

Controlling deposition location in atmospheric-pressure spatial atomic layer deposition

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.

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Statement of Contributions

All the depositions with the lab-scale AP-SALD system in Sections 3.2.1 and 3.2.2 were performed by Ahmed Shahin and Denys Vidish, respectively. Louis Delumeau performed the depositions with the industrial-scale AP-SALD system in Section 3.3.3.

Farman Ullah and Denys Vidish assisted in the depositions with the lab-scale AP-SALD system in Sections 4.2 and 4.3, respectively.

EDX analysis of the samples in Section 3.3.1 were performed by Farman Ullah. The EDX analysis described in other sections in this thesis were performed by Denys Vidish.

The study of powder formation on 3D printed AP-SALD reactors dip-coated with growth inhibitors discussed in Chapter 3 of this thesis is part of an international patent application, (United States Provisional Patent Application No. 63/413,440), assigned worldwide to Nfinite Nanotechnology Inc.

Abstract

Nanoscale thin films exhibit unique properties and functionalities and are significant in a wide variety of applications and various sectors such as microelectronics, energy harvesting and storage applications, optoelectronics, sensing, and various other emerging technologies such as flexible electronics, 2D materials, quantum computing, micro electromechanical systems (MEMS), and packaging. Atomic Layer Deposition (ALD) is one method for producing thin films; its advantages include atomic-scale precision and control over film properties, which are vital for these applications. On the other hand, ALD is carried out under vacuum and therefore the process is expensive and slow. Atmospheric-Pressure Spatial Atomic Layer Deposition (AP-SALD) is an advanced technique for fabrication of thin films with properties similar to ALD but under atmospheric conditions and up to 2 orders of magnitude faster than ALD.

AP-SALD is advantageous for its ability to deposit uniform, conformal and pinhole-free thin films. However, formation of powder can be observed during deposition using lab-scale and industrial-scale AP-SALD systems. A major reason for the formation of airborne powder particulates is due to intermixing of precursor gases. This can be a disadvantage as it can lead to non-uniform film growth, an increase in surface roughness and poor adhesion, film quality and properties. Moreover, formation of powder around the perimeter of the AP-SALD reactor head and the channels due to undesired material deposition can affect the performance and efficiency of the system. In addition to unwanted powder formation, AP-SALD is a coating technique that deposits a film over the entire substrate area, whereas selective deposition of a patterned film is sometimes desired. To overcome these challenges, methods to control the location of material deposited by AP-SALD are crucial. Therefore, the objective of this work includes developing methods to (1) either prevent or minimize the powder formation on 3D-printed AP-SALD reactor heads and (2) control what parts of the substrate are coated by depositing thin films at specific regions on the substrate.

Several advanced strategies revolving around exhaust systems, in-situ monitoring and process optimization are being explored at the Functional Nanomaterials Group to prevent powder formation and effective removal of powders. In addition to these methods, coating the AP-SALD reactor head with materials that passivate the surface against gas-phase reactions may reduce powder formation on the reactor head. Area-selective atomic layer deposition (AS-ALD) by area deactivation is a technique in which thin films are selectively deposited on specific regions or patterns of a substrate (growth area)

by coating the undesired regions (non-growth area) with growth inhibitors. In this work, the effect of dip-coating a custom AP-SALD reactor head with growth inhibitors to prevent material nucleation and powder formation is studied. Samples made of the same material as the reactor head are dip-coated with various growth inhibitors: polymers including poly(methyl methacrylate) (PMMA) and poly(vinyl pyrrolidone) (PVP) and self-assembled monolayers including octadecylphosphonic acid (ODPA) and dodecanethiol (DDT) for different durations up to 6 hours and 53 hours 30 minutes, respectively. Then AP-SALD depositions are performed on the samples to assess the effectiveness of the inhibitors. Some of the selected inhibitors demonstrate a clear ability to limit film growth on the 3D-printed samples. When 3D-printed reactors are coated with the promising growth inhibitors PVP and ODPA, powder formation is still observed on the reactor after performing depositions, although slightly less powder formation is observed when the reactor was coated with ODPA.

Using 3D printing, AP-SALD reactors with complex channels that cannot be fabricated with conventional manufacturing methods can be fabricated. Fabricating custom reactor heads with channels that deliver precursors at desired locations on the substrate can enable direct selective deposition. In this work, novel area-selective AP-SALD reactors are developed to selectively deposit thin-film patterns on a silicon substrate. Two types of reactors are designed and tested; to deposit wide and narrow patterns separated by a small and large gap, respectively. Using the former type of reactor, a pattern is visually observed after depositions, however film growth with approximately half the thickness of the patterns is observed in the gaps due to precursor leakage and intermixing. Closely spaced narrow patterns are deposited using the latter type of reactor by slightly offsetting the reactor head relative to the substrate in subsequent depositions. This method can also be extended to depositing wide patterns and represents a significant advancement in the ability to deposit high-throughput patterned films by AP-SALD.

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Dedication

To my parents

To my grandparents

To my uncle

To my brother

To my friends

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List of Abbreviations

ALD	Atomic layer deposition
AP-SALD	Atmospheric pressure spatial atomic layer deposition
AS-ALD	Area selective atomic layer deposition
CFD	Computational fluid dynamics
CFM	Cubic feet per minute
CVD	Chemical vapor deposition
DDT	Dodecanethiol
DEZ	Diethylzinc
EDX	Energy dispersive X-ray
EPE	Edge placement error
eV	Electronvolt
FDT	<i>1H,1H,2H,2H</i> -perfluorodecanethiol
FESEM	Field-emission scanning electron microscopy
HVAC	Heating, ventilation, and air-conditioning
ICP	Inductively coupled polymerization
MEMS	Microelectromechanical systems
ODPA	Octadecylphosphonic acid
OS	Octadecylsilane
OTS or ODTS	Octadecyltrichlorosilane
PMMA	Poly(methyl methacrylate)
PVP	Poly(vinyl pyrrolidone)
SAM	Self-assembled monolayer

SCCM	Standard cubic centimeter per minute
SCVD	Spatial chemical vapor deposition
SEM	Scanning electron microscopy
SLA	Stereolithography
SMI	Small molecule inhibitor
TMA	Trimethylaluminum
UV	Ultraviolet

Nomenclature

μm	Micrometer
Al	Aluminum
$\text{Al}(\text{CH}_3)_3$	Trimethylaluminum
Al_2O_3	Alumina
Au	Gold
C	Carbon
CH_4	Methane
cps	Counts per second
Δ_x and Δ_y	displacement of the disturbed ray
ϵ_x and ϵ_y	the angular deflection of the disturbed ray
H_2O	Water
nm	Nanometer
N_2	Nitrogen
O	Oxygen
θ_{ga}	Film thickness in growth area
θ_{nga}	Film thickness in non-growth area
Zn	Zinc
ZnO	Zinc oxide

Chapter 1

Introduction

1.1 Functional nanoscale thin films and deposition techniques

Thin layers or coatings of materials with thickness typically in the range of tens of nanometers and less than 1 μm are referred to as functional nanoscale thin films. Thin films possess specific properties or functionalities at the nanoscale that differ from their bulk counterparts. They play a pivotal role in nanotechnology by:

- i. enabling miniaturization and integration into nanoscale devices, making them essential for the development of nanoelectronics, nano sensors, and nanodevices [1],
- ii. providing materials with tailored properties (such as mechanical, structural, optical, electrical conductivity, magnetic, biocompatibility, etc.) [2],
- iii. enhancing device performance by protecting the surface from moisture, oxygen, and pollution [3].

They find applications in microelectronics, energy harvesting and storage, optoelectronics, sensing, etc. and various other emerging technologies such as flexible electronics, biomedical devices, 2D materials, quantum computing, micro electromechanical systems (MEMS), and packaging [1-3].

Thin films can be deposited by a variety of techniques, as shown in Figure 1.1, and the deposition technique is chosen based on the application or requirements and the desired properties [4].

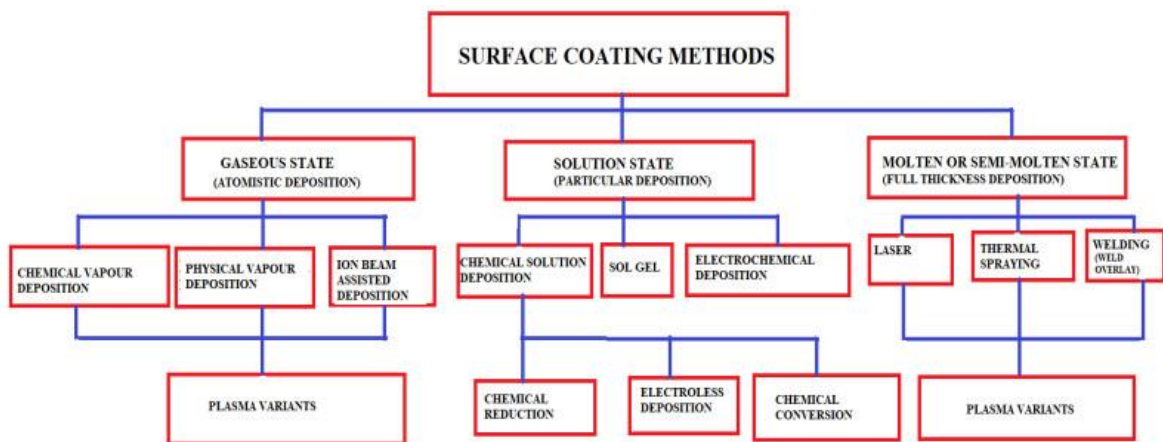


Figure 1.1 Various thin film deposition techniques. Reproduced with the permission of the authors and AIMS Press from [4].

1.2 Atomic Layer Deposition

In recent years, atomic layer deposition (ALD) has emerged as a powerful and versatile thin-film-deposition method and has been widely used to meet the challenge of continuous downscaling of devices. ALD offers precise control over film thickness and composition, uniformity and conformality, which becomes essential as the feature sizes decrease and aspect ratio of the structures increase [5,6].

ALD is a vapor-phase, bottom-up, ultrathin film fabrication technique based on chemical vapor deposition (CVD) [7]. ALD is a cyclic process based on the principle of sequential, self-limiting surface half reactions between precursor molecules and the substrate surface. ALD achieves atomic layer control by depositing materials one layer at a time (a monolayer), resulting in precise control over film thickness, uniformity, and composition [8].

The steps involved in an ALD process, as shown in Figure 1.2, are as follows [9]:

1. Precursor pulse and reaction: The first precursor, typically a volatile compound that can undergo a self-limiting reaction is pulsed into the reaction chamber. The chamber is maintained at a controlled temperature to optimize the surface reaction kinetics. The precursor molecules adsorb onto the substrate surface, forming a monolayer and the reaction stops once the surface sites are saturated.
2. Excess precursor and by-product removal: In this step, an inert gas, such as nitrogen or argon is introduced, or a vacuum is generated to purge the excess first precursor molecules and reaction by-products to prevent their interference with the reaction in the following steps.
3. Precursor pulse and reaction: The second precursor or co-reactant is introduced into the chamber to react with the precursor molecules on the substrate from the previous pulse step.
4. Excess precursor and by-product removal: Excess second precursor molecules and by-products are evacuated from the chamber by purging.

Steps 1 to 4 are repeated in a cyclic manner until the desired film thickness is achieved.

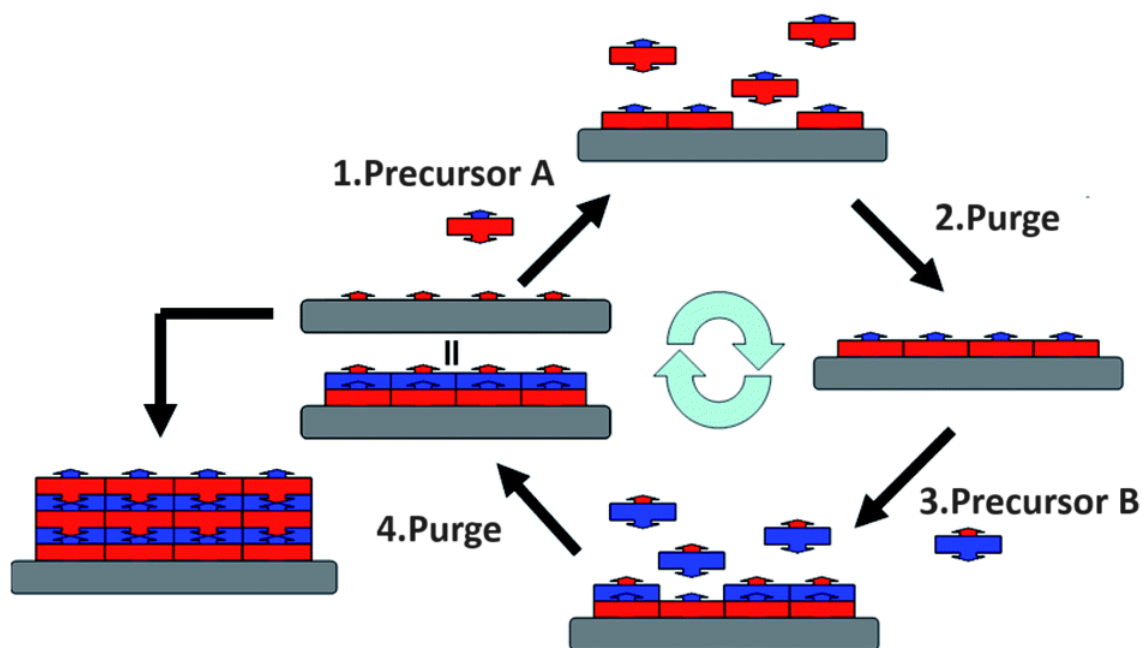


Figure 1.2 ALD process stages showing two self-limiting reactions. Reproduced with permission from [10]. Copyright 2021 The Royal Society of Chemistry.

A wide variety of thin films such as pure metals, metal oxides, metal nitrides and metal sulfides can be deposited through ALD [8]. The chemical precursor that delivers the oxygen required for the reaction to take place is referred to as “an oxidant”. A major difference between ALD and CVD, as shown in Figure 1.3, is the presence of the precursors in the reaction chamber [9]. In ALD the precursor and oxidant are pulsed separately into the reaction chamber with an inert gas purge step in between the pulses, whereas in CVD both the precursor and the oxidant are introduced simultaneously [9].

ALD is a slower process due to the long precursor pulse and purge steps involved and the pulse and purge times increase with the size of the ALD reaction chamber, which affects the throughput. Also, ALD operates under vacuum which affects scaling of the process as it is expensive. ALD has numerous advantages including atomic layer control, uniformity, and conformal coating on complex structures while CVD offers faster deposition rates. Faster deposition rates and atmospheric conditions are preferable for the commercialization of ALD [11].

