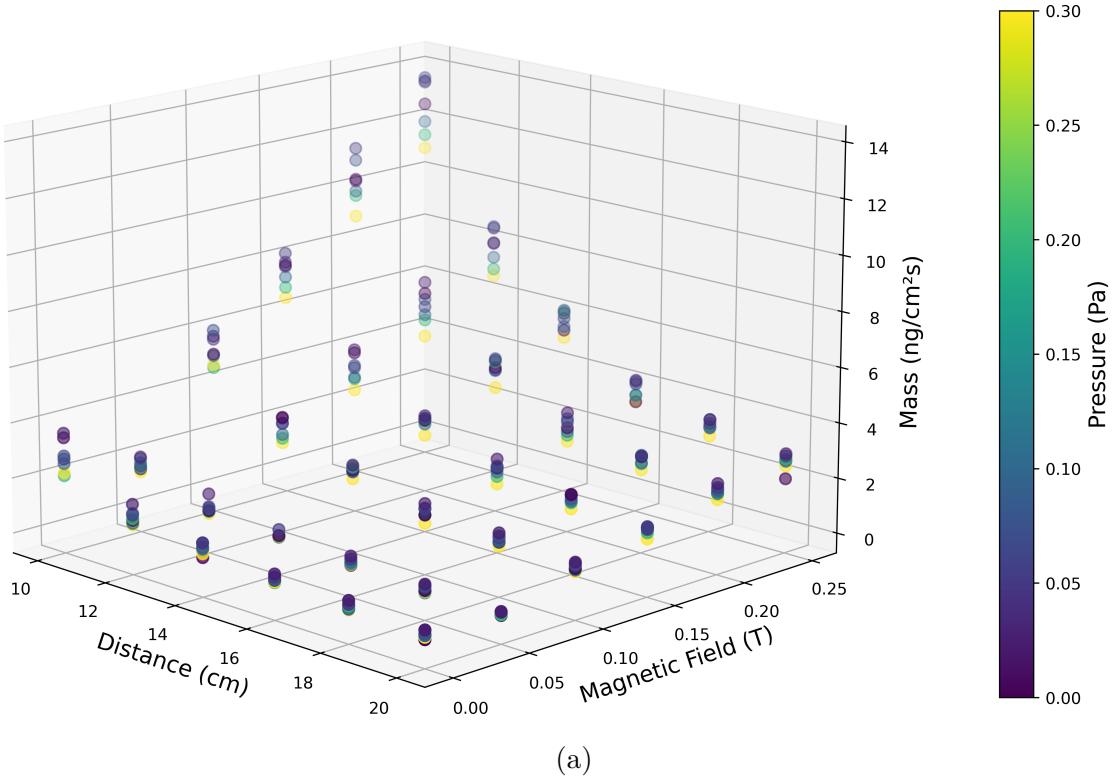
### 4.1 Mass Deposition Rate and Ion Current Measurements

To systematically characterize the plasma dynamics and deposition behavior, measurements were conducted using a quartz crystal microbalance (QCM) for mass deposition rate 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 D.1. At this stage, the raw quantities mass deposition rate (in  $\text{ng cm}^{-2} \text{ s}^{-1}$ ) and ion current (in mA) are presented to establish trends before flux calculations in Section ??.

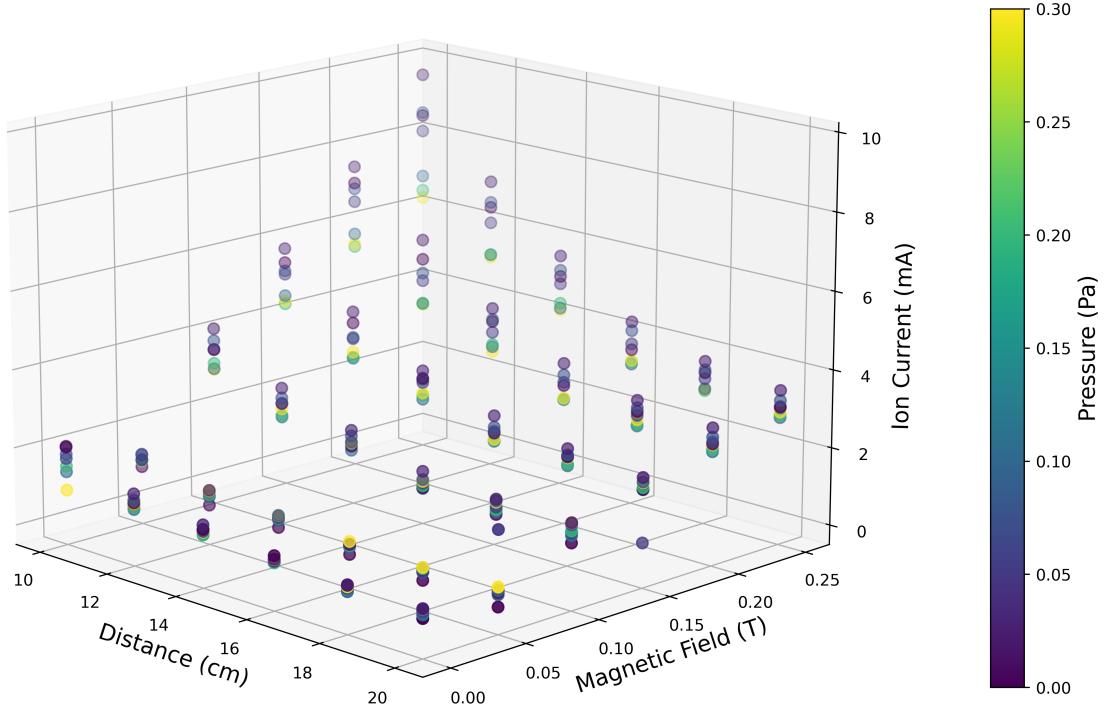
Figure 4.1 provides a three-dimensional visualization of the complete dataset, illustrating how mass deposition rate and ion current vary simultaneously with all three control parameters. Several global trends are immediately apparent: both quantities decrease with increasing distance due to plasma expansion, 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 4.1: Three-dimensional visualization of (a) mass deposition rate ( $\text{ng cm}^{-2} \text{s}^{-1}$ ) and (b) ion current (mA) as functions of distance (10–20 cm), magnetic field strength (0–0.25 T), and nitrogen pressure (0–0.3 Pa). Measurements performed over 64 arc pulses at 5 Hz repetition rate.

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 (no nitrogen, Section 4.1.1) to establish baseline behavior without reactive gas complications. Sections 4.1.2–4.1.4 then isolate the effects of distance, magnetic field, and nitrogen pressure. The parameter combinations analyzed in detail—distances of 10, 14, and 20 cm; magnetic fields of 0, 0.15, and 0.25 T; and nitrogen pressures of 0.1 and 0.3 Pa—were selected because they correspond to conditions used for energy-resolved mass spectrometry (ERMS) measurements and thin film deposition, enabling direct correlation between plasma diagnostics and film properties in later sections.

#### 4.1.1 Metallic Case (No Nitrogen)

In the absence of reactive gas, plasma expansion and deposition dynamics are governed solely by geometric dilution and magnetic confinement. Figure 4.2 presents mass deposition rate and ion current as functions of magnetic field strength for three representative distances.

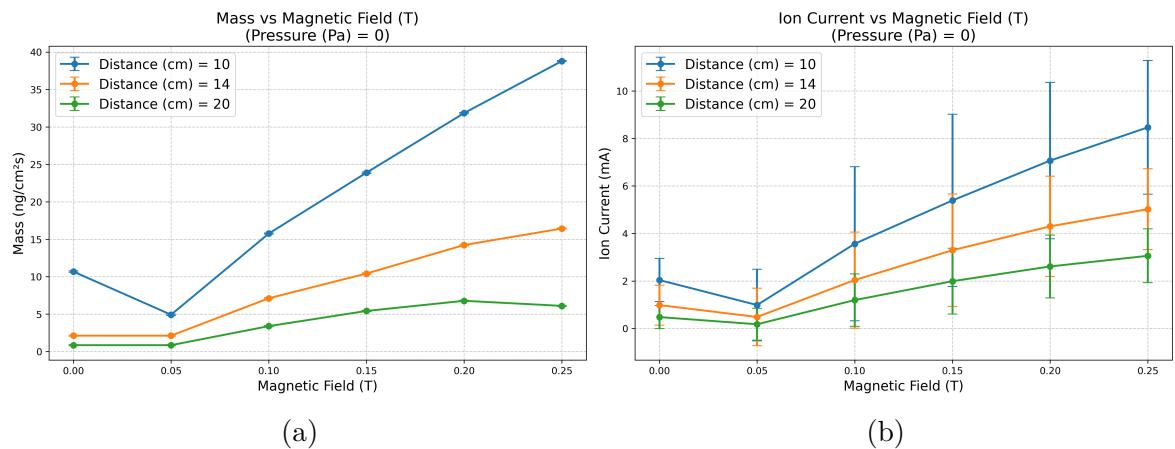


Figure 4.2: Metallic case measurements showing (a) mass flux and (b) the ion current, each plotted as a function of magnetic field strength. Data selected for three distances (10, 14, 20 cm), with error bars representing variation within pulses.

As shown in Figure 4.2, both mass deposition rate and 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 before recovering and increasing at higher fields (0.1 T and above). Similar behavior is observed across all experimental conditions involving increasing magnetic field strength.

### 4.1.2 Distance as a variable

Figure 4.3 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.

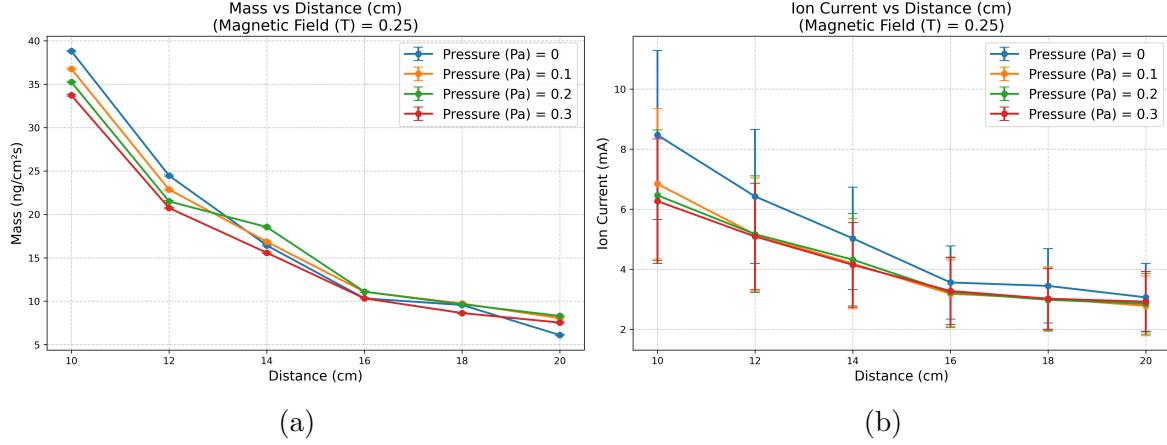


Figure 4.3: Mass deposition rate and ion current as functions of distance at 0.25 T magnetic field for four nitrogen pressures. (a) Mass deposition rate shows moderate pressure dependence. (b) Ion current exhibits much stronger pressure dependence, particularly at short distances. Error bars represent intra-pulse variability.

Both mass deposition rate and ion current decrease with distance, reflecting plasma expansion and dilution. In metallic mode (0 Pa), mass deposition rate follows an approximate  $1/r^2$  dependence expected for free expansion [3, Chap. 4.3], with 20 cm values approximately 25–30% of those measured at 10 cm.

Ion current exhibits a far more dramatic pressure dependence than mass deposition rate. When nitrogen is introduced, the measured current drops steeply, while the QCM mass deposition rate shows more modest changes. The contrast between the two measurements is most pronounced at short distances and diminishes at 14–20 cm.

Additional measurements at constant magnetic field (0 T) and varying distance show similar trends and are presented in Appendix C.2.

### 4.1.3 Magnetic Field as a variable

Figure 4.4 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.

