

Advancing the Industrialization of Thin Film Deposition: Tools for Mitigating Powder Formation in Spatial-ALD Systems and for Real-time, In-situ Metrology

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of Contributions

The samples used for analysis in Chapter 3.3.2.5 were created by Louis-Vincent Delumeau.

The Reactor head used for all the Chapter 3 experiments was created by Nfinite Nanotechnology.

The “555” circuit (Appendix A.2.3) and flow-valve controller circuit (Appendix A.2.5) were developed by Neil Griffett.

Abstract

Thin-film manufacturing through Spatial Atomic Layer Deposition (SALD) offers high throughput and cost-saving advantages, but challenges such as powder formation and the lack of real-time in-situ metrology hinder its industrial-scale viability. This thesis focuses on improving the reliability of the SALD process in two key ways: mitigating the powder formation in SALD systems which tends to diminish film quality and identifying in-situ metrology techniques to assure the quality of SALD films.

The first section investigates the influence of deposition variables, including precursor concentration, reactor-substrate gap spacing, and temperature, on powder formation. A novel powder quantification module, based on exhaust filter resistance measurements, enables systematic investigation of these parameters. This approach was used to identify optimal parameters for minimizing powder (e.g., Gap = 0.5mm, Curtain > 4000 SCCM, Temperature > 100°C). Additionally, a method to assess SALD precursor isolation, a critical factor in reducing powder formation, is introduced. These quantification methods represent a significant step toward reducing powder in industrial SALD systems as there have been few attempts at systematically quantifying the effects of deposition conditions on powder formation.

In the second section, three metrology techniques (Absorbance spectroscopy, reflectometry, and ellipsometry) are evaluated for their efficacy in measuring SALD-produced films. These techniques are evaluated using Al₂O₃- and ZnO-coated flexible PLA samples. This study finds that while absorbance was effective in measuring small ZnO thicknesses (12 nm-85 nm), it could not be used for Al₂O₃ films. We also found that while small film thicknesses were discernable with both ellipsometry and reflectometry raw data, generating models to calculate thickness would not be straightforward. This work demonstrated that ellipsometry modelling would need to incorporate substrate orientation and reflectometry modelling would need to incorporate refraction through multiple films.

Overall, this thesis contributes significant insights into overcoming key obstacles in the industrialization of the SALD process, offering practical solutions for powder reduction and film quality assurance.

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List of Abbreviations

1. **ALD**: Atomic Layer Deposition
2. **Al₂O₃**: Aluminum Oxide
3. **CFD**: Computational Fluid Dynamics
4. **CVD**: Chemical Vapor Deposition
5. **H₂O**: Water
6. **LPM**: Litres per minute
7. **MBE**: Molecular Beam Epitaxy
8. **MOCVD**: Metal Organic Chemical Vapor Deposition
9. **PE**: Polyethylene
10. **PHA**: Polyhydroxyalkanoates
11. **PLA**: Polylactic Acid
12. **PVD**: Physical Vapor Deposition
13. **R2R**: Roll-to-Roll
14. **SALD**: Spatial Atomic Layer Deposition
15. **SCCM**: Standard Cubic Centimeters per Minute
16. **SEM**: Scanning Electron Microscopy
17. **SiO_x**: Silicon Oxide (where X represents the varying amount of oxygen)
18. **TMA**: Trimethylaluminum
19. **UV-Vis**: Ultraviolet-Visible (spectroscopy)
20. **ZnO**: Zinc Oxide

1. Introduction

1.1 Spatial atomic layer deposition

Conformal thin films are ubiquitous in our world today and play a critical role in various industries, ranging from microelectronics to food packaging to energy storage. Some common applications of conformal thin films are as follows:

1. **Semiconductors:** Thin films of materials like silicon dioxide or various metal layers are used in integrated circuits and microelectronics.
2. **Optics:** Thin films are used to create anti-reflective coatings, mirrors, and optical filters.
3. **Solar Cells:** Thin films of materials like amorphous silicon or cadmium telluride are used to convert sunlight into electricity.
4. **Magnetic Storage:** Thin films of ferromagnetic materials are used in hard drives.
5. **Protective Coatings:** Thin films can be used to protect surfaces from corrosion or wear.
6. **Food packaging:** Thin films are used to improve barrier properties of regular and biodegradable packaging.

High utilization of thin films, together with the drive towards advancement in these fields, make high throughput manufacturing of these thin films critical. Currently, thin films are manufactured with an array of techniques including molecular beam epitaxy (MBE), chemical vapor deposition (CVD), metal-organic CVD (MOCVD), sputtering, evaporation, and spin coating. Atomic layer deposition (ALD) trumps these other techniques in its ability to give precise control over the thickness of the film being deposited.

In the conventional ALD process, two self-terminating precursor gases (Precursor A and Precursor B) are sequentially passed over a substrate in a vacuum chamber, with evacuation and purge steps in-between these exposures. This process leads to a monolayer of the product of these precursors. Repeating this process multiple times leads to a build up of film, with atom-scale control of the thickness of the film. [1], [2], [3]. A schematic of this process for building up Al_2O_3 is shown in Figure 1. In step 1, Precursor A, Trimethylaluminum ($\text{Al}(\text{CH}_3)_3$ or TMA)

molecules react with the starting surface which contains hydroxyl groups but not with itself, leaving a methoxy monolayer and methane (CH_4) byproducts. In step 2, the byproducts and excess TMA are evacuated and replaced with an inert gas. In step 3, Precursor B, Water Vapor (H_2O), replaces the inert gas in the chamber, which reacts with the methoxy monolayer. In step 4, the excess H_2O and byproducts are evacuated, and the chamber is filled with an inert gas, leaving behind a hydroxy surface on which the sequence can be repeated.

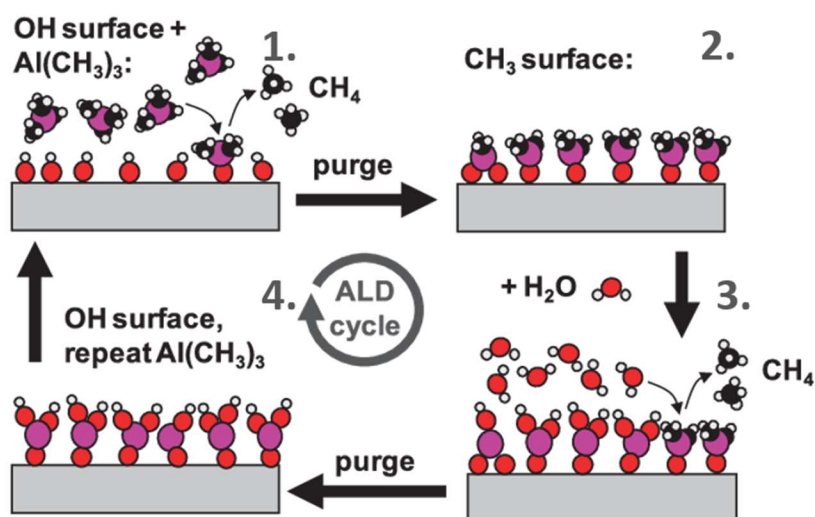


Figure 1: Schematic of ALD synthesis of Al_2O_3 . Source: Reprinted (adapted) with permission from [4].

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Spatial ALD (SALD) improves the speed of the ALD process by eliminating the sequential evacuation and purge steps required in conventional ALD. It does this by simultaneously emitting both gasses from a reactor which oscillates across the surface of the substrate. This way, each gas hits any given location on the substrate sequentially - achieving ALD with a separation of precursor gas reactions in space instead of time. Precursor separation is achieved using high-flow inert gas curtains and evacuation (of byproducts, inert gas and excess precursors) is accomplished by exhaust suction, as shown in Figure 2 [5].

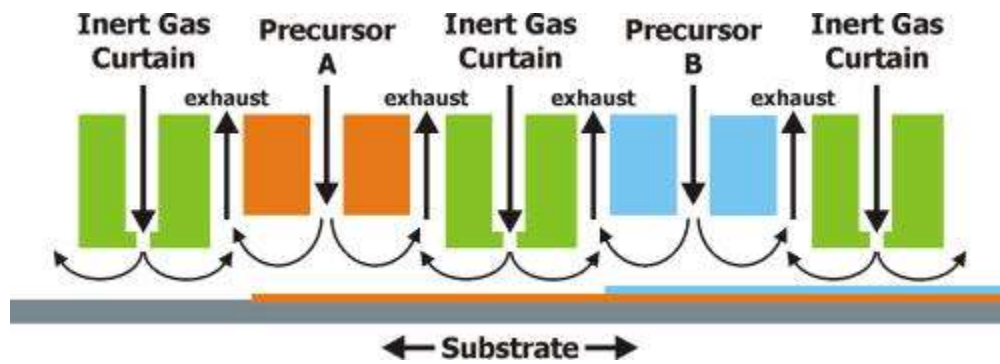


Figure 2: “Close-proximity” SALD configuration showing the arrangement of slits. Source: Reprinted with permission from [5]. Copyright 2011, American Vacuum Society.

For a deeper understanding of the two processes, conventional ALD and SALD are juxtaposed in Figure 3 below. Here, a plot of the process of conventional ALD (I) as well as a schematic of a typical ALD reactor (II) is shown. In contrast, the translation of the substrate to be coated through precursor zones is represented by III, while IV shows a 3D schematic of a SALD reactor head, delivering gases to the substrate oscillating underneath it.

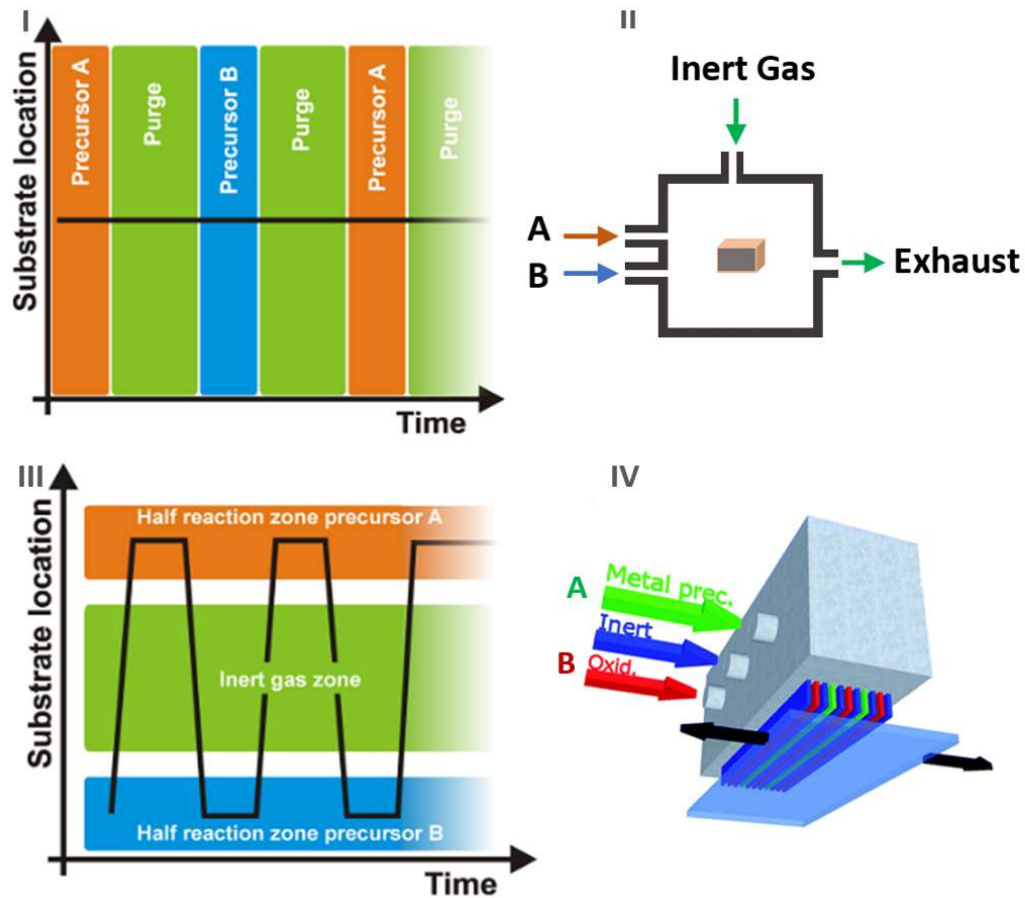


Figure 3: Conventional and spatial ALD schematics. The plot (I) shows how in conventional ALD, a vacuum chamber (II) is filled with precursor A, which is evacuated and replaced with an inert gas in a Purge step, followed by filling the chamber with precursor B and then purging that. III shows the translation of the substrate to be coated through precursor zones in spatial ALD. IV shows a 3D schematic of a SALD reactor head with the substrate oscillating underneath it. Sources: (I,III) Reprinted with permission from [5]. Copyright 2011, American Vacuum Society.(IV) Reprinted with permission from [6]. Copyright 2013, American Vacuum Society.

In one SALD oscillation, a substrate will go through all the ALD steps (1-4) outlined above [6]. By oscillating the substrate underneath the reactor, the sequence of steps is repeated multiple times, adding a monolayer each time. One big advantage of SALD is that it can be done in atmospheric pressure. Another major advantage of SALD is the speed of deposition. SALD allows for 100 times faster depositions [7]. It achieves this by eliminating the evacuation and

purge steps needed in conventional ALD. Another advantage is scalability. Due to the absence of a need for a vacuum, SALD can be scaled by simply increasing the number of reactor heads delivering precursor to the surface. Thus, the speed, modularity, atmospheric pressure, and thickness control features of SALD make it ideal for high throughput applications.

A Note on Colloquialism

Throughout literature and in practice, the different gas-delivery slits used in SALD systems are sometimes referred to by the functions they carry out. This can be seen in Figure 3 IV, where Precursor A is labeled as the Metal precursor, because Precursor A carries the metal atoms that will coat the surface. Precursor B is labeled as the Oxidant Precursor, as it oxidizes the methoxy layer left by precursor A. This functional naming convention will be used throughout this thesis to emphasize that the methods specified in this thesis can be applied to any SALD system regardless of the various combination of gases used to achieve different coatings.

For the rest of the text, the slits delivering Precursor A will be called the metal slits. The slits delivering Precursor B will be called the oxidant slits. The slits delivering the inert gas will be referred to as the curtain slits, as their function is to separate the oxidant and metal gases from reacting.

1.2 The Problems (Motivation)

As shown above, SALD is an excellent technique for high throughput thin-film manufacturing. There are, however, many challenges to be overcome before widespread industrial-scale thin-film manufacturing is achieved with SALD systems. This thesis is dedicated to enhancing the reliability of the SALD process to make it more suitable for industrial-scale production. Towards this, this thesis focuses on two challenges:

- a. **Powder formation in SALD systems:** This is one issue that is often encountered while depositing using SALD systems [8] [9]. Due to unideal deposition conditions, precursors react to form powder/dust at various sites – on the substrate, on the reactor head, and in the exhaust line. We see this often at the Functional Nanomaterials Lab, and our industry partner Nfinite Nanotechnology reports this as well. As will be expanded on in Section 2.2,

powder formation negatively impacts the uniformity of the films created with SALD and creates a need for additional maintenance of the SALD systems. Both of these issues inhibit the industrialization of SALD.

- b. Real-time, in-situ thickness measurements of films created in SALD:** Another issue plaguing the industrialization of SALD is the inability to measure the thickness of the films created by a high-throughput system. An ideal high-throughput system would include an in-situ monitoring subsystem for troubleshooting as well as quality assurance. Thickness measurements of the films created using SALD is challenging due to the minute thickness of the films that can be created – films can theoretically be made a few atoms thick. This difficulty has led to the absence of systems capable of achieving this feat, as highlighted in the most recent, exhaustive review of such techniques by Maize et al. [10]. Identifying suitable in-situ metrology techniques becomes imperative for evaluating the quality of films produced in industrial SALD.

1.3 The Solutions (Thesis Objectives)

This thesis seeks to address the two challenges outlined in Section 1.2 by:

- a. Preventing Powder Formation through Process-Variable Optimization:**

To do this, dedicated methods will be developed to quantify the amount of powder SALD systems generate during depositions. These methods are then used to systematically investigate the impact of various deposition parameters on powder formation.

- b. Evaluating Techniques for Real-Time Nano-Thin Film Metrology:**

To be able to measure the films created with SALD, multiple metrology techniques are explored. These techniques are ranked based on benchmarking criteria and tested for feasibility.

1.4 Synopsis

This thesis begins with a Literature Review in Chapter 2. In Section 2.1, a comparative analysis of thin-film deposition techniques is presented, highlighting the advantages of Spatial Atomic Layer Deposition (SALD) for high-throughput thin film manufacturing. Section 2.2 delves into the prevalent issues associated with powder formation in SALD systems, referencing both literature

and experiences from our industry partner, Nfinite Nanotechnology. This section also explores both the known and suspected causes of powder formation. Section 2.3 will discuss potential methods for the real-time thickness characterization of SALD films, based on established research, and detail the mechanisms of three selected methods.

Chapter 3 will detail a series of experiments developed to measure powder formation in SALD qualitatively, and then quantitatively. It begins with Section 3.1, which reiterates the underlying motivation of the research. Section 3.2 describes the experimental apparatus and standardized procedures for investigating powder formation. Subsequently, Section 3.3 outlines a series of experiments, detailing both methodologies and results, to examine the mechanisms behind powder formation in SALD.

Chapter 4 shifts focus to real-time, in-situ film characterization methods. Section 4.1 introduces the criteria provided by our industry sponsor for method selection. Section 4.2 describes the various samples and instrumentation employed, along with the methodologies for data collection. In Section 4.3, the results are presented and each method's viability for in-situ, real-time characterization is evaluated against the criteria set by the industry sponsor.

The thesis concludes with Chapter 5, summarizing the findings and providing recommendations for the industrialization of SALD.

2 Background and Literature Review

2.1 Comparison of SALD With Other Thin Film Deposition Techniques

For comparison, brief descriptions of some common thin film deposition techniques are presented below followed by a table (Table 1) comparing them. Some of the factors that are considered for each technique are the materials it can deposit, the speed of deposition, if a vacuum is required for the technique, if roll-to-roll is possible, conformality of the film it produces and the technique's applications.

ALD occurs by chemical reactions of two or more precursors injected alternately into a chamber where a substrate is placed at a given temperature and pressure to enable materials deposition on the substrate's surface layer by layer. [11]

SALD is a variation of ALD which eliminates the evacuation and purge steps by spatially separating precursor delivery to the substrate. [12]

Physical vapor deposition (PVD) describes a variety of vacuum deposition methods which can be used to produce thin films and coatings. PVD is characterized by a process in which the material goes from a condensed phase to a vapor phase and then back to a thin film condensed phase. [12] Examples include sputtering and evaporation.

Chemical vapor deposition (CVD) is a vacuum deposition method used to produce high quality, and high-performance, solid materials. Precursors are introduced simultaneously into a chamber and react on a heated substrate to form a thin film. The process is often used in the semiconductor industry to produce thin films. [13]

Spin coating is a technique used to spread uniform thin films on flat substrates by centrifugal force. [14]

Metal Organic Chemical Vapor Deposition (MOCVD) is a form of CVD utilizing metalorganic compounds for one or more of the precursors. [15]

Molecular beam epitaxy sublimates (or evaporates in the case of a liquid source) material from effusion cells, thus forming molecular beams that are incident upon a heated sample.

Table 1: Table comparing different thin-film deposition techniques based on the materials they can deposit, the speed of deposition, if vacuum is required for it, if roll-to-roll is possible, conformality and applications.

	Materials	Speed (nm/hr)	Vacuum Required	Roll-to-roll	Conformal	Applications
ALD	Fluoride, Metal Oxides, Metal Nitrides on variety of substrates. [16]	36 – 360 [7]	Yes [16]	No [7]	Yes [17]	Fuel cells, microelectronics, capacitors, oxides, catalysts, etc. [11]
SALD	Metal Oxides, Metal Nitrides on variety of substrates. [16]	3600 – 36,000 [7]	No [7]	Yes [7]	Yes [7]	Fuel cells, desalination, microelectronics, capacitors, oxides, catalysts, etc. [11]
PVD	Vaporizable materials (Metals, Nitrides, Carbides, oxides etc) on most surfaces [18]	360 – 36,000 [18]	Yes [19]	Yes [20]	No [19]	Fuel cells, batteries, microelectronics, optical and conducting surfaces, etc. [11]
CVD	Metal Oxides, Metal Nitrides [21] on variety of substrates. [16]	1800 – 36,000 [7]	Yes [22]	Yes [22]	Yes [22]	Microelectronics, solar cells, fuel cells, batteries, etc. [11]
Spin Coating	Organic (polymers) and inorganic materials [23], Epitaxial films [23]	120 – 1200 [24]	No [23]	No [23]	No [23]	Photoresists, insulators, organic semiconductors, synthetic metals, nanomaterials, etc. [11]
MOCVD	Epitaxial semiconductor films [25]	2000 – 3000 [26]	No [26]	No (Typically) [26]	Yes [26]	Light-emitting diodes (LEDs), laser diodes, and photodetectors [26]
MBE	III-IV compounds like GaAs [27]	360 [28]	Yes [27]	No [27]	No [27]	MOSFETs, Diodes, lasers [29]

From the above table, it can be gleaned that SALD has major speed, cost and conformality advantages. This makes it an excellent candidate for high throughput thin-film manufacturing.

2.2 Powder Formation in SALD Systems

Because powder formation is a known deterrent to the industrialization of SALD [5] [8] [9], many potential causes have been identified. The following is a summary of those causes and their effect on powder formation:

2.2.1 Known Causes of Powder Formation

Unwanted intermixing of precursor gases: Intermixing occurs when there is mixing between the metal and oxidant flow profiles in the deposition zone. This mixing has been cited as a cause of powder formation [16]. In Figure 4, the concentration of precursors along the substrate for a set of conditions that results in intermixing is shown. The region in orange shows the region where intermixing occurs. The greater the intermixing, the greater the level of powder formation, thus any variable that contributes to intermixing, will contribute to powder formation. Some of the variables cited to affect intermixing are as follows: Gap Spacing [8], Precursor Concentration [17], Reactor Head Geometry, Exhaust Flowrate, and Precursor and Curtain Flowrates [16]. Their effect on powder formation is detailed below.