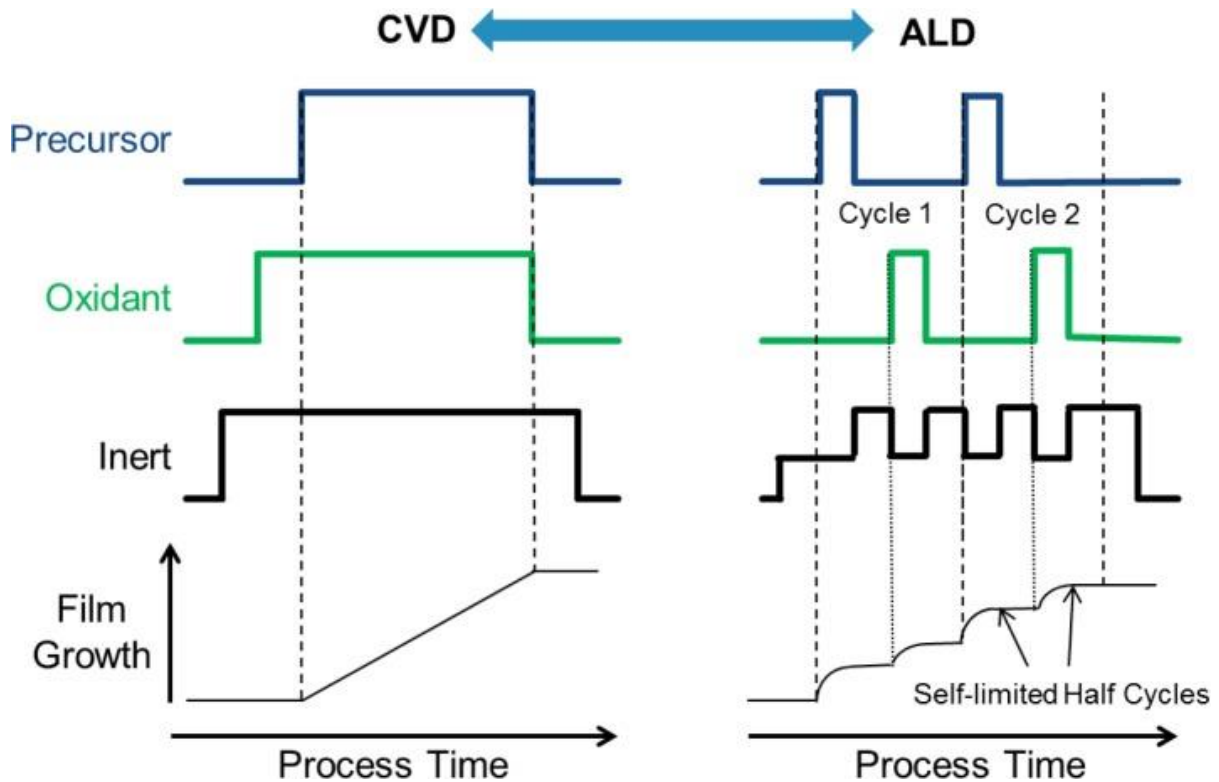


Figure 1.3 Precursor flow profile and expected film growth profile vs. process time for ALD and CVD process. Adapted with permission from [9]. Copyright 2014 MPDI.

1.3 Atmospheric-Pressure Spatial Atomic layer deposition (AP-SALD)

The throughput and scalability of traditional ALD methods are limited by the low deposition rate and need for a vacuum chamber, respectively. To overcome this, atmospheric-pressure spatial atomic layer deposition (AP-SALD) has emerged as a promising alternative in recent years. AP-SALD enables large-area, high-throughput, and cost-effective thin film deposition under ambient conditions.

As mentioned earlier, ALD relies on sequential, self-limiting surface reactions. As shown in Figure 1.4, the key difference between conventional ALD and spatial ALD is how the substrate is exposed to the precursors [12]. In conventional ALD, two precursors are introduced sequentially, allowed to react on the substrate surface to form a monolayer, with purge steps introduced in between to remove excess precursor and reactant by products. Therefore, the exposure of the substrate to the precursors is separated by time with a purge step in conventional ALD. In spatial ALD, the precursor exposure is separated in space by moving the substrate between different precursor zones. The substrate oscillates

between the zones, exposing it to the different precursor gases without a slow purge step, allowing for faster deposition rates, up to 2 orders of magnitude faster than conventional ALD [6,13].

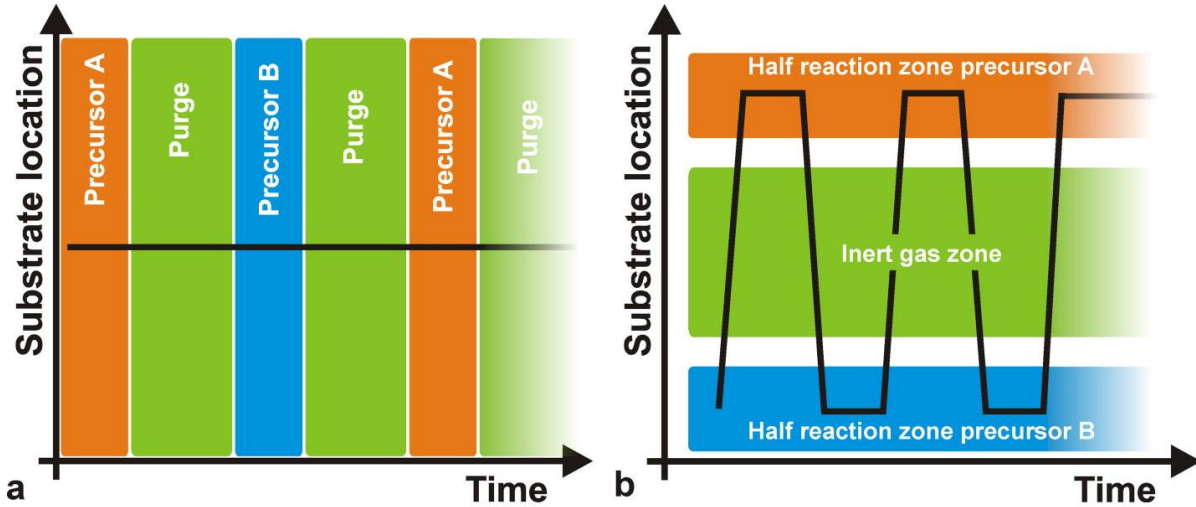


Figure 1.4 Process schematics for (a) conventional ALD and (b) spatial ALD. Adapted with permission from [12]. Copyright 2011 AIP Publishing LLC.

There are various spatial ALD techniques and AP-SALD has been gaining popularity recently due to its ability to operate under open-air conditions [1,13]. This eliminates the need for vacuum conditions, therefore making AP-SALD a faster, cheaper, and scalable alternative to ALD. In this method, also known as “close-proximity SALD” the substrate and the reactor head are separated by a small gap, typically less than 100 μm to prevent the precursors mixing. The precursor vapors generated by bubbling inert gas through liquid precursors and inert gas are fed separately to the reactor head [14]. Figure 1.5 (a) presents the schematic of an AP-SALD reactor head. The reactor head consists of parallel channels separated by a small distance to distribute the precursors into the respective reaction zones and separated by inert gas shielding in between. As the substrate passes through the first precursor zone, a monolayer is formed as the precursor molecules are adsorbed by the reactive sites on the substrate surface and the excess precursor atoms along with reaction by products are removed as it passes through the inert gas zone as shown in Figure 1.5 (b). As the substrate passes through the second precursor zone, a monolayer of the desired material is formed as the precursor reacts with the previous monolayer as shown in Figure 1.5 (c). The substrate is oscillated back and forth until the desired film thickness is obtained. Since the ALD cycles and reactions are reproduced, the films produced are of the same quality as ALD films; uniform, conformal and pin-hole free. Another advantage of AP-SALD depicted in

Figure 1.6 is that it can be switched between close-proximity mode and atmospheric-pressure spatial chemical vapor deposition (AP-SCVD) mode by adjusting the reactor head-substrate spacing. For larger spacings, intermixing of the precursors takes place leading to CVD-type reactions.

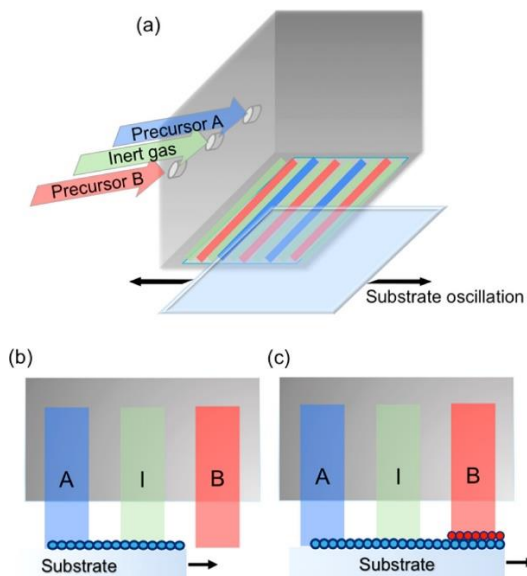


Figure 1.5 (a) AP-SALD reactor head with alternating precursor and nitrogen-shielding channels. (b) The substrate first enters precursor A zone, absorbing a monolayer of the precursor, and then through the inert gas shielding (I) to remove excess precursor and by-products. (c) The substrate then enters precursor B zone, which reacts with the previously formed monolayer to form a monolayer of the desired material. Reproduced with permission from [1]. Copyright 2016 American Chemical Society.

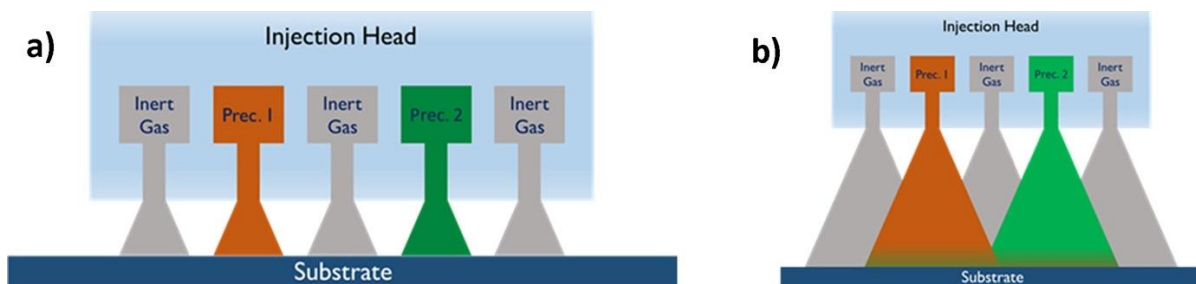


Figure 1.6 (a) SALD mode: close proximity between the substrate and reactor prevents precursor mixing. (b) CVD like deposition due to precursor mixing as the reactor (injection) head-substrate spacing increases. [13]

1.4 Lab scale AP-SALD system at the University of Waterloo

Canada's first lab-scale AP-SALD system built at the University of Waterloo under the supervision of Dr. Kevin Musselman is shown in Figure 1.7. The reactor head-substrate gap spacing can be adjusted manually with the help of micrometer adjustment knobs. The heated stage reciprocates along the linear actuator during deposition. Films up to 50 mm by 50 mm in area can be deposited using the system for research purposes. Figure 1.8 presents a schematic of the AP-SALD system; the precursors are bubbled and carried to the reactor head by nitrogen gas during the deposition. A recent publication used this system for uniform and conformal coating of polypropylene fabrics used as outer and inner layers of N95 respirators and cotton fabrics [15].

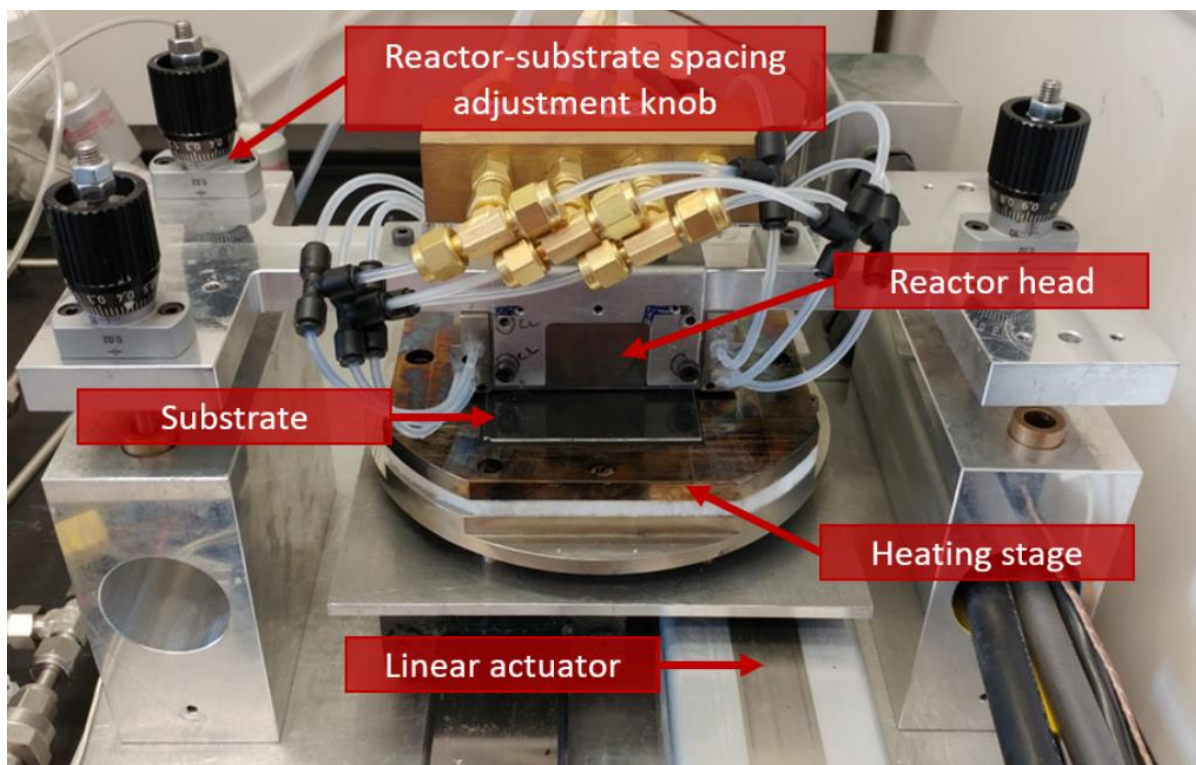


Figure 1.7 A photo of Dr. Kevin Musselman's lab-scale AP-SALD system at the University of Waterloo. Reproduced with permission from Chee Hau Teoh [16].