The magnetic mirror anomaly at 0.05 T, clearly visible in the 10 cm metallic data (Figure 4.2), is significantly attenuated at 14 cm. Both mass deposition rate and ion 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

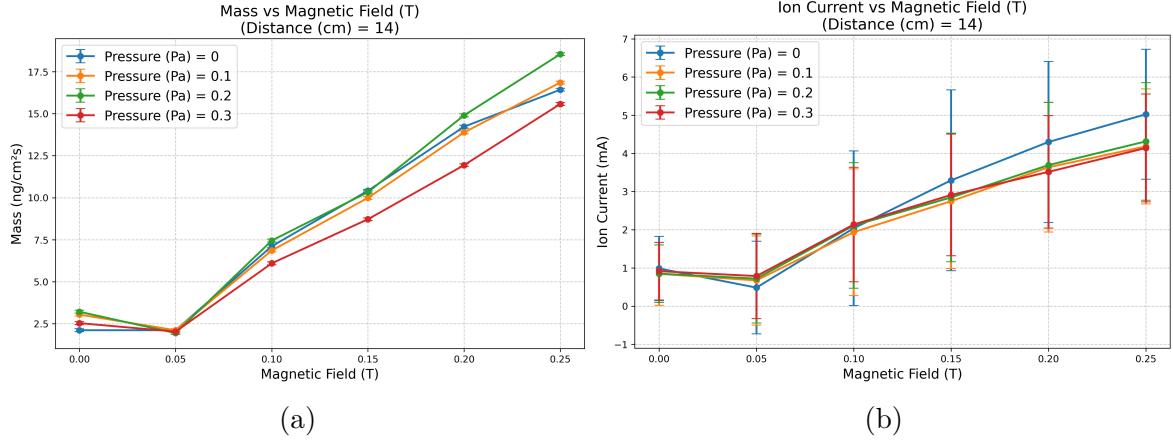


Figure 4.4: Mass deposition rate and ion current as functions of magnetic field strength at 14 cm distance for four nitrogen pressures. (a) Mass deposition rate increases monotonically above 0.1 T. (b) Ion current shows pronounced divergence between metallic and reactive conditions at high fields. Error bars represent intra-pulse variability.

increased statistical noise at this intermediate distance.

Above 0.1 T, both quantities show a clear, consistent increase for all conditions, confirming that magnetic confinement enhances plasma density and flux at the substrate. The enhancement is approximately linear with field strength in the 0.1–0.25 T range. Mass deposition rate (Figure 4.4a) increases by a factor of approximately 5–6× from zero field to 0.25 T, with all pressure conditions following similar trajectories. This similarity indicates that the magnetic field effect on total mass flux is largely independent of nitrogen pressure at this distance.

Ion current (Figure 4.4b) also increases with magnetic field, but exhibits greater variability, particularly in reactive mode. At 0.25 T, the ion current in metallic mode (0 Pa) reaches approximately 5 mA, while reactive mode conditions (0.1–0.3 Pa) show currents in the range of 4 mA with substantial error bars. The overlap between metallic and reactive conditions at high fields, combined with the large variation of ion current during a pulse, makes it difficult to draw definitive conclusions about pressure effects on ion current at 14 cm distance.

The similar behavior of mass deposition rate across all pressures, combined with the more variable ion current measurements, suggests that at 14 cm the magnetic field primarily affects the total particle flux rather than selectively enhancing ionization. The reduced contrast between metallic and reactive mode compared to the 10 cm measurements (Section 4.1.2) is consistent with the plasma having undergone substantial expansion and equilibration by this distance.

To isolate the effect of nitrogen pressure more clearly, the next section examines pressure as the primary variable under fixed magnetic field conditions.

#### 4.1.4 Nitrogen pressure as a variable

Figure 4.5 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).

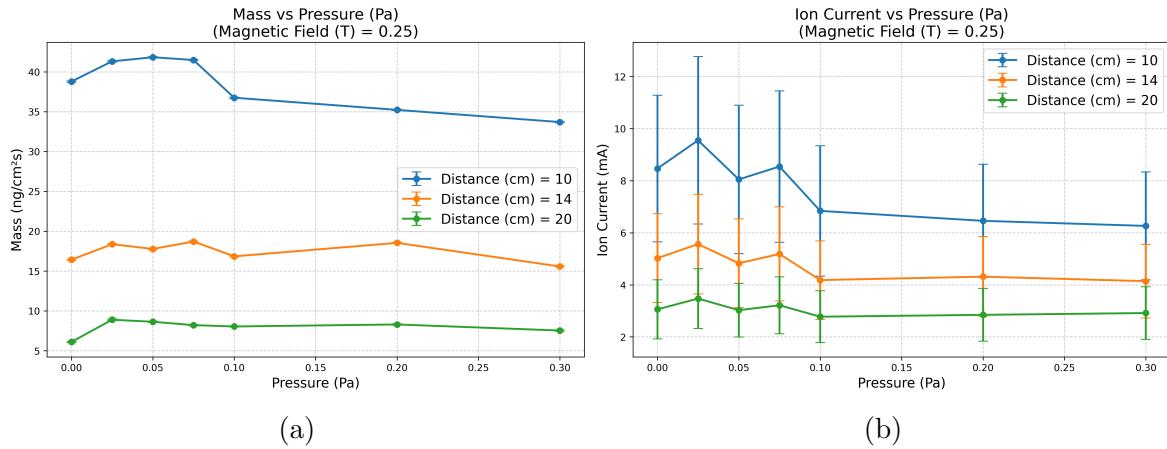


Figure 4.5: QCM and Ion Probe measurements showing (a) mass flux and (b) the ion current, each plotted as a function of Pressure. Data shown for representative pressures, with error bars representing variation within pulses.

At 10 cm, the mass deposition rate exhibits non-monotonic pressure dependence, with a local maximum near 0.05–0.1 Pa before decreasing at higher pressures. The ion current shows substantial scatter across the low pressure ranges this is an artefact from the experimental setup. A general decreasing trend is evident despite the variability.

At 14 cm and 20 cm, both mass deposition rate and ion current become largely independent of nitrogen pressure. Within experimental uncertainty, both quantities remain essentially constant across the 0–0.3 Pa range investigated.

The measurements presented in this section establish the macroscopic trends in mass deposition rate and ion current across the experimental parameter space. However, these raw quantities do not directly reveal the underlying plasma composition. To address these questions, energy-resolved mass spectrometry was performed under selected conditions to characterize the ion energy distributions and mean charge states, as presented in the following section.

## 4.2 Energy-Resolved Mass Spectrometry Results

Energy-resolved mass spectrometry (ERMS) measurements were performed to characterize charge-state distributions and ion energies under selected conditions corresponding to film depositions. The measurements provide charge-state-resolved ion energy distribution functions (IEDFs) for  $\text{Al}^{1+,2+,3+}$ ,  $\text{Ti}^{1+,2+,3+,4+}$  and  $\text{N}/\text{N}_2^{1+}$ , from which mean charge states  $\langle Q \rangle$ , kinetic energies  $E_{\text{kin}}$ , and potential energies  $E_{\text{pot}}$  are derived. All measurements were performed at 0.25 T magnetic field strength, with particular emphasis on the 14 cm distance selected for systematic film depositions, as well as for all the above mentioned species, even if nitrogen should not be present in metallic plasmas.

### 4.2.1 Distance Dependence

Figures 4.6 and 4.7 present mean charge states, potential energies, and kinetic energies as functions of distance for metallic mode (0 Pa) and reactive mode (0.3 Pa  $\text{N}_2$ ), respectively.

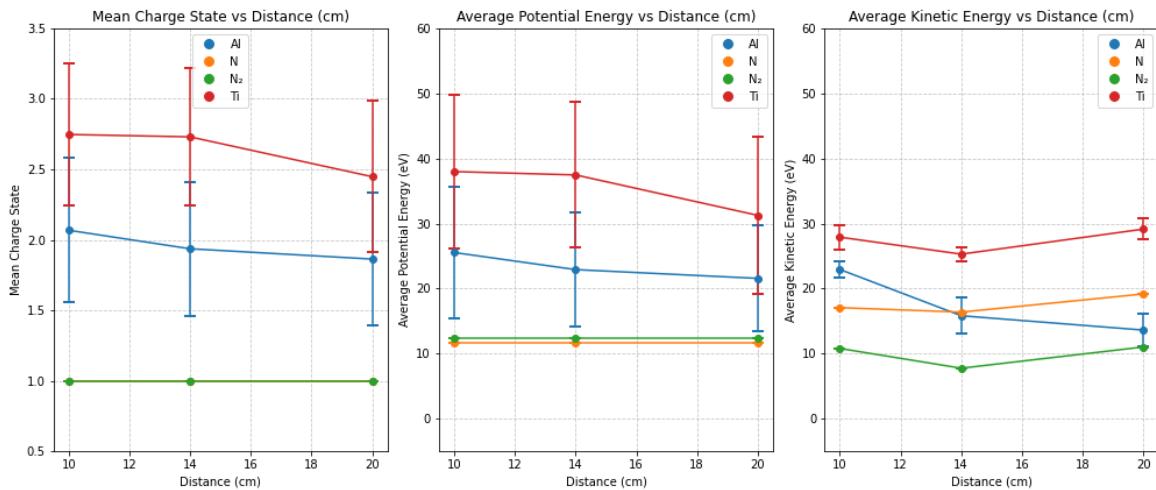


Figure 4.6: Mean charge state, potential energy, and kinetic energy as functions of distance in metallic mode (0 Pa, 0.25 T). Al and Ti show mean charge states of  $\langle Q \rangle \approx 2.0$  and 2.7 respectively, with minimal variation across 10–20 cm. Total ion energies remain above 40 eV at all distances.

In metallic mode (Figure 4.6), titanium ions exhibit  $\langle Q \rangle \approx 2.6$  and aluminum ions  $\langle Q \rangle \approx 2.0$  across all distances. These charge states reflect the high electron temperatures ( $T_e \approx 5\text{--}10$  eV) characteristic of cathode spot plasmas. The mean charge states remain remarkably constant with distance, varying by less than 10% between 10 and 20 cm, indicating that recombination is negligible during the transit time through this region on the order of  $\sim 100$   $\mu\text{s}$  scale.

Potential energies scale directly with charge state, with Ti showing  $E_{\text{pot}} \approx 38$  eV and Al  $E_{\text{pot}} \approx 26$  eV, remaining nearly constant across the measurement range. Kinetic energies are in the range of 20–30 eV for both species, with a slight decreasing trend with distance due to minor collisional thermalization. Importantly, total ion energies ( $E_{\text{kin}} + E_{\text{pot}}$ ) exceed 40 eV at all distances, well above the  $\approx 30$  eV threshold for subplantation-driven densification [3, Chap. 8.1]. This confirms that energetic condensation should remain accessible across the entire 10–20 cm range without substrate heating.

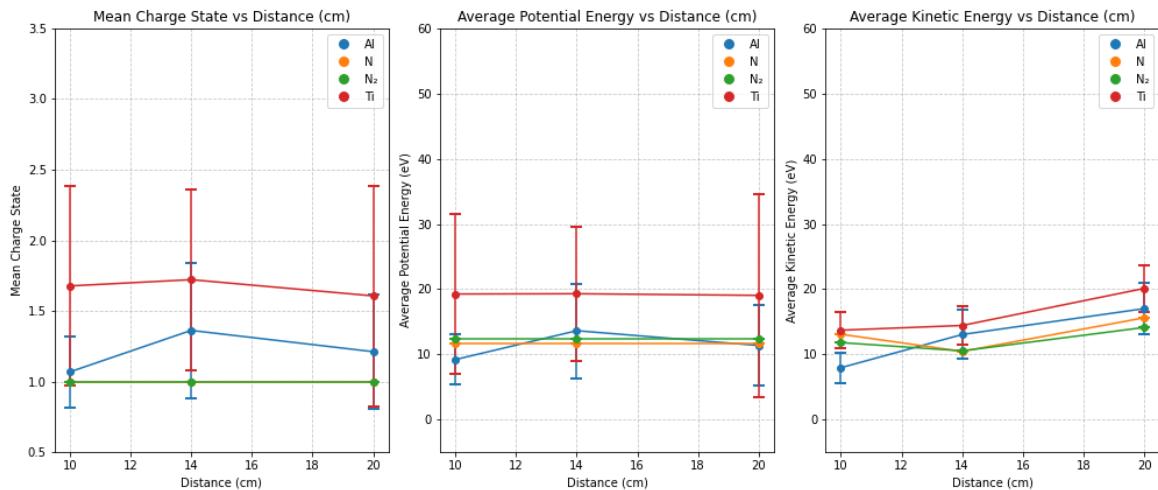
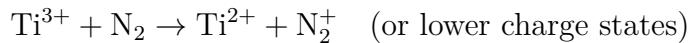


Figure 4.7: Mean charge state, potential energy, and kinetic energy as functions of distance in reactive mode (0.3 Pa N<sub>2</sub>, 0.25 T). Metal ion charge states decrease by 20–30% compared to metallic mode due to charge-exchange collisions. Kinetic energies show increased scatter due to collisional thermalization.