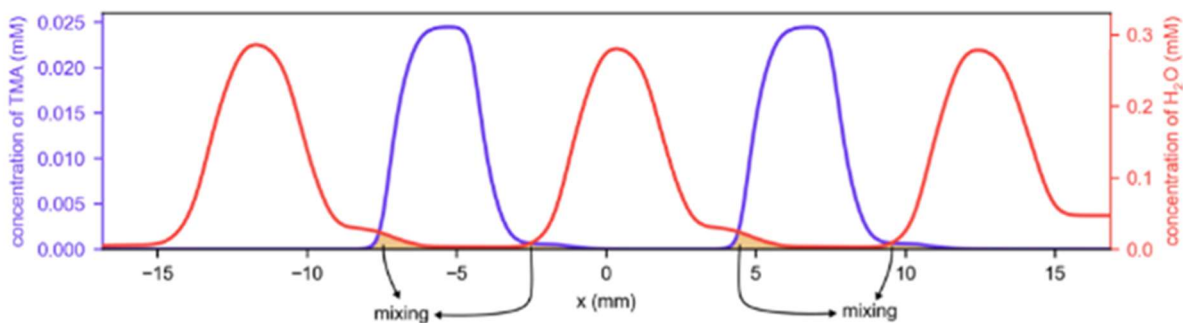


Figure 4: Precursor concentration profiles along the substrate for a set of conditions that result in intermixing of precursors. The orange area under the concentration profiles of TMA and H_2O marks the proportion of the substrate with precursor intermixing, where precursors react with each other and the film grows by CVD. Source: Adapted from [16]. CC BY 4.0

1. **Gap Spacing:** This is the distance between the substrate and the reactor head. It greatly influences intermixing of gases as it can determine the level of intersection of the gas

flow profiles in SALD. A smaller gap spacing can lead to a separation of gas profiles, which would alleviate mixing, as shown in Figure 5 [8] [7]. Conversely, reducing gap spacing could also lead to higher turbulence in the deposition zone, which would increase mixing. Optimizing gap spacing is thus crucial for minimizing intermixing and ensuring uniform deposition.

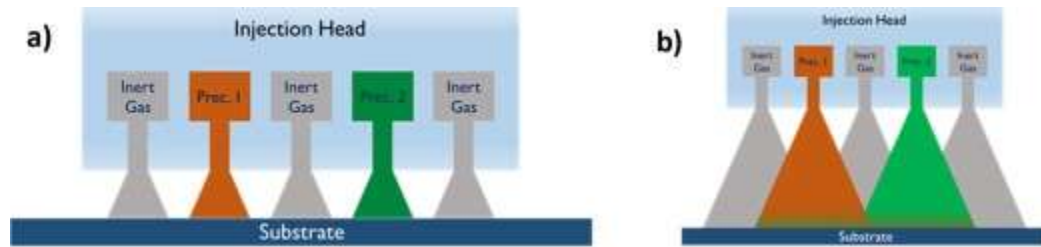


Figure 5: Schematic of an SALD reactor and substrate to show that an Increase in reactor-substrate gap spacing can result in an intersection of gas profiles, and, thus, intermixing. a) A shorter gap-spacing with all the gas profiles separated b) a larger gap spacing with intersections between the gases. Increase in reactor-substrate gap spacing can result in intermixing. Source: [7] CC BY 4.0

2. **Reactor Head Geometry:** The design of the reactor head, such as the spacing between the gas slits, and the width of the slits affects the flow dynamics [16]. Certain geometries, such as smaller spacing between the slits would enhance mixing, thus increasing powder formation risk.
3. **Precursor and Curtain Flowrates:** Balancing the flowrates of the precursors and curtains is crucial as they determine the flow profiles in the deposition zone. It has been reported that high curtain flowrates reduce intermixing [16]. It is important to note that excessively high flowrates can cause turbulence, increasing mixing in the deposition zone.
4. **Exhaust Flowrate:** Inadequate exhaust flow can result in excess precursors lingering in the deposition zone, creating opportunities for intermixing. Past works have used CFD

simulations [18], analysis [16] and experiments [19] to show that an increase in exhaust flowrates could reduce the amount of intermixing.

Precursor Concentrations: Since the oxidation of the metal precursor is known to be the primary cause of powder formation [8], changing the concentration of the metal precursor should directly impact the rate of powder formation.

Combining Metal and Oxidant Precursor Exhaust Lines: According to the literature, directing both metal and oxidant precursors to a shared exhaust line can lead to their interaction and subsequent powder formation [20]. This is because any scenario allowing the precursors to mix contributes to powder creation.

Precursor leaking outside the deposition zone: Similar to intermixing, precursor leakage occurs when the balance of deposition variables is not optimal, failing to spatially isolate the precursors as intended in SALD. In this case of imbalance, Metal precursors leak out of the deposition zone under the reactor head and react with the surrounding water vapor in air to form powder. Powder formation due to leaking has been cited in literature [8], but has also been seen in our lab, while running depositions without oscillating the substrate.

In the same vein, leaks in the metal and exhaust lines could also cause powder to form.

Low temperature: Low temperatures in SALD have been known to create powder during depositions [9] . Past works have reported an ideal ALD temperature window (Figure 6), where lower temperatures will lead to precursor condensation and slow incomplete reactions, and too high temperatures will lead to chemical desorption of the precursor from the surface and precursor decomposition [21] [22]. The existence of this ALD temperature window seems to suggest optimal temperatures at which opportunistic, powder-forming reactions would be minimized.

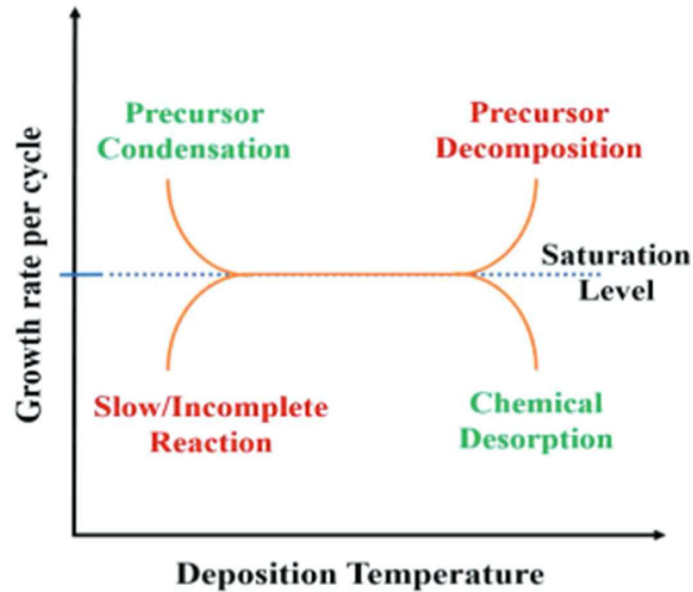


Figure 6: Schematic representation of the growth rate per cycle as a function of temperature. The ALD Window is shown. Source: Reprinted with permission from [22].

Virtual leaks: Another potential cause of powder formation in SALD is the so-called virtual leak [23], which has been identified to cause powder formation in conventional ALD. In conventional ALD, a virtual leak occurs when precursor B gets adsorbed onto the walls of the chamber and then, as a result, encounters precursor A during the first step in the deposition sequence. In Spatial ALD, a similar virtual leak could occur if precursor B (H_2O) is adsorbed on the surface of the reactor in a region intended to only encounter precursor A.

Nucleation sites: The presence of nucleation sites was also identified as a cause of powder formation [23]. In other words, the larger the surface area, the more chances of powder formation on that surface. Thus, a surface with powder has higher chances of forming more powder either from virtual leaks or other unexpected chemical processes.

While there are many mentions of powder in SALD systems, there have been few attempts to quantify it. Given this fact, this work will focus on quantifying the amount of powder formed in SALD systems.

2.2.2 Known Effects of Powder Formation in SALD systems

The problems resulting from powder formation in SALD systems include:

Powder on the Film: Literature reports the presence of powder on films being deposited [9]. The presence of powder at the deposition site compromises the film's conformality. It adheres to the surface, disrupting the formation of subsequent atomic layers and potentially affecting the film's uniformity and functional properties. Figure 7 shows a silicon wafer with Al_2O_3 film deposited using a circular SALD with some powder visible at near the center.

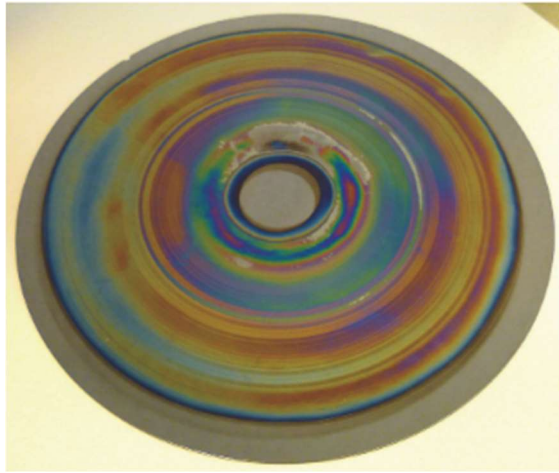


Figure 7: A silicon wafer with Al_2O_3 film with some powder visible at near the center. Source: Reprinted with permission from [9]. Copyright 2011, American Vacuum Society.

Exhaust-Line Clogging: To manage powder formation, the exhaust line (shown in Figure 8) is fitted with a nano-particle filter that catches the powder while evacuating the unreacted gases and byproducts. Over time, this powder accumulates in the filter and the tubes leading up to it, clogging the exhaust slits. These clogs impact the suction and result in the following issues:

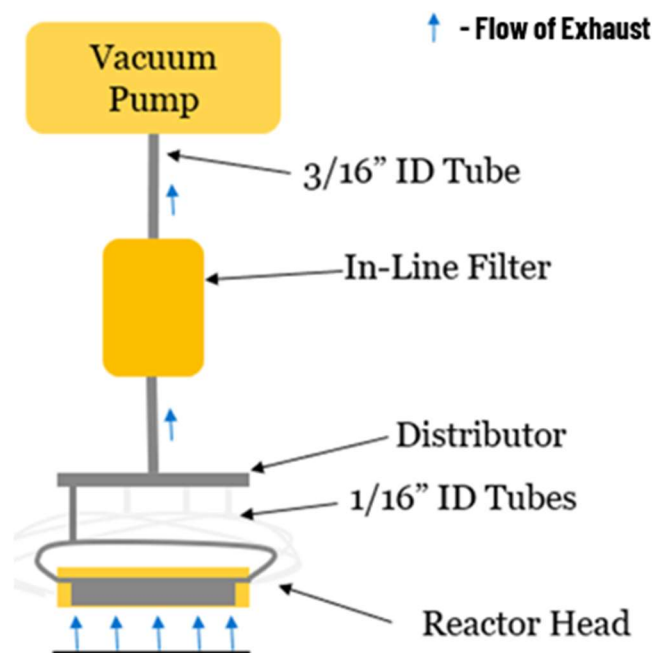


Figure 8: A schematic representing the exhaust line of an SALD system showing a cross section of the reactor head and the in-line filter used to separate the powder from the exhaust gases. Powder has been seen to accumulate throughout the line.

- a. **Non-uniform films:** As different exhaust slits accumulate varying amounts of powder, they clog at a different rates. This nonuniform clogging of exhaust slits leads to different suction rates, which, in turn, cause uneven evacuation of by-products and precursors across the substrate. As a result of the varied suction rates, different areas of the substrate undergo deposition under differing conditions, culminating in films with non-uniform thickness and potentially varied material properties. Figure 9b-d juxtaposes films created with clean exhaust lines with films affected by clogged exhaust lines.

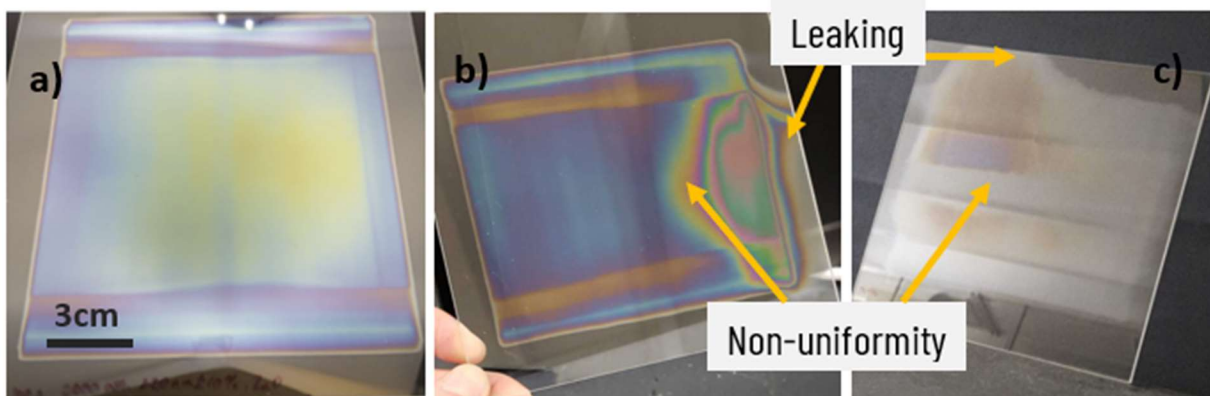


Figure 9: Clogging in Exhaust line and effects on film quality. a) A film deposited with clean exhaust lines. b-c) Films deposited with clogged exhaust lines. Courtesy of Nfinite Nanotechnology. Notice the difference between a film deposited with clean exhaust lines and films deposited with clogged exhaust lines – there is non-uniformity (marked by interference fringes) and leaking outside of the intended deposition area in the latter.

- b. Unwanted intermixing of the precursor gases:** Impaired suction from exhaust line clogging disrupts the balance of flow rates essential for optimal SALD film creation. This imbalance promotes intermixing of precursor gases in the deposition zone, leading to less precise CVD-like film growth and further exacerbates powder formation [7]. CFD simulations [18], calculations [16] and experiments [19] have shown that efficient suction prevents intermixing.
- c. Additional maintenance requirements:** Powder formation and accumulation in SALD system further hinders industrialization by necessitating regular maintenance to remove said powder. Failure to clean the exhaust lines, as we have seen, can lead to clogging which in turn causes the myriad of problems outlined above. The team at FNG currently cleans the exhaust slits daily. This would be undesirable for a full-scale industrial system.

The outlined causes and effects demonstrate a self-reinforcing cycle: powder formation leads to conditions that favor further powder formation, such as clogging-induced precursor intermixing. This cyclical issue emphasizes the need for effective strategies to mitigate powder formation in high-throughput SALD systems.

Safety Hazards of Powders Formation: The formation of powders in SALD systems, while a technical challenge, also presents significant health hazards as the generated powders tend to be nanoparticles [24]. These particles, owing to their small size and large surface area, can be inhaled and penetrate deep into the respiratory system, potentially causing pulmonary and systemic effects [25]. The generation of nanoparticles, especially from metal oxides like Al_2O_3 in SALD processes, is a particular concern. If not effectively managed and contained, these nanoparticles could become airborne, posing risks to researchers and operators [26]. Therefore, mitigating powder formation is not only crucial for improving process efficiency and film quality but also for ensuring occupational health and safety.

2.3 Real-time, In-situ Film Thickness Measurements in SALD systems

In-situ metrology is essential for assessing the quality of films in industrial Spatial Atomic Layer Deposition (SALD) systems. It allows for the real-time evaluation of film characteristics, crucial for maintaining uniformity and optimizing the manufacturing process. Given the precision required in SALD for film uniformity and thickness control, as highlighted in Section 1.2, identifying suitable in-situ metrology techniques becomes imperative for evaluating the quality of films produced in industrial SALD.

There is a myriad of technologies that could be used to measure the film thickness in real-time, in-situ in SALD systems. In a recent review paper, Kerry Maize et. al conveniently compiled a comprehensive list of real-time metrology techniques for roll-to-roll systems [9]. They provide a table which summarizes the capabilities of the techniques they identified.

Our industry partner, particularly interested in in-situ thickness measurements for their Roll-to-Roll SALD system, defined some criteria which they would require. These criteria include the ability to measure:

- a thickness range of 1nm to 150nm, with an accuracy of +/- 1nm
- single and multi layer stacks of a combination of Al_2O_3 and ZnO films

- films deposited on different substrate material such as polyethylene (PE), polypropylene (PP), polylactic acid (PLA), and plastic-coated paper.

Given the above, most of the techniques on the list were immediately deemed unsuitable for our application and the following were explored further for their potential ability to characterize the thickness of the films: UV-Visible (UV-Vis) Absorbance Spectroscopy, Reflectometry and Ellipsometry.

2.3.1 UV-Vis Absorbance Spectroscopy

UV-Vis absorbance spectroscopy operates on the fundamental principle that materials absorb light in accordance with the Beer-Lambert Law [27] [28]. This law is mathematically represented as

$$I = I_0 e^{-\mu t} \quad (1)$$

where I is the intensity of the light transmitted through the material, I_0 is the initial light intensity, μ is the absorption coefficient, and t is the thickness of the material. The intensity of light attenuates as it travels through the material.

The technique is crucial for assessing the uniformity and composition of thin films, particularly when dealing with multi-component films. It effectively gauges light absorption over a wide wavelength spectrum.

To execute this method, the intensity of the incident light on the sample (I_0) and the intensity of the light that has passed through the sample (I) are measured. Absorbance (A) is then calculated using the formula:

$$A = \ln(I_0/I) \quad (2)$$

Given that $A = \mu t$, a direct relationship is anticipated at specific wavelengths, allowing for the deduction of film thickness from absorbance values.

The use of absorbance (and by extension, transmittance) for measuring thin film thickness is a recognized technique, particularly for metal films [29]. In previous studies, such as those reported by Heavens O., absorbance measurements of thin gold, silver, and aluminum films as

thin as 5nm demonstrate nearly linear trends at certain wavelengths [30]. These absorbance patterns are instrumental in estimating film thickness.

An in-line system for absorbance measurement would comprise of a light source and a spectrometer (or detector) both connected via a fiber optic cable, with the film positioned in between them. This setup has been utilized in the context of organic photovoltaics to evaluate thin film thicknesses [31].

2.3.2 *Ellipsometry*

Ellipsometry is a highly precise and non-destructive optical technique utilized for measuring the thickness of thin films. It is particularly renowned for its remarkable sensitivity and accuracy in determining film thickness, even at the nanometer and micrometer scales [32]. This broad range allows ellipsometry to be used in various applications, from ultra-thin films in semiconductor manufacturing to thicker protective coatings in industrial processes [33]. This method operates on the principle that the polarization of light changes upon reflection on surfaces (a result of electromagnetic interactions). Ellipsometry is the art of detecting subtle changes in the polarization state of incident light and inferring surface characteristics, such as film thickness, from it.

The polarization state of light is characterized by two perpendicular components, p- and s-polarized light. The change in the polarization of incident light can be defined by two parameters: Psi (Ψ), representing the ratio of the reflection coefficients for the p- and s-polarized light, and Delta (Δ), indicating the phase difference between the p- and s-polarized light upon reflection. Ellipsometry involves measuring Psi (Ψ) and Delta (Δ) values and using models (Cauchy, Tauc-Lorentz, etc.) to determine surface characteristics, such as the thickness of a thin film.

The primary challenge in ellipsometry is the complexity involved in modeling. In order to build a representative model of the film, which would enable thickness calculations from measuring Psi (Ψ) and Delta (Δ), the surface properties (both the film and substrate) need to be well understood. Some models require only electrical and optical properties of the film and substrate, while others require additional factors like surface roughness and film inhomogeneity

to be known [33] [34]. Such an in-depth understanding of the material can sometimes be impossible to ascertain. Thus, many ellipsometers collect multiple ellipsometry measurements with varying incident angles and wavelengths with the hope of building a model with this additional information [32]. Some, such as the Film Sense Model Builder, even goes as far as using multiple models and automatically selecting the best one for the particular measurement – the one with the least fitting error [35].

Modelling films deposited with SALD can be particularly challenging as the optical properties of the films may vary with deposition conditions [36]. This complexity is further amplified in the case of multilayer coatings where additional intermediate ellipsometry measurements between each layer during deposition are needed to solve for the thickness of each layer [36]. The complexity escalates with flexible substrates, where optical characteristics vary depending on the inspection axis, a phenomenon known as anisotropy [37]. To deal with this, Mueller matrix characterization of flexible plastic substrates have been suggested [37].

Toward this modelling issue, machine learning approaches for solving ellipsometry problems have been developed. One example is the "SUNDIAL" method, which automatically calculates film properties like thickness using both ellipsometry measurements with intensity-based transmission and reflection spectroscopies for a comprehensive analysis [38]. This novel approach drastically outperforms traditional methods and takes the guess work out of ellipsometry. This enables automatic, rapid, high-throughput optical characterization of films and is compatible with existing ellipsometers.

Major advances have been made in in-line, real-time ellipsometry for high throughput manufacturing. Inline measurements for single point ellipsometry have been used to characterize 30nm -100nm polymer thin films within 1 nm at substrate speeds of 4m/min [36]. This was done using a commercially available Horiba spectroscopic ellipsometer. 2-dimensional ellipsometry has even been developed and demonstrated. This 2D in-line imaging/mapping ellipsometer, used a beam expander to perform ellipsometry on a scanline, and was able to measure thicknesses of 6nm with material moving at speeds of 10cm/min [39].

In conclusion, ellipsometry is a powerful and sensitive technique for measuring thin film thickness. Its ability to provide precise and non-invasive measurements makes it an essential tool in both research and industrial applications, particularly in fields where film thickness control is crucial for product performance and quality. That it is one of the technologies at the forefront of thin-film measurement in high throughput systems, warrants its consideration here.