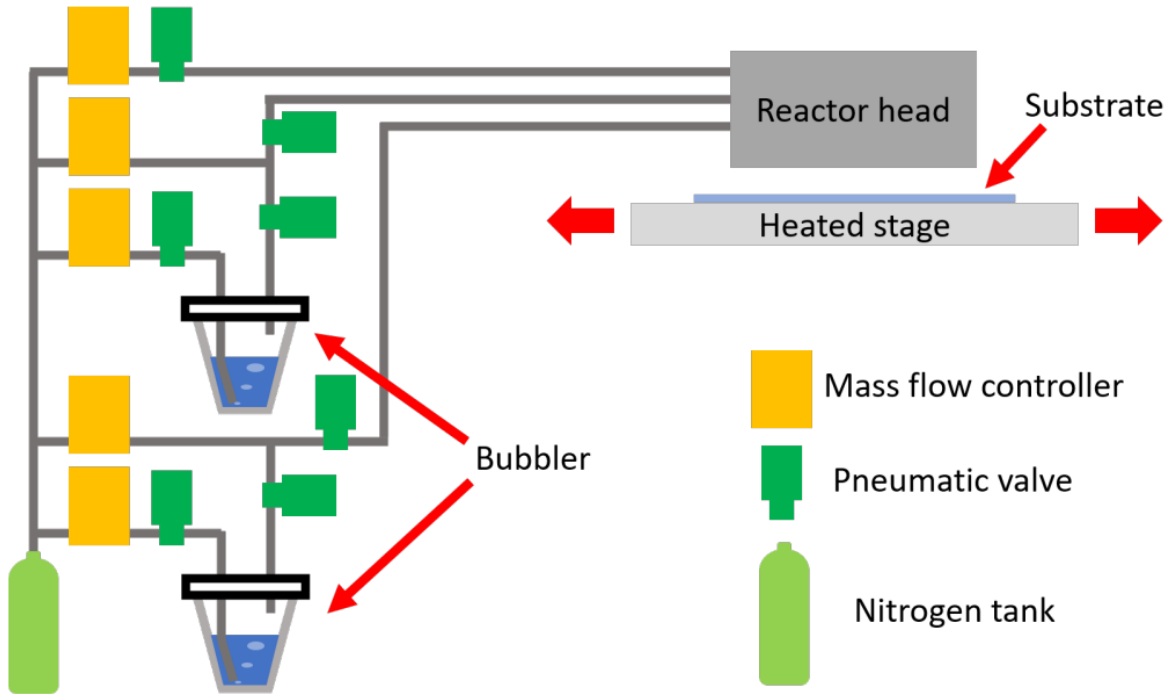


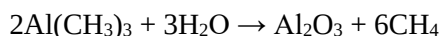
Figure 1.8 A schematic of Dr. Kevin Musselman’s lab-scale AP-SALD system at the University of Waterloo. Adapted with permission from Chee Hau Teoh [16].

1.5 Location of film deposition during ALD

A challenge for ALD and AP-SALD thin-film deposition techniques is controlling the location of film deposition. These techniques are coating processes that completely coat all the surface area that is exposed to the precursor gases, whereas in many applications, patterned films are desired.

Furthermore, these techniques are prone to unwanted powder formation. During ALD of alumina with trimethylaluminum (TMA) and water (H_2O) and the reactor chamber maintained at a temperature between 100°C to 200°C , physisorption of H_2O molecules at the cold spots along the chamber walls takes place and does not fully desorb after the purging step [17,18]. The H_2O desorbs from the walls gradually and the phenomenon is called virtual leak [18]. In the following TMA pulse, the desorbed H_2O reacts with TMA and leads to CVD-like continuous film growth on the substrate, while the remaining H_2O can lead to CVD and the formation of white alumina (Al_2O_3) powder on the walls of the reactor [17,18]. As powder accumulates on the cold region on the wall, it will increase the surface area that may adsorb H_2O from subsequent oxidant pulses, causing the virtual leaks due to H_2O physisorption to grow with time. [17,18].

On the other hand, in spatial ALD, when the precursors are ineffectively isolated, precursor mixing takes place and leads to formation of powder, which can deposit on the reactor head or end up in the thin film. Powder formation is caused due to the intermixing of the metal precursor and the oxidant (either from oxidant channel or from ambient atmosphere) in the reactor-substrate gap. For example, during alumina deposition using TMA and water, alumina powder is formed when the following reaction takes place in the reactor-substrate gap due to ineffective isolation of precursors [19]:



In addition, during thermal ALD at low temperatures, the partial pressure of water plays a crucial role. A higher partial pressure can lead to excess adsorption of water (due to its high coefficient of sticking), which can eventually lead to powder formation and affect film quality. Therefore, the temperature and partial pressure must be controlled carefully to deposit high-quality thin films and avoid powder formation. Figure 1.9 shows a non-homogenous alumina film deposited using spatial ALD at 75°C, with powder formation evident [20].

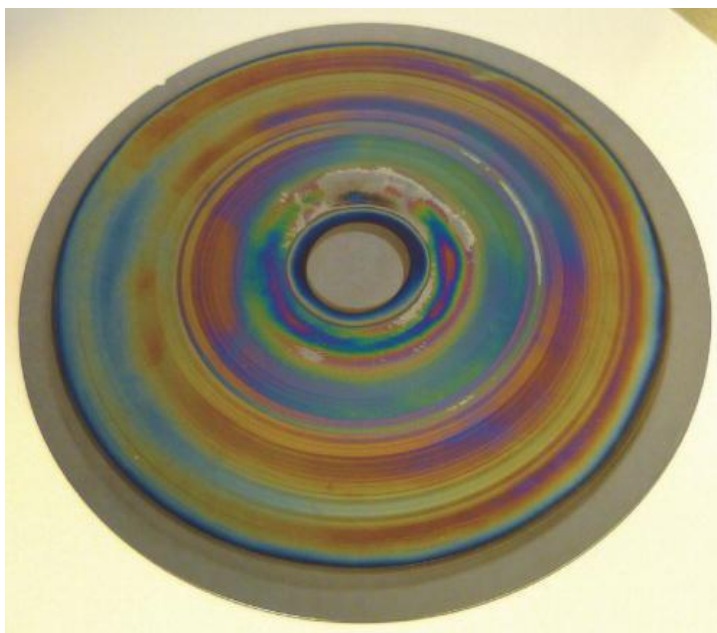


Figure 1.9 Al_2O_3 deposition at 75°C with TMA and water using a rotary spatial ALD reactor and water partial pressure optimized for a deposition temperature of 200°C. The powder formation was caused by CVD like reaction near the center due to multilayer adsorption of water. Reproduced with permission from [20]. Copyright 2011 AIP Publishing LLC.

1.6 Thesis objectives and overview

This thesis will focus on developing strategies to control the location of material deposition in AP-SALD systems. Objectives include:

- Reduce the amount of unwanted powder deposition on AP-SALD reactor heads
- Develop the ability to deposit patterned, high-throughput films by AP-SALD.

In Chapter 2, relevant literature will be reviewed, including film-patterning techniques, area-selective ALD that uses growth inhibitors to prevent film deposition, direct selective AP-SALD methods that direct the precursors onto specific areas of the substrates, and computational fluid dynamics modelling of AP-SALD reactors. In Chapter 3, coating AP-SALD reactor heads with chemical growth inhibitors will be investigated as a strategy to prevent powder formation of the reactor heads. In Chapter 4, a new direct selective AP-SALD reactor will be developed to enable high-throughput deposition of patterned films. Finally, in Chapter 5, key conclusions will be reviewed, and future work discussed.

Chapter 2

Literature Review

2.1 Patterning

In nanofabrication, patterning or nanopatterning refers to the process of creating specific nanoscale patterns or features. Nanopatterning techniques are essential for achieving precise control over the arrangement and placement of components at the nanoscale. It plays a significant role in modern science and technology, including semiconductors, biomedical, optics, and energy harvesting, etc. According to Moore's law, the number of transistors per chip on an integrated circuit (IC) doubles every two years, leading to a rapid increase in computing power and a decrease in cost per transistor [21]. In order to achieve this, the IC industry is driven by continuous downscaling of the components of an IC, so more transistors could be packed into a smaller space thereby increasing the performance and reducing the cost.

Conventional nanoscale patterning is a top-down or subtractive approach involving a series of deposition, lithography, and etch cycles as shown in Figure 2.1 (a) that are repeated to create a series of patterned layers [22].

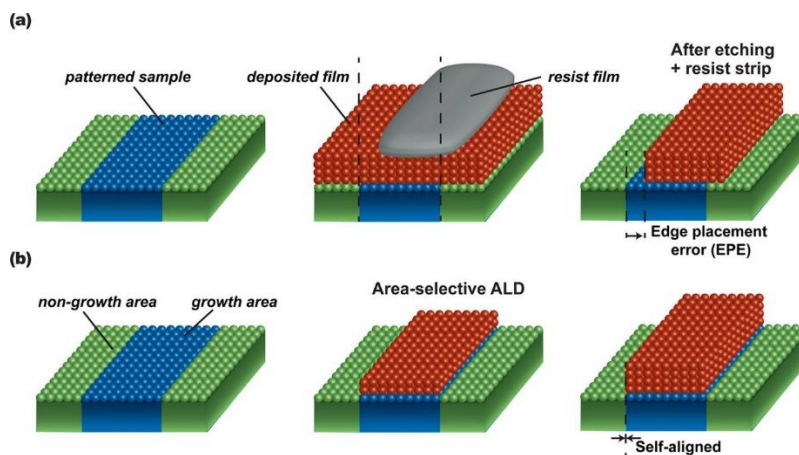


Figure 2.1 (a) Process flow for conventional patterning. A film is deposited (red) on the sample, which is coated with a photoresist (grey). The photoresist is then patterned using lithography, but it becomes challenging to align the resist along the desired pattern on the sample. Therefore, when the pattern is then transferred to the film by etching, the feature is misaligned. This results in so-called edge-placement errors (EPEs). (b) Schematic illustration of self-aligned fabrication. In area-selective ALD, the edge placement errors are eliminated since the material is deposited only in the desired regions. Reproduced with permission from [22]. Copyright 2022 American Chemical Society.

Photolithography is the widely used technique in industry for fabrication of microelectronics, whereas other techniques such as electron-beam lithography, soft lithography and imprint lithography are used for research purposes [23]. Photolithography is the key enabling technology that has played a central role in driving the continuous miniaturization of feature sizes and meeting the increasing complexity of semiconductor devices, leading to more powerful and efficient electronic devices. However, as the feature sizes become smaller and smaller, the complexity and the cost of the device fabrication increases. Fabrication of 2D multilayer or 3D nanostructures with smaller feature sizes can be challenging with photolithography as it can cause alignment issues with the structures relative to one another (edge placement errors) and involves a large number of lithography and etch steps [24]. The misalignments may result in open circuits or unwanted shorting of the circuit structure and energy loss in the system [25].

In order to overcome current challenges in nanofabrication, self-aligned fabrication processes using area-selective atomic layer deposition have proven an effective tool, as the material is deposited only on the desired regions of a substrate, thus eliminating misalignments and processing steps. Area-selective ALD is a bottom-up or additive nanofabrication technique, hence it provides better control and accuracy in defining nanoscale features, reduces fabrication complexities (number of lithography and etch steps), and improves device performance and yield. It is particularly advantageous when dealing with sub-5 nm scale features, where conventional patterning methods face significant challenges in maintaining precise alignment [26].

2.2 Area Selective Atomic Layer Deposition (AS-ALD)

Area-selective atomic layer deposition enables dimension control in the lateral direction along with atomic level thickness control and high conformality. Since ALD is based on sequential, self-limiting surface half reactions between precursor gas and the substrate surface, the deposition characteristics strongly depend on the surface chemistry of the substrate [27]. By tailoring surface chemistry and functionalization, localized regions can be created that preferentially prevent interaction with precursor molecules during the ALD process, leading to targeted deposition. As shown in Figure 2.1 (b), the regions on the substrate or the material where growth is desired is referred to as “growth area” while the regions of the substrate or materials where growth is undesired is referred to as “non growth area”. A major challenge with implementation of AS-ALD widely is the loss of selectivity after tens of cycles due to the change in characteristic of the non-growth area with exposure to ALD precursors [28,29].

2.2.1 Mechanism of Area-Selective ALD

There are various approaches to achieve area-selective ALD, as shown in Figure 2.2 [30]. The selective deposition of the film on the growth area depends on the principle of nucleation delay, i.e., during the ALD process, the thin film readily nucleates on specific regions on the substrate (referred to as growth area) whereas there is an inhibition or delay of the initial nucleation and growth of thin film on other areas (referred to as non-growth area) of the substrate. For example, metal oxides readily nucleate on -OH terminated surfaces, whereas nucleation begins after a short time on -H terminated surfaces [31]. In the inherent selective approach, the substrate comprises of different materials and deposition does not occur on some of the materials due to the surface properties of different materials and precursor preference to surface chemistry. As a result, selectivity is inherent in the specific ALD process. Since the inherent selectivity may last only for a few cycles, the surface is commonly pretreated to either activate or deactivate the growth area or the non-growth area, respectively [30]. Selective deposition takes place when parts of the substrate are deactivated and rendered inert by using photoresist or self-assembled monolayers or small-molecule inhibitors. These materials are known as growth inhibitors and this type of approach is known as area deactivation. In contrast to this, when the surface is activated with surface activators before deposition, for example, by depositing an ultrathin seed layer, the technique is called area activation. There are no subtractive steps such as etching involved with this type of deposition. Hence, the area activation approach is also known as direct-write ALD.

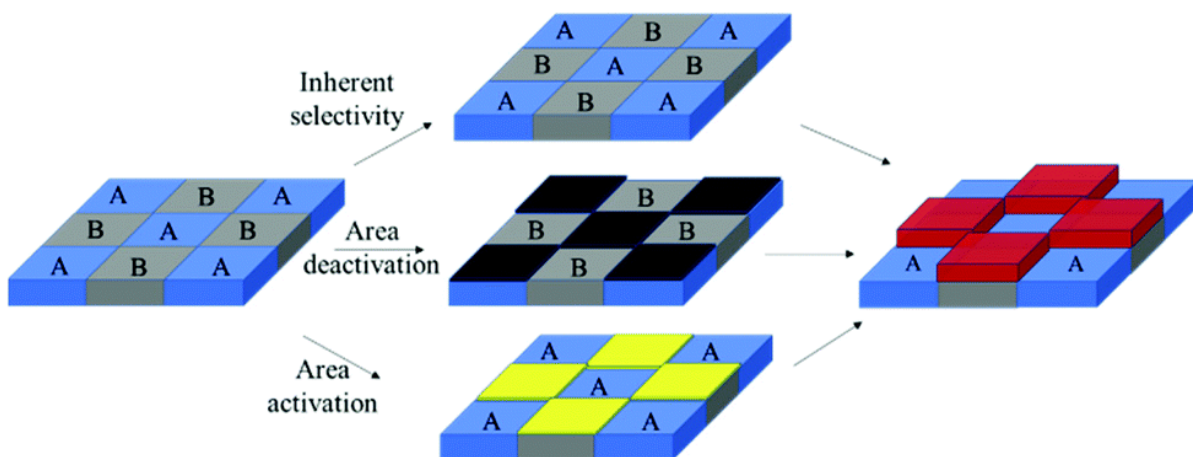


Figure 2.2 Mechanisms of various AS-ALD approaches (A and B are the non-growth area and growth area, respectively): inherent selectivity to the specific ALD process, area deactivation or area activation. Reproduced with permission from [30]. Copyright 2022 The Royal Society of Chemistry.

The nucleation behavior of an area-selective ALD process is shown in Figure 2.3 (a). The substrate consists of two chemically different surfaces: growth area and non-growth area. In the growth area, nucleation of the precursors begins almost immediately, resulting in film growth in a linear fashion with increasing number of ALD cycles. In contrast, film growth is delayed on the non-growth area for a number of ALD cycles before the nucleation begins, referred to as the nucleation delay. The number of cycles for which the film growth is observed only on the growth area and the thickness of the film on the non-growth area remains zero is known as the selectivity window. The selectivity S is given by

$$S = \frac{\theta_{ga} - \theta_{nga}}{\theta_{ga} + \theta_{nga}} \quad (1)$$

where θ_{ga} and θ_{nga} represent the thickness of the material after deposition on the growth and non-growth area, respectively [32]. As shown in Figure 2.3 (b), the selectivity of an area-selective ALD process is a function of film thickness [33].