Introducing nitrogen at 0.3 Pa substantially alters the plasma composition (Figure 4.7). Metal ion charge states decrease by up to 50%, coinciding with charge-exchange conditions where multiply charged metal ions interact with nitrogen molecules [7]:



Potential energies decrease proportionally with the reduced charge states, falling from  $\approx 35$ –40 eV (metallic) to  $\approx 20$ –30 eV in reactive mode. Kinetic energies show a slight increase in reactive mode. Despite these changes, total ion energies remain in the range of 30 eV at 10 cm and 35 eV at 20 cm. At the 14 cm deposition distance, energies are approximately 25–35 eV.

## 4.2.2 Pressure Dependence

Figures 4.8 and 4.9 present the pressure dependence of charge states and ion energies at 10 cm and 14 cm, respectively. The 14 cm measurements are emphasized as this distance was selected for film depositions.

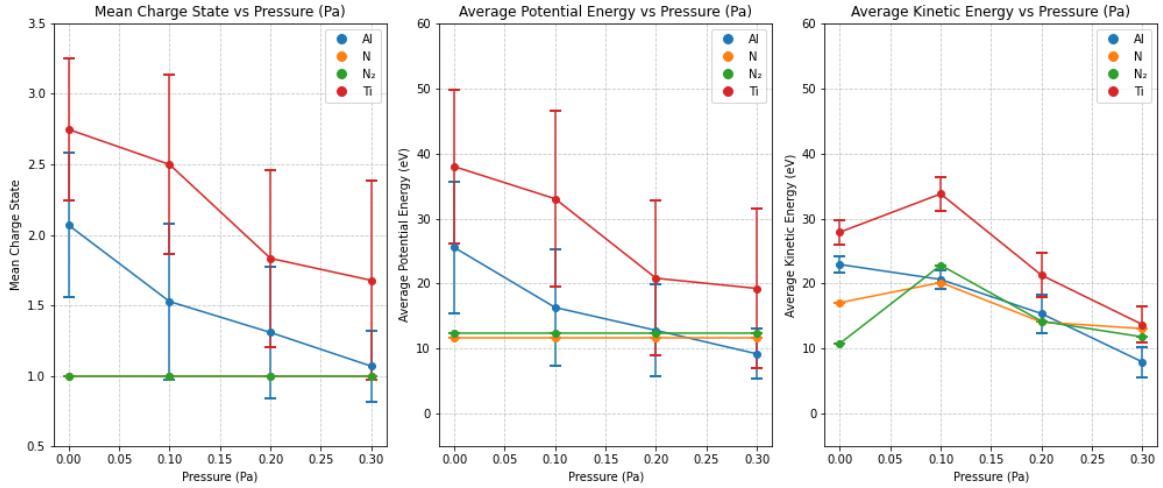


Figure 4.8: Mean charge state, potential energy, and kinetic energy as functions of nitrogen pressure at 10 cm distance (0.25 T). Only metal ion (Al, Ti) charge states are shown. Metal ion charge states decrease systematically with increasing pressure due to charge-exchange collisions. Kinetic energies exhibit non-monotonic behavior, with a local maximum near 0.1 Pa.

At both distances, metal ion charge states generally decrease with increasing nitrogen pressure as charge-exchange collisions accumulate. At 14 cm, Ti decreases from  $\langle Q \rangle \approx 2.7$  (0 Pa) to  $\approx 1.7$  (0.3 Pa), and Al from  $\approx 1.9$  to  $\approx 1.3$ . This trend is non-monotonic, with a slight increase observed between 0.2 and 0.3 Pa at 14 cm. This deviation from systematic reduction suggests that charge-exchange collisions are not the sole process affecting charge-state distributions. The overall charge-state reduction is qualitatively similar at both distances.

Kinetic energies show more complex behavior. At both 10 cm and 14 cm, Ti and Al exhibit non-monotonic trends with a local maximum near 0.1 Pa. This behavior may reflect competing effects: at low pressures, nitrogen collisions reduce forward momentum through elastic scattering, while at intermediate pressures, reactive processes at the cathode surface (type-1 vs. type-2 spot transitions [3, Chap. 9.3]) may alter the initial ion velocity distribution. The kinetic energy measurements also show increased scatter at higher pressures, consistent with collisional thermalization. Despite this complexity, the general trend toward slightly reduced kinetic energy with increasing nitrogen pressure is evident at both distances.

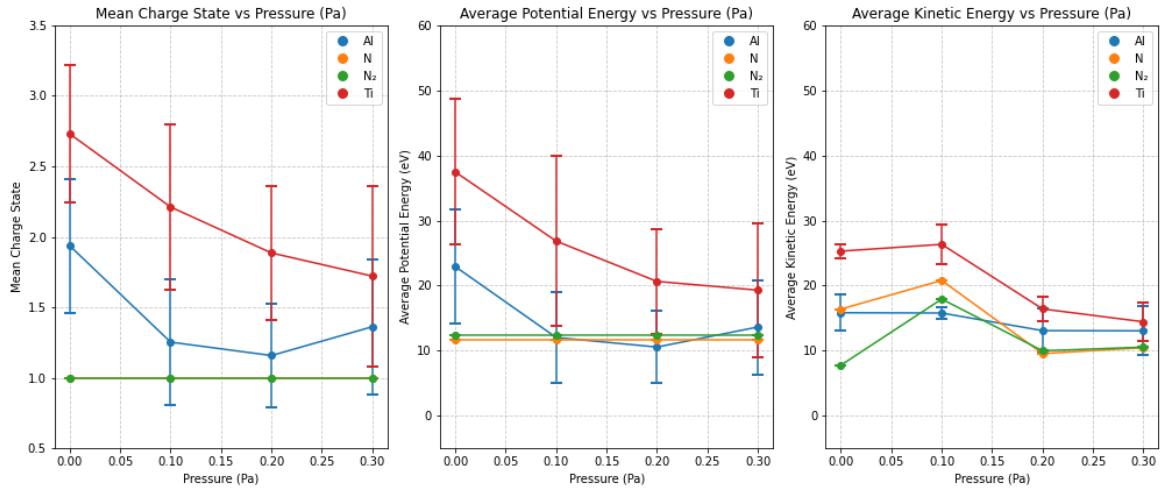
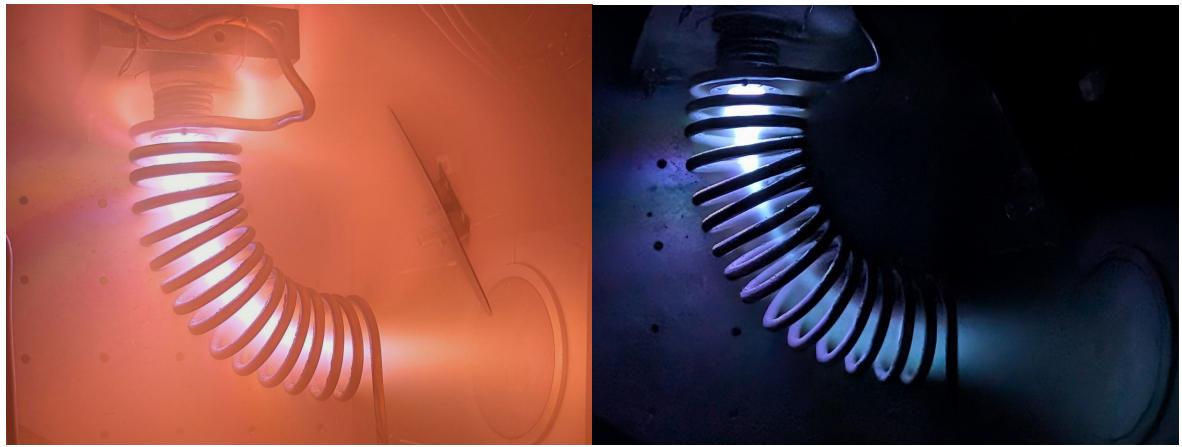


Figure 4.9: Mean charge state, potential energy, and kinetic energy as functions of nitrogen pressure at 14 cm distance (0.25 T). Only metal ion (Al, Ti) charge states are shown. Trends are similar to 10 cm but with reduced absolute values due to plasma expansion. This distance was selected for film depositions (Section 4.3).

The similarity in pressure-dependent trends between 10 cm and 14 cm and especially the increased kinetic energy around 0.1 Pa nitrogen pressure, makes these configurations especially interesting.

### 4.3 Thin Film Characterization

Thin films were deposited on Si(100) substrates positioned at 14 cm from the macroparticle filter exit under conditions listed in Table D.1. The substrates were mounted on the substrate holder with the same positions in space used for QCM and ion probe measurements to ensure identical positioning. Films were deposited under four representative conditions spanning the parameter space: metallic mode (0 Pa) and reactive mode (0.1, 0.2, 0.3 Pa) and at high magnetic field strength (0.25 T). All depositions used 850 A arc current, 1 ms pulse width, and 5 Hz repetition rate.



(a) Reactive mode (0.3 Pa N<sub>2</sub>) (b) Metallic mode (vacuum)

Figure 4.10: Visual comparison of cathodic arc plasma plumes exiting the macroparticle filter. (a) Reactive mode operation with 0.3 Pa N<sub>2</sub> background pressure shows broader, more diffuse plasma emission with characteristic orange-red glow from nitrogen excitation. (b) Metallic mode in vacuum shows tighter confinement of the ionized metal plasma plume with blue-white emission characteristic of highly ionized Ti and Al species. (Camera settings: f/1.7, 1/100 s, ISO 90.)

### 4.3.1 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.

To compensate for the reduced deposition rate observed in reactive mode, the number of pulses for nitrogen-containing depositions was increased from 6000 (metallic mode) to 8000 pulses. This adjustment aimed to achieve film thicknesses sufficient

for reliable characterization while maintaining comparable total deposition times. All resulting thickness values are summarized in Table 4.1.

Table 4.1: Profilometry thickness measurements for the deposited films at the two positions where the QCM and Ion probe were before

Film ID	Distance (cm)	Pressure (Pa)	Pulses	Thickness QCM (nm)	Thickness Ion probe (nm)
8	14	0	6000	73	68
9	14	0.3	6000	42	35
10	14	0	6000	65	57
11	14	0.3	8000	60	42
13	14	0.1	8000	59	41
14	14	0.2	8000	46	38

The measured thicknesses show good agreement between QCM-derived values and profilometry, with differences on the order of 10 %, which is within the combined measurement uncertainties of both techniques. Films deposited in metallic mode (films 8 and 10, 6000 pulses) show thicknesses of 57–68 nm by profilometry, while films deposited in reactive mode show lower values despite the increased pulse count to 8000. This reduction reflects the lower mass deposition rate in reactive mode observed in Figure 4.5a, which is not fully compensated by the increased pulse count.

Several competing effects influence the thickness trends. Films 8 and 10 (metallic mode, 6000 pulses) show thicknesses of 65–73 nm by profilometry, while films deposited in reactive mode show lower values despite the increased pulse count. Film 11 (0.3 Pa, 8000 pulses) achieved 60 nm. This reduction reflects the lower mass deposition rate in reactive mode (Figure 4.5a), which is not fully compensated by the increased pulse count.