2.3.3 Reflectometry

Spectroscopic reflectometry is a well-established technique for indirectly gauging the thickness and properties of dielectrics, thin film metals, and semiconductors [10] [40]. The technique uses the intensity of reflected light from the film surface to determine film thickness and uniformity. For reflectometry measurements, broadband light is directed onto a spot on the surface and the spectrum of the reflected light is then recorded. As shown in Figure 10, the illumination and sensor components can be integrated into a single compact instrument head to control and process equipment. The measured spectra can then be used to estimate film thickness using various models and techniques.

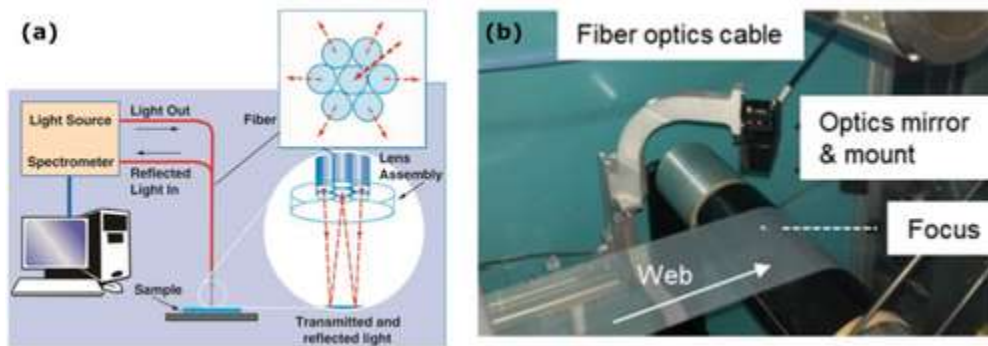


Figure 10: Broadband illumination reflectometry with single spot probe sensor. a) Schematic representation of measurement apparatus. A fiber optic bundle guides broadband illumination incident normal to sample and reflected light back to spectrometer. b) A picture of reflectometry apparatus integrated into an SALD system. Source: [10] CC BY 4.0

As with Ellipsometry (Section 2.3.2), modeling the reflectance of thin films can be challenging, especially for the nano-thin films created using SALD. One way of resolving film thickness from reflectance spectra involves employing Fresnel relations, which model the relationship between reflectance, angle of incidence, and the film's refractive index [30]. Here, again, knowledge of the optical characteristics of the film is necessary. The fact that films deposited with SALD have

variable optical properties [36] can make thickness estimation from spectra difficult. For the same reason, reflectometry modelling on multi-layer films is also more difficult. To mitigate this, other methods which do not require specific knowledge of the film have been employed.

One such method for estimating thickness using spectral information includes using Fourier transforms of the spectra [41]. Because the oscillatory features of the Reflectance spectra vary with thickness (thicker films tend to have high frequency oscillations while thinner films have low frequency oscillations), different thicknesses result in resolvable differences in the frequency domain of reflectance spectra. The frequency can be mapped to thickness using films of known thickness. Figure 11, shows this method being used to resolve films created with ALD. The geometric thickness, ascertained by mapping the raw reflectance's Fast Fourier Transform (FFT) to the film thickness, is seen to increase (shift right) with more deposition cycles.

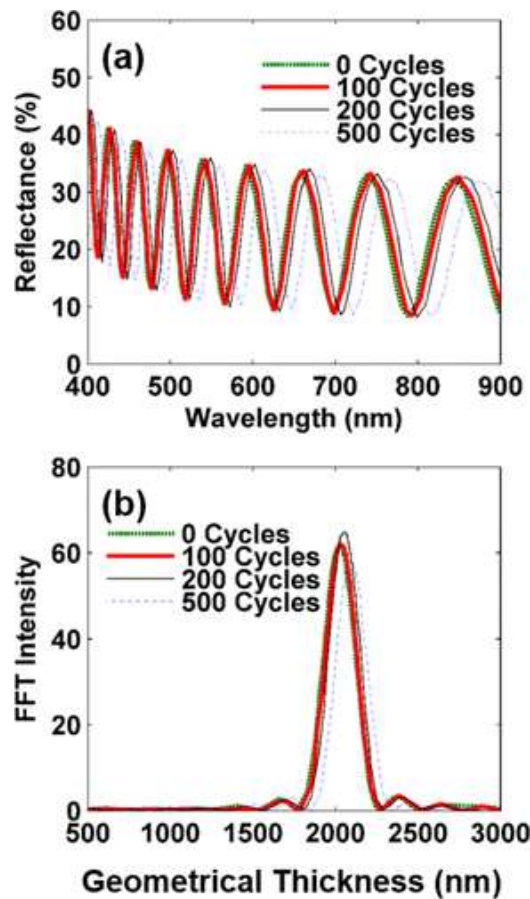


Figure 11: The figure above shows extraction of film thickness from reflectance spectra using FFT (a) Ex situ reflectance spectra for 100, 200, and 500 cycles of ALD SiO_2 films (300 °C deposition) grown on $\sim 2 \mu\text{m}$ thick SiO_2 are shown. (b) FFT peaks were calculated from the reflectance spectra in (a) using

FILMeasure 7.0 and correspond to the total geometrical SiO₂ film thicknesses. Source: Reprinted with permission from [41]. Copyright 2016 American Chemical Society.

Other methods for thickness estimation without precise knowledge of the refractive index exist. One includes using machine learning to map spectra features to films of different thicknesses [42]. Another includes error-minimizing algorithms which generate reflectance spectra from a guess refractive index and checks the fit to the measured spectra [43].

Software for resolving thicknesses from reflectance spectra using these methods are commercially available [44]. Modern commercial reflectometry systems claim a thickness error of 2 nm for films thinner than 500 nm and 0.4% for films greater than 500 nm [10] [8]. These purported measurements are feasible for films ranging from 1 nm to 1 mm, including multilayer film stacks [8].

Single-point spectroscopic reflectometry has been successfully demonstrated for inline measurement of thin film thickness [10] , including on an SALD system, reaching web speeds of 1 m/s [10] [8]. The setup in Figure 10b succeeded in measuring 100-nm-thick Al₂O₃ with an uncertainty of ± 2 nm. This measurement allowed for the tuning of deposition parameters in real-time to optimize thickness without the need to stop the system for offline characterization.

The work that follows in Chapter 3.3.2.5 details efforts to validate the effectiveness of UV-Vis Absorbance Spectroscopy, Reflectometry and Ellipsometry for SALD thin films produced by our industry partner, Nfinite Nanotechnology.

3 Study of Powder Formation

3.1 Introduction

In the realm of Spatial Atomic Layer Deposition (SALD) systems, a profound understanding of powder formation mechanisms is critical for advancing towards efficient industrial-scale manufacturing as it is a known deterrent to SALD [5] [8] [9]. The significance of this research area stems from SALD's potential as a high-throughput method for thin-film manufacturing, which is currently hindered by various challenges, including powder formation. This chapter delves into the potential causes and explores ways to measure and mitigate powder formation in SALD systems, a pivotal aspect for advancing this technology for industrial use.

As expanded in Section 2.2, the literature has identified multiple causes of powder formation, such as unwanted intermixing of precursor gases [18] [16] [19], temperature [9] [21] [22], and precursor leaking [8] [23]. However, there have been few attempts to quantify powder formation. Quantifying powder formation in SALD systems would open the door for fine tuning of deposition parameters to minimize it.

In this chapter, I demonstrate two methods for quantifying powder formation in SALD systems. One method is direct and in-situ, involving capture of the powder and measuring how much accumulates in an ultrafine nano-pore filter, and the other method involves using deposit patterns on the substrate to infer ideal deposition conditions. All experiments are done with physical SALD systems. The methods are first established and are then used to study the causes of powder formation outlined in the literature.

The outcomes of this research are expected to advance the current understanding and control of powder formation in SALD systems. Using the developed methods, this study confirms, in a quantitative manner, some suspected effects of pertinent variables (temperature, gap spacing and curtain flowrate) on powder formation in SALD systems. While these findings provide insights for process optimization in SALD systems, the primary contribution of this research lies in establishing a robust method for quantifying powder formation. This method could be used to further analyze the impact of the many SALD deposition parameters on powder formation,

serving as a tool for system optimization, but also feed-back control and real-time troubleshooting.

3.2 Methodology: Common Experimental Parameters and Apparatus

3.2.1 Typical Deposition Conditions

Since mitigating powder formation was of particular interest to our industry partner, the parameters and equipment used for these experiments replicated their SALD process parameters. To achieve this, Dr. Kevin Musselman's lab-scale SALD system was modified to replicate deposition conditions in the production-ready SALD system (details in Appendix A.2.1). All the studies were done on the deposition of Al_2O_3 because our industry collaborator and other lab SALD users reported that it resulted in the most powder residue.

Precursor delivery is achieved via the bubbling system shown in Figure 12. Here, nitrogen flows into the Bubbler through the Bubbler Line, generating precursor vapor which combines with additional nitrogen from the Carrier Line. The result is a precursor-nitrogen mixture which is sent to the reactor head. The concentration of the precursor is thus defined by the vapor pressure of the precursor and the ratio between the flowrates of the carrier and the bubbler

lines, which are set independently with mass flow controllers (MFC). The resulting precursor flowrate is the sum of the carrier and the bubbler flowrate.

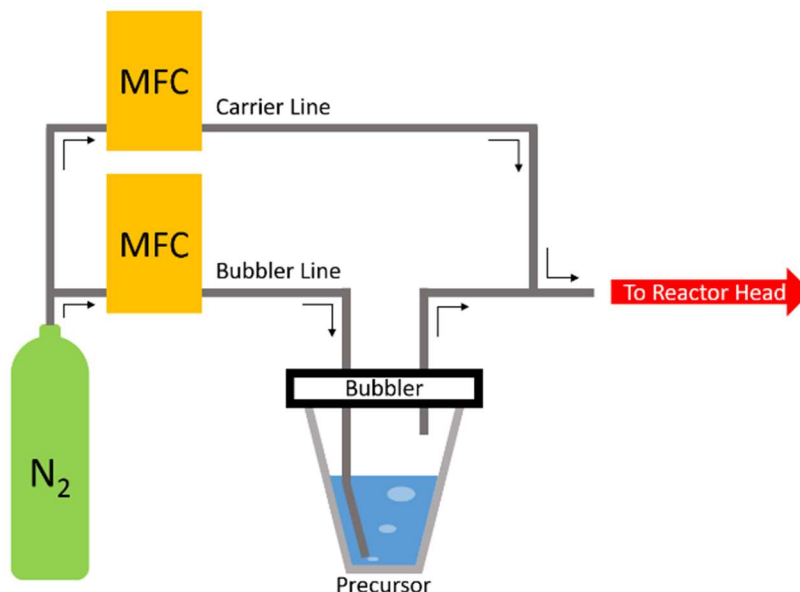


Figure 12: Schematic illustrating the bubbling system used for delivering precursor gases to the Reactor Head. Nitrogen flows into the Bubbler through the Bubbler Line generating precursor vapor which combines with additional Nitrogen from the Carrier Line. Concentration of the precursor is set by controlling the mass flow controllers (MFC). Source: Reprinted with permission from [45]

Unless otherwise stated, the following parameters were used for depositions in the experiments described in 3.3 (summarized in Figure 13). All experiments in this chapter were on a glass substrate and simulated the deposition of Al_2O_3 . The metal precursor (Precursor A/ Trimethylaluminum/ $Al_2(CH_3)_6$ /TMA) typically had a bubbler flowrate of 50 SCCM and a carrier flowrate of 400 SCCM resulting in a bubbler-carrier ratio of 0.125 and a total flowrate (F_M) of 450 SCCM delivered to one of the metal slits. The oxidant (H_2O) had a bubbler flow rate of 50 SCCM and a carrier flow rate of 750 SCCM and was distributed to two oxidant slits in the reactor head. This resulted in a total oxidant flowrate (F_O) of 800 SCCM. The inert nitrogen curtains had a total flowrate (F_C) of 6000 SCCM and was delivered to two curtain slits in the reactor head. The total flowrate of the metal exhaust slits (F_{ME}) - exhaust slits adjacent to the metal precursor slits - was typically 8000 SCCM or 0.80 lpm. F_{ME} was divided amongst three metal exhaust slits and would reduce with time as the exhaust filter accumulates powder. The oxidant exhaust slits – exhaust slits adjacent to the oxidant slits – were typically left without suction. The substrate

temperature (T) was typically 70 °C and the reactor-substrate gap spacing (G) was typically 0.5 mm. All tests in the chapter were done without oscillating the substrate (i.e., static depositions).

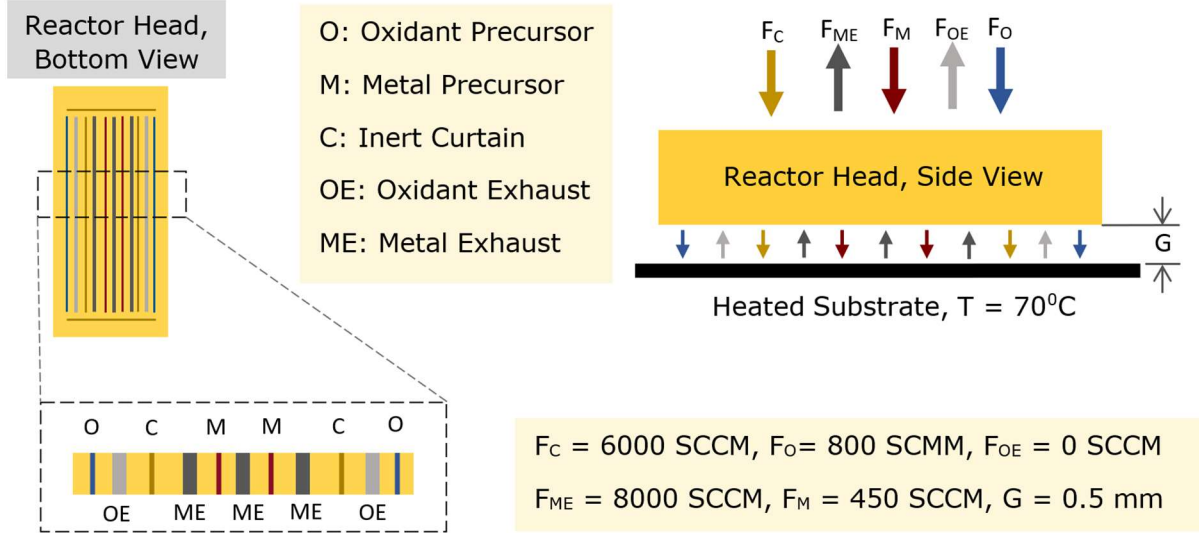


Figure 13: Schematic of the SALD system used for experiments in this chapter. The reactor head side view shows how the precursor, curtain and exhaust flows are distributed on the substrate. Pertinent deposition variable values used throughout this chapter are shown, including flowrates (F_x), reactor-substrate gap spacing (G), and Temperature (T).

3.2.2 Monitoring Powder formation

After a myriad of failed attempts (detailed in Appendix A.1), a method for decidedly quantifying the amount of powder trapped in a filter in the exhaust line of the SALD system was devised. This method involves calculating the instantaneous flow resistance of the filter based on the pressure across the filter and the resulting flowrate during a deposition.

$$Resistance, R = \frac{Pressure, \Delta P}{Flowrate, F} \quad (3)$$

This simple model is Darcy's law [46] and is used to model the flow of fluids through porous media. Though its applicability to compressible fluids (such as the gasses used for these depositions) may be questionable [47], computational simulations suggest that pressure-driven gas transport in nanoscale pores would behave in a manner consistent with Darcy's law [48].

To measure the resistance of the filter as powder from the exhaust line accumulates in it during deposition, an SMC PF2M7 flowmeter and an Ashcroft G2 Compound pressure transducer were connected to the filter in series (see Figure 14). Only one pressure gauge was used to attain the pressure differential across the filter because the other end of the filter was exposed to atmospheric pressure. For continuous flowrate and pressure sampling, the flowmeter and pressure sensor were originally connected to an Arduino but then a National Instruments DAQ USB 6100 data acquisition device was implemented to improve the noise-to-signal ratio, as discussed in Appendix A.2.6, and a LabView program was developed to collect the data. A proportional flow control valve was included in the module to give the ability to control the flowrate of the exhaust line.

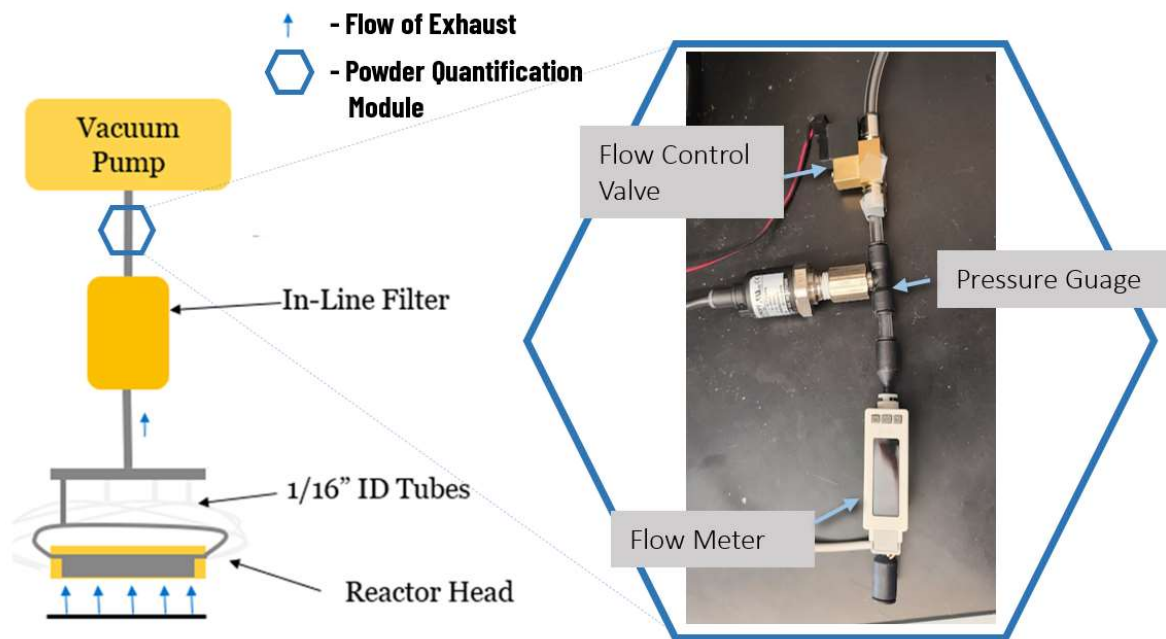


Figure 14: The schematic above shows the location of the Powder Quantification Module in the metal exhaust line of the SALD system. The Flow meter and Pressure Gauge are used to collect the differential pressure and flowrates used to calculate resistance. The Flow Control Valve regulates the flow of the exhaust line.

As a test for the validity of Darcy's law for our system, the driving pressure across the exhaust filter was varied using the in-built pressure regulator on the vacuum pump. The pressure was varied across the range of pressures typically experienced by a typical deposition, with no

precursors flowing, such that no powder was produced. Since no powder was produced, the filter resistance is expected to be unchanged. The resultant flowrate and resistance are shown in Figure 15.

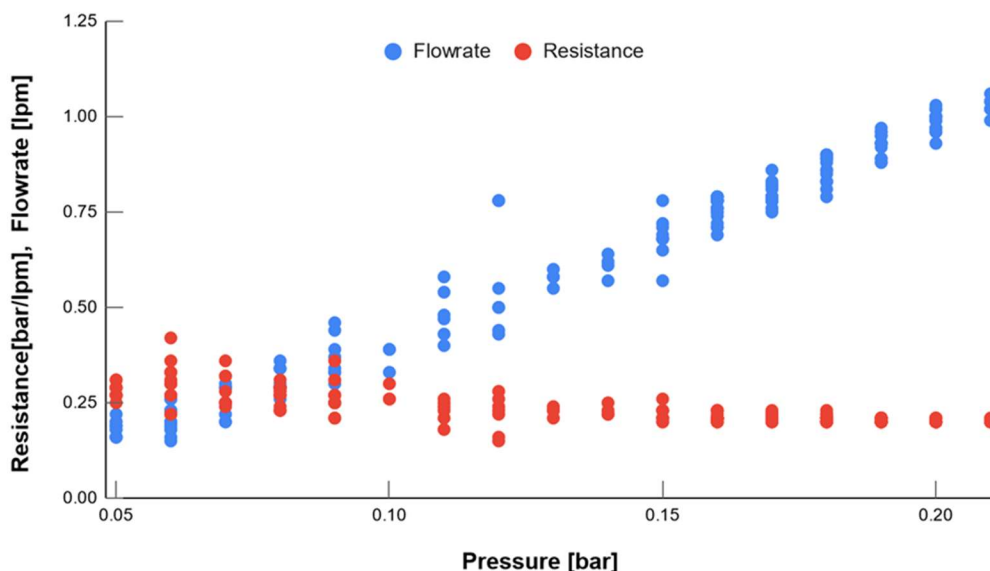


Figure 15: Resistance of the filter at different pressures following Darcy's law. Resistance can be seen staying constant for as the Flowrate varies linearly with pressure.

It can be seen from Figure 15 that the resistance stays largely constant as the pressure and flowrate varies. This suggests that for the range of pressure and flowrates explored, the resistance would be independent of the pressure and flowrate. Consequently, compressibility factors could be ignored in this range.

3.3 Powder Study Results and Discussion

3.3.1 Qualitative Powder Exploration

Visual Tubing Inspection

It was initially unclear where in the system the powder may have been forming. Since powder formation is formed by the Metal Precursor reacting with an Oxidant, it could occur anywhere the highly reactive metal precursor travels – the metal line and slits, in the deposition zone, and in the exhaust line. Given this uncertainty, the first step in exploration of powder formation was to identify where the powder was ending up in the system.