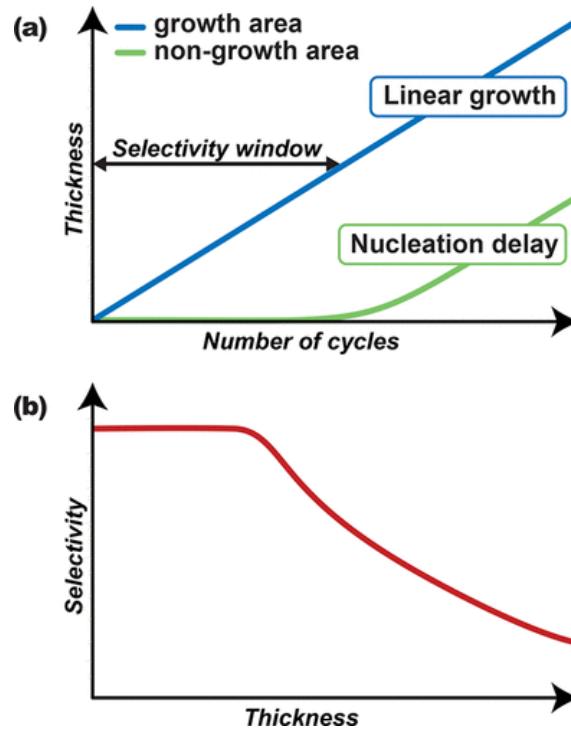


Figure 2.3 (a) Nucleation behavior on the growth and non-growth areas during area-selective ALD, resulting in linear growth and nucleation delay on the growth and non-growth area, respectively. The number of ALD cycles for which the growth is delayed on the non-growth area is referred to as the selectivity window. (b) Selectivity of area-selective ALD process as a function of film thickness calculated from equation (1). Reproduced with permission from [22]. Copyright 2022 American Chemical Society.

In this thesis, direct selective deposition of patterned films by AP-SALD will be investigated (Chapter 4), rather than chemical modification of the substrate. However, previously reported growth inhibitors will be employed in Chapter 3 to prevent powder formation on AP-SALD reactor heads. With this in mind, relevant growth inhibitors are reviewed in the next section.

2.2.2 Previously reported growth inhibitors for AS-ALD of Al_2O_3 and ZnO and their coating techniques

Area-selective ALD has been reported for the self-aligned fabrication of various materials such as noble metals and metal oxides. The most common method employed to achieve area-selective ALD is area deactivation by surface functionalization with growth inhibitors [34].

Our research group frequently deposits alumina (Al_2O_3) and zinc oxide (ZnO) thin films for a variety of applications, using trimethylaluminum (TMA), diethylzinc (DEZ) and deionized water ($\text{DI H}_2\text{O}$) as the precursors. Focus will therefore be placed on these materials. Growth inhibitors reported for alumina and zinc oxide deposition using these precursors are listed in Table 2.1 and 2.2, respectively.

Table 2.1 Previously reported growth inhibitors for AS-ALD of alumina

Type of growth inhibitor	Growth inhibitor used	Inhibitor deposition technique	Reference
Polymer	Poly(methyl methacrylate) (PMMA)	Spin coating	[43]
	Poly(vinyl pyrrolidone) (PVP)	Spin coating	[44]
Self-assembled monolayer	Dodecanethiol (DDT)	Vapor deposition	[38], [40]
	Octadecylphosphonic acid (ODPA)	Dip coating	[39], [41], [46]
	Octadecyltrichlorosilane (OTS or ODTS)	Dip coating	[48]
	1H,1H,2H,2H-perfluorodecanethiol (FDT)	Dip coating and vapor deposition	[48]

Table 2.2 Previously reported growth inhibitors for AS-ALD of zinc oxide

Type of growth inhibitor	Growth inhibitor used	Inhibitor deposition technique	Reference
Polymer	Poly(methyl methacrylate) (PMMA)	Spin coating	[35]
	ICP-polymerized fluorocarbon (CF _x)	Plasma polymerization	[36]
	Poly(vinylpyrrolidone) (PVP)	Spin coating	[37]
Self-assembled monolayer	Octadecylsilane (OS)	Dip coating	[35]
	Dodecanethiol (DDT)	Dip coating and vapor deposition	[38], [40], [42]
	Octadecylphosphonic acid (ODPA)	Dip coating	[39], [41], [47]
	Octadecyltrichlorosilane (OTS or ODTs)	Dip coating	[45]

The commonly used growth inhibitors include unreactive polymer blocking layers, self-assembled monolayers (SAMs), and small molecule inhibitors (SMIs) to deactivate the non-growth surface against reactions with the ALD precursor. Unfortunately, there is currently very limited knowledge on the growth inhibitor and substrate combinations for AS-ALD [34].

Polymer inhibitors are often applied by spin coating and then patterned by photolithography. The most widely established technique in literature is the use of SAMs to deactivate the reactive surface sites on the non-growth area by chemical modification [35,38-42,45-47,49]. In addition to the SAMs in Table 2.1, several other SAMs have been reported for selectively depositing other metals and metal oxides. The SAMs can be deposited either by wet chemistry or vapor deposition. SAMs consist of long-chain organic molecules that spontaneously order on surfaces through physical or chemical adsorption [49,50]. The molecules are amphiphilic and consists of three key parts as shown in Figure 2.4 [51].

They have a reactive head group that adheres to the substrate with high affinity, a long chain backbone that causes the SAM to be ordered due to the Van Der Waals force of interaction with neighbouring chains and a tail group that modifies the surface properties to prevent interaction with ALD precursors [50,51]. The process of SAM formation on a substrate is shown in Figure 2.5 [52]. The first step is the adsorption of the reactive head group with the substrate and the molecules lie on the surface in a flat and tilted manner. As the concentration of molecules on the surface increases, the molecular order on the surface changes due to the van der Waals forces resulting in formation of disordered clusters. Eventually, this process leads to the formation of a densely packed uniform and conformal layer of molecules on the surface, approximately normal to the surface.

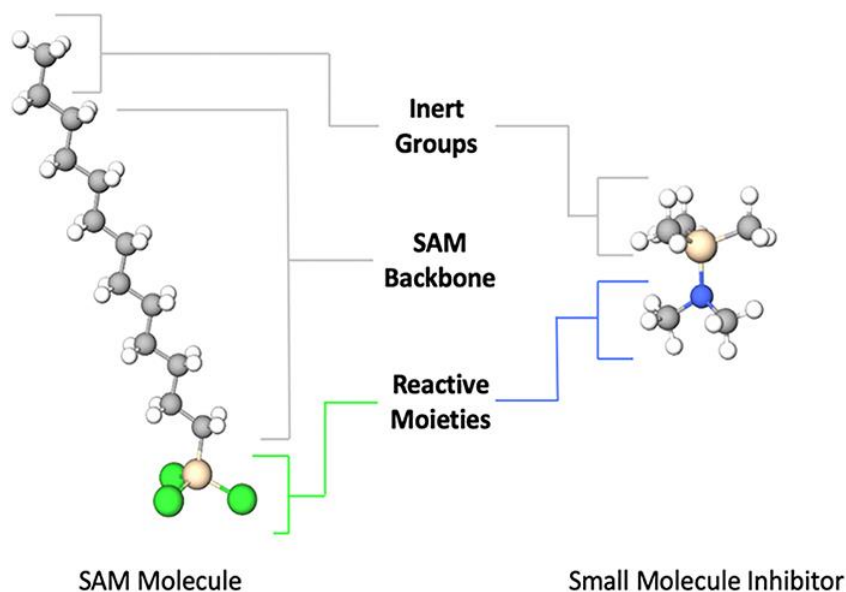


Figure 2.4 Difference between SAM and SMI. Reproduced with permission from [51]. Copyright 2021 AIP Publishing LLC

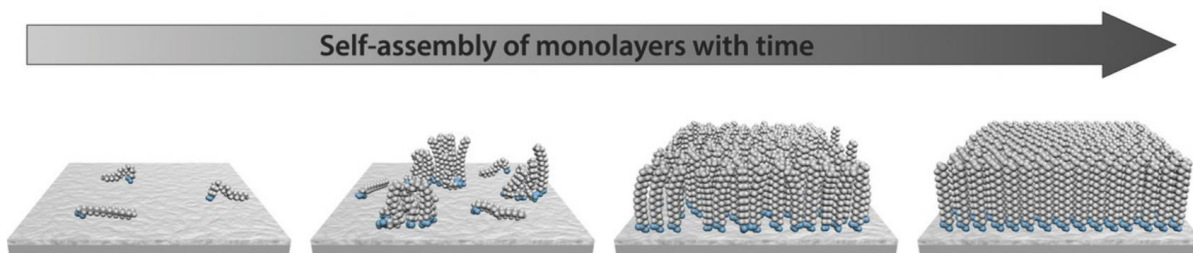


Figure 2.5 Graphical representation of the self-assembly process of SAM molecules into monolayers. [52]

Solution deposition of SAMs involves dip coating the specimen in the solution for more than 24 hours to form a monolayer [53]. The deposition time can be reduced by switching to vapor deposition of SAMs; thiol SAMs have drawn significant attention in AS-ALD of Al_2O_3 and ZnO on Cu substrates because of their much shorter deposition times and vaporizable processes [42]. It is noted that DDT vapor deposition for 30s facilitated AS-ALD of ZnO for 200 ALD cycles and regenerating the DDT at intervals of 150 cycles aided the selective deposition for up to 650 ALD cycles [54].

Recently, small molecules inhibitors (SMIs) were reported for AS-ALD, which are similar to SAMs. SMIs only have a reactive head group and functional tail group, as shown in Figure 2.4, and therefore, lack self-assembly. Small molecule inhibitors are highly volatile and can be deposited in the vapor phase by “ABC-type” cycles as shown in Figure 2.6 [55]. This method is similar to the SAM regeneration technique; however, in this type of AS-ALD, inhibitor molecules are dosed every cycle. Each cycle comprises of three doses: an inhibitor dose (A), the precursor dose (B) and the co-reactant exposure (C). In dose A, the inhibitor molecules are introduced which selectively adsorb on the non-growth area. When the precursor molecules are dosed during step B, it only adsorbs on the growth area while the small molecule inhibitors block precursor adsorption. Lastly, the co-reactant is dosed in step C. The co-reactant removes the ligands from the adsorbed precursor resulting in selective deposition on the growth surface. When plasma is used as the co-reactant, a part of the inhibitor is also removed [56]. By repeating the cycles, material can be selectively deposited on the growth area. The nucleation delay of SMIs are shorter when compared to SAMs, as shown in Figure 2.7 [51]. Since SMIs are deposited in the vapor phase and the nucleation begins earlier, they are not considered for this study. Different polymer- and SAM-based inhibitors will be studied in Chapter 3 to prevent powder formation on AP-SALD reactor heads.

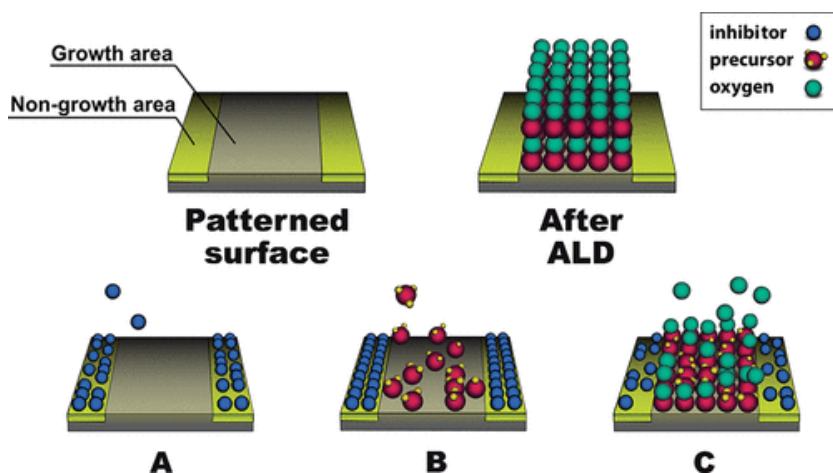


Figure 2.6 Ideal area-selective ALD process using growth inhibitor molecules and ABC-type ALD cycles. In this type of AS-ALD, inhibitor molecules are dosed during every cycle. Each cycle comprises of three doses: an inhibitor dose (A), the precursor dose (B) and the co-reactant exposure (C). In dose A, the inhibitor molecules are introduced which selectively adsorb on the non-growth area. When the precursor molecules are dosed during step B, it only adsorbs on the growth area while the small molecule inhibitors block precursor adsorption. Lastly, the co-reactant is dosed in step C. The co-reactant removes the ligands from the adsorbed precursor resulting in selective deposition on the growth surface. By repeating the cycles, material can be selectively deposited on the growth area. Reproduced with permission from [55]. Copyright 2022 American Chemical Society.

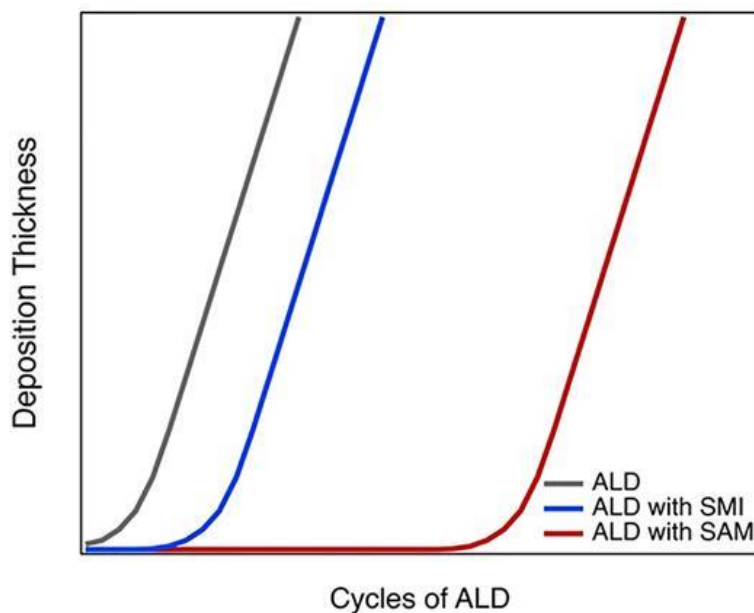


Figure 2.7 Generalized graph for film growth during ALD with and without SAMs and SMIs. Reproduced with permission from [51]. Copyright 2021 AIP Publishing LLC.

2.3 Direct selective film deposition by AP-SALD

Direct selective methods attempt to deposit patterned AP-SALD films without any patterning or chemical modification of the substrate. As in inkjet printing, patterned films are produced by physically directing the film deposition on specific areas of the substrate. Masse de la Huerta, C. *et al* demonstrated selective deposition of zinc oxide using an AP-SALD system [57]. The exhaust channels are used to remove excess precursor gases and reaction by products. Poor exhaust may lead to CVD type reactions even in “close proximity” SALD mode. However, during static depositions by placing the reactor on top of the substrate at close proximity, and by suppressing the movement of the substrate relative to the reactor head, localized intermixing of the gases can be achieved at reduced exhaust efficiency that enable selective deposition [57]. Figure 2.8 (a) and (b) shows the simulation and experimental results of a static AP-SALD deposition [57]. When the exhaust efficiency and the distance between the reactor and the substrate was maintained at 4.5% and 150 μm for the simulation, depositions in the CVD regime were observed at localized regions as shown in Figure 2.8 (a) [57]. The simulation result was verified by performing a deposition using a reactor head with an exhaust efficiency of 10.1% under static mode for 30 seconds; strips of zinc oxide were deposited on the substrate similar to the simulation results, as shown in Figure 2.8 (b) [57].