An apparent inconsistency emerges when comparing films 9 (0.3 Pa, 6000 pulses, 35 nm) and 11 (0.3 Pa, 8000 pulses, 42 nm). The thickness increase from 35 to 42 nm represents only a 20 % gain for a 33 % increase in pulses, suggesting either non-linear deposition behavior or position-dependent variations. Additionally, Figure 4.5a shows that at 14 cm, the mass flux should remain relatively constant across the pressure range (0–0.3 Pa), yet film 9 shows substantially lower thickness than predicted by this trend.

[NOTE: Add discussion of apparent inconsistency at 14 cm between Figure 4.5a trend (constant mass flux vs pressure) and observed film thicknesses. Potential explanations: spatial gradients between QCM/substrate positions, pulse-to-pulse variability (Table 4.1).]

### 4.3.2 X-ray Diffraction (XRD)

X-ray diffraction measurements were performed to characterize the crystallographic structure and phase composition of the deposited films as a function of nitrogen pressure. Figure 4.11 shows the stacked diffraction patterns for films deposited at 14 cm distance with 0.25 T magnetic field under varying N<sub>2</sub> pressures from 0 Pa (metallic mode) to 0.3 Pa (reactive mode).

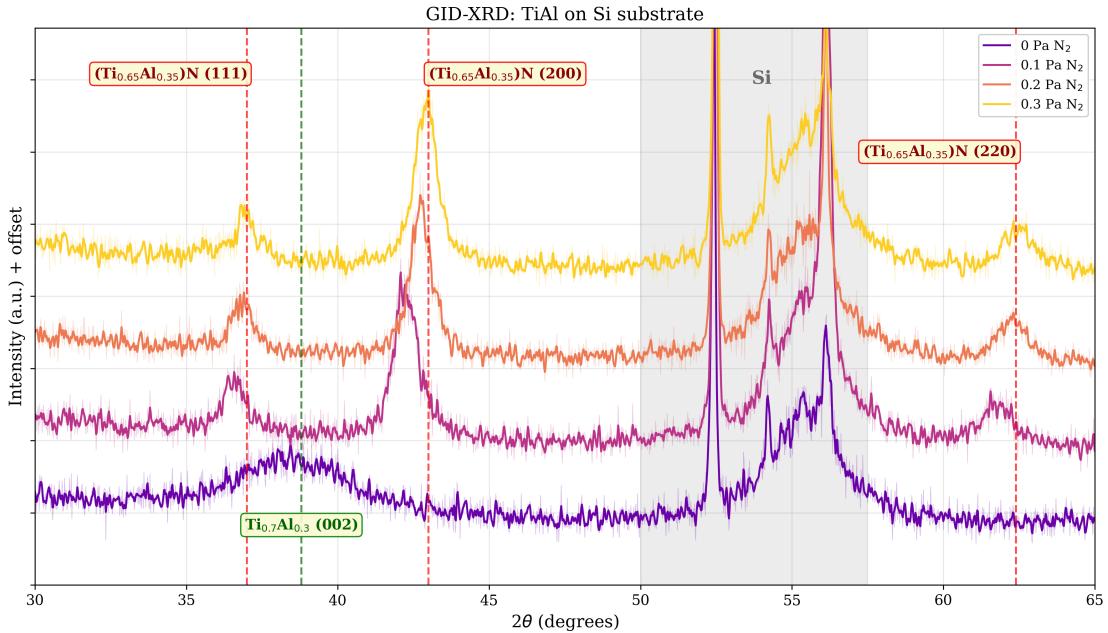


Figure 4.11: Grazing incidence XRD patterns for Ti–Al and Ti–Al–N films deposited at different nitrogen pressures. Films were deposited at 14 cm distance with 0.25 T magnetic field. The intense peaks between 52° and 57° originate from the Si substrate. Vertical dashed lines indicate reference positions for cubic (Ti<sub>0.65</sub>Al<sub>0.35</sub>)N (111), (200), and (220) reflections at 37.0°, 43.0°, and 62.5° respectively (ICDD PDF 04-017-5094), as well as hexagonal Ti<sub>0.7</sub>Al<sub>0.3</sub> (002) at 38.8° (ICDD PDF 04-004-9157).

### Phase Identification

The diffraction patterns reveal a clear transition from metallic to nitride phases with increasing nitrogen pressure:

**Metallic mode (0 Pa N<sub>2</sub>):** At zero nitrogen pressure, the film exhibits a weak, broad peak at approximately 38.8°, consistent with the (002) reflection of hexagonal Ti<sub>0.7</sub>Al<sub>0.3</sub> (space group P6<sub>3</sub>/mmc, PDF 04-004-9157). The (101) reflection expected at 40.9° (I/I<sub>max</sub> = 100% in the reference pattern) is not observed.

**Reactive mode (0.1–0.3 Pa N<sub>2</sub>):** Introduction of nitrogen fundamentally alters the film structure. At 0.1 Pa N<sub>2</sub>, three distinct peaks emerge at approximately 37°,

43°, and 62°, corresponding to the (111), (200), and (220) reflections of the cubic B1 (NaCl-type) ( $\text{Ti}_{0.65}\text{Al}_{0.35}$ )N phase (space group  $\text{Fm}\bar{3}\text{m}$ , PDF 04-017-5094). The hexagonal TiAl peak disappears completely, indicating full conversion to the nitride phase.

As the nitrogen pressure increases to 0.2 Pa and 0.3 Pa, all three nitride reflection peaks sharpen and their positions align more closely with reference values. The (200) peak at 43° becomes the most prominent reflection, matching the highest relative intensity in the reference pattern ( $I/I_{\max} = 1000$ ) [27].

Peak positions at 0.2 Pa and 0.3 Pa agree closely with reference values. Small deviations at 0.1 Pa correlate with the lower nitrogen content measured by EDX (33 at.% vs 39 at.%). The reference cubic nitride exhibits a lattice parameter of  $a = 4.202 \text{ \AA}$  and a calculated density of  $4.8 \text{ g cm}^{-3}$  [27], which will be compared with the film densities determined by XRR (Section 3.3.3).

### 4.3.3 XRR

#### 4.3.4 Energy dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectroscopy was performed to determine the elemental composition of the deposited films as a function of nitrogen pressure. All films were deposited at 14 cm distance with a magnetic field of 0.25 T. Three measurement points were taken on each sample and averaged to obtain representative composition values.

Table 4.2: EDX film composition (atomic %) as a function of nitrogen pressure and the resulting effective molar mass of the films (deposited at 14 cm, 0.25 T)

Nitrogen (Pa)	N (at.%)	Al (at.%)	Ti (at.%)	$M_{\text{eff}}$ (g · mol $^{-1}$ )
0.0	0	21	79	43.5
0.1	33	17	50	33.2
0.2	38	15	47	31.9
0.3	39	14	47	31.8

The results in Table 4.2 reveal several key trends:

**Metallic mode (0 Pa):** In vacuum deposition, the film composition shows a Ti:Al ratio of approximately 79:21, compared to the cathode composition (62.8 at.% Ti; 37.2 at.% Al). The effective molar mass is  $43.5 \text{ g} \cdot \text{mol}^{-1}$ , between pure aluminum ( $27.0 \text{ g} \cdot \text{mol}^{-1}$ ) and pure titanium ( $47.9 \text{ g} \cdot \text{mol}^{-1}$ ).

**Reactive mode (0.1–0.3 Pa N<sub>2</sub>):** Nitrogen incorporation reaches approximately 33 at.% at 0.1 Pa and saturates near 39 at.% above 0.2 Pa. The final composition at 0.3 Pa is  $\text{Ti}_{0.47}\text{Al}_{0.14}\text{N}_{0.39}$ , close to the reference material composition used for XRD

analysis [27]. The Ti:Al ratio shifts from approximately 3.75:1 in metallic mode to approximately 3.4:1 in reactive mode.

**Effective molar mass trends:** The effective molar mass decreases from  $43.5 \text{ g}\cdot\text{mol}^{-1}$  (metallic mode) to approximately  $32 \text{ g}\cdot\text{mol}^{-1}$  (reactive mode), a reduction of approximately 25%. The molar mass saturates above 0.2 Pa at  $M_{\text{eff}} \approx 31.8 \text{ g}\cdot\text{mol}^{-1}$ , consistent with the compositional saturation observed in nitrogen content.

The effective molar mass is calculated from the atomic fractions  $x_i$  and atomic masses  $M_i$  according to:

$$M_{\text{eff}} = \sum_i x_i M_i = x_{\text{Ti}} \cdot 47.867 + x_{\text{Al}} \cdot 26.982 + x_{\text{N}} \cdot 14.007 \quad (4.1)$$

where the atomic fractions sum to unity ( $x_{\text{Ti}} + x_{\text{Al}} + x_{\text{N}} = 1$ ).

#### 4.3.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was performed to examine the surface morphology of selected TiAl and TiAlN films. Figure 4.12 shows representative images for films deposited under different conditions.

The metallic TiAl film [Fig. 4.12(a)] exhibits localized surface swelling features, likely resulting from stress relaxation induced by energetic ion bombardment ( $E_{\text{tot}} \approx 60 \text{ eV}$ ). Scattered macroparticles are visible as bright spots across the surface, consistent with typical cathodic arc deposition despite magnetic filtering.

The high-magnification image [Fig. 4.12(b)] shows a direct comparison between secondary electron imaging (left, sensitive to topography) and backscattered electron imaging (right, sensitive to atomic number contrast) of the same macroparticle on a TiAlN film. The absence of compositional contrast in the BSE image confirms that the macroparticle has the same elemental composition as the surrounding film, indicating it originated from molten cathode material rather than external contamination.

The reactive TiAlN film [Fig. 4.12(c)] macroparticle are present, but lower quantities than for the metallic case. The overall surface remains relatively smooth between defects, with no evidence of large-scale roughening or columnar grain boundaries at this magnification.

These observations confirm that the magnetic macroparticle filter effectively reduces but does not completely eliminate macroparticle contamination, consistent with the filtered cathodic arc deposition process described in Section 3.

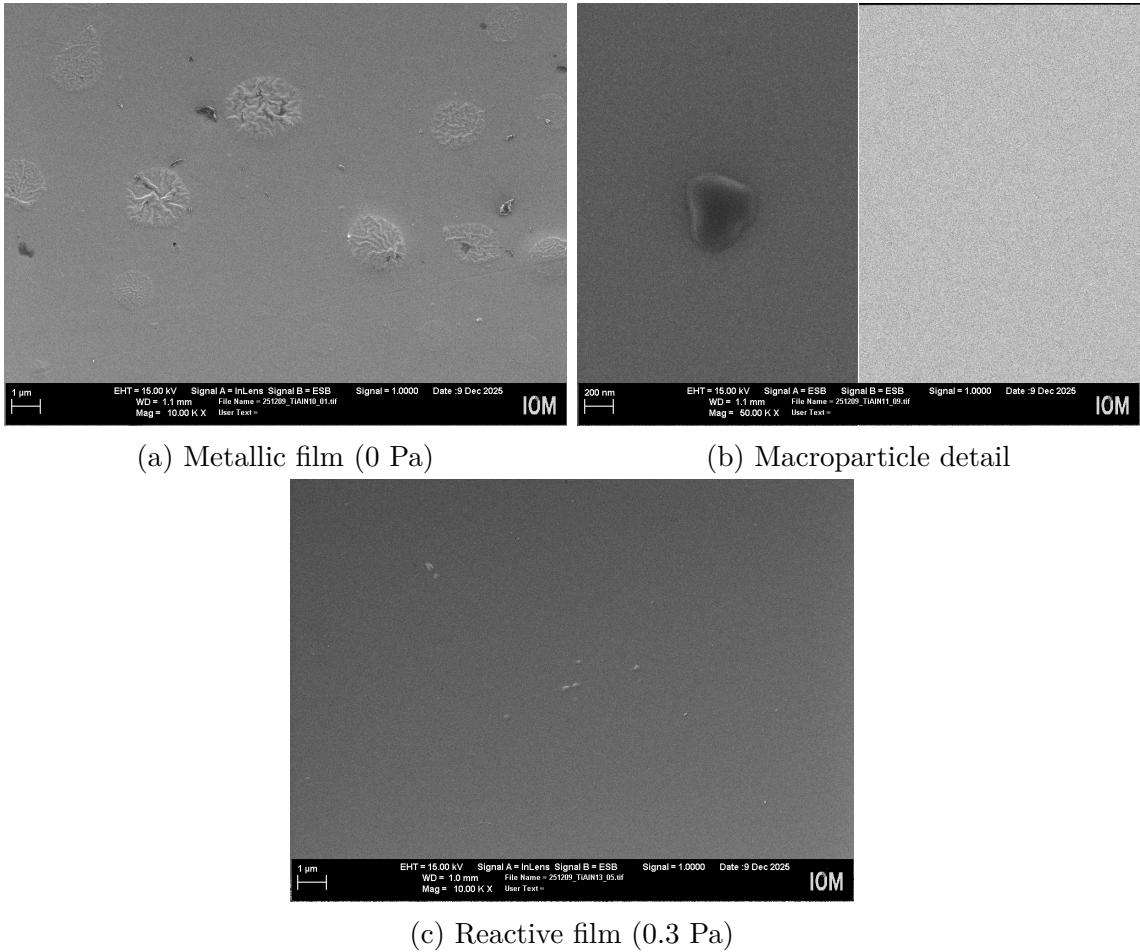


Figure 4.12: SEM surface morphology of deposited films at 14 cm distance, 0.25 T magnetic field: (a) metallic TiAl film showing surface swelling features and scattered macroparticles ( $10,000\times$ ,  $1\ \mu\text{m}$  scale), (b) higher magnification view of an individual macroparticle on a reactive TiAlN film ( $50,000\times$ ,  $200\ \text{nm}$  scale), (c) reactive TiAlN film with characteristic splash patterns from macroparticle impacts ( $10,000\times$ ,  $1\ \mu\text{m}$  scale).