The first approach to this was inspecting the tubing used for depositions. Over time, as the SALD system is used for depositions, clear tubing used to carry precursor gases to the reactor head and out the exhaust line become white/cloudy. This seems to indicate formation or accumulation of powder along the walls of the tubing. Figure 16a shows new exhaust tubing juxtaposed with old tubing. The whiter hue of the old tubing indicates an accumulation of powder. Further a cross-section of a piece of old tubing in Figure 16b shows powder lining its walls.

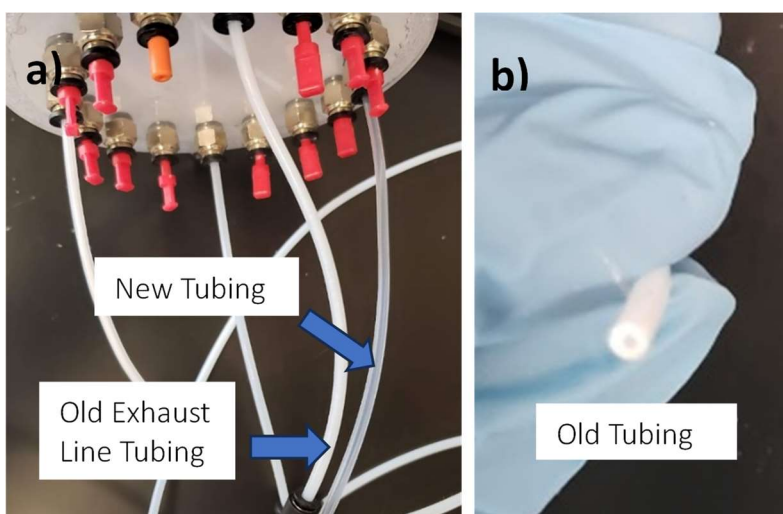


Figure 16: Figure showing new tubing juxtaposed with old SALD exhaust tubing. a) New and old tubing (labeled) connected to an SALD exhaust manifold. b) A wall of powder can be seen to have accumulated in old SALD tubing. These pictures demonstrate the accumulation of powder in the exhaust tubes over time in the metal and exhaust lines but never in the oxidant and curtain lines.

Inspection of all the tubing showed that, over months of use, only tubing in two locations whitened:

- The metal line leading to the metal slit of the reactor head.
- The exhaust line leading away from the metal exhaust slits of the reactor head.

The other tubing showed no signs of powder formation. This would suggest that powder may be formed in the metal lines as well as the exhaust line.

It is unclear how the metal precursor encounters oxidant in the metal lines. It might be due to incomplete purging of the line before introducing the precursor. The metal precursor could have also reacted with residual water or oxygen stuck to the wall of the lines.

Reactor Head Face Inspection

Next the reactor head was inspected. A great deal of powder can be seen on the face of the reactor heads – the surface in contact with the deposition zone. Investigation after a typical deposition showed that the powder was isolated to the center of the face where the metal slit is located. Powder can be seen in the metal slit and the surrounding exhaust slits.

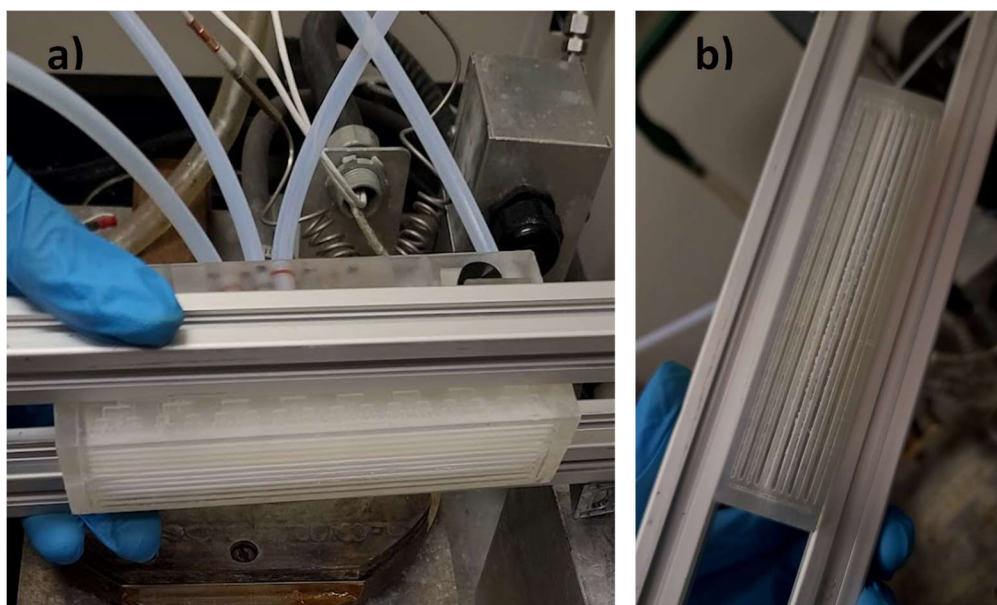


Figure 17: Picture of reactor head with powder on its face from depositions. a) Side view of the reactor head, showing tubing. b) The face (or under-side) of the reactor head.

Extracting Powder from Reactor Head

To investigate which parts of the reactor head accumulate the most powder, the powder in different areas of the reactor head was extracted in a fume hood as follows:

- Prior to a film deposition, the reactor head was cleaned by lightly scraping the face and slits with a razor blade and blowing compressed air through all the reactor head's slits.
- Al_2O_3 was deposited on a glass substrate using typical parameters, while keeping the stage static, as opposed to oscillating it.

- The face of the reactor head was lightly scraped with a razor blade over a wet brown piece of paper.
- The walls of the slits were lightly scraped with a razor blade over a wet brown piece of paper.
- Compressed air was then forced through the slits to push the powder on the wet paper.

The above procedure was done twice. One of those trials is shown in Figure 18. It can be seen that the metal slits and the face of the reactor had little powder compared to the powder in the exhaust slits. The oxidant and curtain slits showed no powder. This would suggest that most of the powder, either ends up in the exhaust slits, or most of the powder is created in the exhaust slits.



Figure 18: Powder from cleaning different areas of the reactor head. a) Powder found in the exhaust slits. b) Powder found on face of the reactor head. c) Powder found in the metal slits of the reactor head.

It is interesting to note that even the exhaust slits next to the oxidant line showed some powder deposits. This would suggest that powder was formed in the deposition zone and was forced into the exhaust slits. Powder forming on the face of the reactor could be because of virtual leaks [23] described in Chapter 2.

Since we found most of the powder in the exhaust line, we focused our attention on quantifying the powder found in the exhaust stream.

3.3.2 Quantitative Powder Exploration

In the above qualitative exploration, we determined that monitoring the rate of powder accumulation in the exhaust line with each deposition would be a good way to estimate the amount of powder formed in the system with each deposition. In the case that the mechanisms for powder formation are different in the exhaust stream than for other parts of the system, this quantification would at least be useful for quantifying powder in the exhaust stream. The powder quantification module described in Section 3.2.2 was therefore employed to monitor the resistance of the exhaust filter.

Figure 19 shows the measured filter resistance for a typical test run over time, using the standard test conditions outlined in Section 3.2.1, sampled every second. The duration of the test run is consistent with a typical film deposition in the Functional Nanomaterials Group, which takes approximately 4 to 30 minutes, depending on the desired thickness. From the plot, it can clearly be seen that after ~700 seconds the resistance changes in a linear fashion. Prior to stabilizing to a linear trend, the resistance seems to change more slowly. This slow change of resistance can be explained by a saturation period, during which some of the precursor is being adsorbed on the internal surface of the metal lines before exiting the SALD reactor. This is consistent with experience; a saturation deposition is typically performed at the start of the day to saturate the surface of the metal lines before proceeding with the deposition of desired samples.

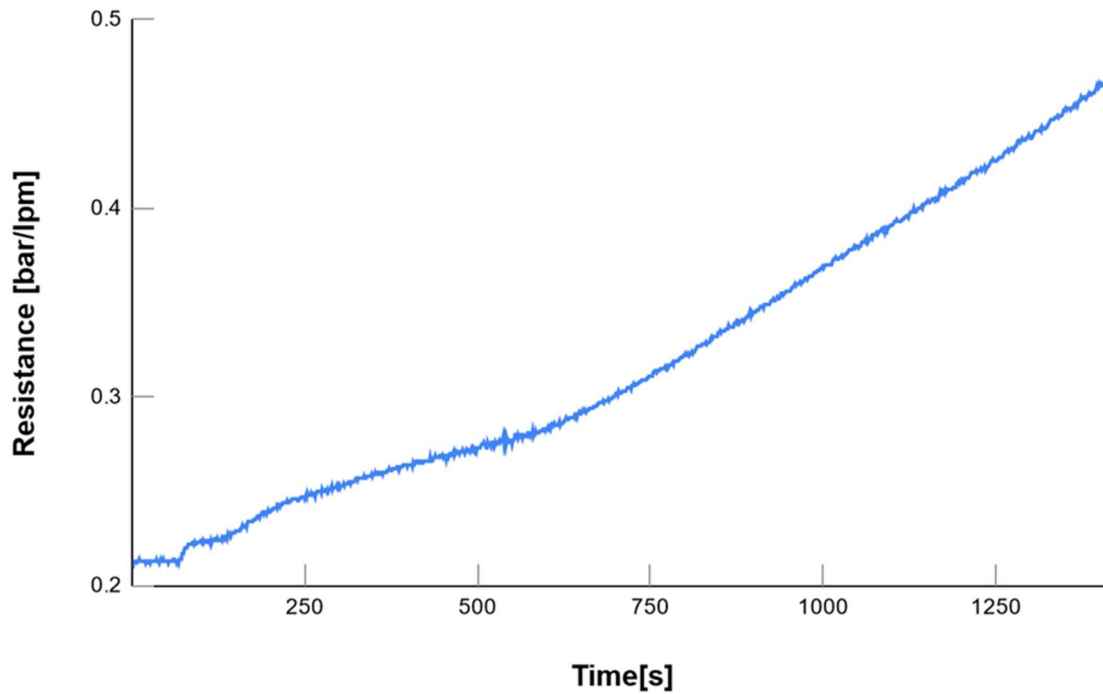


Figure 19: Resistance of the exhaust filter of an SALD system over time, as precursors are delivered to the reactor. Note how the slope becomes linear over time, this indicates a stable rate of powder formation.

Two more standard static depositions were performed, where for each deposition:

- The exhaust filter was cleaned by forcing compressed air through one end for 1 second and then the other end for 1 second. This was done multiple times for > 1 minutes using an automated filter cleaner that was developed for this work (see appendix A.2.3).
- A typical test was run for 15 minutes (900 seconds).

The resulting resistance plots are shown in Figure 20. From the plots, it can be gleaned that the saturation run results in a slower increase in filter resistance (i.e., slower powder formation) than the rest of the plots. As no precursors flow between the tests, some purging of the Metal line is expected (removal of Metal precursor from the walls of the line), which would partially reverse the effect of the saturation run. However, it is clear in Figure 20 that for each test after the initial saturation deposition, it took less time for saturation to occur (i.e., the effect of the

saturation run was not significantly reversed). Note that each of the runs begins at the same resistance $\sim .20\text{bar/lpm}$. This is because the filter was cleaned before each deposition.

It is also worth noting that the slope of each resistance plot is different after saturation even though the deposition parameters are identical. This variance in slope between test runs (signifying variance in the rate of powder formation) likely results from experimental errors (e.g., specific placement of the reactor head, variation in filter cleanliness, etc.) and will pose a challenge to comparing resistance results from different test runs. To mitigate for this random variance, deposition parameters can be changed during a particular test run and the change in resistance observed for a more direct, unobstructed view of the effect of changing said parameters.

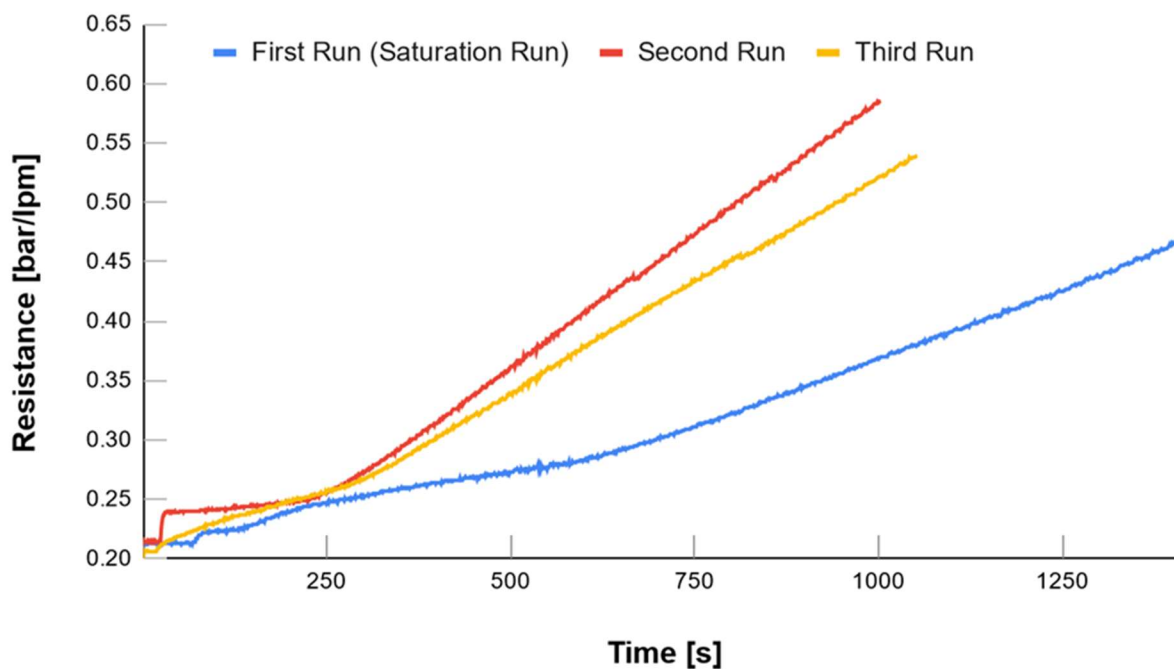


Figure 20: Resistance plots for 3 consecutive depositions. Notice how saturation periods (periods when the powder formation rate is lower because some of the precursor is being adsorbed on the surface of the metal lines before exiting the SALD reactor) are shorter for runs after the first run, which is also known as the saturation run.

To clearly show any changes in the rate of powder formation, the slope of the filter resistance curve, dR/dt , was plotted in real-time. This curve was helpful in determining the stability of the

rate of powder formation which is crucial as a stable rate of powder formation signals that the SALD system has reached equilibrium. For illustration, consider the third run from Figure 20, isolated in Figure 21a. The resulting, dR/dt plot is shown in Figure 21(b). To reduce the noise, the interval for evaluating the slope dR/dt was chosen to be 50 seconds. This means that there is a 50 second delay between the resistance and dR/dt plots. It also means that any instantaneous signal will register for 50 seconds on the dR/dt graph.

The dips in the dR/dt curve at ~ 650 s and ~ 850 s can be attributed to momentary perturbations of the system which can be seen on the resistance curve. While the cause of these perturbations is unknown, the perturbations could have been from unintended impact of the filter, a mass movement of the powder in the filter, or fluctuations in the flow regulator valve. These fluctuations register in the flowrate and pressure signals which in turn appear in the resistance plot. Since the dR/dt returned to the same level after the perturbations, the perturbations were ignored and regions of stable dR/dt were used for experiments. To further clarify the trends in the dR/dt plot, 10 points were averaged to yield the red line drawn over the Raw dR/dt .

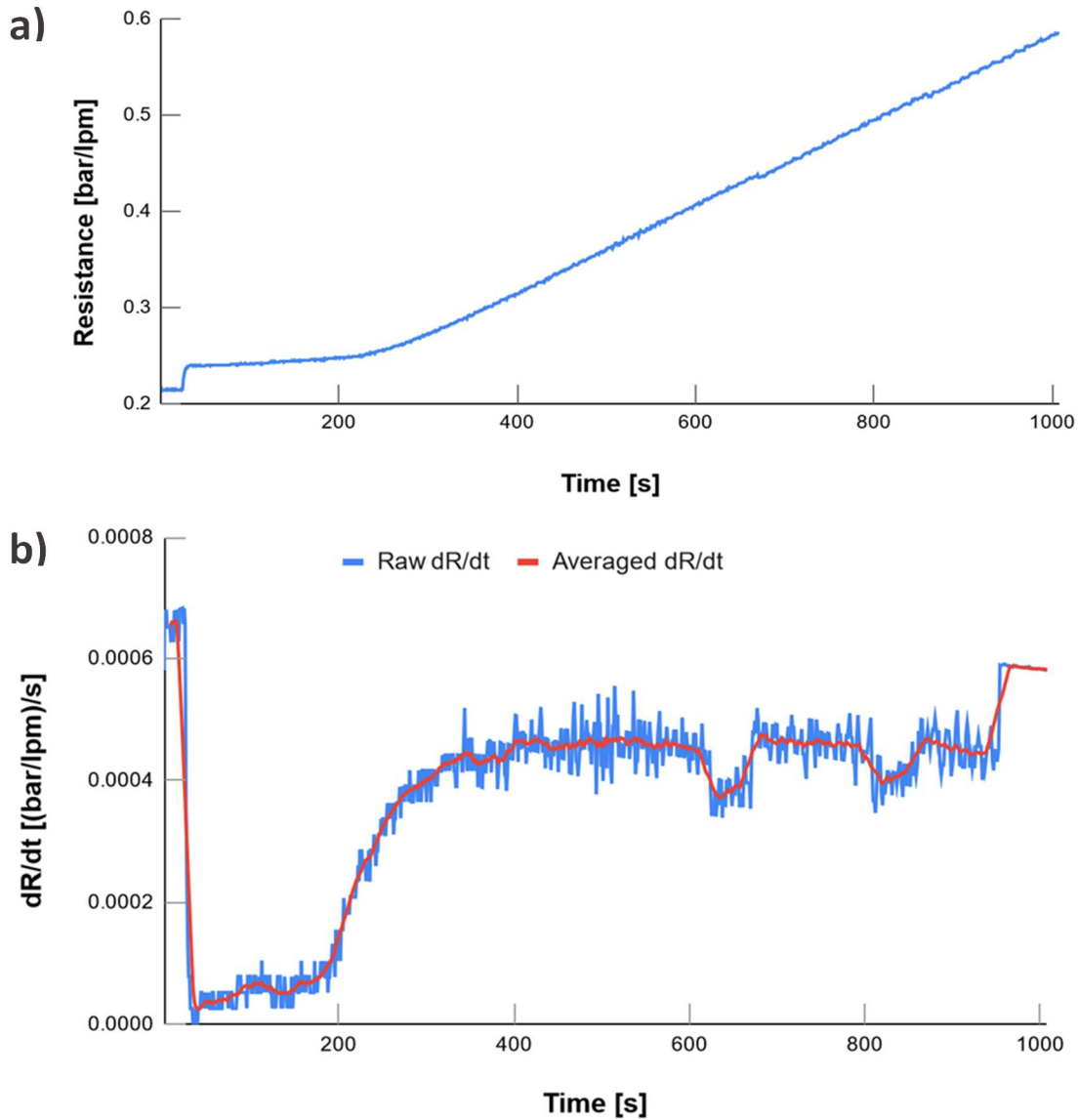


Figure 21: a) Resistance of the filter in the exhaust line plotted against time and b) dR/dt over time. dR/dt was used to gauge stability of powder formation rates. The slope was averaged over a 50 second interval resulting in a 50 second lag between the two plots. Another consequence is that instantaneous perturbations in the Resistance appear as 50 second perturbations in the Resistance Slope.

With the ability to monitor the rate of powder formation in the exhaust filter established (based on dR/dt), attention was turned to quantifying the effect of different SALD parameters on the powder formation rate. Two methods were considered for quantifying the effect of changing parameters:

- Keeping parameters constant during a deposition and changing them between each deposition. This method is time consuming, requiring 1hr for each data point and multiple trials to be statistically significant. Variation of powder formation due to random, un-noted variables may add to the variance in the data gotten from this method.
- Changing parameters during a deposition after the powder formation rate is stable and monitoring the resulting change in slope (dR/dt). This method saves time and gives a real-time response to changing variables. Variation of powder formation due to random, un-noted variables is minimized with this method.

Figure 22a show the results of changing a parameter (here the curtain flowrate) during a test run. It begins with the curtain at 2000 SCCM then is changed to the standard value of 6000 SCCM at 563 s, then 4000 SCCM at 1100 s, and finally, 2000 SCCM at 1600 s. The slope of the Resistance curve (Figure 22b) changes when the curtain is changed, which indicates a change in rate of powder formation. Armed with this revealing method for powder quantification, different deposition parameters were investigated for the effect they had on powder formation.