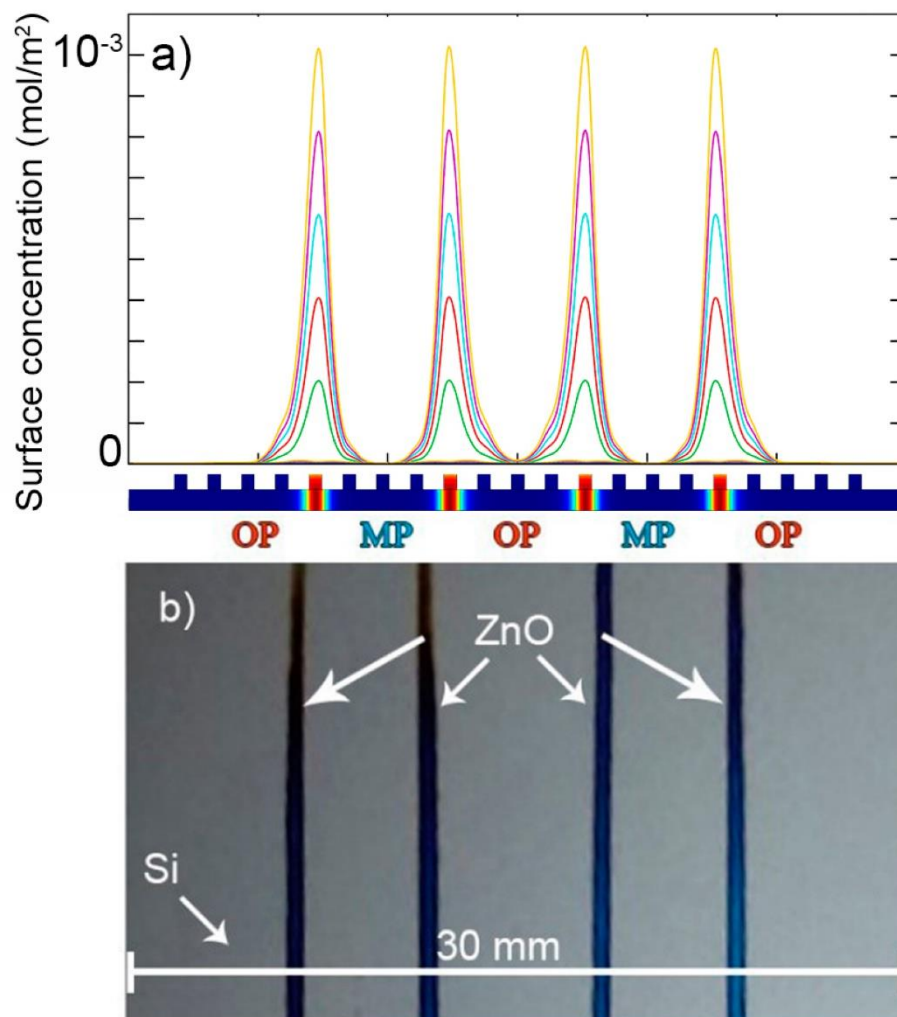


Figure 2.8 Simulation and experimental result of a static deposition using AP-SALD: (a) Simulation result with exhaust efficiency of 4.5% showing localized deposition in the CVD regime, and (b) pattern obtained after the static deposition of ZnO on a Si substrate using a reactor with an exhaust efficiency of 10.1 %. Reproduced with permission from [57]. Copyright 2018 MPDI.

Another example of selective deposition was demonstrated by the same research group using 3D printed custom reactors with concentric circular channels [58]. This led to the deposition of a circular pattern in the static spatial CVD mode as shown in Figure 2.9 (a) and the film thickness can be controlled by modifying the process parameters such as deposition time and flowrate. Another unique 3D-printed reactor referred to as a “SALD pen”, consisting of circular gas channels arranged in a concentric manner is shown in Figure 2.9 (b) [58]. The channels are positioned with the configuration: metallic precursor/exhaust/nitrogen/exhaust/oxidant precursor. This particular design can be used to deposit in

any direction, since the substrate will be exposed to precursors alternatively [60]. Figure 2.9 (c) shows the schematic of the setup to deposit in desired directions using the SALD pen by moving the substrate on a plate, and a circular ZnO pattern deposited by moving the plate is shown in Figure 2.9 (d) [58].

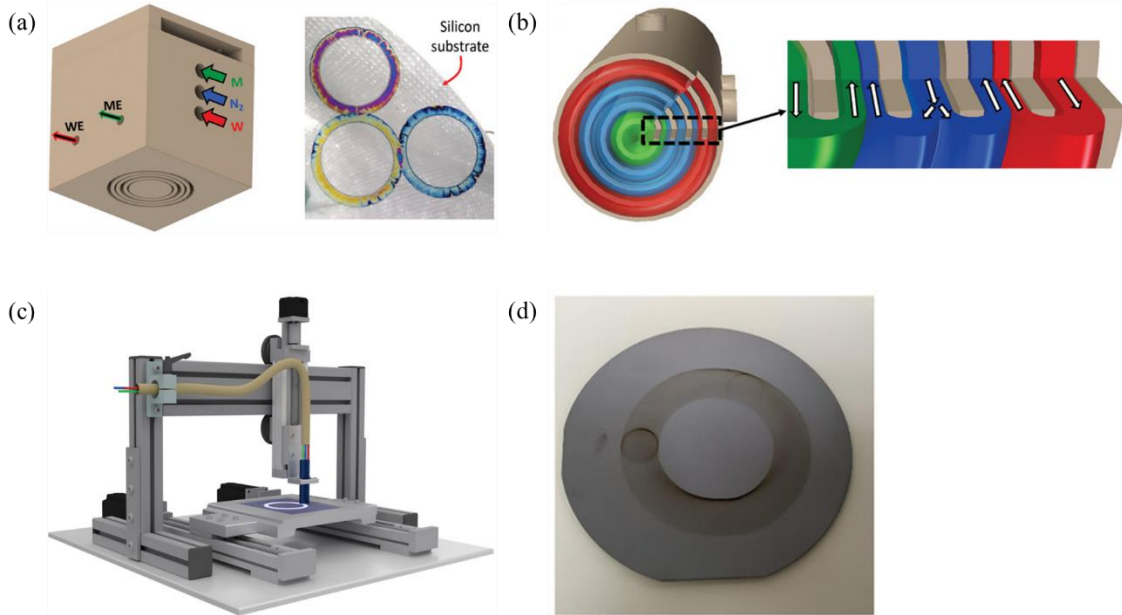


Figure 2.9 (a) Schematic of the reactor used to deposit circular ZnO patterns in the spatial CVD mode (left) and circular patterns of different thicknesses (right). (b) Reactor used in the SALD pen approach consisting of concentric circular gas outlets allowing freeform deposition. (c) Schematic of the setup to deposit a pattern using SALD pen. (d) Circular ZnO pattern deposited using the SALD pen. Reproduced with permission from [58]. Multiple images are combined together into a single image. Copyright 2020 Wiley.

The lateral resolution of the deposited patterns depends on the diameter of the exhaust channel adjacent to the metal precursor channel, as this determines the region of the substrate exposed to the metal precursor. Using the SALD pen, the lateral resolution achieved was in the range of a few millimeters. The resolution reported by ATLANT 3D Nanosystems with a similar design as the SALD pen (metallic precursor/exhaust/nitrogen/oxidant precursor/exhaust) was 400 μm and 150 μm using a standard nozzle and an advanced microfluidic nozzle respectively [59]. The resolution is much larger than what is achievable with the AS-ALD methods discussed in Section 2.2. Improvement in this resolution is warranted; however, even these modest resolutions are suitable for patterning requirements in some applications, e.g., cell patterning in perovskite solar modules.

2.4 CFD modelling of AP-SALD system and flow visualization

Computational fluid dynamics (CFD) is a branch of fluid mechanics that focuses on the numerical analysis and simulation of systems involving fluid flow, heat transfer and other related phenomena by means of computer simulations. CFD is a powerful tool utilized in a wide variety of industrial and non-industrial applications including aerospace, automotive, biomedical, electronics, energy, hydrology, HVAC, and metrology. CFD involves using computer simulations to solve the governing equations of fluid motion and heat transfer in order to predict how fluids behave in various situations.

The workflow of a CFD process consists of three major stages: pre-processing, solving, and post-processing. The pre-processing stage involves geometry creation, mesh generation, selection of physics and fluid properties and setting boundary conditions. The first step in a CFD process is the generation of the fluid flow region, i.e. the computational domain in 2D or 3D using suitable CAD tools. In meshing, the system is discretized into smaller elements. In the next step, the flow physics is selected which exactly represents the features of the flow phenomena being analysed. The boundary conditions are specified in the next step which include specifying the pressure, temperature, and velocity etc. Using the CFD solver, the computer solves the set of equations describing the physics of each cell or element in the mesh. This is an iterative process and continues until a converged solution is obtained. Finally, the post-processing stage involves analyzing and interpreting the results of the simulation.

Numerical simulation has proven to be a valuable tool in understanding and optimizing spatial ALD. It can play a vital role in the design of reactor heads and in adjusting the process parameters. As mentioned earlier, the type of deposition (either SALD type or SCVD type) depends on the reactor-substrate gap as precursor intermixing takes place as the gap is increased. In spatial ALD, the precursors are separated in space with nitrogen curtains in between. The precursors must be effectively isolated from each other and the ambient in order to achieve uniform and conformal films since precursor intermixing leads to CVD type reactions and affect film quality [60,61]. In addition to this, spatial ALD systems can be used to deposit thin films at a faster rate when compared to conventional ALD. The deposition rate not only depends on the design of the reactor head, but also on the rate at which the precursors react with the substrate [61]. To saturate all surface sites, the precursors should be in contact with the substrate for a sufficient time period. Therefore, uniform deposition depends upon the speed at which the substrate oscillates [61]. Moreover, the effective precursor isolation and reaction kinetics are temperature

dependent [61]. Therefore, the reaction rate and maximum substrate speed for a specific design of the reactor head varies depending on the temperature.

During the design stage, by modifying the various process parameters (such as reactor-substrate gap, flow rates, substrate speed, substrate temperature, pumping pressure etc.) and reactor-design parameters (such as channel width, wall thickness of the channels etc.) in the CFD model, the effect of different reactor designs and process parameter can be evaluated, and the optimal parameters can be obtained with the help of computer simulations.

Experiments are required to verify CFD simulation results. Observation of the properties of the deposited films provides some indirect evidence; however, direct visualization of the gas flows would facilitate verification of the CFD simulations and optimization of the process and reactor-design parameters. Various flow visualization techniques exist for visualizing liquids and gases [62]. The commonly used methods for flow visualization include visualization by addition of foreign materials and optical methods.

2.4.1 Flow visualization by addition of foreign materials

Since most fluids are transparent, it is difficult to directly visualize the motion of the fluid. The most common method to visualize fluid flow is achieved by adding a foreign material to the fluid in motion. These materials are also known as tracers. Commonly used tracers include dyes for visualizing liquids such as water and smoke for visualizing gases such as air [63]. Other tracers for gaseous flows include dust particles, oil droplets, etc., whereas particles, neutrally buoyant spheres, hydrogen bubbles, etc. are used for visualizing liquids. Flow visualization by this technique is still an indirect method as the fluid motion is estimated by visualizing the motion of the tracers. Therefore, the tracer must be selected such that the density of the tracer is similar to the fluid to avoid any errors due to a difference between the fluid and tracer motion.

2.4.2 Optical methods

Optical flow visualization techniques are often applied in the field of research involving compressible flows [64]. The three principal optical flow visualization techniques include shadowgraph, schlieren imaging and interferometry. These methods rely on the varying density of the fluid flow. The refractive index is a function of fluid density, so any variation in density affects the refractive index. The basic principle of this method is as follows: the properties of the light wave transmitted through the fluid

flow may be affected due to changes of the refractive index of the fluid. A light wave transmitted through the flow with refractive index changes is affected in two different ways; the light wave is deflected from its original direction of propagation, and the phase of the disturbed light wave is shifted with respect to the undisturbed light wave, as shown in Figure 2.10.

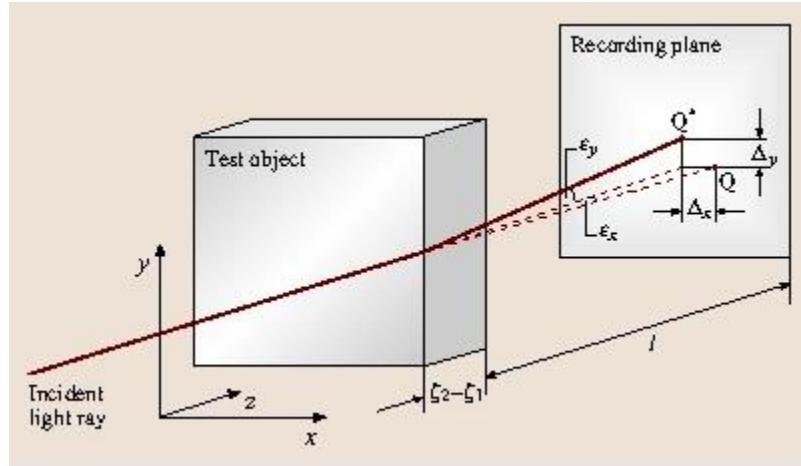


Figure 2.10 Deflection of light rays when passing through an inhomogeneous flow field. [63]. Reproduced with permission from [63]. Copyright 2007 Springer-Verlag.

An optical device records the uneven illumination caused by the phase change in the light beam as it passes through the compressible flow being studied. If a recording plane is placed behind the disturbing media, three quantities can be measured: the displacement of the disturbed ray (Δ_x and Δ_y), the angular deflection of the disturbed ray with respect to the undisturbed one (ϵ_x and ϵ_y) and the retardation of the deflected ray, i.e., the phase shift between both rays.

To-date, however, gas flows from AP-SALD reactor heads have not been successfully visualized. Initial trials will be conducted to test different flow visualization methods on an AP-SALD reactor. These are discussed briefly in Chapter 3, with details in Appendix C.

Chapter 3

Coating AP-SALD reactors with growth inhibitors to prevent powder formation

3.1 Overview

During depositions using the Functional Nanomaterial Group's AP-SALD systems, white powder formation is observed along the reactor head perimeter and the channels as shown in Figure 3.1. Powder formation is due to the undesired intermixing of precursor gases or due to the interaction of the metal precursor with oxidant from ambient and nucleation on the reactor head.