## 4.4 Particle Flux Calculations

The ion current and mass deposition rate measurements represent electrical and mass quantities that must be converted to particle fluxes using charge-state data from ERMS (Section 4.2) and compositional data from EDX (Section 4.3.4). This section presents the derived ion flux  $\Gamma_{\text{ion}}$  and total atomic flux  $\Phi_{\text{total}}$  for the 14 cm deposition distance.

### 4.4.1 Calculation Methods

The ion flux ( $\text{ions}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ) is calculated from the ion current measurements:

$$\Gamma_{\text{ion}} = \frac{I_{\text{ion}}}{e\langle Q \rangle A_{\text{probe}}} \quad (4.2)$$

where  $I_{\text{ion}}$  is the measured ion current,  $e = 1.602 \times 10^{-19}$  C,  $A_{\text{probe}} = 0.196$  cm<sup>2</sup>, and  $\langle Q \rangle$  is the weighted mean charge state from ERMS:

$$\langle Q \rangle = \frac{\sum_i Q_i \cdot I_i^{\text{ERMS}}}{\sum_i I_i^{\text{ERMS}}} \quad (4.3)$$

where the sum includes all charge states of Ti and Al.

The total atomic flux (atoms·cm<sup>-2</sup>·s<sup>-1</sup>) is calculated from QCM measurements:

$$\Phi_{\text{total}} = \frac{\Delta m \cdot N_A}{A_{\text{QCM}} \cdot \Delta t \cdot M_{\text{eff}}} \quad (4.4)$$

where  $\Delta m$  is the mass change over time interval  $\Delta t$ ,  $A_{\text{QCM}} = 0.5027$  cm<sup>2</sup>,  $N_A = 6.022 \times 10^{23}$  mol<sup>-1</sup>, and  $M_{\text{eff}}$  is the effective molar mass from Table 4.2.

#### 4.4.2 Flux Measurements at 14 cm Distance

Figure 4.13 presents the calculated ion flux and atomic flux as functions of nitrogen pressure at 14 cm distance with 0.25 T magnetic field.

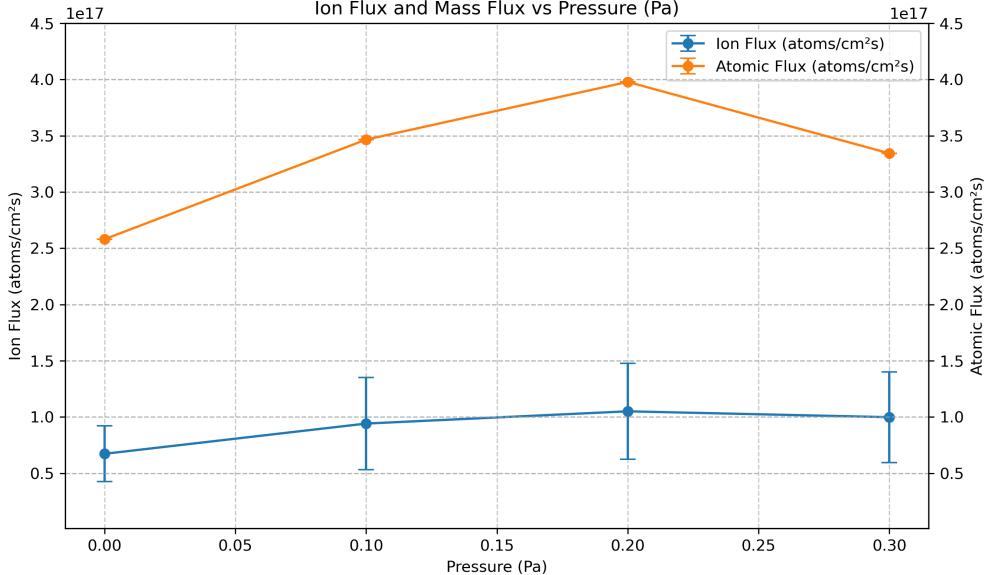


Figure 4.13: Ion flux and atomic flux as functions of nitrogen pressure at 14 cm distance with 0.25 T magnetic field. Ion flux (blue, left axis) remains approximately constant at  $(0.7\text{--}1.0) \times 10^{17}$  ions·cm<sup>-2</sup>·s<sup>-1</sup> across the pressure range. Atomic flux (orange, right axis) exhibits non-monotonic pressure dependence with a maximum near 0.2 Pa. Error bars on ion flux represent combined uncertainties from probe current and ERMS charge-state measurements.

The ion flux remains relatively constant at  $(0.7\text{--}1.0) \times 10^{17}$  ions·cm<sup>-2</sup>·s<sup>-1</sup> across the measured pressure range, with large error bars ( $\pm 30\text{--}50\%$ ) reflecting the combined un-

certainties from probe current measurements and ERMS charge-state determination. The pressure independence is consistent with the ion current behavior observed in Figure 4.5b at 14 cm distance.

The atomic flux shows non-monotonic pressure dependence, increasing from  $2.6 \times 10^{17}$  atoms·cm $^{-2} \cdot$ s $^{-1}$  in metallic mode to a maximum of  $4.0 \times 10^{17}$  atoms·cm $^{-2} \cdot$ s $^{-1}$  at 0.2 Pa, before decreasing slightly to  $3.3 \times 10^{17}$  atoms·cm $^{-2} \cdot$ s $^{-1}$  at 0.3 Pa.

#### 4.4.3 Observations on Flux Magnitudes

The atomic flux is systematically higher than the ion flux by factors of 3–4 across all pressure conditions. In metallic mode (0 Pa), where film composition is purely Ti and Al without nitrogen, the atomic flux is approximately 3.7 times larger than the ion flux. This ratio increases to approximately 4 in reactive mode.

Several factors may contribute to this discrepancy:

- The QCM to flux conversion using  $M_{\text{eff}}$  of the resulting film instead of the plasma
- Systematic errors in probe collection or measurement resistance values

The origin of the flux magnitude difference requires further investigation. The relative trends (pressure independence of ion flux, non-monotonic behavior of atomic flux) are considered robust, while the absolute magnitudes carry larger systematic uncertainties. Detailed analysis of this discrepancy is deferred to future work.

# CHAPTER 5

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## Discussion of Results

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This chapter interprets the experimental findings presented in Chapter 4 and connects them to the theoretical framework established in Chapter 2. The discussion is organized around three central themes: plasma transport and composition, film growth mechanisms, and the correlation between plasma parameters and film properties. Measurement limitations and comparison with previous (V,Al)N work are addressed in the final sections.

## 5.1 Plasma Transport and Magnetic Field Effects

### 5.1.1 Magnetic Mirror Effect at Low Fields

The anomalous decrease in both mass deposition rate and ion current at 0.05 T magnetic field (Figure 4.2) reflects a magnetic mirror effect at the entrance of the EM-coil. When plasma transitions from the weak fringing field ( $\sim 0.01$  T) outside the coil into the stronger field (0.05 T) inside, conservation of the magnetic moment  $\mu = mv_{\perp}^2/2B$  causes electrons with significant perpendicular velocity components to be reflected [28]. The reflection condition is met when:

$$\frac{v_{\perp}^2}{v_{\parallel}^2} > \frac{B_{\max} - B_{\min}}{B_{\min}} \quad (5.1)$$

For the transition from 0.01 T to 0.05 T, electrons with pitch angles greater than approximately  $60^\circ$  are reflected, creating a localized space-charge layer that retards ion flow. This temporarily reduces both ion flux and deposition rate despite the nominally increased magnetic confinement. At higher fields (0.1 T and above), the beneficial

effects of plasma compression and enhanced ionization [6] overcome this mirror loss, restoring the monotonic increase expected from magnetic confinement.

The persistence of this effect across all distances and pressures indicates it is a fundamental feature of the plasma-coil interaction rather than a transient or distance-dependent phenomenon. Future system optimization could minimize this loss by tapering the magnetic field profile at the coil entrance, reducing the field gradient that drives electron reflection.

### 5.1.2 Spatial Expansion and $1/r^2$ Scaling

In metallic mode, mass deposition rate follows approximate  $1/r^2$  dependence (Figure 4.3a), consistent with free expansion of a quasineutral plasma from a point source [3, Chap. 4.3]. The 20 cm flux is approximately 25–30% of the 10 cm value, close to the geometric factor  $(10/20)^2 = 0.25$ . Small deviations from perfect  $1/r^2$  scaling arise from the finite source size (cathode diameter 6.35 mm) and magnetic field effects that partially collimate the plasma plume.

Ion current also decreases with distance but more steeply than  $1/r^2$  in reactive mode, reflecting the additional effects of charge-exchange neutralization. The spatial profiles of mass deposition rate and ion current progressively diverge as nitrogen pressure increases, indicating that charge-exchanged neutral metal atoms follow ballistic trajectories while ions can be guided by residual magnetic fields from the filter coils.

## 5.2 Reactive Mode Plasma Chemistry

### 5.2.1 Charge-Exchange Collisions and Neutral Formation

The pressure dependence of ion current exhibits complex behavior at close distances (Figure 4.5b). At 10 cm, the ion current initially increases from 0 to approximately 0.05 Pa before decreasing at higher pressures. This non-monotonic behavior reflects two competing mechanisms operating in different pressure regimes.

At low nitrogen pressures (0–0.1 Pa), the initial increase may result from enhanced plasma generation at the cathode. Nitrogen incorporation into the cathode surface can alter spot dynamics, potentially increasing the erosion rate and metal ion production. Simultaneously, ion molecule reactions begin to produce nitrogen ions ( $N^+$ ,  $N_2^+$ ) that contribute to the total measured probe current.

At higher pressures (above 0.1 Pa), charge exchange collisions dominate, reducing

the metal ion contribution to the measured current:



The resulting fast neutral metal atoms are invisible to the biased probe, leading to apparent current reduction even though total metal flux (measured by QCM) remains substantial. The charge-exchange cross section increases with collision energy and is largest for highly ionized species [3, Chap. 9.4].

ERMS measurements confirm this mechanism: average mean charge states decrease from  $\langle Q \rangle \approx 2.4$  (metallic) to  $\langle Q \rangle \approx 1.6$  (0.3 Pa reactive), with the charge-state distribution shifting toward lower ionization levels (Figures 4.6 and 4.7). Potential energy decreases proportionally with charge state, while kinetic energy shows modest variations reflecting the competing effects of elastic scattering and cathode chemistry changes [7].