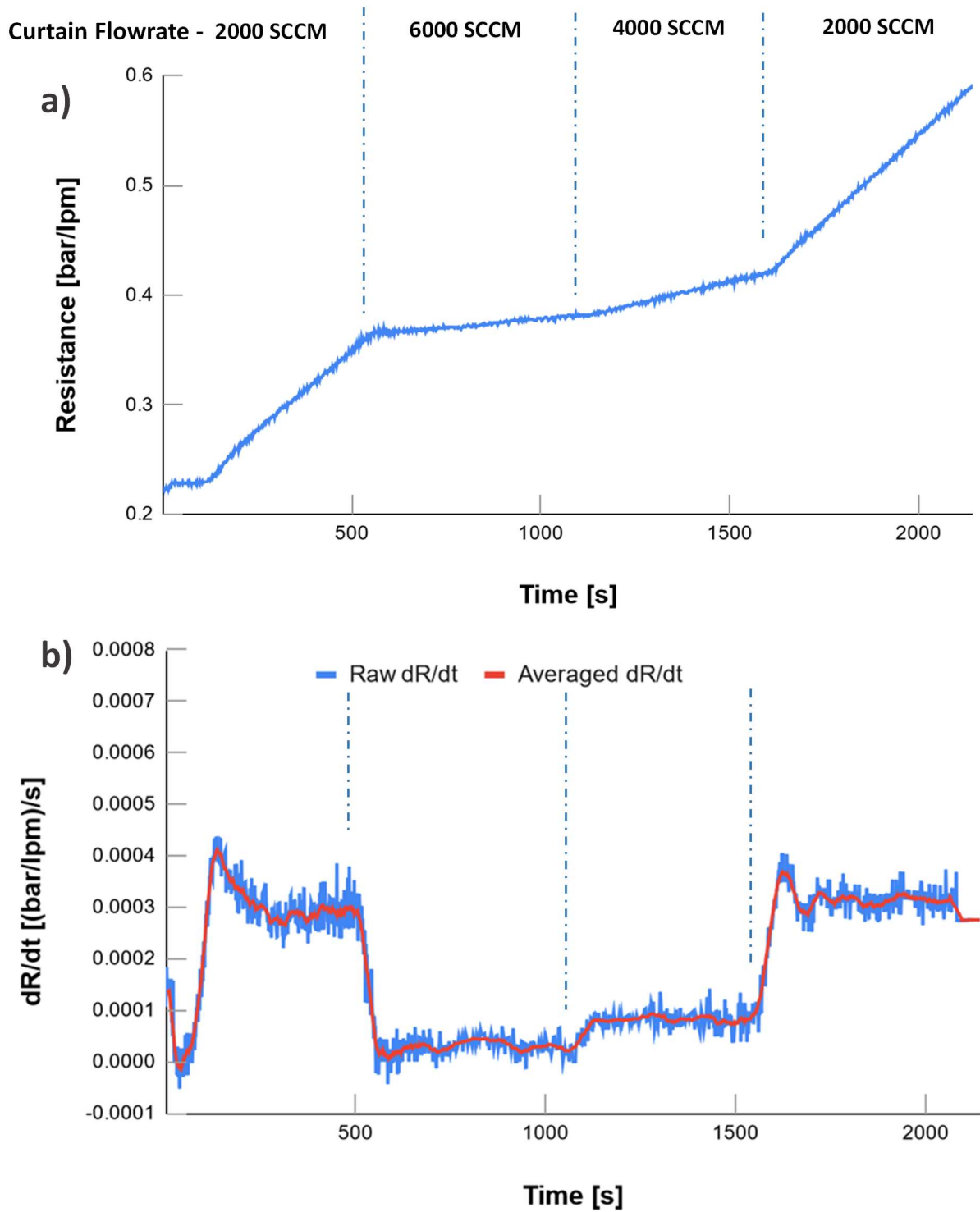


Figure 22: a) Resistance and b) dR/dt plots when changing the curtain flowrate during a deposition. This deposition began with the curtain at 2000 SCCM then is changed to 6000 SCCM at 563 s, then 4000 SCCM at 1100 s, and finally, 2000 SCCM at 1800 s.

3.3.2.1 Metal Concentration and Exhaust Flowrate

First, the effects of the concentration of the metal precursor and the exhaust flow rate on powder formation were explored. Since the oxidation of the metal precursor is known to be the primary cause of powder formation [8], changing the concentration of the metal precursor should directly impact the rate of powder formation. Confirming this proportional relationship was needed to validate this new method for continuous monitoring and quantification of powder formation.

Filter resistance data was obtained with the metal line having bubbler-to-carrier flowrate ratios of 0.1, 0.075 and 0.04. These ratios were selected based on the limitation of the flowmeters we had available, keeping the ratio close to that used in typical depositions (0.1). The flowrates used to attain those ratios were:

- 0.1 - Bubbler flowrate of 50 SCCM and Carrier flowrate of 450 SCCM
- 0.075 - Bubbler flowrate of 35 SCCM and Carrier flowrate of 465 SCCM
- 0.04 - Bubbler flowrate of 20 SCCM and Carrier flowrate of 480 SCCM

Additionally, stability of the measured dR/dt with changing exhaust flowrate was important to confirm the validity of the method because in typical depositions, the exhaust flowrate reduces as the exhaust filter accumulates powder. A typical deposition begins with an exhaust flowrate of 0.8 lpm, which reduces gradually as the exhaust filter accumulates powder. To see the effect of this dropping flow rate and to confirm the stability of the measured dR/dt value while powder accumulates in the filter, the flowrate was varied from 0.8 lpm to 0.6 lpm and 0.4 lpm using a custom PID flow controller (see Appendix A.2.5).

The metal concentration and exhaust flowrate were varied in tandem to ensure the change in metal concentration was visible through monitoring dR/dt , regardless of a fall in flow rate. The rate of powder formation (dR/dt) was measured after the system stabilized – i.e., the real-time plot of dR/dt was constant. The slope of the resistance plot in the region of interest was then obtained using a least-squares fit (see appendix A.3). The resulting data is plotted in Figure 23.

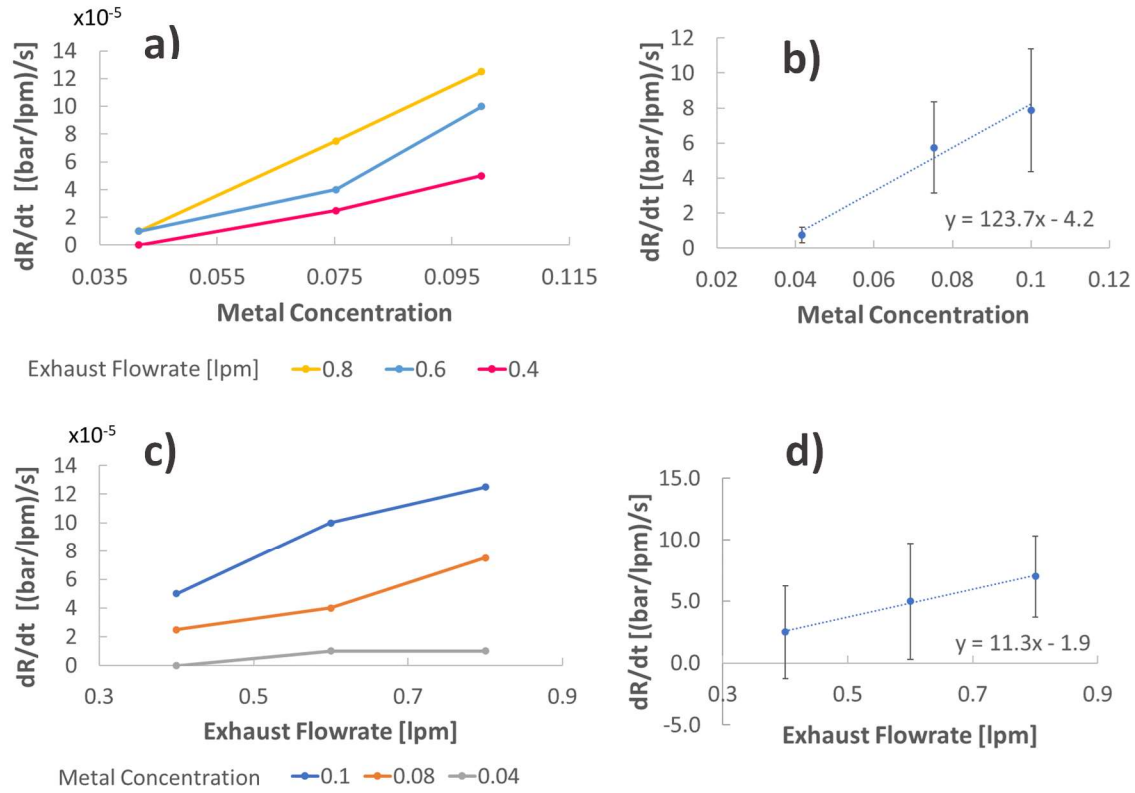


Figure 23: The effect of Metal Concentration and Exhaust Flowrate on powder formation, dR/dt . a) dR/dt vs. Metal Concentration for different Exhaust Flowrates. b) The average dR/dt across different Exhaust Flowrates vs. Metal concentration. c) dR/dt vs. Exhaust Flowrate for different Metal Concentrations. d) The average dR/dt across different Metal concentrations vs. Exhaust Flowrate. The error bars are ± 1 standard deviation. Trendlines on b) and d) indicate that the Metal Concentration has a much greater impact on dR/dt than the Exhaust Flowrate.

From Figure 23a it can be concluded that for the range explored, the rate of powder formation in the exhaust line (as measured by dR/dt) increases with the metal concentration, as expected. This further confirms that for the range of exhaust flowrates considered, the rate of change of resistance (dR/dt) is a good measure for the rate of powder formation.

From Figure 23c it is clear that there is also some effect of changing the exhaust flowrate on the rate of change of resistance (dR/dt). Using this method, it is difficult to determine the mechanism behind the effect of the exhaust flowrate on dR/dt . When the exhaust flowrate is changed, resulting changes in dR/dt could be from greater suction throwing off the chemical balance of precursors in the deposition zone, causing more precursor intermixing and, thus,

powder formation, or it could be a result of greater suction mechanically taking more powder up to the filter. The fact that it has been reported that higher exhaust flowrates *reduce* intermixing and, thus, powder formation [8] [16] hints that the dominating mechanism in this range of exhaust flowrates is the mechanical action of sucking more powder into filter.

The average dR/dt across different metal concentrations is plotted against the flowrate in Figure 23d. For comparison, the average dR/dt (measured at different flowrates) against the corresponding concentration is also plotted (Figure 23b). Assuming that the exhaust flowrate and concentration affect dR/dt independently, the effect of the metal concentration on dR/dt is seen to be more significant than that of the exhaust flowrate, based on the fitted slopes in Figure 23b and d.

That the effect of the exhaust flowrate on dR/dt is small for relevant flowrates suggests that this powder quantification method can be used to explore the effect of other deposition parameters, as long as these other parameters have a larger effect on dR/dt , as was the case for the metal precursor concentration.

To stay with replicating the industry partner's SALD process, where the lack of a flow controller in the exhaust stream results in the gradual diminishing of exhaust suction, the remaining variables will be explored without regulating the flowrate. The effect of any systematic reduction of the exhaust flowrate (which we have shown is small in this range) will be accounted for by randomizing the values being explored, where feasible.

3.3.2.2 Effect of Temperature

The temperature of the substrate stage was varied during test runs while all other deposition parameters were fixed at their standard values noted in Section 3.2.1. The temperature was varied between 20°C (room temperature), 70°C, and 100°C, with two trials per temperature point. One set of trials was done all in one test run – the temperature was raised from room temperature to 70°C and then to 100°C.

The measured dR/dt values are plotted against the temperature in Figure 24, with the standard deviation as error bars.

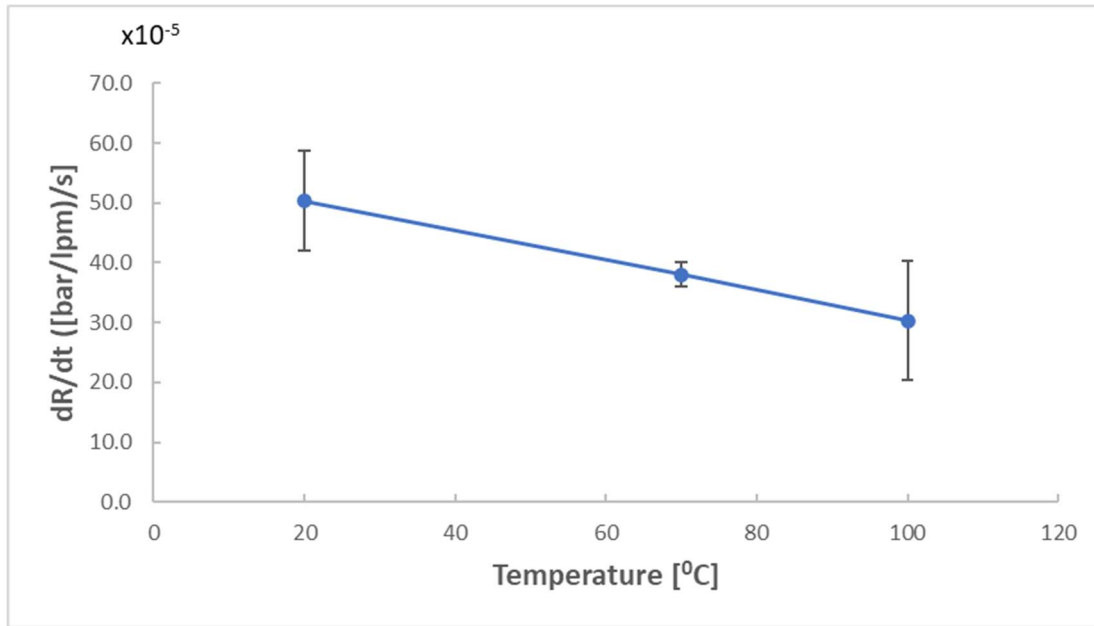


Figure 24: Effect of Temperature on Powder Formation rates (dR/dt). Notice the clear decrease in powder formation with increasing temperature. The error bars are ± 1 standard deviation.

The plot shows a clear decrease in powder formation in the exhaust line with increasing temperature in this regime. This is consistent with experiments reported in literature for low temperature deposition of Al_2O_3 [9]. It also makes sense theoretically since the expected ALD window for TMA (the Al_2O_3 precursor) is around 100°C - 300°C [49] [50]. As discussed in Section 2.2.1, the increase of powder formation with lower temperatures here may be due to precursor condensation in the gas phase, a decrease in substrate adsorption, and slow, incomplete reactions on the substrate surface that result in more precursors in the exhaust stream [24] [21].

3.3.2.3 Effect of Gap Spacing

The typical gap spacing used for depositions with the studied SALD reactor is 0.5mm, thus the gaps that were investigated were 0.3 mm, 0.4 mm, 0.5 mm and 0.7mm. To achieve these gap spacings, the initial gap was set to 0.7mm then the appropriate metal shims were added to the bottom of the glass substrate. To remove systematic errors, the sequence in which the gaps were explored were randomized. Two trials were done for each spacing. The average dR/dt values are plotted in Figure 25, with the standard deviation as error bars.

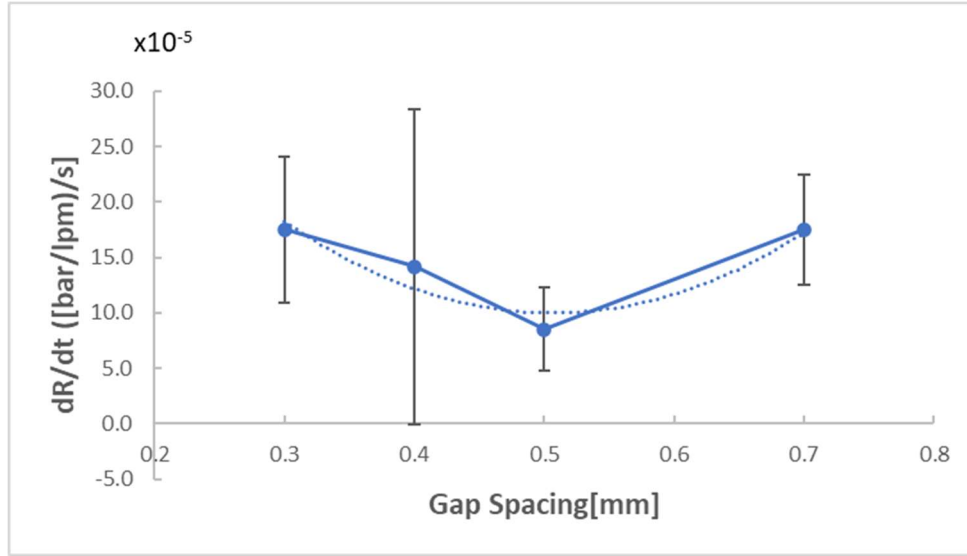


Figure 25: Effect of Gap Spacing on powder formation rate (dR/dt). Powder formation is minimized at a gap spacing of 0.5mm. The error bars are ± 1 standard deviation. Trendlines are provided as visual guides.

From Figure 25, it can be concluded that powder formation is minimized at or around the standard gap spacing of 0.5 mm. This is reasonable, as this gap spacing was selected from CFD model optimizations by our industry sponsor and the standard flows for this reactor have been optimized over time for a 0.5 mm spacing. The mechanism for the increase in powder formation with increased gap spacing could be the intersection of precursor gas profiles leading to intermixing (see Section 2.2.1). This effect is well documented in the literature [8] [7]. The mechanism behind the increase in powder formation with decreased gap spacing could be more turbulent collisions in the deposition zone, causing more mixing.

3.3.2.4 Effect of curtain Flow rate

The standard curtain flowrate was 4000 SCCM, thus the curtain flowrates explored were 1500 SCCM, 2000 SCCM, 4000 SCCM and 6000 SCCM. The flowrate was modified by a flowmeter during depositions, and a dR/dt value was obtained after the rate of powder formation stabilized. To account for systematic errors, the sequence of curtain values tested was randomized. Two trials were done for each curtain flowrate. The average dR/dt are plotted in Figure 26, with the standard deviation as error bars.

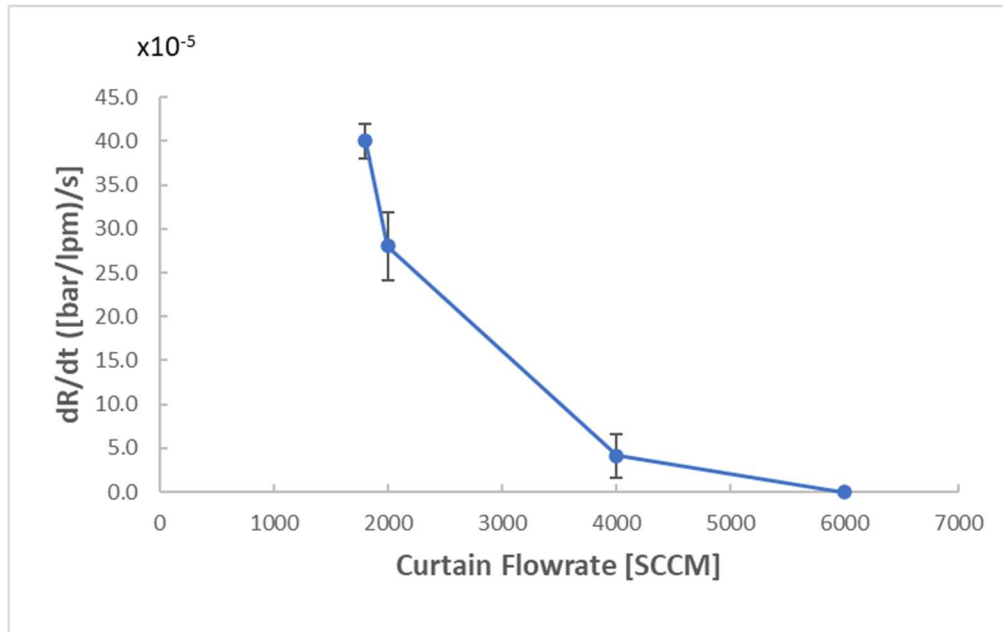


Figure 26: Effect of Curtain Flowrate on powder formation rates (dR/dt). Powder formation decreases as curtain flowrate increases.

From Figure 26, it can be concluded that the curtain flow rate has a significant impact on the formation of powder that ends up in the exhaust line - the lower the curtain flowrate, the higher the rate of powder formation. This makes sense since the curtain directly separates the profiles of the precursor gases; without the curtain the profiles would be allowed to mix. As was discussed in Section 2.2.1, this agrees with the literature which has reported less intermixing with more curtain flowrate [16].

In summary, Metal Concentration, Temperature, Gap spacing, and Curtain flowrate all seem to influence the amount of powder that ends up in the exhaust line in various ways. The powder quantification method outlined above could thus be an invaluable tool for industrial-scale SALD, enabling engineers to evaluate reactor head designs as well as optimize deposition parameters. It could be used for making long-term decisions for those designs and deposition parameters but also for real-time feedback control of SALD systems as it gives a concrete quantity for powder formation.

3.3.2.5 Avoiding Precursor Leaking and Intermixing by Monitoring Substrate Patterns

As we established in 2.2.1, intermixing and precursor leaking, both of which are caused by an imbalance of flowrates in the SALD reactor, exacerbate the formation of powder. A simple way to confirm the balance of flowrates is through a static deposition (one without substrate oscillation), followed by substrate inspection. In such depositions, regions of mixing, as depicted schematically in Figure 4 and Figure 5 become visible on the substrate. This visibility is due to CVD-like growth [7] [16] and powder forming in the regions of mixing.

Figure 27a shows an example of a deposition condition that yielded mixing on a glass substrate. For contrast, a glass substrate without much mixing is shown in Figure 27b. Given that the metal precursor is only emitted from the reactor head's middle slits (see Figure 27c), and is surrounded by inert gas curtains, we would ideally expect to see a localized pattern in the middle of the deposition zone. Figure 27b shows an example of ideal conditions where the metal precursor is properly isolated, with minimal mixing. Notice how much powder and film growth we see outside of the expected central region in Figure 27a. This spread signifies that there is flow from the metal slits in the center of the reactor to other regions of the reaction zone. Features of these deposited patterns were used to glean insight about the balance of precursors.