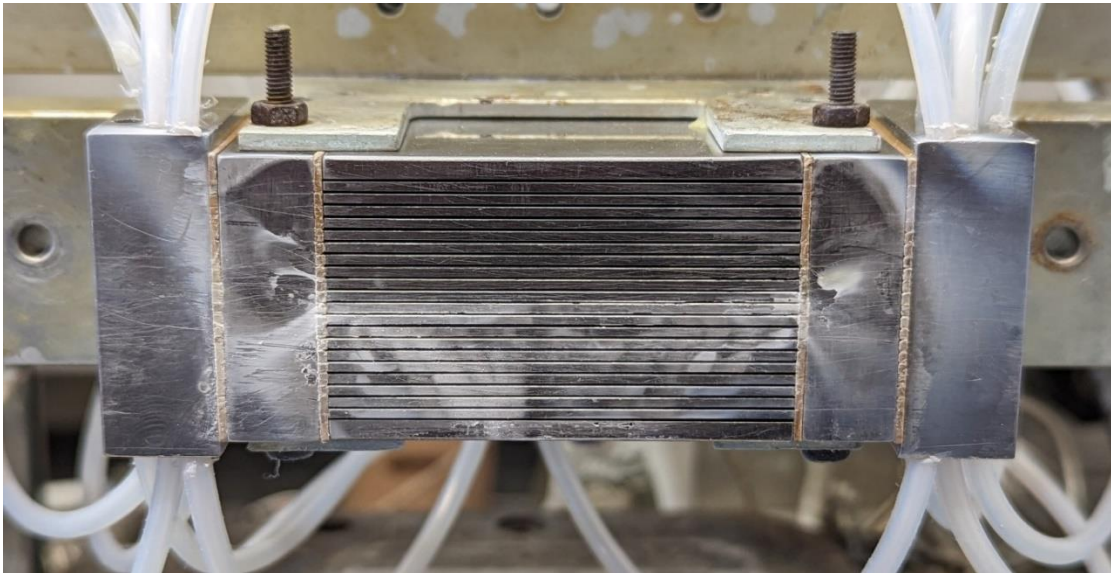


Figure 3.1 Powder formation around the perimeter of a reactor head after deposition.

The powder formation can have the following effects on the reactor head:

- **Reactor Contamination:** Continuous powder formation on the reactor head leads to the build-up of solid particles. This can obstruct gas flow paths, restrict precursor access to the substrate, and result in non-uniform deposition on the substrate.
- **Clogging and Pressure Drop:** Powders can accumulate along the exhaust channels, tubing, and the filters. This can cause clogging, leading to an increase in pressure drop. Increased pressure drop may negatively impact the excess precursor and by product removal, resulting in non-uniform deposition and reduced film quality.

- Precursor nucleation: Powder formation on the reactor head acts as nucleation sites for more precursors. This can intensify the powder formation issue with time.

Therefore, methods to minimize powder formation on the reactor head and effective removal of the powders become crucial. The aim of this chapter is to dip coat the reactor head with growth inhibitors reported previously in area-selective ALD processes to achieve selective deposition by preventing precursor nucleation. For this study, four commonly reported growth inhibitors for alumina and zinc oxide depositions are selected for dip coating the reactor head: these include PMMA, PVP, ODPA and DDT.

Most reactor heads used in the Functional Nanomaterials Group's AP-SALD systems are 3D printed using Formlabs Form 3 SLA 3D printer. The material used for 3D printing the reactors is High Temp Resin from Formlabs. It is a proprietary material made of liquid photopolymers to print parts for high temperature applications. Therefore, in order to determine if the inhibitors are compatible with 3D printed parts, samples of size 11.25 mm by 11.25 mm by 2 mm were 3D printed with the High Temp Resin, as shown in Figure 3.2 (a). Figure 3.2 (b) represents a schematic of the patterns on the top face of the sample; the topmost region (red) is referred to as the peak whereas the bottom region (green) is referred to as the base. The samples are dip coated in various growth inhibitor solutions for different time periods.

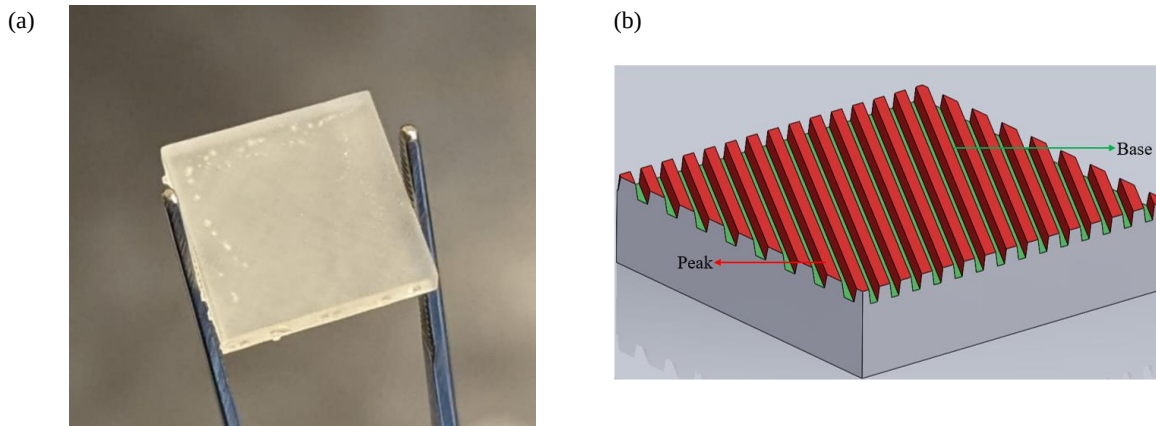


Figure 3.2 (a) 3D printed High Temp Resin sample of size 11.25 mm by 11.25 mm by 2 mm. (b) A schematic representation of a 3D printed sample using SLA 3D printer. The topmost region (shown in red) and the bottom region (shown in green) are referred to as the peak and base, respectively.

3.2 Experimental details

3.2.1 Deposition of Al_2O_3 on 3D printed samples coated with growth inhibitors

To prepare the PMMA solution, 10 g/L PMMA ($M_w = 350$ KDa) was dissolved in isopropanol-water mixture (20% water) at 55°C , and the solution was then cooled down to room temperature. Three 3D printed samples were immersed in the solution for up to 4 hours and 15 minutes. The PVP solution was prepared by dissolving 0.25 wt.% PVP K-30 in diacetone alcohol and three samples were immersed in the solution for up to 4 hours and 10 minutes. For coating the samples with ODPA SAMs, four samples were immersed in 1mM ODPA solution prepared using toluene and maintained at 50°C . Similarly, four samples were immersed in 10 mM DDT solution in pure ethanol maintained at $\sim 40^\circ\text{C}$ for up to 48 hours. After dip coating, all the samples were taken out from the solution, dried under nitrogen, and placed together on a sample holder as shown in Figure 3.3 (a). The position of each sample on the sample holder is shown in Figure 3.3 (b). Two 3D printed samples with no inhibitor coating were placed at the top right and the bottom left along with the other dip coated 3D printed samples. The different dip-coating times were based on previous reports of these inhibitors for alumina and zinc oxide, although it is recognized that different substrates were used in these previous reports.

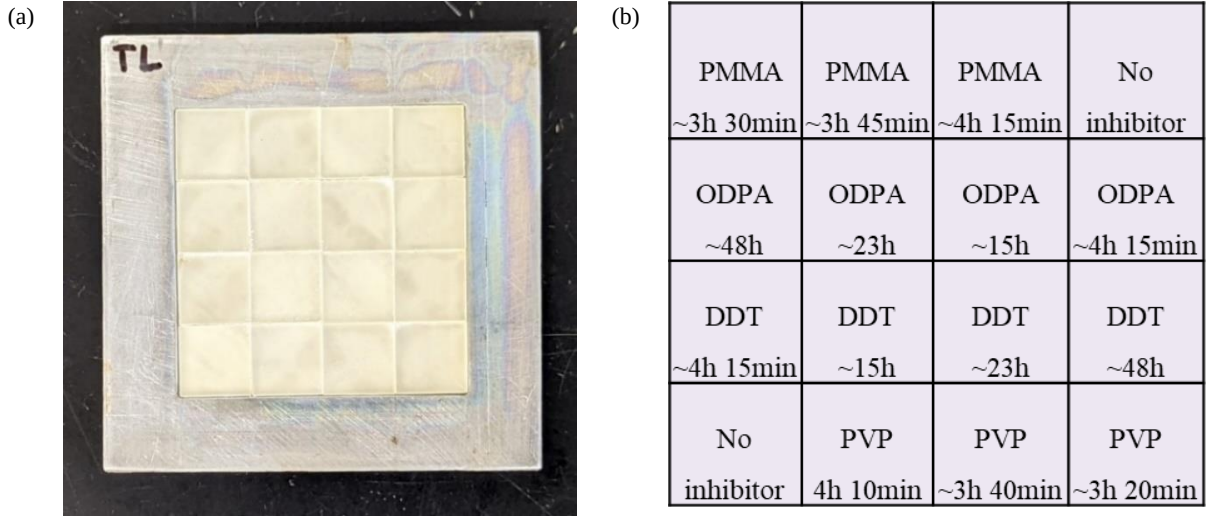


Figure 3.3 (a) Sample holder with 3D printed samples dip coated with growth inhibitors for different time periods and (b) position of each 3D printed sample on the sample holder for deposition of Al_2O_3 .

The deposition parameters for Al₂O₃ are listed in Table 3.1. The lab-scale AP-SALD system in the Functional Nanomaterials Group was used. For the deposition, nitrogen gas was bubbled through the trimethylaluminum precursor at 45 sccm and combined with a 105 sccm nitrogen carrier flow. Similarly, water was bubbled at 100 sccm and combined with a 150 sccm nitrogen carrier flow. A 750 sccm nitrogen curtain was used to separate the precursors and remove excess unreacted precursors or by-products. A reactor-substrate spacing of 300 µm was used. Two batches of samples were deposited: one at 100 °C and one at 70 °C. For the depositions, the stage was oscillated at a speed of 60 mm/s for 500 oscillations. The depositions were carried out in batches in order to maintain uniform deposition conditions on all the samples on the sample holder, as shown in Figure 3.4.

Table 3.1 Al₂O₃ AP-SALD conditions

Deposition temperature (°C) for 1st batch		100
Deposition temperature (°C) for 2nd batch		70
Number of oscillations		500
Oscillation speed (mm/s)		60
Flow per channel (sccm)		150
Gas flows for TMA	Metal bubbler (sccm)	45
	Metal carrier (sccm)	105
Gas flows for H₂O	Water bubbler (sccm)	100
	Water carrier (sccm)	150
N₂ rate (sccm)		750
Reactor height (µm)		300

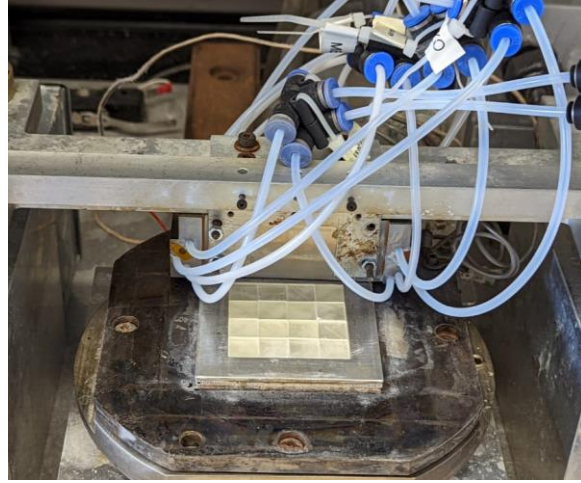


Figure 3.4 Sample holder along with all the samples placed on the heated stage for deposition.

3.2.2 Deposition of ZnO on 3D printed samples coated with growth inhibitors

The growth inhibitor solutions were prepared by the same procedure mentioned in section 3.2.1. However, the dip coating times were different for zinc oxide deposition, as compared to alumina deposition. The PMMA, PVP, ODPA and DDT samples were coated for up to 6 hours, 53 hours 30 minutes, 53 hours 30 minutes and 6 hours, respectively. After dip coating, all the samples were taken out from the solution, dried under nitrogen, and placed together on a sample holder at different positions as shown in Figure 3.5. Two 3D printed samples with no inhibitor coating were placed at the top left and the bottom right along with the dip coated 3D printed samples.

No inhibitor	PMMA ~5h 20min	PMMA ~5h 40min	PMMA ~6h
ODPA ~53h 30min	ODPA ~29h 30min	ODPA ~21h 30min	ODPA ~6h 30min
DDT ~6h 30min	DDT ~21h 30min	DDT ~29h 30min	DDT ~53h 30min
PVP ~6h	PVP ~5h 40min	PVP ~5h 20min	No inhibitor

Figure 3.5 Position of each 3D printed sample dip coated with growth inhibitors for different time periods on the sample holder for zinc oxide deposition.

For the deposition of ZnO, the lab-scale AP-SALD system was again used. Nitrogen gas was bubbled through a diethylzinc precursor at 23 sccm and combined with a 127 sccm nitrogen carrier flow. Water was bubbled at 45 sccm and combined with a 255 sccm nitrogen carrier flow. A 900 sccm nitrogen curtain was used to partially separate the precursors and remove excess unreacted precursors or by-products. A reactor-substrate spacing of 100 μm was used. Two batches of samples were deposited; one at 100 °C and one at 50 °C. For the depositions, the stage was oscillated at a speed of 60 mm/s for 500 oscillations. The deposition parameters for ZnO deposition are listed in Table 3.2.

Table 3.2 ZnO AP-SALD conditions

Deposition temperature (°C) for 1st batch		100
Deposition temperature (°C) for 2nd batch		50
Number of oscillations		500
Oscillation speed (mm/s)		15
Flow per channel (sccm)		150
Gas flows for DEZ	Metal bubbler (sccm)	23
	Metal carrier (sccm)	127
Gas flows for H₂O	Water bubbler (sccm)	45
	Water carrier (sccm)	255
N₂ rate (sccm)		900
Reactor height (μm)		100

3.2.3 Characterization methods

Initial characterization of the samples was performed using an OMAX trinocular lab compound microscope . The various magnification options were 4X, 10X, 40X and 100X, and all the images were obtained under 10X magnification. Energy-dispersive x-ray spectroscopy (EDX) was used to characterize the surface composition of the samples and was done either on a Zeiss LEO 1530 field emission scanning electron microscope (SEM) or Zeiss Ultra Plus field emission SEM.

3.3 Results and discussion

3.3.1 Deposition of Al_2O_3 at 100°C on 3D printed samples coated with growth inhibitors

For simplicity, the samples are classified into three groups: uncoated samples (no inhibitor or alumina present on the sample), Al_2O_3 -deposited samples without inhibitor and Al_2O_3 -deposited samples dip coated with inhibitor.

Initially, all the 3D printed samples were characterized using a bench-top optical microscope. The microscope images of an uncoated sample (on which no inhibitor or alumina is present) are shown in Figure 3.6 (a), (b) and (c). Figures 3.6 (a) and 3.6 (b) correspond to the top face of the sample focused on the peak and the base, respectively, while Figure 3.6 (c) corresponds to the bottom face of the sample.

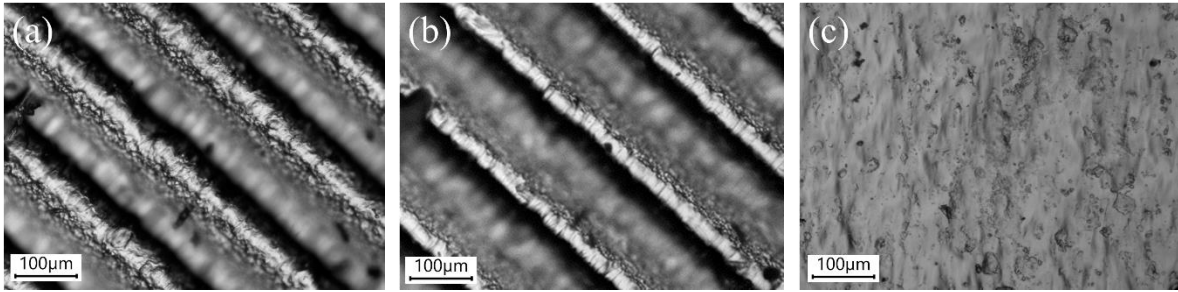


Figure 3.6 10X magnification images of the uncoated sample. (a) & (b) Focused on the peak and base on the top face of the uncoated sample, respectively, and (c) focused on the bottom face of the uncoated sample.