Additionally, nitrogen ions ( $\text{N}^+$ ,  $\text{N}_2^+$ ) contribute less current per particle than multiply charged metal ions because their charge states are predominantly 1+. A probe measuring 10 mA of  $\text{Ti}^{2+}$  current corresponds to  $3 \times 10^{16}$  ions·s<sup>-1</sup>, while the same 10 mA of  $\text{N}^+$  represents  $6 \times 10^{16}$  ions·s<sup>-1</sup>. This explains part of the apparent current reduction when nitrogen ions displace metal ions in the plasma composition.

### 5.2.2 Cathode Poisoning and Spot Transitions

The non-monotonic pressure dependence of mass deposition rate at 10 cm (Figure 4.5a), with a maximum near 0.05–0.1 Pa, reflects competing effects of cathode poisoning and reactive film growth. At low nitrogen pressures, the cathode surface remains predominantly metallic (type-2 spots), with nitrogen adsorbing on the growing film rather than the cathode [3, Chap. 9.2–9.3]. This enhances deposition through compound formation without significantly reducing the metal emission rate.

As pressure increases beyond 0.1 Pa, a compound layer (TiN or mixed TiAlN) forms on the cathode surface, transitioning to type-1 (poisoned) spots. Type-1 spots have lower erosion rates and altered emission characteristics, reducing the total material flux. Simultaneously, collisional deflection becomes significant: nitrogen molecules scatter metal ions through momentum transfer, broadening the spatial distribution and reducing flux at the measurement position [29].

At 14 cm and 20 cm, the pressure independence of both mass deposition rate and

ion current (within uncertainties) indicates that the plasma has already undergone extensive scattering and equilibration. Collisional mean free paths at 0.1–0.3 Pa are on the order of centimeters, so multiple collisions occur during transit to these distances. Further pressure increases produce no additional deflection because the plasma is already thermalized and broadly distributed.

### 5.2.3 Activated Nitrogen Species

EDX measurements (Table 4.2) show substantial nitrogen incorporation in reactive mode films (33–39 at.%), while ERMS detects only modest  $\text{N}^+/\text{N}_2^+$  signals (10–28 at.%) compared to metal ions. This imbalance suggests that nitrogen arrives predominantly through neutral channels: either ground-state  $\text{N}_2$ , vibrationally/electronically excited  $\text{N}_2^*$ , or atomic nitrogen radicals  $\text{N}^*$  produced by dissociative electron impact in the cathode spot plasma [7].

The quantitative relationship between ion flux measurements and atomic flux calculations (Figure 4.13) shows systematic differences that require further investigation. Potential contributions include calibration uncertainties in the flux conversion factors and time averaging effects between pulsed and continuous measurements.

## 5.3 Film Growth Mechanisms and Microstructure

### 5.3.1 Energetic Condensation and Room-Temperature Crystallization

ERMS measurements confirm that total ion energies ( $E_{\text{kin}} + E_{\text{pot}}$ ) remain above 30 eV across all experimental conditions (Figures 4.6 and 4.7), well above the threshold for subplantation-driven densification [3, Chap. 8.1]. In metallic mode, total energies reach 60–80 eV, while in reactive mode they remain in the 30–50 eV range despite charge-exchange reduction of potential energy.

This energetic condensation enables room temperature film growth through two mechanisms: (1) shallow implantation of ions below the surface, occupying interstitial sites and displacing near-surface atoms through knock-on collisions and (2) localized atomic-scale heating from kinetic and potential energy deposition, enhancing adatom mobility on nanosecond timescales without global substrate heating [3, Chap. 8.2].

XRD results validate this mechanism. In metallic mode without nitrogen, films exhibit weak and broad diffraction (Figure 4.11, 0 Pa), consistent with limited crys-

tallinity despite energetic ion bombardment. The low intensity and broad peak width suggest small crystallite size or incomplete crystallization, typical of vapor deposited alloys without substrate heating [11]. The absence of the expected (101) reflection indicates either strong (002) texture or predominantly amorphous structure with small hexagonal domains.

In reactive mode, nitrogen incorporation fundamentally alters film growth. The appearance of sharp cubic TiAlN peaks at 0.1 Pa and their continued sharpening at higher pressures reflects progressive crystallization driven by the chemical driving force for nitride formation (formation enthalpy approximately -200 kJ/mol for TiN and AlN [1]) combined with energetic ion bombardment. The complete disappearance of the hexagonal TiAl peak indicates full conversion rather than phase coexistence.

### 5.3.2 Composition and Stoichiometry

EDX measurements show systematic deviations from cathode stoichiometry. In metallic mode, the Ti:Al ratio shifts from 62.8:37.2 (cathode) to 79:21 (film). This deviation likely arises from: (1) Different erosion rates: titanium's higher melting point (1668°C vs 660°C) and cohesive energy may lead to preferential aluminum emission from the explosive cathode spots. (2) Ionization efficiencies: aluminum's lower ionization potentials (5.99 eV for  $\text{Al}^{1+}$  vs 6.83 eV for  $\text{Ti}^{1+}$ ) could favor Al ionization, but charge state distributions show  $\text{Ti}^{2+}$  is more abundant than  $\text{Al}^{2+}$ , suggesting ionization is not the primary factor. (3) Transport through the macroparticle filter: multiply charged ions with higher m/Q ratios experience stronger magnetic deflection, potentially causing differential transmission.

In reactive mode, the Ti:Al ratio shifts to 3.4:1, closer to the cathode composition. This suggests that nitrogen incorporation alters the emission process, possibly through cathode poisoning that reduces overall erosion rates and equalizes Ti/Al emission. The nitrogen saturation at 39 at.% (0.2–0.3 Pa) is close to stoichiometric  $(\text{Ti}_x,\text{Al}_{1-x})\text{N}$  (50 at.% N), with the deficiency attributable to a multitude of factors.

## CHAPTER 6

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final words or smt like thanks everyone

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# APPENDIX A

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## Experimental Methods supplementary

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### A.1 Longer QCM depositions

For larger mass loadings of the QCM, the linear approximation fails and the Z-match<sup>TM</sup> technique is used. This method, introduced by Lu and Lewis in 1972 on the basis of Miller and Bolef's theoretical treatment [30, 31], 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  $\mu$  denoting the density and shear modulus of quartz ( $q$ ) and film ( $f$ ), respectively [32]. 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  $\sim 0.4F_q$ .

### A.2 Holder Assembly Design

The integrated holder assembly (Figure A.1) enabled simultaneous QCM and ion probe measurements with minimal spatial separation. The aluminum mount positioned both diagnostics as close as practicable to bring the flux and plasma conditions as close as

possible between measurement locations.

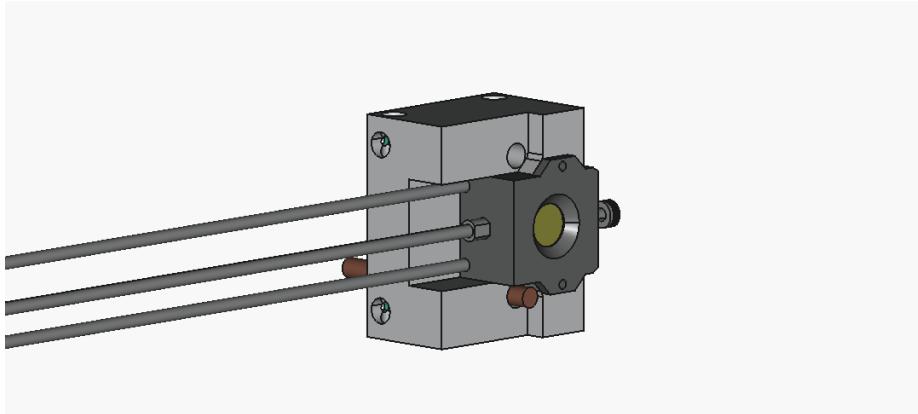


Figure A.1: Holder Assembly for In-Situ Plasma Diagnostics: Integrated QCMs and Langmuir Ion Collector Probe (interactive 3D model; static preview shown in non-Adobe viewers).

## A.3 Data Processing Workflow

Experimental data were processed using custom Python scripts to ensure consistency and reproducibility across all measurements. This section describes the data handling procedures and processing workflows used throughout this work.

### A.3.1 Data Organization and Logbook System

A central Excel logbook served as the reference for all measurements, with each measurement identified by a unique suffix and linked to its corresponding data files. The logbook recorded:

- Date and time of measurement
- Spatial parameters: distance from macroparticle filter (10–20 cm)
- Gas parameters: N<sub>2</sub> flow rate (MFC setting in sccm), working pressure (Pa)
- Vacuum system parameters: cryopump gate valve position, base pressure
- Power supply settings: arc voltage and current, EM-coil voltage and current
- Pulse characteristics: frequency (Hz), pulse width (ms), number of pulses
- QCM frequencies: initial ( $f_0$ ) and final ( $f_1$ ) values for mass determination

Associated oscilloscope waveforms were stored as CSV files for ion current analysis, with filenames linked to the logbook suffix for traceability.

### A.3.2 Ion Current Data Processing

Ion current waveforms were recorded using a Tektronix MSO64 oscilloscope. For each measurement condition, multiple pulses were recorded and processed as follows:

1. **Pulse averaging:** Individual pulse waveforms were averaged to obtain the mean ion current waveform.
2. **Time-integrated current:** The mean ion current over the pulse duration (0–1 ms) was calculated by integrating the averaged waveform and dividing by the pulse width.

The Python script automatically matched logbook entries to oscilloscope CSV files and compiled all parameters into CSV files for analysis.

### A.3.3 ERMS Data Processing

Energy-resolved mass spectrometry data were evaluated with a Python script that performed the following operations:

1. **Spectral integration:** Raw energy distribution functions (EDFs) for each  $M/Q$  value were averaged over the two measurement window of 20 ms.
2. **Mass transmission correction:** Applied correction factors to account for mass-dependent detection efficiency of the quadrupole mass filter and detector.
3. **Energy extraction:** For each ion species ( $Q = 1^+, 2^+, 3^+, 4^+$ ), the measured  $E/Q$  distributions were multiplied by  $Q$  to obtain energy distributions in eV.
4. **Statistical parameters:** Mean ion energy  $\langle E \rangle$ , standard deviation  $\sigma_E$ , and peak energy  $E_{\text{peak}}$  were extracted for each charge state and species.
5. **Charge state analysis:** Mean charge state  $\langle Q \rangle$  was calculated as a weighted average:

$$\langle Q \rangle = \frac{\sum_Q Q \cdot I_Q}{\sum_Q I_Q} \quad (\text{A.3})$$

where  $I_Q$  is the integrated ion current for charge state  $Q$ .

6. **Energy decomposition:** Total ion energy was separated into kinetic and potential components following the procedure described in [6].

The processed results were visualized and exported to CSV files for correlation with ion probe and QCM measurements.

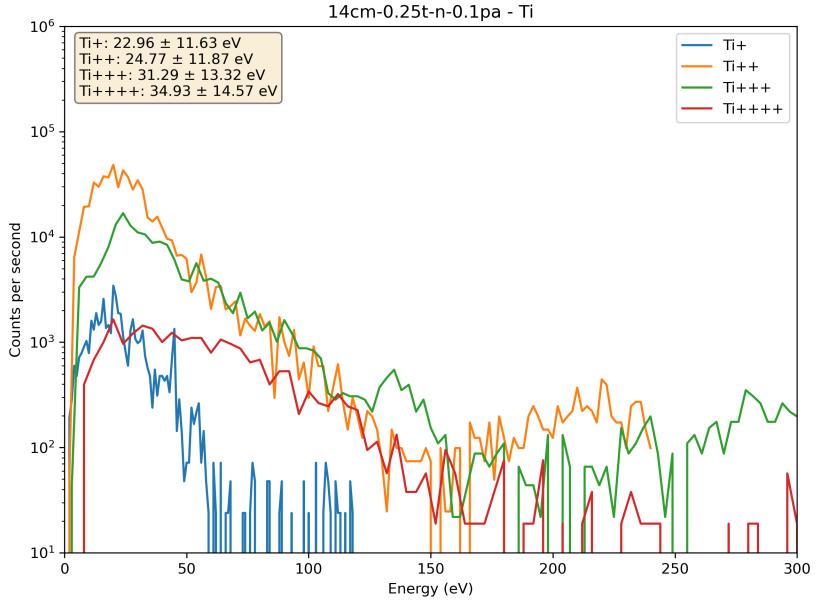


Figure A.2: Charge-state-resolved ion energy distribution functions for  $\text{Ti}^+$  through  $\text{Ti}^{4+}$  measured at 14 cm distance with 0.25 T magnetic field and 0.1 Pa  $\text{N}_2$  pressure. Mean kinetic energies and standard deviations are shown in the legend.