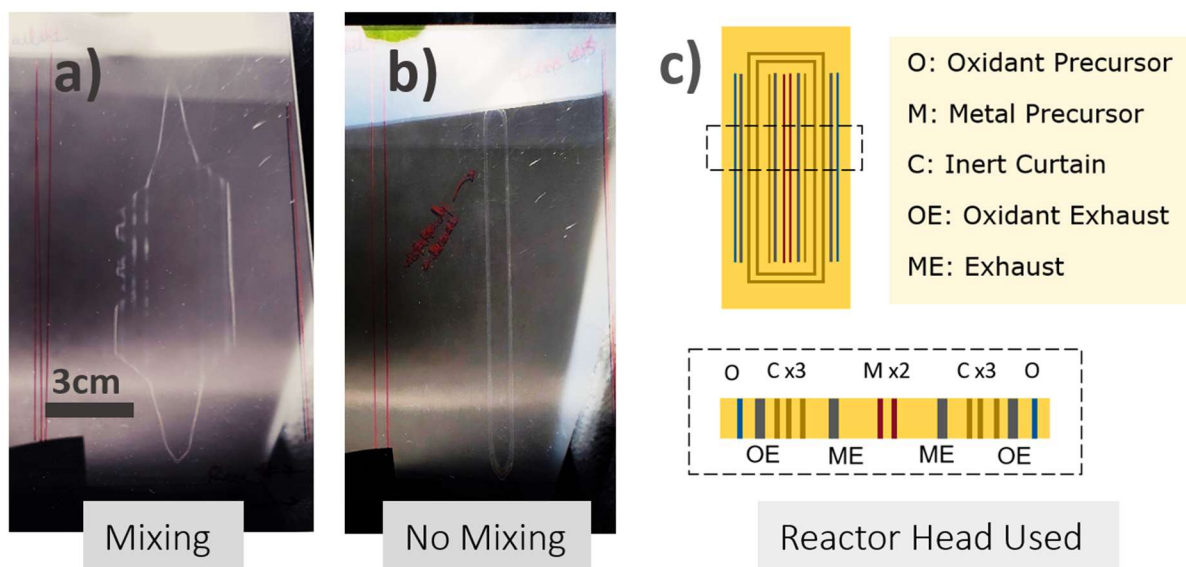


Figure 27: Patterns on substrate signaling the presence of a) mixing b) no mixing. c) A schematic showing the reactor head used for these experiments

To investigate the effect of different parameters on these substrate patterns, static depositions were performed on glass substrates with the deposition conditions shown in Table 2. Other deposition parameters such as precursor flowrates and concentrations stayed the same as the typical depositions described in Section 3.2.1. A different reactor head, shown in Figure 27c was used for these experiments. For clarity, only some of the conditions tested are shown.

Table 2: Deposition conditions used to investigate the effect of curtain flowrate, gap spacing, exhaust pressure and temperature on substrate patterns.

Index	Curtain Flowrate (SCCM)	Gap (mm)	Metal Exhaust Pressure (bar)	Temperature (°C)
4	4000	0.6	-0.15	30
10	6000	0.6	-0.1	80
12	6000	0.4	-0.1	30

Figure 28 shows the resulting patterns on the substrate. Each pattern has been annotated with labels of the Index (the specific deposition condition used in accordance with Table 2) and measured features of the resulting substrate pattern. The length and max width values represent the length and maximum width of the pattern as shown in Figure 28a and b. The % Isolation, illustrated in Figure 28c, is defined as how much of the pattern follows the localized pattern we expect from ideal precursor isolation.

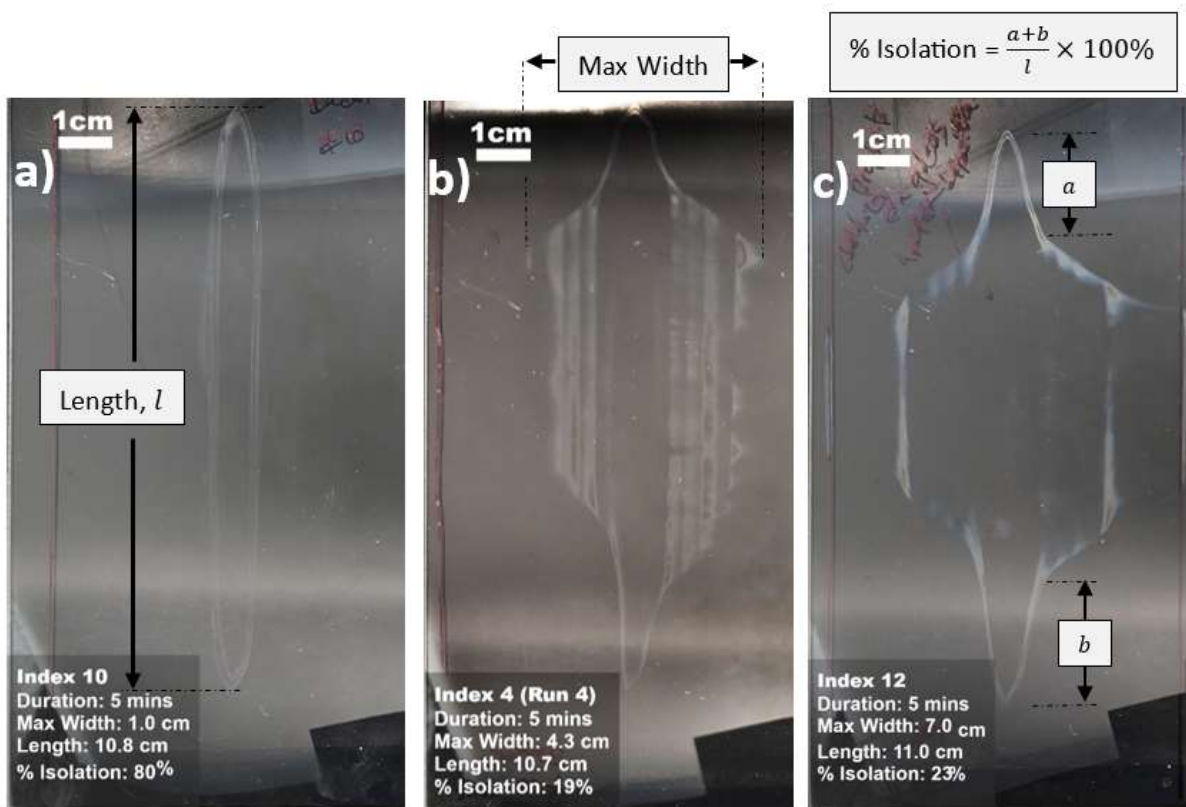


Figure 28: Resulting deposition patterns on the substrate and variables used to quantify them.

As can be seen in Figure 28, different deposition parameters yield different levels of % isolation and max width. For some conditions, such as that seen in Figure 28c, the pattern even spilled past the width of the deposition zone, signifying flow of the metal precursor outside the deposition zone (precursor leaking). The width the deposition pattern on the substrate can thus be used to confirm isolation of metal precursors after setting deposition parameters; a more spread-out pattern signals the need to modify deposition conditions.

While variations in substrate patterns are clear from the data, the above experiment is flawed as it set the pressure across the exhaust filter without cleaning the filter each time. This resulted in varying exhaust flowrates for the same exhaust pressure setting. Thus, more work is needed to determine the relationship between the deposited patterns and deposition variables.

3.4 Powder Exploration Conclusions

This chapter has presented a comprehensive study on powder formation in Spatial Atomic Layer Deposition (SALD) systems, an essential aspect for advancing this technology towards efficient industrial-scale manufacturing.

Exhaust Monitoring Apparatus Developed: The chapter introduced a novel exhaust monitoring apparatus designed to quantify powder formation in the exhaust of SALD systems. This apparatus, utilizing an ultrafine nano-pore filter in the exhaust line, calculates powder accumulation by measuring the instantaneous flow resistance of the filter. This method has been validated and proven effective for real-time monitoring and quantification of powder formation during the SALD process.

Results of Powder Formation Study: A series of experiments were conducted to understand how different SALD parameters affect powder formation. Key findings include:

- **Saturation Periods:** One insight our studies revealed was the presence of saturation periods in all depositions. This information can inform process considerations for any SALD system.
- **Metal Precursor Concentration:** Our measurements showed that higher metal precursor concentrations led to increased powder formation. This was the first validating step as more metal precursor was expected to produce more powder.
- **Exhaust Flowrate:** Though the mechanism behind the influence of the exhaust flowrate was not clear, we saw a slight increase in dR/dt with exhaust flowrate in the range measured. This could simply be the mechanical action of pulling more powder into the exhaust stream at higher flowrates.
- **Temperature:** Increasing the substrate temperature showed a clear decrease in powder formation. This aligns with the literature that places optimal Al_2O_3 temperature windows at $125^\circ\text{C} - 300^\circ\text{C}$. Lower temperatures may be leading to precursor condensation and slow, incomplete reactions.
- **Gap Spacing:** Optimal powder formation was observed at a gap spacing of 0.5 mm, consistent with the parameters optimized by our industry sponsor.

- **Curtain Flowrate:** Higher curtain flowrates effectively reduced powder formation by better separating the precursor gases and minimizing their intermixing.

The developed method for quantifying powder formation is a significant tool that can be utilized to optimize deposition parameters in various SALD reactors and systems, aiming to minimize powder formation. However, it's important to note that while reducing powder formation is crucial, these parameters also influence other aspects of the deposition process, such as deposition rate and film uniformity. For instance, a higher curtain flow may reduce powder formation but could also potentially slow down the growth rate of films. Future studies should integrate these findings with the characterization of films formed under different deposition parameters to achieve a holistic optimization of the SALD process.

Furthermore, it's crucial to recognize that this method primarily evaluates powder in the exhaust line. While the qualitative observations suggest that most powder forms in the exhaust line for the specific SALD reactor studied, this might not be the case for other reactors or under different standard deposition conditions. Future research should develop techniques to measure powder formation in other system components, such as on the substrate or the reactor face.

Preliminary Work on Visualizing Precursor Isolation: The chapter also discussed initial efforts to visualize precursor isolation using static depositions. These patterns on the substrate could be further quantified in future studies to characterize precursor intermixing and leakage. Such quantification is pivotal as these factors not only influence powder formation but also directly impact the film quality.

In summary, this chapter has laid a foundational framework for understanding and controlling powder formation in SALD systems, offering methodologies that can be further refined and applied for optimizing industrial-scale SALD processes.

4 Metrology

4.1 Introduction

When creating large throughput of thin films, methods to ensure the quality are important. Techniques used to monitor films created with high-throughput roll-to-roll SALD systems would need to be able to measure nano-scale thicknesses and be able to spot micro-scale cracks, pin holes and impurities. In Section 2.3, based on a literature review, we isolated absorbance spectroscopy, ellipsometry and reflectometry as potential methods for measuring the thickness of our industry partner's thin films. This chapter details experiments conducted to test the feasibility of characterizing samples of PLA coated with thin films of Al_2O_3 and ZnO using these three potentially suitable techniques: UV-vis absorbance spectroscopy, ellipsometry, and reflectance spectroscopy.

4.2. Experimental Methodology

This section describes the setups for the different metrology methods that were investigated as well as the rationale behind the samples chosen to be characterized.

4.2.1 Sample Sets

For this study, various sample sets were provided by collaborator Louis-Vincent Delumeau. These samples comprised of a polymer substrate and a combination of Aluminum Oxide (Al_2O_3) and Zinc Oxide (ZnO) coatings. The sample sets below were deposited by SALD and designed to simulate film growth in-situ monitoring equipment would experience in Nfinite Nanotechnology's applications. The samples were selected to represent intermediate steps during the growth of a coating on a PLA substrate. To represent *Growing Al_2O_3 on PLA*, Blank PLA as well as PLA samples with 4-nm and 12-nm-thick Al_2O_3 coatings were used. To represent *Growing ZnO on PLA*, Blank PLA, as well as PLA samples with 4-nm, 10-nm, 15-nm, 30-nm, and 85-nm-thick coatings of ZnO were used.

4.2.2. UV-Vis Absorbance Measurements

The absorbance spectra of the samples were obtained using a HORIBA Scientific QuantaMaster 8000 as follows:

- The wavelengths of interest, slit widths and integration time were adjusted to maximize signal without saturation.
- A blank PLA sample was placed in the sampled holder and used to attain the reference spectrum, $I_0(\lambda)$.
- A coated PLA sample was then placed in the sampled holder and used to attain the sample spectrum, $I(\lambda)$.
- The 'Absorbance calculation cell' of the Fluorescence software was used to calculate the absorbance.

4.2.3. Ellipsometry Measurements

A Film Sense FS1EX Ellipsometer was used to collect ellipsometry measurements with incident light of 410.5-nm wavelength. To collect raw ellipsometry data (Psi and Delta), a given sample was placed on the Film Sense default x-y stage. Multiple data points were taken by automatically translating the x-y stage to points 3 mm apart. To investigate the influence of sample orientation on the ellipsometry data, each sample was placed on a custom rotary stage (Figure 29) and multiple 3 mm-spaced data points were taken at each orientation.



Figure 29: Custom rotary stage used to take ellipsometry data of a sample at different orientations.

4.2.4. Reflectometry Measurements

For reflectometry measurements, a reflectometry fibre-optic probe from Ocean Optics (EOS-A6177351-2) was connected to an Ocean Optics DH-2000 dual deuterium-halogen lamp and an oceanHDX miniature spectrometer, as shown in Figure 28. To measure the reflectance spectrum of each sample:

- Both the deuterium and halogen lamps were turned on and allowed to stabilize for 15 minutes.
- A dark spectrum was saved to the OceanView software by covering the probe.
- A reference spectrum was taken on OceanView by placing a reflective silicon substrate below the probe.
- Integration times were adjusted to maximize signal and avoid saturation.
- The sample was placed underneath the probe on a dark matte surface and the reflectance was captured.

After each set of samples, the reference spectrum was retaken due to fluctuations in the intensity of the light source.



Figure 30: Apparatus used for reflectometry. a) The reflectance probe (EOS-A6177351-2) and stand. b) The DH-200 light source. c) The oceanHDX spectrometer.

4.3 Metrology Results

4.3.1 UV-Vis Absorbance Analysis

The absorbance spectra of the four ZnO-coated samples from the *Growing ZnO on PLA* set (10-nm, 15-nm, 30-nm, and 85-nm-thick films) described in 4.2.1 are shown Figure 31a. The ZnO-coated film samples show absorbance peaks around 320 nm, as expected for ZnO, and the magnitude of the absorbance peaks increases with the expected thickness of the film. This indicates that absorbance could be used as a technique for characterizing the ZnO thickness. The absorbance value at 320 nm for four different locations on the samples were plotted in the graph in Figure 31b. Minimal variation in absorbance is observed for the different measurement locations and the absorbance is seen to increase linearly with film thickness, as expected.

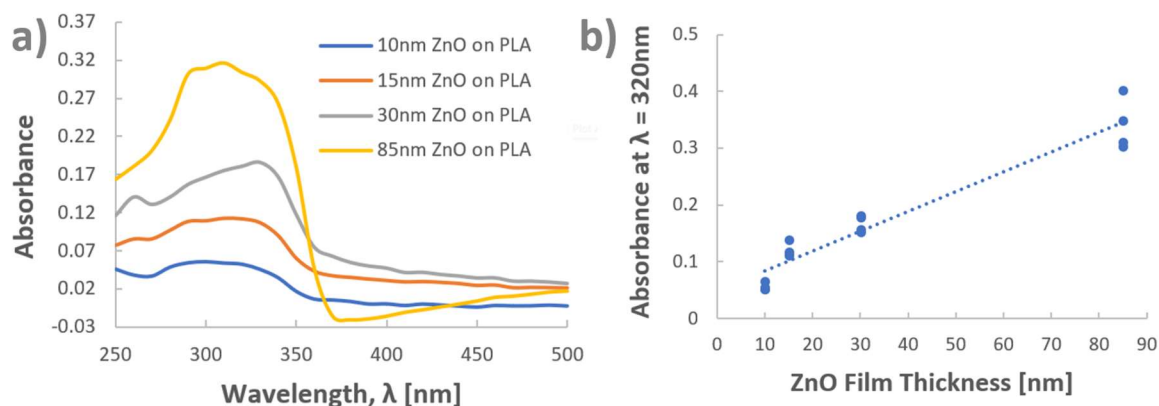


Figure 31: a) Absorbance spectra of various ZnO-coated PLA film samples with varying ZnO thicknesses. b) The absorbance at 320 nm for four ZnO films at four different spots on the film. The absorbance increases with the thickness of the film. A trendline shows a near-linear correlation between film thickness and absorbance intensity ($R = .95$)

The absorbance spectra for Al_2O_3 -coated PLA samples, which can be seen in Figure 32, showed no absorbance peaks. The different colors in Figure 32 represent different spots on the same sample. Because of this, discerning thickness differences with this method would be impossible. This result is not surprising, given the large optical bandgap of Al_2O_3 . Literature reports small absorbance peaks for Al_2O_3 for much thicker films (71 nm) [51], but the above spectra do not show those peaks – absorbance is negligible throughout the wavelengths measured.

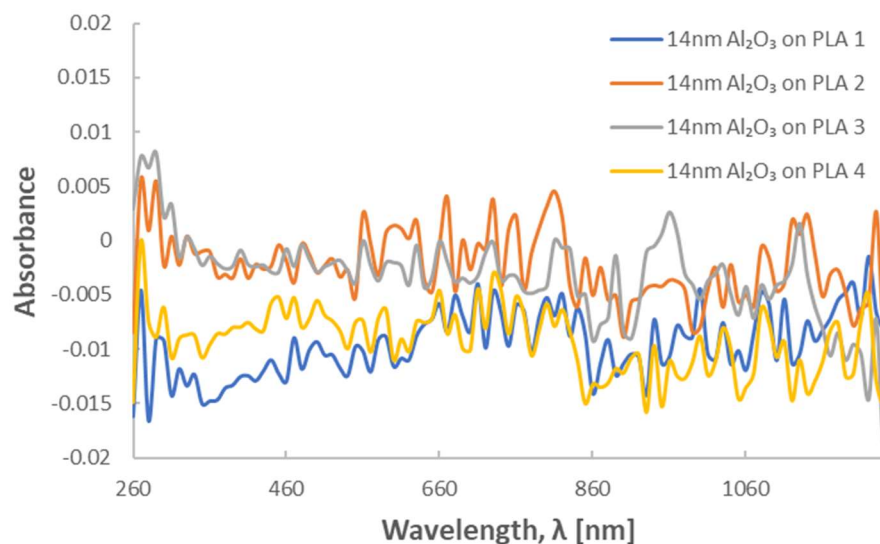


Figure 32: Absorbance spectra of multiple samples of 14nm of Al_2O_3 on PLA. No clear absorbance peaks are observed.

4.3.2 Ellipsometry Analysis

For this ellipsometry analysis, three thicknesses (0 nm, 4 nm, and ~ 10 nm) from the two different film sets (*Growing ZnO on PLA* and *Growing Al_2O_3 on PLA*) were investigated. The raw ellipsometry data (Psi and Delta) from those samples are plotted in Figure 33 to see whether these small differences in film thickness resulted in discernable differences in the ellipsometry data. As noted previously, multiple measurements were taken for each sample, at different locations on the sample surface.

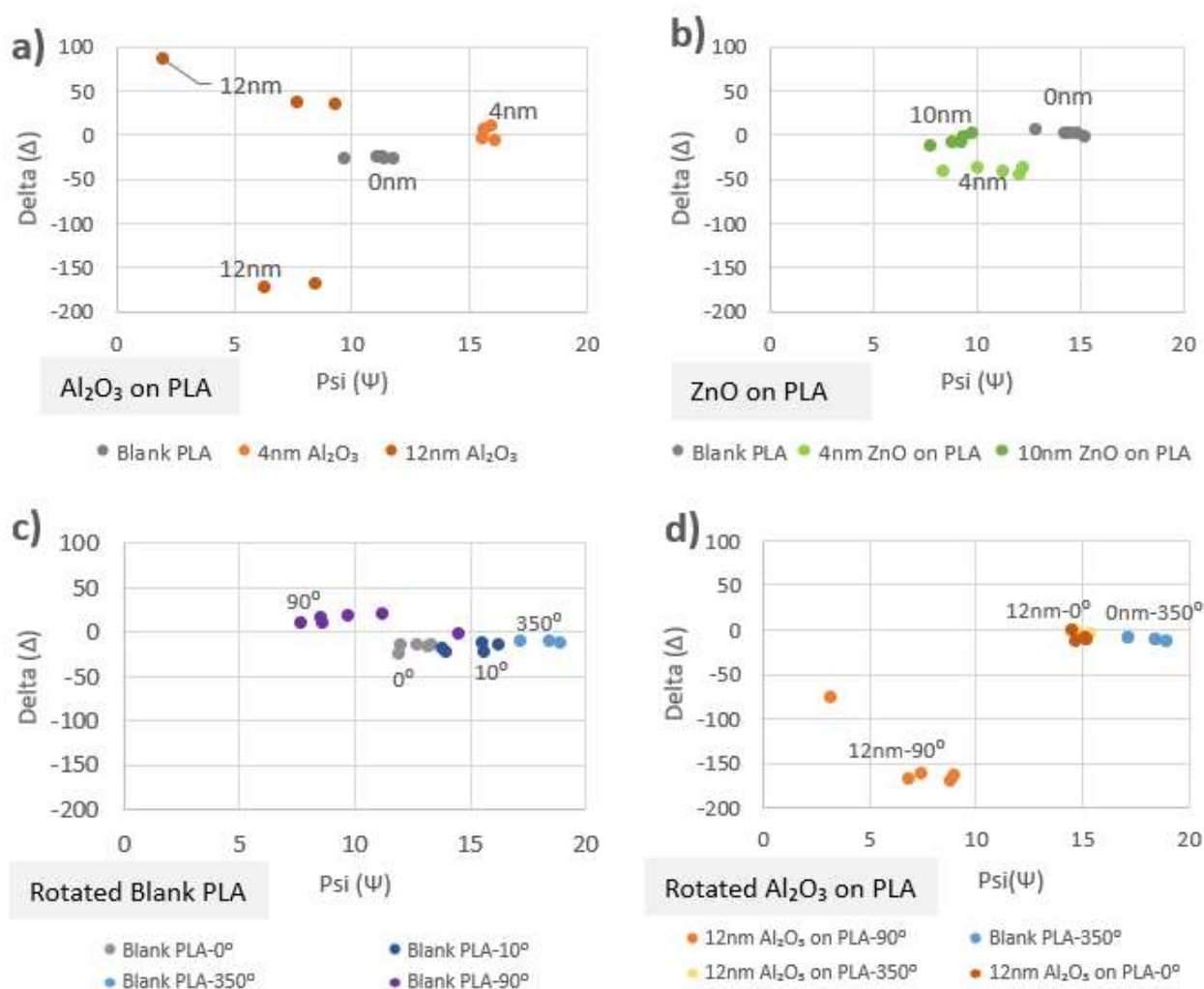


Figure 33: Raw ellipsometry data for three thicknesses (0 nm, 4 nm, and ~10 nm) of Al₂O₃ and ZnO on PLA. On all plots, each measurement is repeated 4 times, translating the sample to a new spot each time. a) Blank and Al₂O₃-coated PLA. Each coating thickness results in localised ellipsometry data. b) Blank and ZnO-coated PLA, along with PLA with 4nm and 10nm ZnO coatings are plotted. Each coating thickness results in localised ellipsometry data. c) Blank PLA taken at different orientations. The localisation region on the Psi-Delta plane changes with orientation d) 12nm Al₂O₃-coated PLA taken at different orientations. The resulting localisation region on the Psi-Delta plane changes with orientation even entering the region of Blank PLA

At first glance, Figure 33a and Figure 33b seem to show good separation between the different thicknesses explored – suggesting a thickness resolution better than 4 nm. However, plotting ellipsometry data of the same samples at different orientations (Figure 33c and Figure 33d) show that orientation, which was not accounted for in Figure 33a and Figure 33b, may be a big

reason for this separation. Figure 33c and Figure 33d show ellipsometry measurements of a blank PLA sample and a 12-nm- Al_2O_3 -on-PLA sample respectively, at different orientations. In ellipsometry measurements for a blank PLA sample (shown in Figure 33c), the localization of data points on the Psi-Delta plane can be seen to change with the orientation, though all data points in this group remain relatively close together (near the Delta = 0 line). The 12nm Al_2O_3 -coated PLA sample (Figure 33d), however, shows a more drastic variation in Psi-Delta values with orientation. The magnitude of variation from orientation alone is similar to that observed for the different film thicknesses in Figure 31a.