The microscope images of the Al_2O_3 -deposited sample without inhibitor (High Temp Resin/ Al_2O_3) are shown in Figure 3.7. When compared to the uncoated sample from Figure 3.6, a difference can be observed between the samples. On the Al_2O_3 -deposited samples without inhibitor, some cracks are visible in a surface coating, as shown in Figure 3.7 (a), 3.7 (b) and 3.7 (c). Al_2O_3 deposited on the top face of the sample without inhibitor is shown in Figure 3.7 (a) and 3.7 (b), focused on the peak and base, respectively. Figure 3.7 (c) corresponds to the Al_2O_3 deposited on the bottom face of the sample without inhibitor

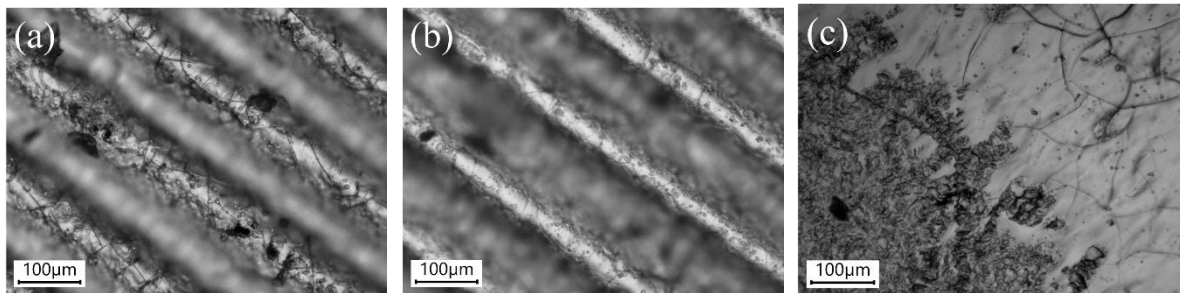


Figure 3.7 10X magnification images of the Al_2O_3 -deposited samples without inhibitor (High Temp Resin/ Al_2O_3). (a) & (b) Al_2O_3 deposited on the top face of the sample without inhibitor, focused on the peak and base respectively. (c) Al_2O_3 deposited on the bottom face of the sample without inhibitor.

Both the samples were then analyzed by EDX-SEM to confirm that the different surface morphology is due to the deposition of Al_2O_3 . The samples were coated with a thin layer of gold for performing EDX-SEM. From Figure 3.8, it is clear that Al_2O_3 is deposited on the sample without inhibitor. In the compositional analysis of the uncoated sample, only carbon and oxygen peaks are detected by EDX-SEM, as shown in Figure 3.8 (a), whereas aluminum peaks can be observed in the EDX-SEM spectrum of the Al_2O_3 -deposited samples without inhibitor in Figure 3.8 (b).

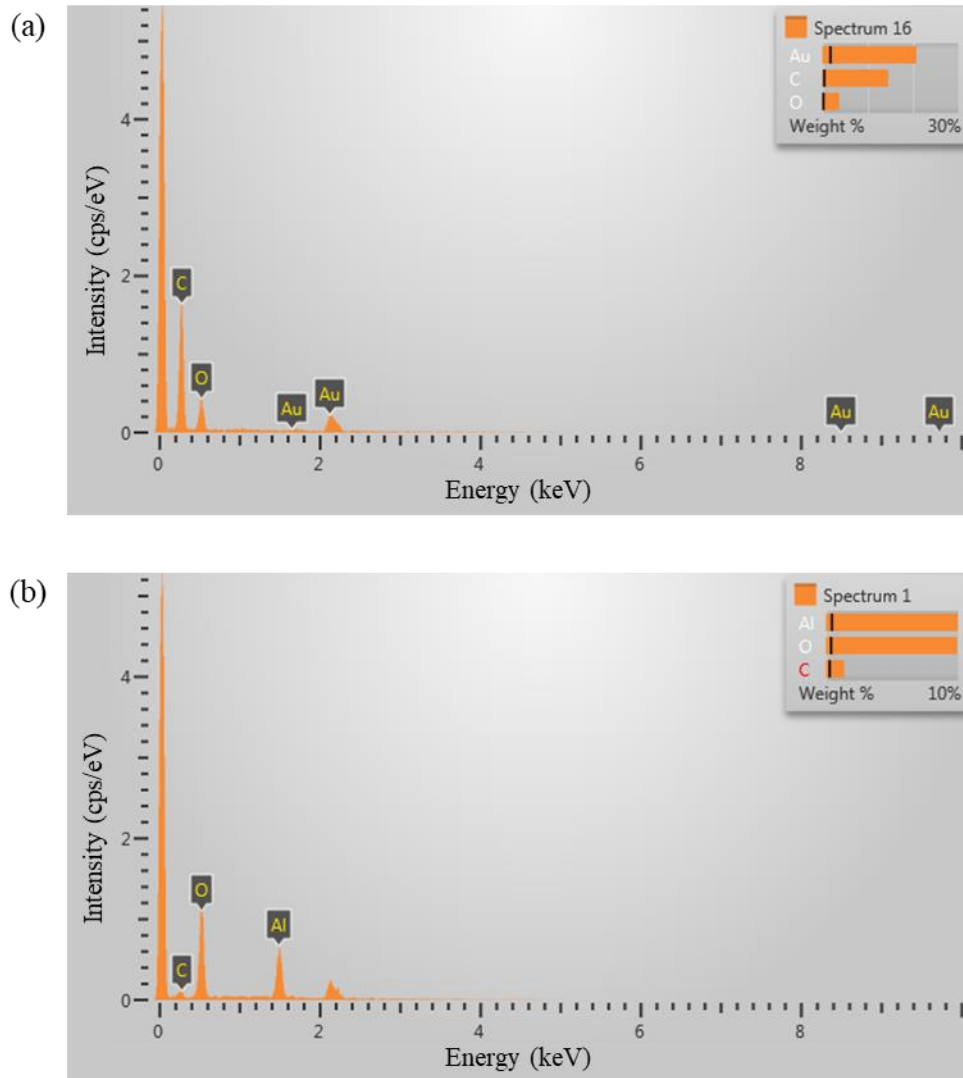


Figure 3.8 EDX spectra of the (a) uncoated samples and (b) Al₂O₃-deposited samples without inhibitor. Only carbon and oxygen peaks are present on the uncoated sample, whereas aluminum peaks are observed on the Al₂O₃-deposited samples without inhibitor. Note: Results generated from the system software using a Zeiss Leo 1530 FESEM coupled with an Oxford Instruments EDS detector.

The samples dip coated with growth inhibitors were also characterized using the optical microscope. Figures 3.9 and 3.10 show the microscope images of the Al₂O₃-deposited samples dip coated for different time periods with PMMA and DDT, respectively. From the images, it is clear that film formation and cracking occurred on all the samples.

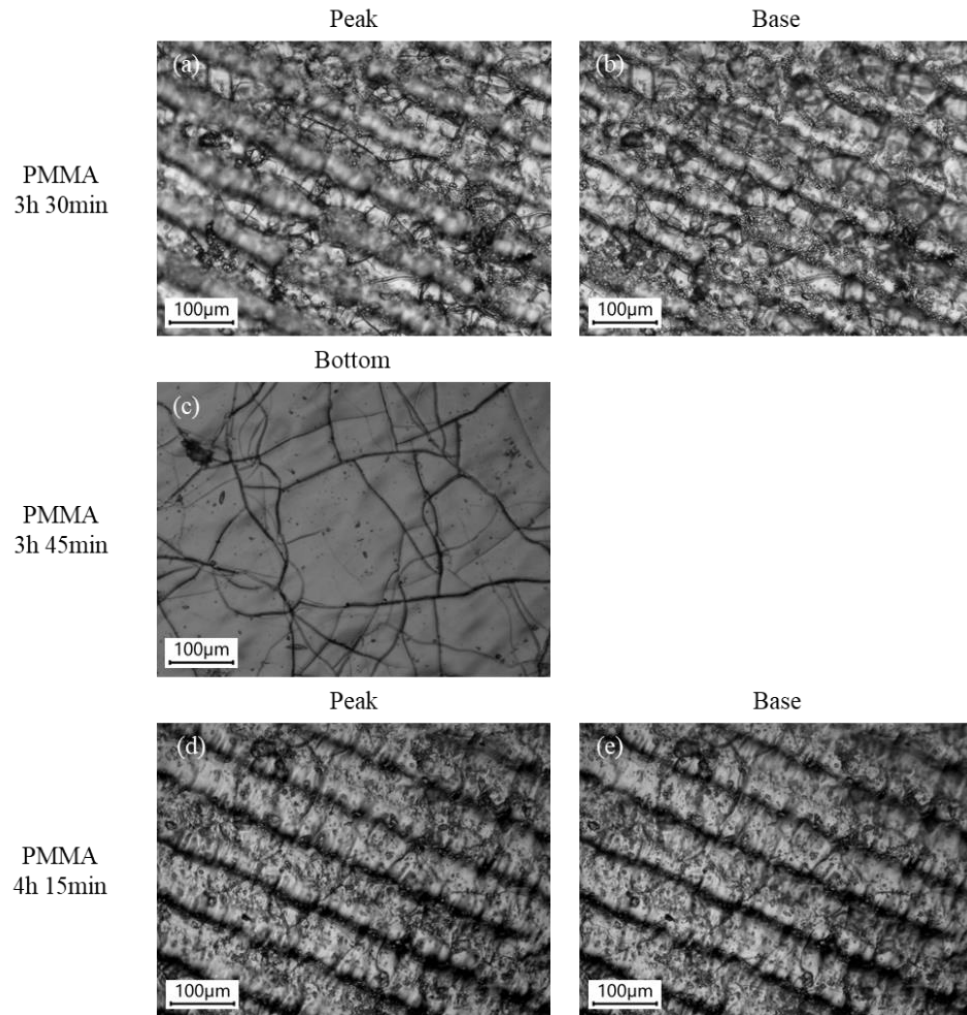


Figure 3.9 10X magnification images of the Al_2O_3 -deposited samples dip coated with PMMA for different time periods (High Temp Resin/PMMA/ Al_2O_3).

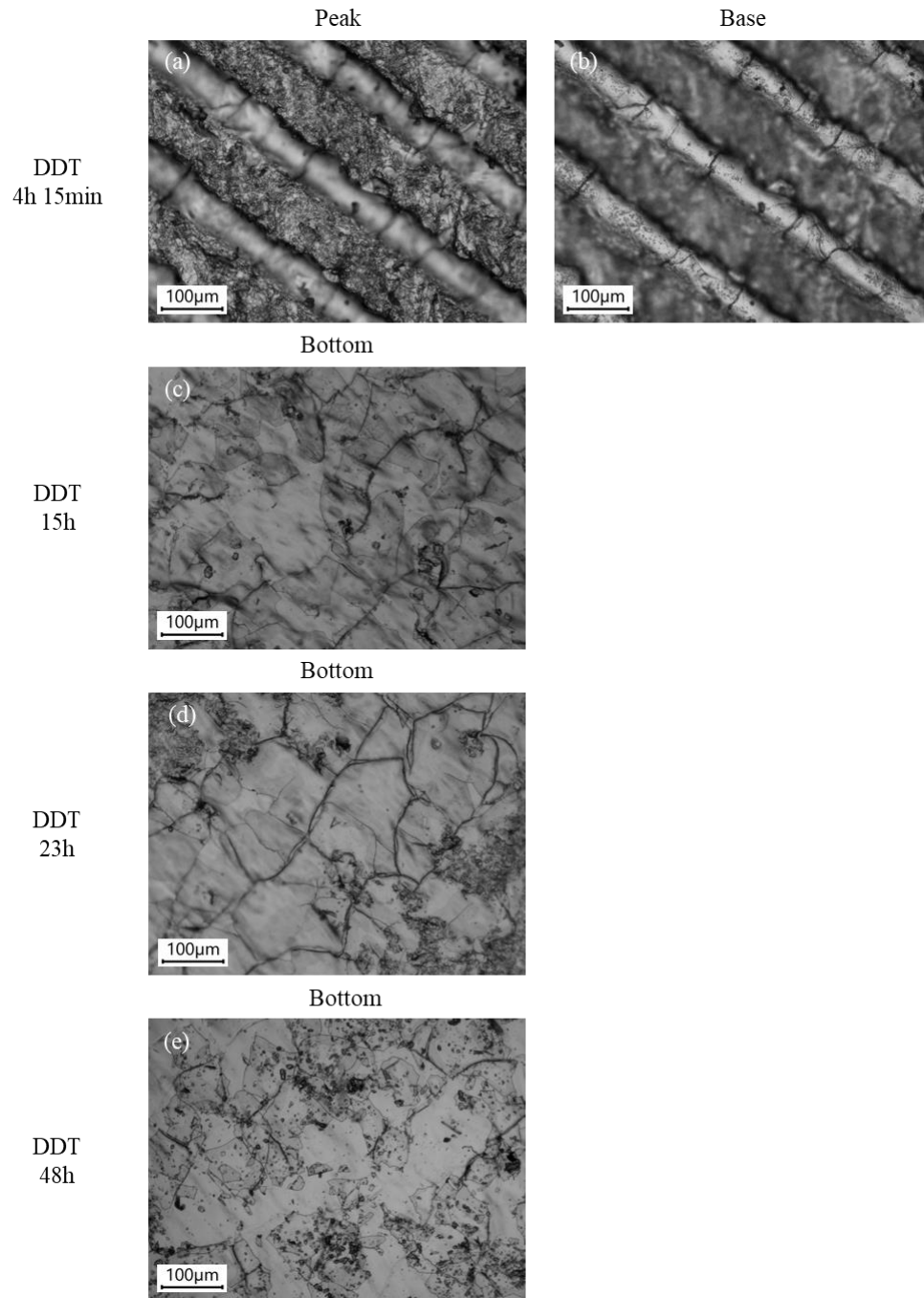


Figure 3.10 10X magnification images of the Al_2O_3 -deposited samples dip coated with DDT for different time periods (High Temp Resin/DDT/ Al_2O_3).

In contrast, when the samples dip coated with ODPA and PVP are observed under the microscope, no film formation and cracking was observed on some of the samples after deposition of Al_2O_3 . The microscope images of the Al_2O_3 -deposited samples dip coated with ODPA and PVP for different time periods are shown in Figure 3.11 and Figure 3.12, respectively. In the case of ODPA, the film formation and cracking was only observed on the sample dip coated for the shortest time period of 4 hours and 15 minutes, as shown in Figure 3.11 (a). The samples in Figure 3.11 (b)-(g) that were dip coated in ODPA for 15 h or longer appear unchanged from the uncoated samples in Figure 3.6. In Figure 3.12, no film and crack formation was observed on any of the samples dip coated in the PVP solution for periods ranging from 3 h 20 min to 4 h 10 min.