### A.3.4 QCM Data Processing

QCM frequency measurements were recorded before and after each set of pulses. The deposited mass was calculated using the Sauerbrey equation (Equation 3.5). The mass deposition rate was obtained by dividing by the number of pulses and the active crystal area.

## A.4 Uncertainty Analysis

This section provides detailed uncertainty analysis for each diagnostic technique, including sources of systematic and random errors, and error propagation through derived quantities.

### A.4.1 ERMS Measurements

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]. For ERMS measurements, the standard deviation  $\sigma_E$  characterizes the pulse-to-pulse variability and is displayed as error bars in energy distribution plots. This statistical approach is well-documented in mass spectrometry literature [33].

The ERMS requires optimization of electrode voltages to ensure stable ion transmission through the analyzer. This tuning process was performed using the cathodic

arc plasma itself and optimized for  $\text{N}_2^+$  ions at their peak energy.

The detection efficiency varies with  $M/Q$  due to the transmission characteristics of the quadrupole mass filter and the detector response. Mass transmission correction factors were applied to account for these effects. The uncertainty in these correction factors is estimated at  $\pm 10\%$ . The energy analyzer has a finite resolution  $\Delta E/E \approx 2\%$  [16], which limits the ability to resolve closely spaced peaks in the energy distribution but does not significantly affect the determination of mean energies.

#### A.4.2 Ion Probe Measurements

For ion current probe measurements, the standard deviation of the time-averaged current over the pulse duration characterizes the within-pulse variability. This variability can be attributed to fluctuations in plasma potential at pulse ignition and termination, charge-exchange reactions between ions and background neutral gas, and variations in arc current due to cathode spot dynamics. Figure A.3 shows an example ion current waveform with typical within-pulse variations.

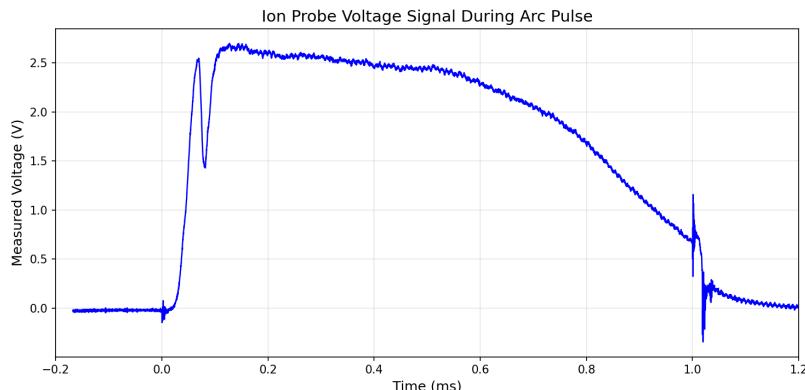


Figure A.3: Example ion current waveform showing variability within a pulse. The voltage signal measured across the  $400 \Omega$  resistor is proportional to the ion current. Rapid transients at pulse ignition (0 ms) and termination (1 ms) are excluded from the time-averaged current calculation.

Pulse-to-pulse variability is examined in Section B.4. For most measurements, ion current waveforms were averaged over multiple pulses (typically 64 pulses) using the oscilloscope's averaging function to reduce noise. The reported uncertainty in these cases reflects within-pulse variability rather than pulse-to-pulse differences.

The ion collection area depends on the sheath thickness, which varies with bias voltage and plasma density. For a cylindrical probe of radius  $r_p = 2.5$  mm biased at  $V_b = -80$  V in a plasma with electron temperature  $T_e \approx 5$  eV, the Debye length is

estimated as:

$$\lambda_D = \sqrt{\frac{\epsilon_0 k_B T_e}{e^2 n_e}} \approx 10^{-5} \text{ m} \quad (\text{A.4})$$

assuming  $n_e \approx 10^{17} \text{ m}^{-3}$ . Since  $r_p \gg \lambda_D$ , sheath expansion effects are negligible and the geometric probe area ( $A = 0.196 \text{ cm}^2$ ) is appropriate. Energetic ions striking the probe surface can induce secondary electron emission, which would reduce the measured ion current. For Cu surfaces bombarded by Ti and Al ions at energies of 30–80 eV, the secondary electron yield is typically  $< 0.1$  [3, Chap. 8.2]. The  $-80 \text{ V}$  bias is sufficient to suppress these secondary electrons, so this effect is considered negligible.

The probe collection area (diameter 5 mm) is smaller than the QCM active area (diameter 7.5 mm), and both are positioned as close as possible to each other. However, radial plasma density gradients inherent to expanding cathodic arc plasmas [3, Chap. 6.2] mean that the probe and QCM sample slightly different regions of the plasma. This effect is most significant at close distances (10 cm) and is discussed in the main text.

### A.4.3 QCM Measurements

The INFICON SQM-160 controller has a frequency measurement uncertainty of  $\Delta f = 0.03 \text{ Hz}$  according to manufacturer specifications [32]. Using the Sauerbrey equation (Equation 3.5), this corresponds to a mass uncertainty:

$$\sigma_m = \frac{N_{\text{AT}} \rho_q \pi r^2}{F_q^2} \cdot \Delta f = 18.8146023 \times 10^{-9} \times 0.03 = 5.6 \times 10^{-10} \text{ g} \quad (\text{A.5})$$

For typical deposited masses in the range 100–1500 ng, this represents a relative uncertainty of 0.04–0.6%, which is negligible compared to other sources of uncertainty.

The QCM is water-cooled to minimize temperature variations, which would cause frequency drift unrelated to mass deposition. The cooling water temperature was maintained at  $20 \pm 1 \text{ }^\circ\text{C}$ . Frequency measurements were recorded immediately before and after each deposition run (total time  $< 1 \text{ minute}$ ) to minimize drift effects. The Sauerbrey equation assumes uniform mass loading across the entire crystal surface. In practice, the deposition profile depends on the plasma expansion geometry. The QCM controller applies no tooling factor correction ( $T_F = 1.00$ ), which is appropriate for directional deposition from a distant source.

For TiAlN films with density  $\rho_f \approx 4.5 \text{ g cm}^{-3}$  deposited on quartz with  $\rho_q = 2.649 \text{ g cm}^{-3}$ , small deviations from linearity are expected at larger mass loadings. However, all measurements were performed in the linear regime ( $\Delta F \ll 0.05 F_q$ ), so Z-match corrections were not required (see Section A.1).

#### A.4.4 Error Propagation in Derived Quantities

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

$$\Gamma_{\text{ion}} = \frac{J_i}{e\langle Q \rangle} = \frac{V_{\text{measured}}}{e\langle Q \rangle A_{\text{probe}} R} \quad (\text{A.6})$$

The primary sources of uncertainty are: ion current measurement ( $\sigma_V/V \approx 5\text{--}15\%$ ), mean charge state determination ( $\sigma_{\langle Q \rangle}/\langle Q \rangle \approx 5\text{--}10\%$ ), probe area ( $\sigma_A/A \approx 1\%$ ), and measurement resistor ( $\sigma_R/R \approx 0.5\%$ ). Assuming independent uncertainties, the standard Gaussian error propagation formula gives [34]:

$$\left(\frac{\sigma_{\Gamma_{\text{ion}}}}{\Gamma_{\text{ion}}}\right)^2 = \left(\frac{\sigma_V}{V}\right)^2 + \left(\frac{\sigma_{\langle Q \rangle}}{\langle Q \rangle}\right)^2 + \left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_R}{R}\right)^2 \quad (\text{A.7})$$

The dominant contributions are from the current measurement and charge state determination, giving a total relative uncertainty of approximately 7–18% depending on measurement conditions.

The total deposited flux  $\Phi_{\text{total}}$  ( $\text{atoms cm}^{-2} \text{pulse}^{-1}$ ) is derived from QCM measurements:

$$\Phi_{\text{total}} = \frac{\Delta m \cdot N_A}{A_{\text{QCM}} \cdot N_{\text{pulses}} \cdot M_{\text{eff}}} \quad (\text{A.8})$$

The primary sources of uncertainty are:

- **Mass measurement** ( $\sigma_m/m \approx 0.5\%$ ): For typical deposited masses of 100–1500 ng over 64 pulses, the frequency shift ranges from 1–50 Hz. With the instrument uncertainty of  $\Delta f = 0.03 \text{ Hz}$  [32], this gives a relative uncertainty of 0.06–3%. However, temperature drift and baseline fluctuations typically add an additional 0.3–0.5%, giving a combined uncertainty of approximately 0.5% for most measurements. This is supported by repeated measurements at identical conditions showing mass reproducibility within 0.4–0.6%.
- **QCM area** ( $\sigma_{A_{\text{QCM}}}/A_{\text{QCM}} \approx 1\%$ ): The active crystal area is defined by the electrode diameter (7.5 mm). Manufacturer specifications for AT-cut crystals indicate electrode diameter tolerances of  $\pm 0.05 \text{ mm}$  [32], corresponding to 0.5% uncertainty in diameter or approximately 1.2% in area.
- **Effective molar mass** ( $M_{\text{eff}}$ ): The effective molar mass depends on film composition determined by EDX. For metallic films (no nitrogen), the Ti:Al ratio was measured by EDX as approximately 4:1 (80 at.% Ti, 20 at.% Al), giving  $M_{\text{eff}} = 46.2 \text{ g mol}^{-1}$ . This differs from the cathode composition (62.8 at.% Ti, 37.2 at.% Al,  $M_{\text{eff}} = 44.2 \text{ g mol}^{-1}$ ) due to differences in ionization efficiency and transport through the magnetic filter [3]. For reactive films, nitrogen content from EDX is added to determine  $M_{\text{eff}}$  for the TiAlN compound.

EDX quantification typically achieves 2–3% relative accuracy for major elements

(>10 at.%) and 5–10% for minor elements under optimal conditions [25]. However, quantitative uncertainty estimates (error bars) were not provided by the EDX analysis software for this work. Therefore, the uncertainty in  $M_{\text{eff}}$  is not included in the error propagation calculations below, and the total flux uncertainties represent lower bounds. Given the exploratory nature of the measurements and the measurement variability from other sources, this simplified approach is considered adequate.

The error propagation for total deposited flux, excluding the unmeasured composition uncertainty, is:

$$\left(\frac{\sigma_{\Phi_{\text{total}}}}{\Phi_{\text{total}}}\right)^2 = \left(\frac{\sigma_m}{m}\right)^2 + \left(\frac{\sigma_{A_{\text{QCM}}}}{A_{\text{QCM}}}\right)^2 \approx (0.005)^2 + (0.01)^2 \quad (\text{A.9})$$

yielding a total relative uncertainty of approximately 1.1%. This represents a **lower bound** on the true uncertainty, as it does not include the contribution from composition measurement uncertainty (typically 2–5% based on literature values for EDX). The actual uncertainty in  $\Phi_{\text{total}}$  is likely in the range of 2–6%, but cannot be precisely quantified without EDX uncertainty data.

The ratio  $\Gamma_{\text{ion}}/\Phi_{\text{total}}$  provides insight into the fraction of deposited material arriving as ions versus neutrals, which is particularly important for distinguishing between metallic and reactive deposition modes. The relative uncertainty in this ratio, excluding composition uncertainty, is:

$$\left(\frac{\sigma_{\text{ratio}}}{\text{ratio}}\right)^2 = \left(\frac{\sigma_{\Gamma_{\text{ion}}}}{\Gamma_{\text{ion}}}\right)^2 + \left(\frac{\sigma_{\Phi_{\text{total}}}}{\Phi_{\text{total}}}\right)^2 \quad (\text{A.10})$$

giving a total uncertainty of approximately 35–44%, completely dominated by the ion flux measurement. The total deposited flux contributes negligibly to the overall uncertainty (<0.3% additional uncertainty).