The variation of the ellipsometry data with sample orientation is attributable to the anisotropic nature of the PLA substrate, which has been reported previously [37]. The observed anisotropy complicates the estimation of film thicknesses using ellipsometry models. For the 12nm Al_2O_3 -coated PLA film shown above, Film Sense's model builder, which uses multiple different classical models and picks the best one, suggested wildly different thicknesses (sometimes 16 nm times 46 nm) for different orientations. This data makes it clear that anisotropy, or at least the material orientation, would need to be accounted for when modeling the thin films created by our industry sponsor.

4.3.3 Reflectometry Analysis

For this reflectometry analysis, the sample set *Growing Al_2O_3 on PLA* was used (Blank PLA, 4 nm Al_2O_3 -coated PLA, 12 nm Al_2O_3 -coated PLA). The raw reflectance spectra of these samples are shown in Figure 34a-b. Notice how different thicknesses have different oscillatory features, particularly around 500 nm. As described in Section 2.3.3, varying oscillatory features in reflectance spectra correspond to varying film thicknesses – higher frequency oscillations correspond to thicker films. We also saw (Figure 10) that the differences in oscillatory features can be further extracted using Fourier transforms [41]. The Fast Fourier transforms of the reflectance spectra were taken and plotted in Figure 34c-d. Notice peaks corresponding to the thickness of the PLA substrate at about 0.03nm^{-1} . In Figure 34d, the Fast Fourier transforms of the reflectance spectra for a smaller frequency range are plotted to show the low-frequency oscillations.

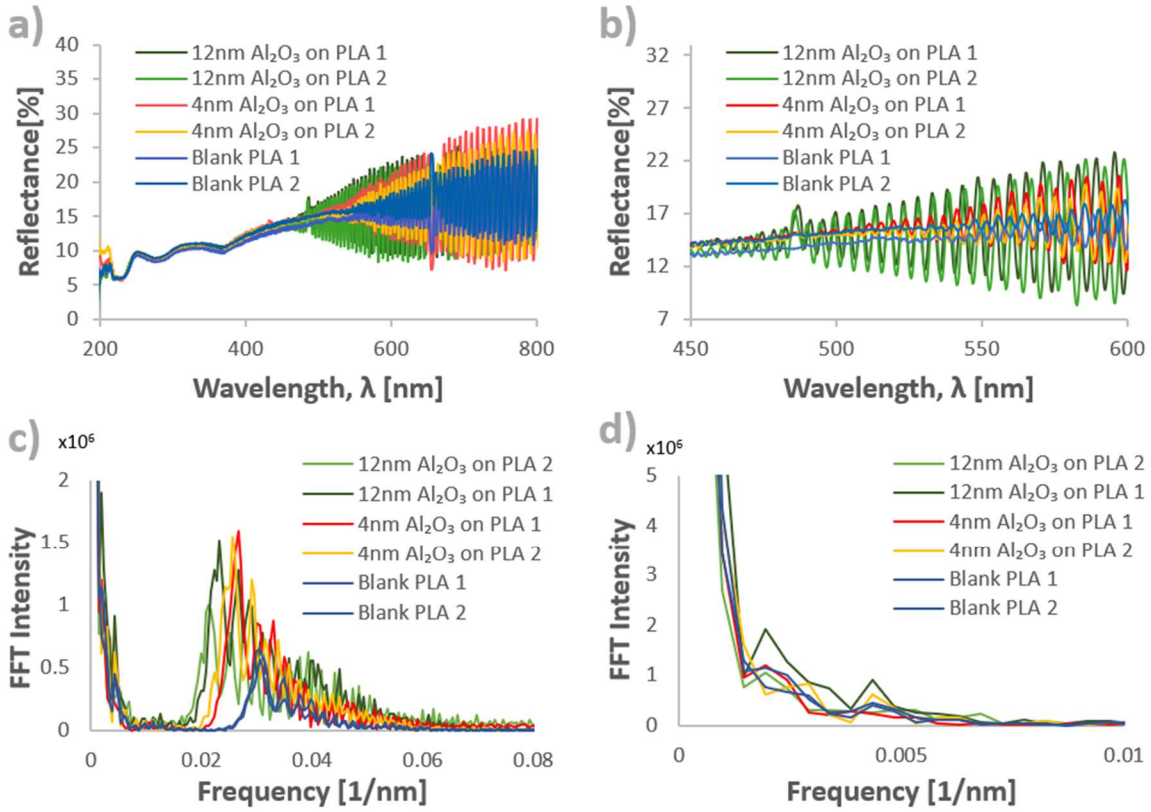


Figure 34: Reflectance spectra of the sample set Growing Al_2O_3 on PLA. a) Full reflectance spectra. The different thicknesses have different oscillatory features, particularly around 500nm. b) Reflectance spectra for a smaller range around 500nm to emphasize the different in oscillatory features. c) The Fast Fourier transforms of the reflectance spectra. Notice peaks corresponding to the thickness of the PLA substrate at about 0.03nm^{-1} . d) The Fast Fourier transforms of the reflectance spectra for a smaller range to show the low-frequency oscillations.

The prominent FFT peak seen at about 0.03nm^{-1} in Figure 34c can be seen to shift left with Al_2O_3 thickness. This is contrary to the expectation set in Section 2.3.3 that thicker films yield higher frequencies. One reason for this is that the reflection of light through multiple materials with different refractive indices (PLA and Al_2O_3) results in a complex interaction that cannot easily be described using changing frequencies. While the minute thicknesses in Figure 34 seem to have discernable FFT peaks, a model would be required to extract meaning thickness information. Fresnel equations, which describe the transmission of light through stacks of films [30], may help describe this behaviour. The peak locations could also be mapped to thicknesses using machine learning/regression techniques.

4.4 Metrology Conclusions

This chapter presented an analysis of potential real-time thickness measurement techniques for films created using SALD. The findings from the UV-Vis absorbance, ellipsometry, and reflectometry measurements offer valuable insights into the challenges to overcome as well as the thickness resolution possible with these methods.

UV-Vis Absorbance: The absorbance spectroscopy measurements successfully identified small differences in ZnO thicknesses, distinguishing between films that were 10 nm, 15 nm, 30 nm, and 85 nm thick. The linear relationship between the thicknesses and absorbance intensities indicates the potential for developing a simple calibration curve to model these measurements. This technique was, however, ineffective for Al₂O₃-coated PLA samples, as evidenced by the absence of absorbance peaks.

The limitations observed in the absorbance spectroscopy experiments highlight the technique's constrained effectiveness with certain materials, including potentially opaque substances like plastic-coated paper. Despite these constraints, the method's ability to discern fine variations in ZnO thicknesses suggests it could be valuable as an adjunct method alongside other techniques for measuring film thickness on various packaging substrates, especially with multilayer films. Further research is needed to explore the full range of thicknesses that absorbance spectroscopy can accurately measure, particularly for ZnO on PLA and for ZnO in multilayer film stacks.

Ellipsometry Measurements: The ellipsometry measurements demonstrated the method's capacity for film thickness measurement, yet they also uncovered significant variability in the results due to the anisotropic nature of the PLA substrates. This anisotropy complicates the use of standard ellipsometry models for accurate film thickness estimation. To address this, developing models that account for the orientation of the substrate, particularly in roll-to-roll systems, is essential. Using Mueller matrices [37] or machine learning models [38] to resolve multi-directional measurements might offer a path forward for more accurate ellipsometry.

One potential method of addressing this, especially for roll-to-roll systems, where the substrate maintains a singular orientation, is to develop models that note the orientation of the substrate which stays constant throughout system. Feasibility studies would need to be done to note the anisotropy of the substrate along this singular axis. Another potential method is to incorporate ellipsometers which take measurements at different orientations. These multi-directional measurements can then be resolved using Mueller matrices [37] or machine learning models [38]. Addressing anisotropy, using these methods, can unlock ellipsometry for thickness measurements of films created using SALD systems.

Reflectometry Measurements: The reflectometry study yielded spectra which were discernable for minute thicknesses (4 nm and 12 nm). These discernable oscillatory features were especially visible in the Fast Fourier Transforms (FFT) of the reflectance spectra, where the frequency was dependent on film thickness. Mapping these changes in the FFT to thickness would be required to use this method for thickness measurements. This mapping could be done with machine learning and could incorporate the interaction of light through multiple layers of film with Fresnel equations [30]. Future work could explore this modelling as well as reflectometry on different materials.

For ellipsometry and reflectometry, efforts to characterize film thickness need to account for variability in physical and optical properties of the substrate (e.g., thickness and refractive index). The substrate properties may vary from manufacturer to manufacturer, between substrate rolls, or just along the length of a roll of one substrate. While using these methods, keeping track the variance in substrate properties quantities might inform complications with interpreting the measurement data.

To prevent the variance in substrate properties from interfering with measurement data, intermediate in-situ measurements, as seen in Figure 11, could be utilized. A witness substrate – a substrate with known characteristics – could also be coated in the same way as the sample being measured to remove any uncertainty introduced by the substrate. Gradient films – films with thicknesses that vary along the substrate – could be used to isolate the effect of changing

thicknesses while minimizing the variance associated with comparing coatings on different substrates.

In conclusion, this study highlights the potential of these metrological techniques to achieve film thickness characterization for films created using SALD. While the data presented here is promising, the effectiveness of any of these techniques boils down to the models used for them.

5 Conclusions and Recommendations

This thesis set out with the aim of addressing two primary challenges hindering the industrial-scale implementation of Spatial Atomic Layer Deposition (SALD) systems: powder formation during the deposition process and the difficulty in performing real-time, in-situ thickness measurement of nano-thin films.

Addressing Powder Formation in SALD Systems

The primary goal of this thesis was to tackle the issue of powder formation in SALD systems, a notable obstacle that hinders uniform film deposition and necessitates regular maintenance. This was investigated by initially identifying areas within SALD systems where powder accumulates, followed by systematic experimentation to demonstrate the effectiveness of a newly developed powder quantification method/module. Utilizing this module, the research provided insights into the impact of various process parameters (such as Temperature, Gap Spacing, Metal Concentration, and Curtain Flowrate) on the accumulation of powder in the exhaust line.

Additionally, a method to quantify precursor isolation, one of the key contributors to powder formation, was also introduced and briefly discussed.

As stated previously, while the mechanisms involved in powder formation have been calculated, theorized, and simulated, there have been no documented attempts to quantify the effects of these mechanisms. Thus, the methodologies presented in this thesis offer a significant improvement to the state of the art and a means to reduce powder formation in SALD systems, enhancing their long-term operational stability and enabling real-time feedback and troubleshooting. This achievement is a considerable step forward in improving the reliability and industrial applicability of SALD technology.

Evaluating Techniques for Real-Time Nano-Thin Film Metrology

In addressing the second objective, this thesis tackled the intricate challenge of accurately measuring the ultra-thin films produced by Spatial Atomic Layer Deposition (SALD) on flexible packaging substrates, a pivotal factor in assuring the quality of high-throughput production. The

research assessed a range of metrology techniques, including absorbance spectroscopy, ellipsometry, and reflectometry. Each method was tested using sample sets that mimicked our industry partner's SALD application, focusing on Al_2O_3 and ZnO coatings on a PLA substrate. Absorbance measurements revealed a direct correlation between film thickness and absorbance intensity for ZnO coatings, although it proved less effective for Al_2O_3 films due to the lack of discernible absorbance peaks. Ellipsometry offered insights into film thickness, but highlighted challenges related to the anisotropy of the substrate. Advanced modeling would be needed to account for material orientation. Reflectometry demonstrated potential in differentiating film thicknesses through oscillatory features in the spectra, although substrate variance posed challenges.

More work is needed to establish any of these techniques as a viable option for comprehensive, in-situ quality control in industrial SALD applications. Future research should focus on refining these methods, particularly in addressing the variability and anisotropy issues, to enhance their precision and reliability.

Overall Impact and Future Directions

Overall, this thesis has made significant contributions to the field of SALD, particularly in enhancing its applicability for industrial-scale production. The findings and developments achieved in this study lay a solid foundation for future research and industrial application. Future work could focus on further refining the optimized process variables for powder reduction and integrating the identified metrology techniques into existing SALD systems, thus moving closer to realizing the full potential of SALD in industrial settings.

Recommendations and Future Work

Based on the findings and accomplishments of this research in addressing the challenges of powder formation and thickness measurement in SALD processes, the following recommendations are proposed for future work and practical application:

For Mitigating Powder Formation in SALD Systems

Optimized Process Variables: The variables found to minimize powder formation in this thesis (Temperature $>100^{\circ}\text{C}$, Gap = 0.5mm, Curtain > 4000) as well as the trends identified can be used directly to optimize SALD system to minimize powder formation.

Further Research on Powder Formation: Continued investigation into the underlying mechanisms of powder formation in SALD processes is needed. The tools identified for quantifying powder formation should be used to optimize each SALD design.

Automating Powder Minimization: Implement automated powder minimizing systems in SALD equipment, using the powder quantification module as a tool for feedback control. This approach will manage powder accumulation, thereby reducing maintenance downtime and improving film quality.

For Enhancing Nano-Thin Film Metrology in SALD

Improving Absorbance for Thickness Measurements: Further refine the absorbance measurement techniques for ZnO coatings, creating calibration curves and noting resolution limitations. Explore additional wavelength ranges to enhance its efficacy for Al_2O_3 films. Research should also focus on the development of calibration models for different film and substrate types and thickness ranges.

Improving Reflectometry for Thickness Measurements: More research is needed to improve the viability of reflectometry for measuring film thickness. The influence of substrate variance can be minimized or quantified using film gradients or witness samples. Additionally modelling techniques for extracting information from spectra is needed. One modelling technique to explore could combine Fresnel Equations with FFT, with the former providing information about how multilayer film FFT should evolve.

Improving Ellipsometry for Thickness Measurements: Address the challenges of anisotropy in ellipsometry using Mueller matrices or machine learning modelling techniques. Explore the feasibility of incorporating multi-directional measurement systems to accurately account for material orientation.

These recommendations aim to build upon the significant progress made in this thesis, directing future efforts towards overcoming the remaining barriers in SALD technology for industrial applications. The ultimate goal is to enable the widespread adoption of SALD, leveraging its advantages in thin-film manufacturing for a variety of industrial applications.

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Appendices

A.1. Failed attempts at monitoring powder.

A great deal of time was spent on trying to quantify the amount of powder generated in the filter. This section will detail some of the missteps taken toward that goal. Find below, a compilation of approaches considered and tried for quantifying the amount of powder captured in the exhaust filter:

Weighing the filter before and after a deposition: The main problem with this method is that the amount of powder generated by a typical deposition was too small to detect on the available scales. Further, exploring the differences between deposition conditions was thought to be too time-consuming as it would require running hours long of depositions to accumulate a significant amount of powder for each data point.

Additionally, this method would be misled by the saturation period we now know exists at the start of every deposition.

Removing the powder from the system and quantifying the residue: This approach involves extracting the powder from the filter using compressed air and trying to quantify it. This takes the qualitative experiments previously described a step further by trying to quantify the powder extracted from the reactor.

This approach would be time consuming as well. It would also be difficult to contain the all the powder extracted from the filter.

This method would also suffer from varying starting saturation conditions.

Width of substrate patterns during deposition: This method (discussed at the end of Section 3.3) involves inferring that metal isolation leads to less powder formation. While information about metal isolation is pertinent to SALD, this method does not directly measure powder formation, experiments would be needed to correlate good metal isolation with less powder formation.

Using either flowrate or pressure of the exhaust line: While the same trends found in the resistance plots can be seen in the flowrate or pressure, I found that the resistance values were less prone to fluctuations. The resistance value reset to the same value (0.2 bar/lpm) every time the ultrafine filter was cleaned. Figure 35 clearly shows the resistance to perturbations of the resistance plots.

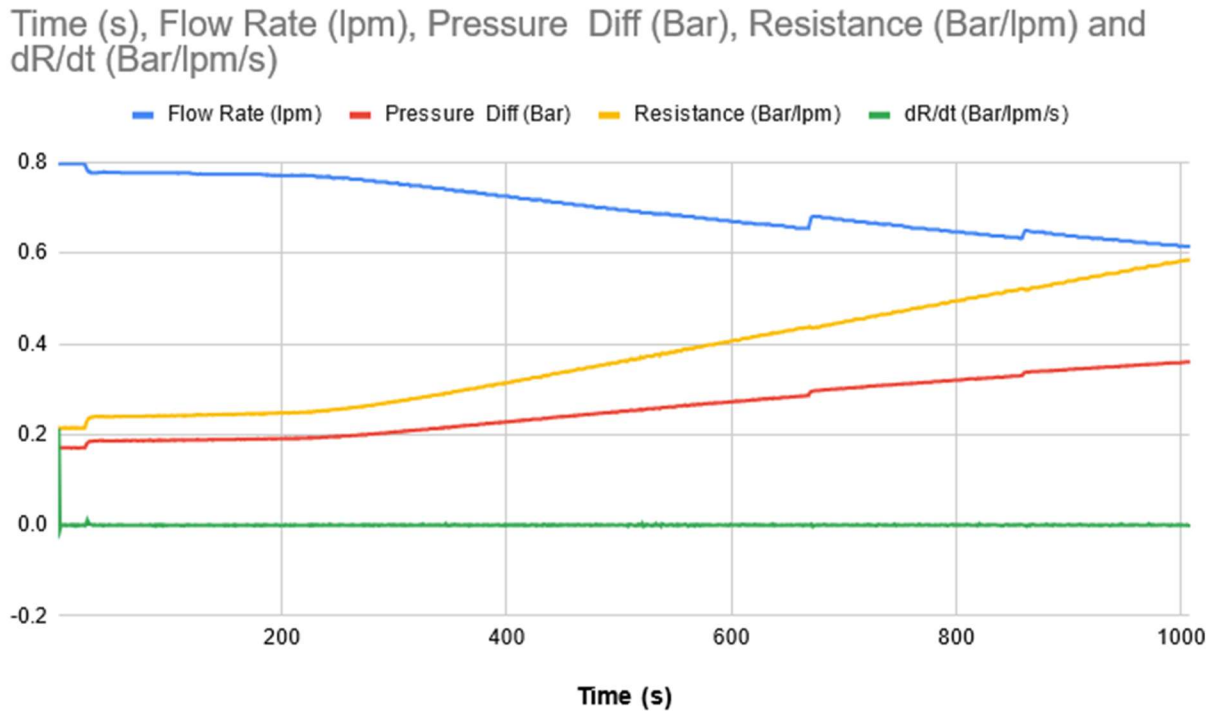


Figure 35: Resistance, dR/dt , Flowrate, Pressure over time

Sampling the filter after long intervals: This method misses significant trends in the powder formation process, particularly the exact moment the trend becomes linear. The continuous sampling presented in the rest of this thesis was done at 1 sample/second.

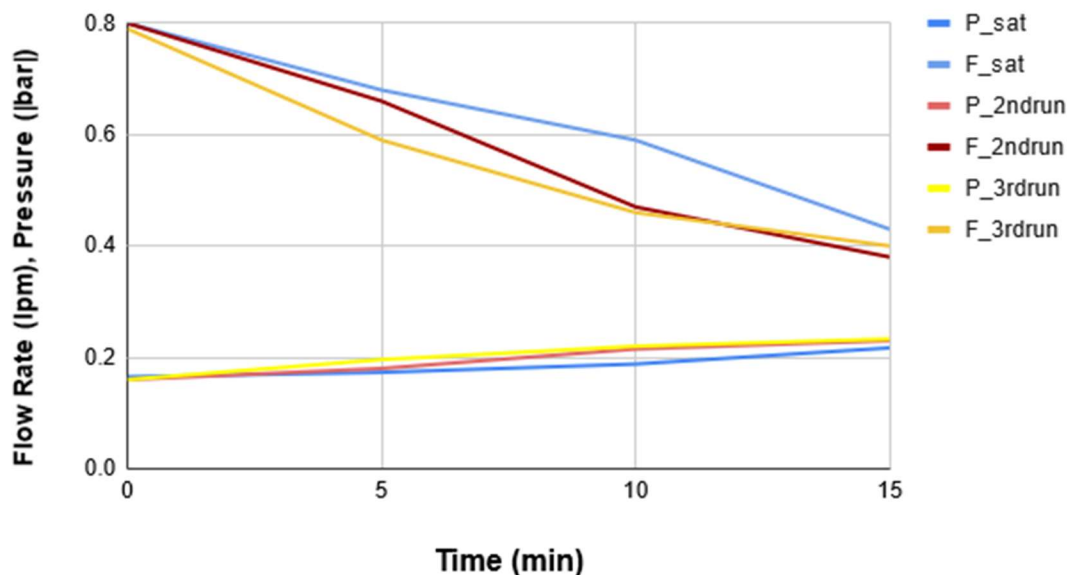


Figure 36: 5min sampling. Continuous sampling at 1 sample/second is recommended.