This large uncertainty in the ion-to-total flux ratio is unavoidable given the fluctuating nature of cathodic arc plasmas.

## APPENDIX B

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### Langmuir Probe Bias Voltage Characterization

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Before plasma diagnostics were performed, the functionality of the custom-built Langmuir probe was verified by characterizing the voltage-current relationship and determining the appropriate negative bias voltage for ion saturation measurements. The goal was to ensure that the probe operates in a regime where the collected current is dominated by ions, excluding contributions from electrons.

## B.1 Validation of Langmuir Probe Operation

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.

The relationship between the collected current  $I$  and the bias voltage  $V$  was analyzed using the modified Langmuir equation [14]:

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

where  $I_{\text{sat}}$  is the saturation current and  $V_0$  is a characteristic voltage. The term  $m$  accounts for plasma sheath expansion and collisional effects at higher bias voltages.

Figure B.1 displays the measured ion current as a function of bias voltage. The blue data points represent the experimental results, while the green line shows the I-V fit to Equation B.1.

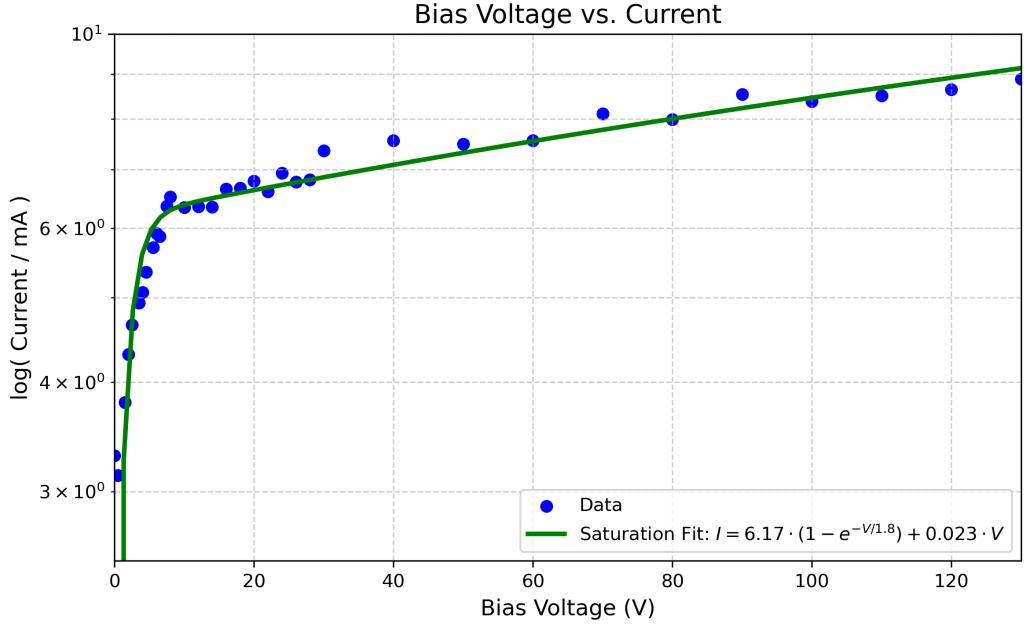


Figure B.1: Measured ion current vs. bias voltage for the Langmuir probe, showing I-V fit  $I = 6.17(1 - e^{-V/1.8}) + 0.023V$ . Conditions: no nitrogen, 10 cm from the macroparticle filter, 0.25 T EM-coil strength.

## B.2 Analysis of the Ion Saturation Curve

As the bias voltage increases, the sheath around the probe grows. At higher voltages, the sheath becomes non-planar, and the probe begins to attract ions not only from directly in front but also from the sides, leading 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. The linear term  $m \cdot V$  in Equation B.1 accounts for these effects and ensures the model accurately describes the probe's behavior across the full range of applied voltages [14, Chap. 7].

The experimental data were fitted to Equation B.1 using a nonlinear least-squares method in Python, yielding the following parameters:

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

The bias voltage test results (Figure B.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 a balance between

the decreasing electron flux and the increasing ion flux.

## 2. Saturation Regime (40 – 130 V):

Beyond approximately 40 V, 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  $m = 0.023$  in the modified Langmuir equation.

## B.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.

## B.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.

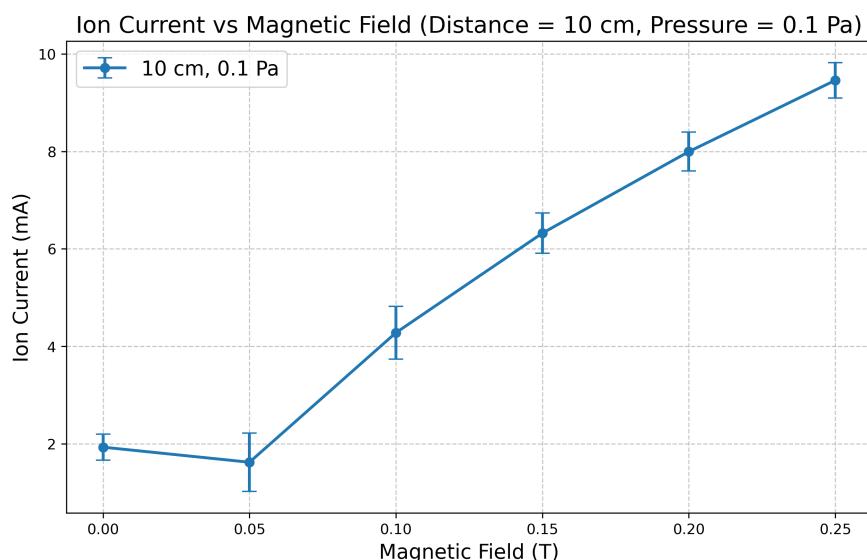


Figure B.2: Pulse to pulse variation in mean ion current at varying magnetic fields (0.1 Pa N<sub>2</sub>, 10 cm distance)

EM-coil field (T)	Mean $I_{\text{ion}}$ (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 B.1: Summary of pulse measurement statistics for varying magnetic field strengths. Note: The 0.05 T data includes variability from unstable arc behavior at this field strength.

In all other measurements, the oscilloscope averaged the voltage signal over multiple pulses to improve signal-to-noise ratio. Therefore, the error reported in subsequent sections primarily reflects variations in ion current within individual pulses, rather than differences between distinct pulses.

## APPENDIX C

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### Additional Plots

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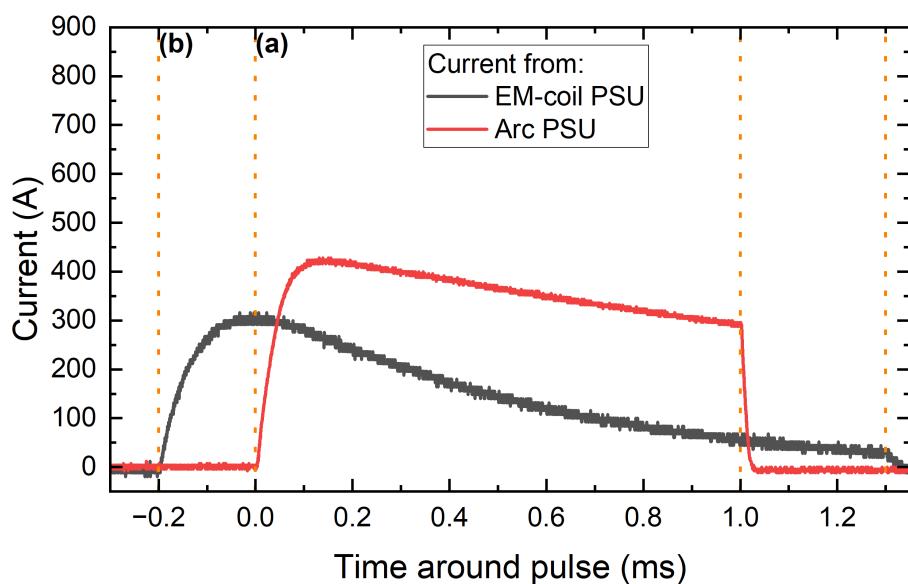
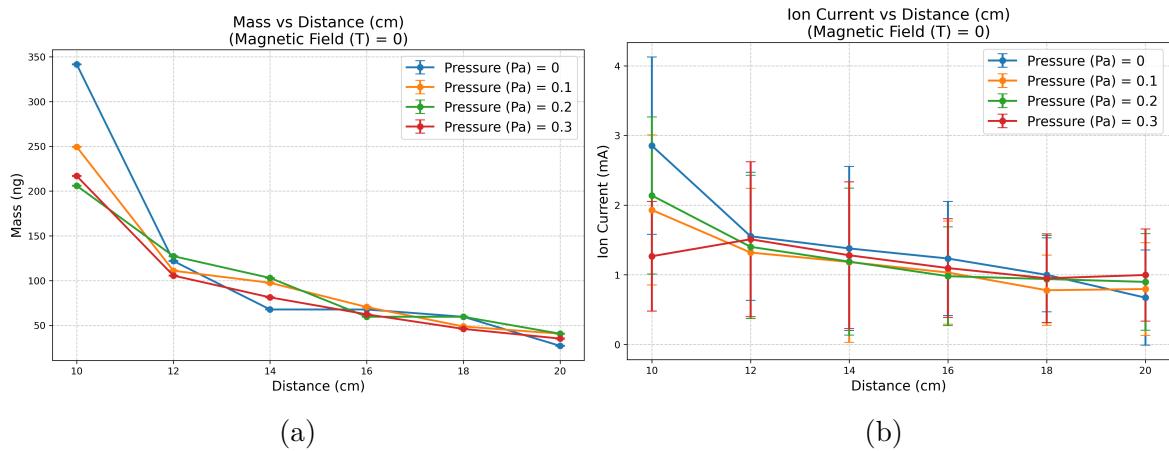


Figure C.1: Additional Pulse waveform with the triggering timings (a) and (b) for the Arc-PSU and the EM-coil PSU marked with the orange dashed line for 100V input



(a)

(b)

Figure C.2: Additional plot for Section 4.1.2. 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 D

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## Python Code and Data Overview

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### D.1 Data Availability

All raw data files, processed datasets, and analysis scripts are archived and available upon request. The main Python scripts used for data processing include:

- `process_ion_probe.py`: Ion current waveform analysis and averaging
- `process_erms.py`: ERMS data integration, mass transmission correction, and energy extraction
- `process_qcm.py`: QCM frequency analysis and mass calculation
- `compile_dataset.py`: Unified dataset generation from logbook and raw data files

Table D.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, 4 deposited films

Distance (cm)	Magnetic Field (T)	Pressure (Pa)	Measurements Performed			Film ID
			Ion/QCM	Mass Spec	Ex-situ	
<b>Systematic parameter scan:</b>						
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	✓	—	—	—
<b>Distance 10 cm — standard conditions:</b>						
10	0.05, 0.1, 0.2	all pressures <sup>†</sup>	✓	—	—	—
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	✓	—	—	—
<b>Distance 10 cm — with mass spectrometry:</b>						
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
<b>Distance 14 cm — standard conditions:</b>						
14	0, 0.05, 0.1, 0.2	all pressures <sup>†</sup>	✓	—	—	—
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	✓	—	—	—
<b>Distance 14 cm — with mass spectrometry:</b>						
14	0.15	0.1	✓	✓	—	—
14	0.25	0	✓	✓	✓	010
14	0.25	0.1	✓	✓	✓	013
14	0.25	0.2	✓	✓	✓	014
14	0.25	0.3	✓	✓	✓	012
<b>Distance 20 cm — standard conditions:</b>						
20	0, 0.05, 0.1, 0.15, 0.2	all pressures <sup>†</sup>	✓	—	—	—
20	0.25	0.025, 0.05, 0.075, 0.1, 0.2	✓	—	—	—
<b>Distance 20 cm — with mass spectrometry:</b>						
20	0.25	0, 0.3	✓	✓	—	—

<sup>†</sup>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

Mass Spec: Energy-resolved mass spectrometry (ERMS)

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