A.2. Tools Developed for Powder Studies

A.2.1. Modification to SALD system

Prof. Kevin Musselman's lab-scale SALD system typically deposits smaller samples than the SALD system used by our industry sponsor, and hence uses lower precursor flow rates. Table 3 shows the deposition parameters typically used by our industry partners against the maximum flow limits the lab SALD system can deliver. It was clear that the flow meters used to deliver the Water Carrier flow and the Curtain flow would (highlighted) need to be replaced or modified.

Table 3: Comparison of maximum flows for lab-scale systems with those needed to replicated industry sponsor's SALD system. The flowmeters that need to be changed are highlighted.

Parameter	Maximum for Lab-Scale System	Needed for Modified System
Metal Bubbler Flowrate (SCCM)	50	50
Metal Carrier Flowrate (SCCM)	500	400
Water Bubbler Flowrate (SCCM)	50	50

Water Carrier Flowrate (SCCM)	500	750
Exhaust Flowrate (SCCM)	-	8000
Curtain Flowrate (SCCM)	2000	4000

The schematic in Figure 37 shows that the Water Carrier Rate was accomplished using two mass flow controllers, each only able to reach 500 SCCM individually. The Curtain rate was accomplished using a manual flow controller.

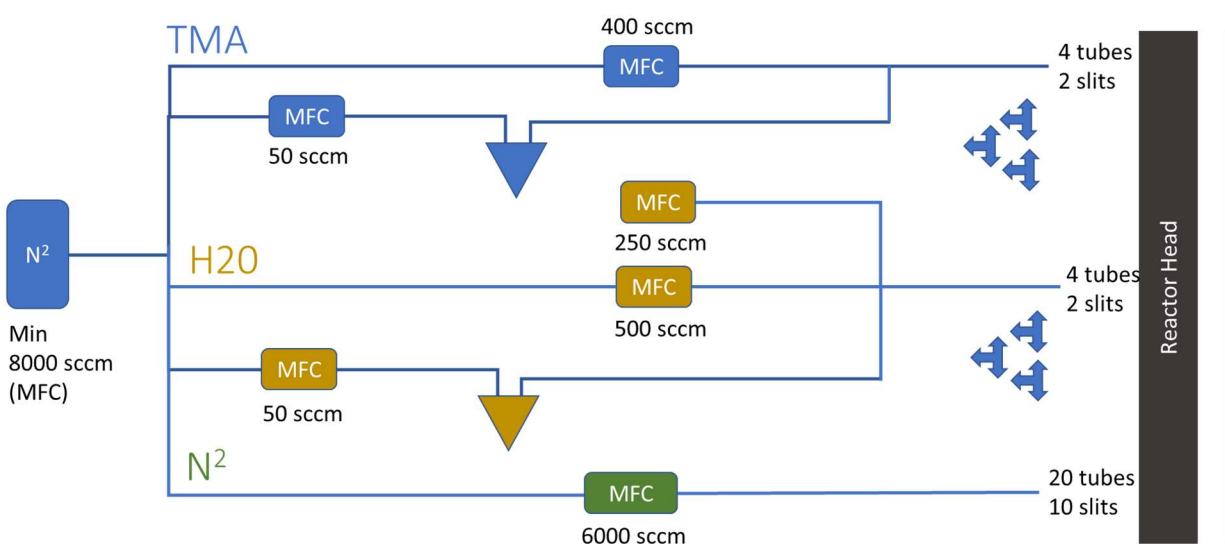


Figure 37: Schematic showing system modifications to replicate industry sponsor's SALD system.

A.2.2. Filters Selection and 3D Printed Filter Adapters

The filter was also selected based on the amount of constriction needed to result in appropriate exhaust flowrate. This function was rendered obsolete with the addition of a proportional valve. Any constrictive flow valve can be used to achieve this function.

Ordering Ultra High Purity filters (filters with pores < 3nm) and filter components were an ordeal, as lead times were upwards of 3 weeks. After acquiring the POU-05-FSV1 GasShield® Fiber POU Gas Filter (P/N: 6700015), we discovered that the proprietary fittings would take just as long to arrive.

To save time and avoid the long lead time, filter adapters were designed and 3D-printed to mate with the proprietary ends of the filter. The part of the adapter, made to mate to ¼" polymer tubing is shown in Figure 38.

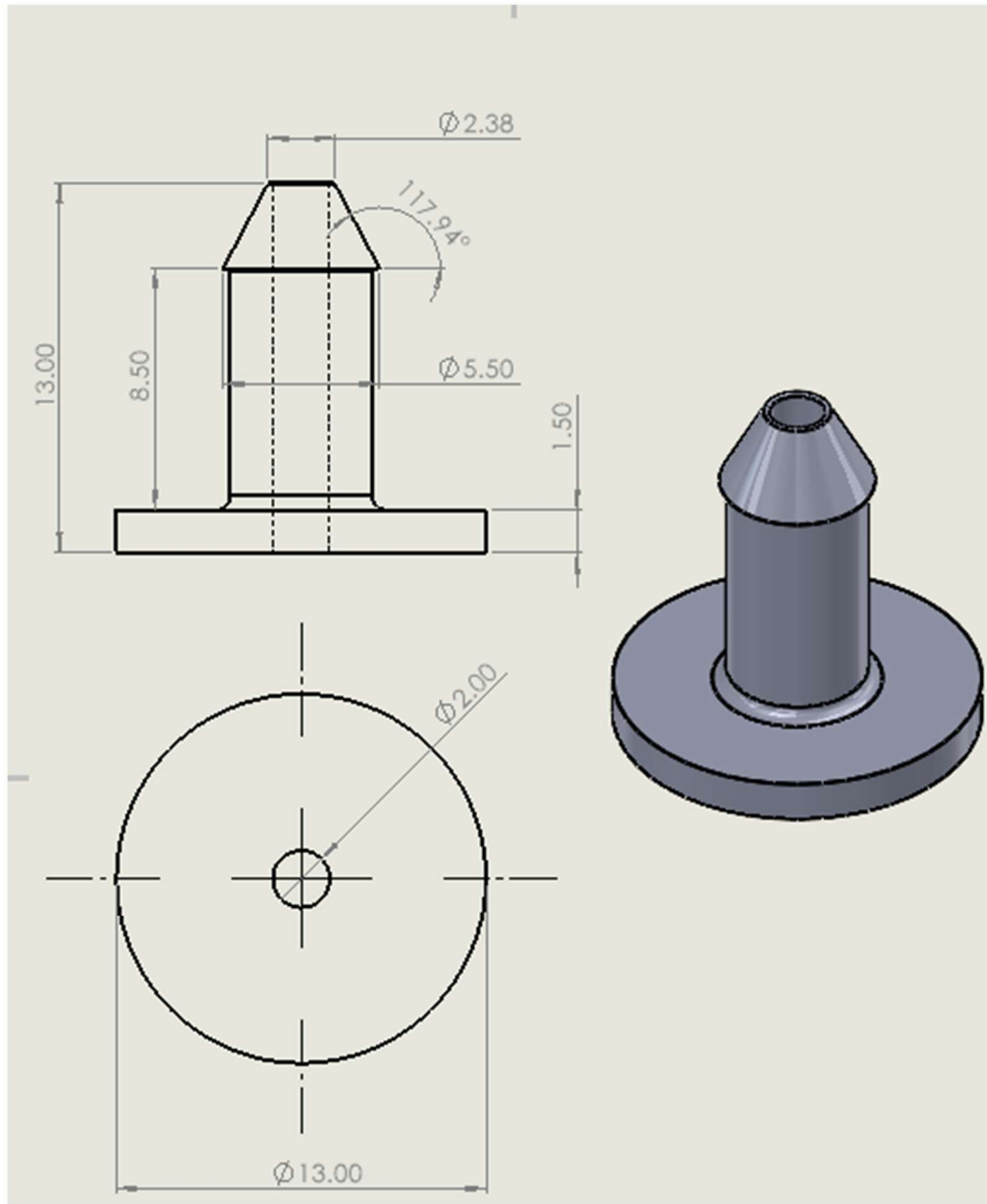


Figure 38: Custom fitting developed to mate tubing to filter.

A.2.3. Filter cleaner

Noting the health hazard as well as the length of time it took to clean a filter, a filter cleaner (Figure 39) was developed to enable safe, remote and rapid cleaning of the filter. This cleaner involved a 5/2 valve that alternates the air flow through the filter being cleaned from an open end to a collector filter on the other end. All the powder is collected in the collector filter.

The filter cleaner was controlled with the help of an NE555N circuit shown in Figure 39.

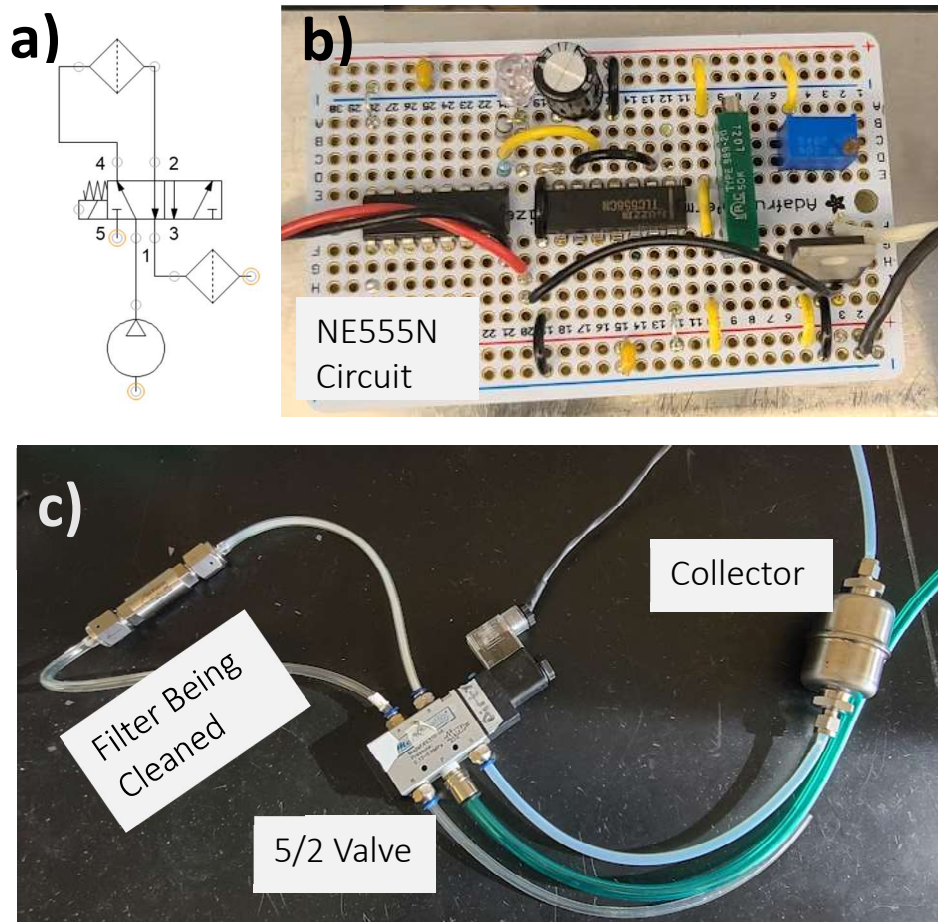


Figure 39: Filter Cleaner Components. a) A schematic of the filter showing air supply, the 5/2 solenoid valve and the collector filter b) NE555N Circuit used to control the filter c) A picture of the filter cleaner assembled.

A.2.4. Powder Quantification Program

To automatically log the pressure and flowrate, a LabView program was created. This program collects the pressure and flowrate signal, appropriately calibrates the signal, and calculates both the resistance and the rate of change of resistance for a given time interval. The dashboard of the program is shown in Figure 40.



Figure 40: Flow Quantification Program dashboard

A.2.5. PID for Flow Control

A PID controller was developed to maintain the exhaust flowrate as the filter got more and more clogged. The PID controller dashboard together with the backend of the PID controller is shown in Figure 41.

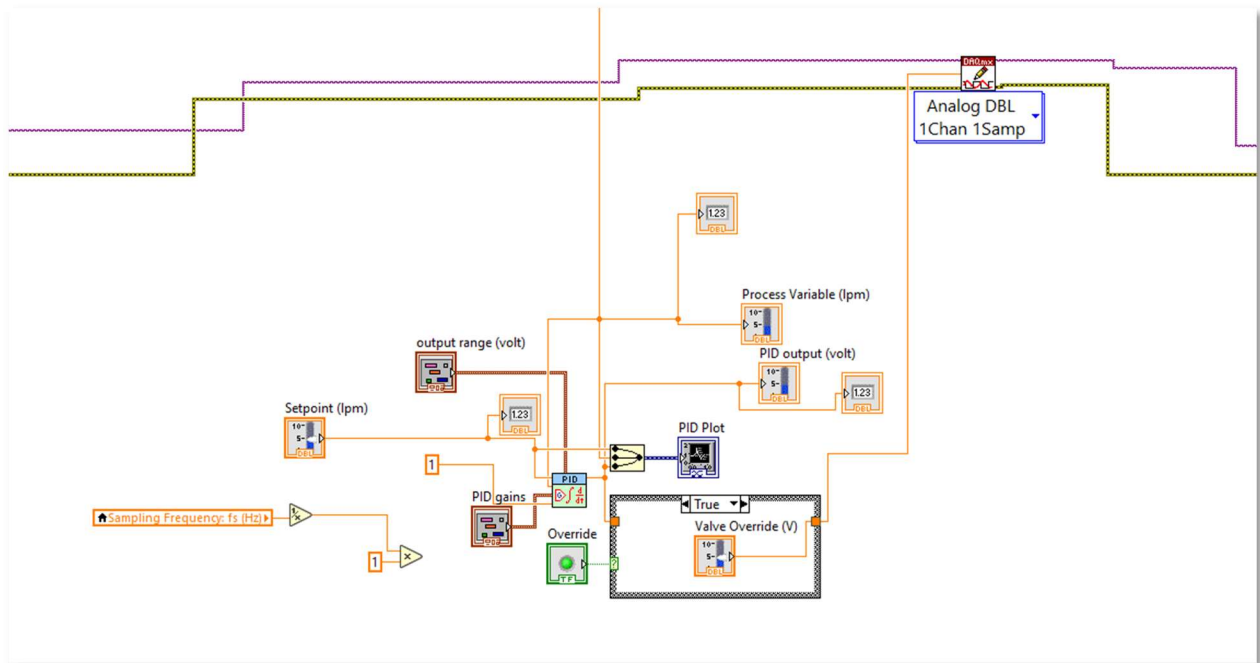
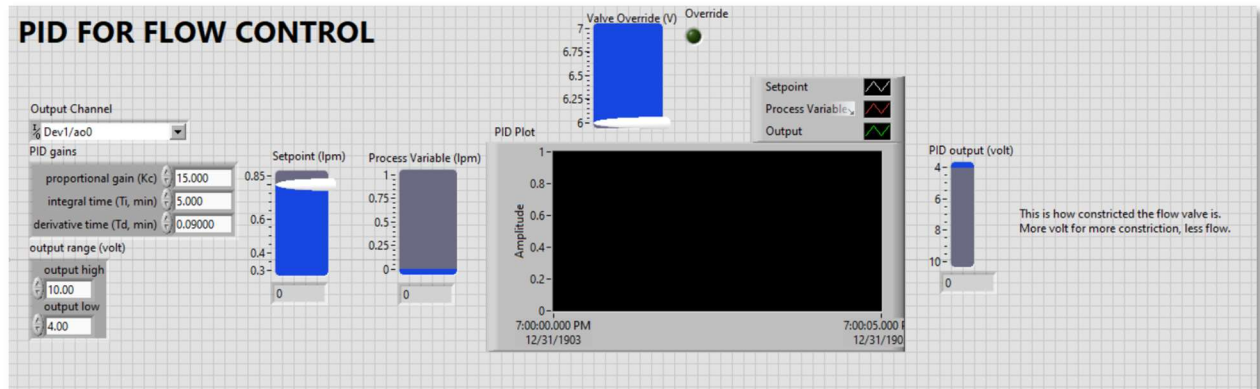


Figure 41: PID Controller for the proportional flow valve used to maintain the exhaust flowrate while the filter gets clogged. The gain values were tuned manually.

A.2.6. Reactor Head Holder

A fixture was designed to hold the reactor head in position for experiments. This fixture included adjustable knobs that acted as set screws, locking the reactor head at appropriate heights. A picture of the fixture is shown in Figure 42.

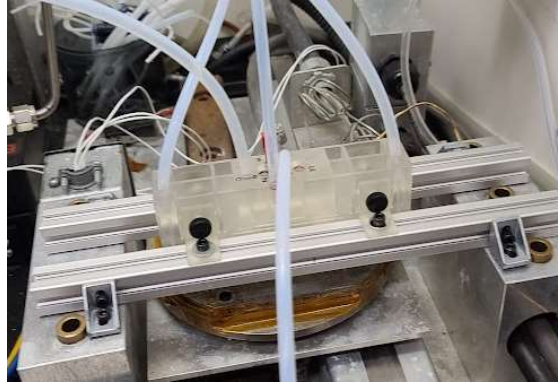


Figure 42: Reactor head holder holding the reactor shown holding the reactor head.

A.2.7. Signal Troubleshooting

Improving the resistance signal was crucial for identifying trends that lead to the success of this project. The largest signal improvement came from maximizing the input voltages to the data loggers, within their respective voltage ratings. Figure 43 shows the signal before and after maximizing the input voltages to the data loggers. The signal was obviously much cleaner after maximizing the input voltages.



Figure 43: The (pressure) signal before and after maximizing the input voltages to the data loggers. Note how much cleaner the signal is after maximizing the input voltages.

A.3. Slope of Resistance Calculations

For slope of resistance calculations, the section of interest of the resistance-time table was copied, pasted into a spreadsheet, and plotted. Using the spreadsheet, a trendline was then fit to the resistance-time plot. The slope of the equation of the trendline was then used as the slope of resistance.

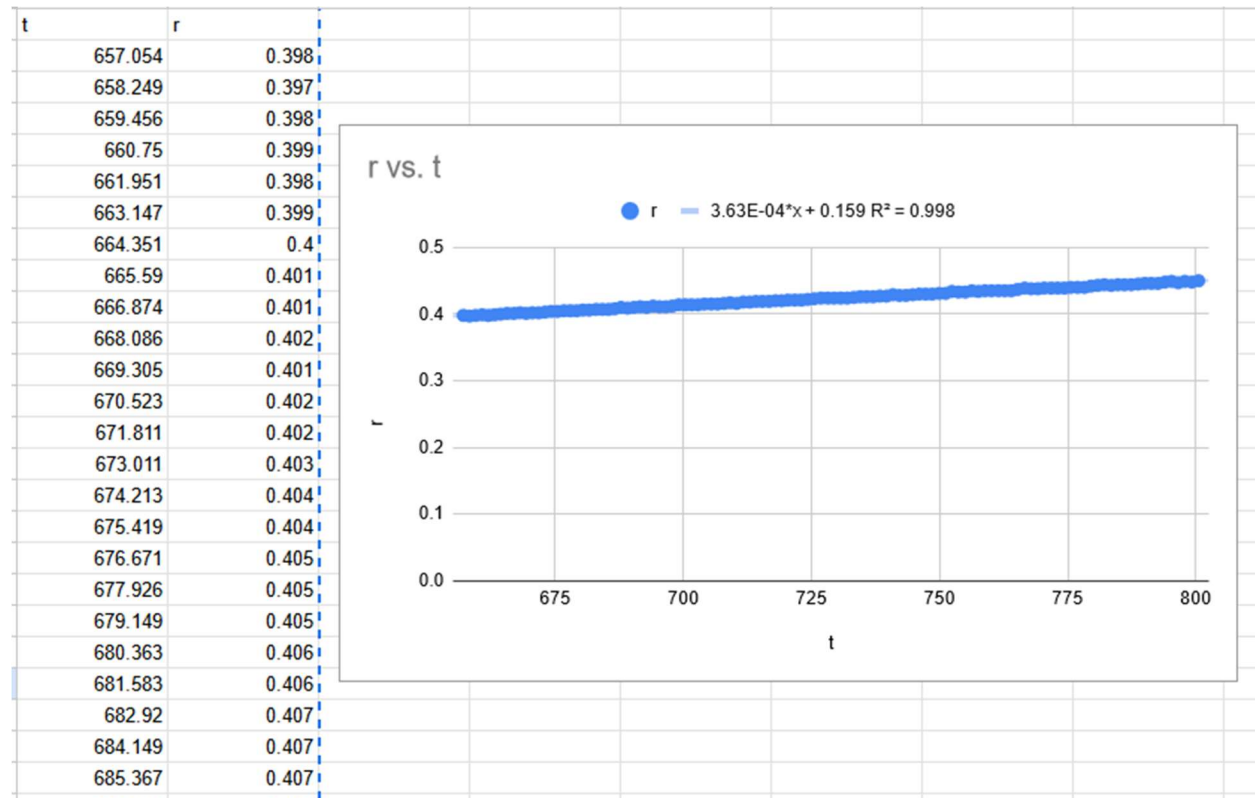


Figure 44: A spread sheet showing the trendline fitting used for slope of resistance calculations. The slope for this particular resistance line is 3.63×10^5