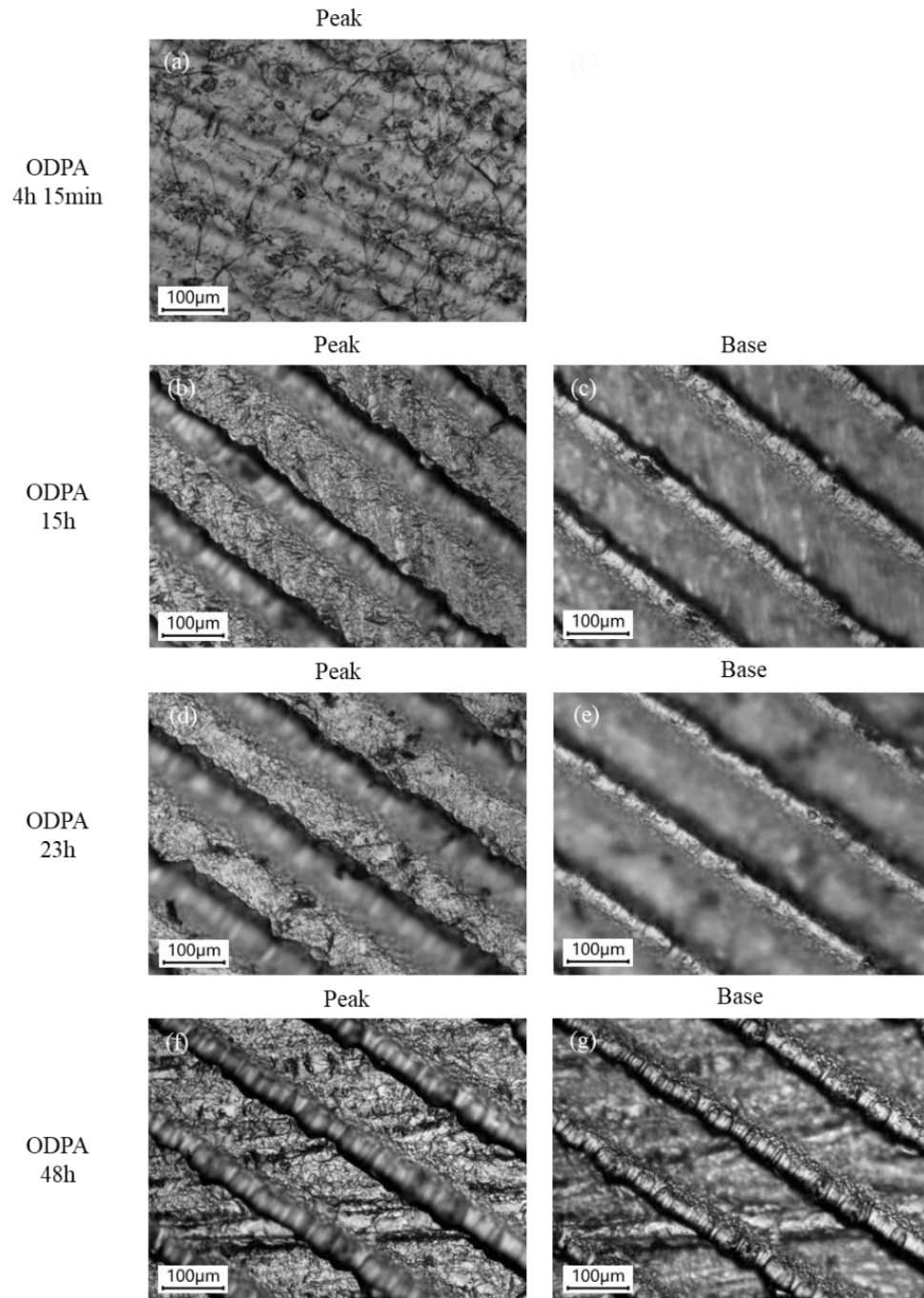


Figure 3.11 10X magnification images of the Al_2O_3 -deposited samples dip coated with ODPA for different time periods (High Temp Resin/ODPA/ Al_2O_3).

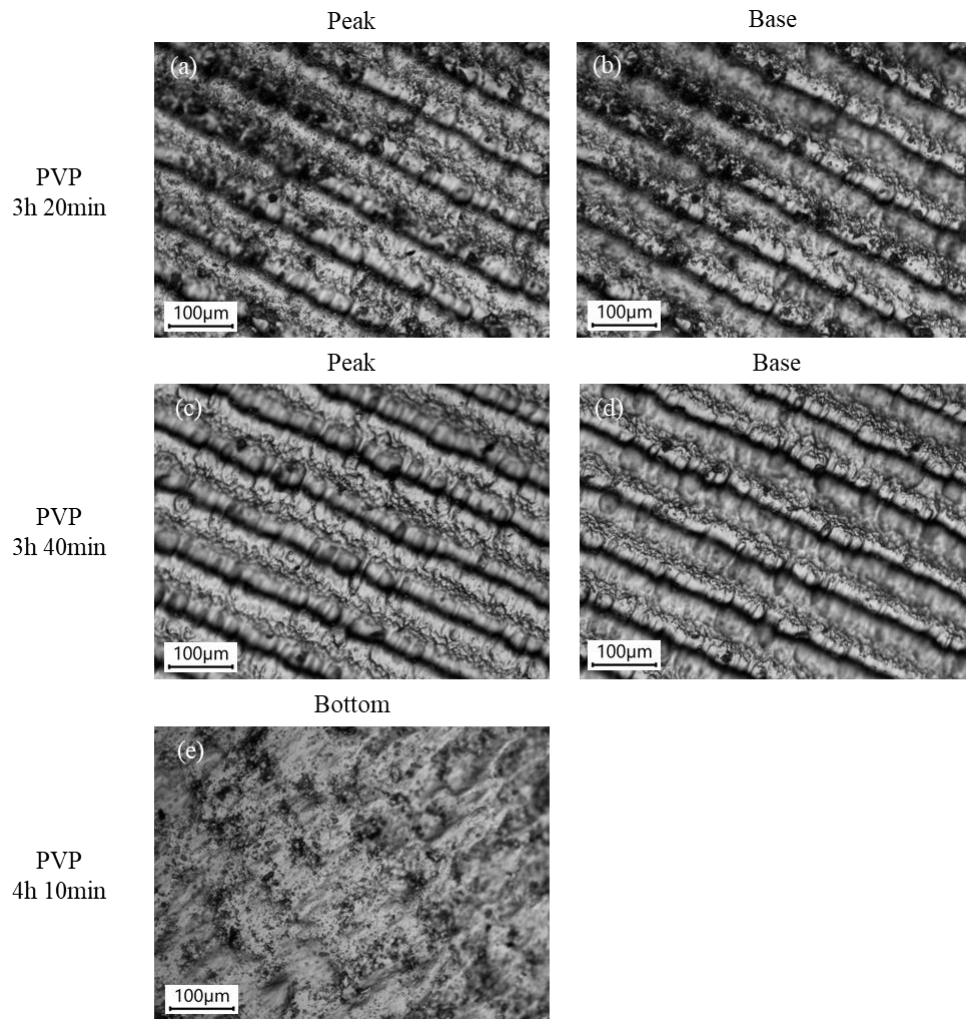


Figure 3.12 10X magnification images of the Al_2O_3 -deposited samples dip coated with PVP for different time periods (High Temp Resin/PVP/ Al_2O_3).

To confirm that the PVP and ODPa growth inhibitors prevented the formation of Al_2O_3 on the High Temp Resin samples, Al_2O_3 -deposited samples dip coated with ODPa and PVP for 48 hours and 4h 10min, respectively, were analyzed by EDX, as shown in Figure 3.13 (a) and Figure 3.13 (b). It can be observed that no aluminum peaks are present for either of the samples.

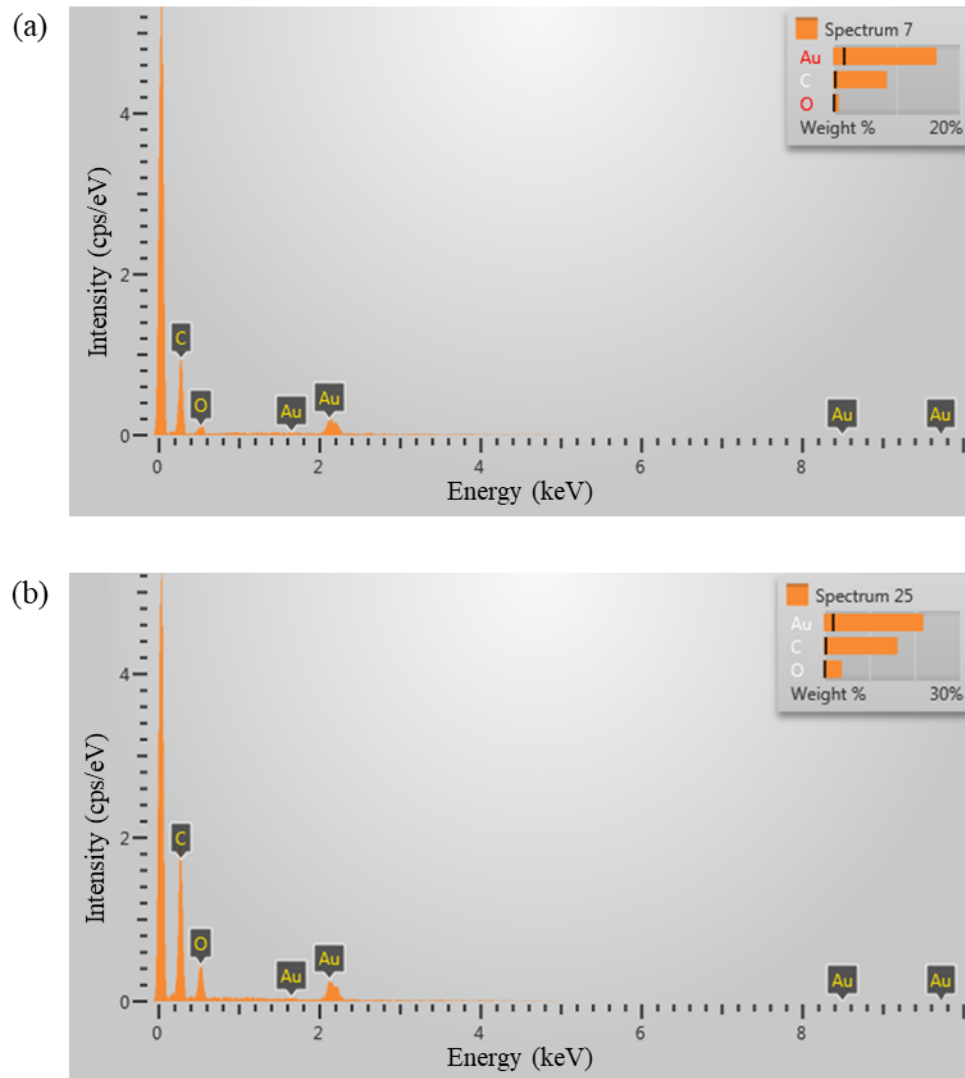


Figure 3.13 EDX-SEM spectra of the Al_2O_3 -deposited samples coated with (a) ODPA for 48h and (b) PVP for 4h 10min. No aluminum peaks are observed. Note: Results generated from the system software using a Zeiss Leo 1530 FESEM coupled with an Oxford Instruments EDS detector.

3.3.2 Deposition of Al_2O_3 at 70°C on 3D printed samples coated with growth inhibitors

The samples on which Al_2O_3 was deposited at 70°C were also characterized using optical microscopy. A microscope image of the Al_2O_3 -deposited sample without inhibitor (High Temp Resin/ Al_2O_3) is shown in Figure 3.14. As seen for the deposition condition of 100°C, film formation and cracking are observed after the deposition of Al_2O_3 .

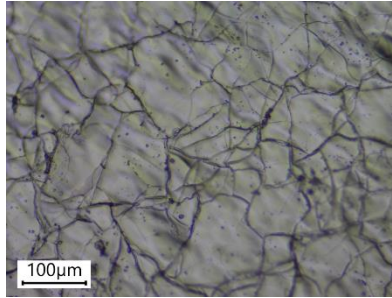


Figure 3.14 10X magnification image of the bottom face of the Al_2O_3 -deposited sample without inhibitor (High Temp Resin/ Al_2O_3).

The microscope images of the Al_2O_3 -deposited samples dip coated with PMMA are shown in Figure 3.15. It can be noted from Figure 3.15 (a)-(c) that film formation is observed on all samples dip coated with PMMA after the deposition of Al_2O_3 .

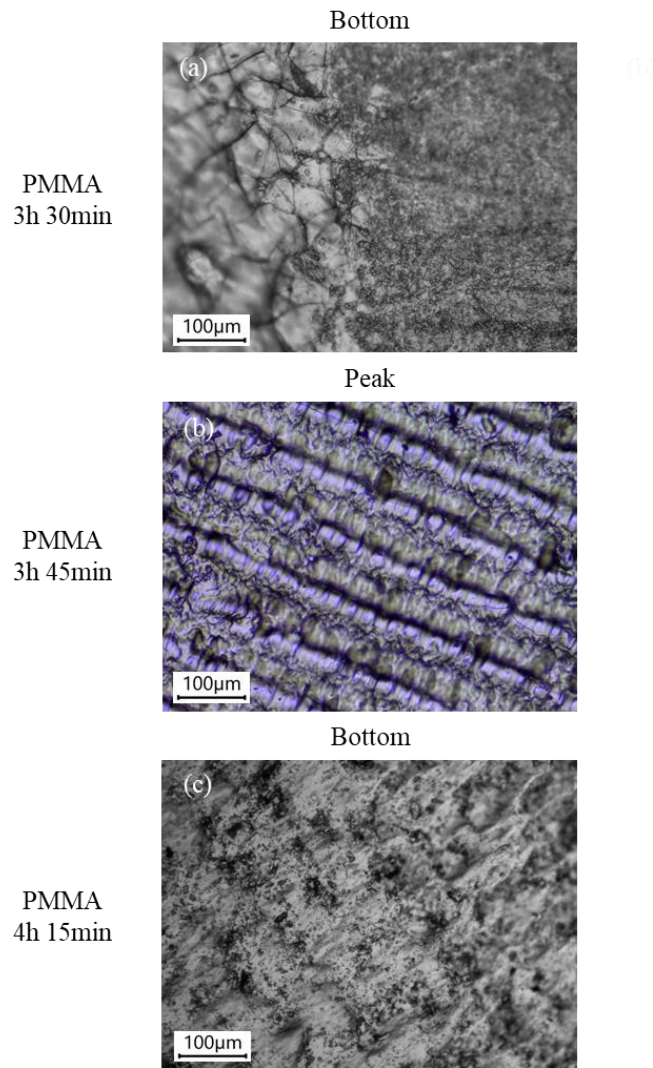


Figure 3.15 10X magnification images of the Al₂O₃-deposited samples dip coated with PMMA for different time periods (High Temp Resin/PMMA/Al₂O₃).

In contrast, in the case of ODPA, film formation and cracking are only observed on the samples coated with ODPA for the shortest time period of 4h 15min, as shown in Figure 3.16 (a), similar to deposition of Al₂O₃ at 100°C.

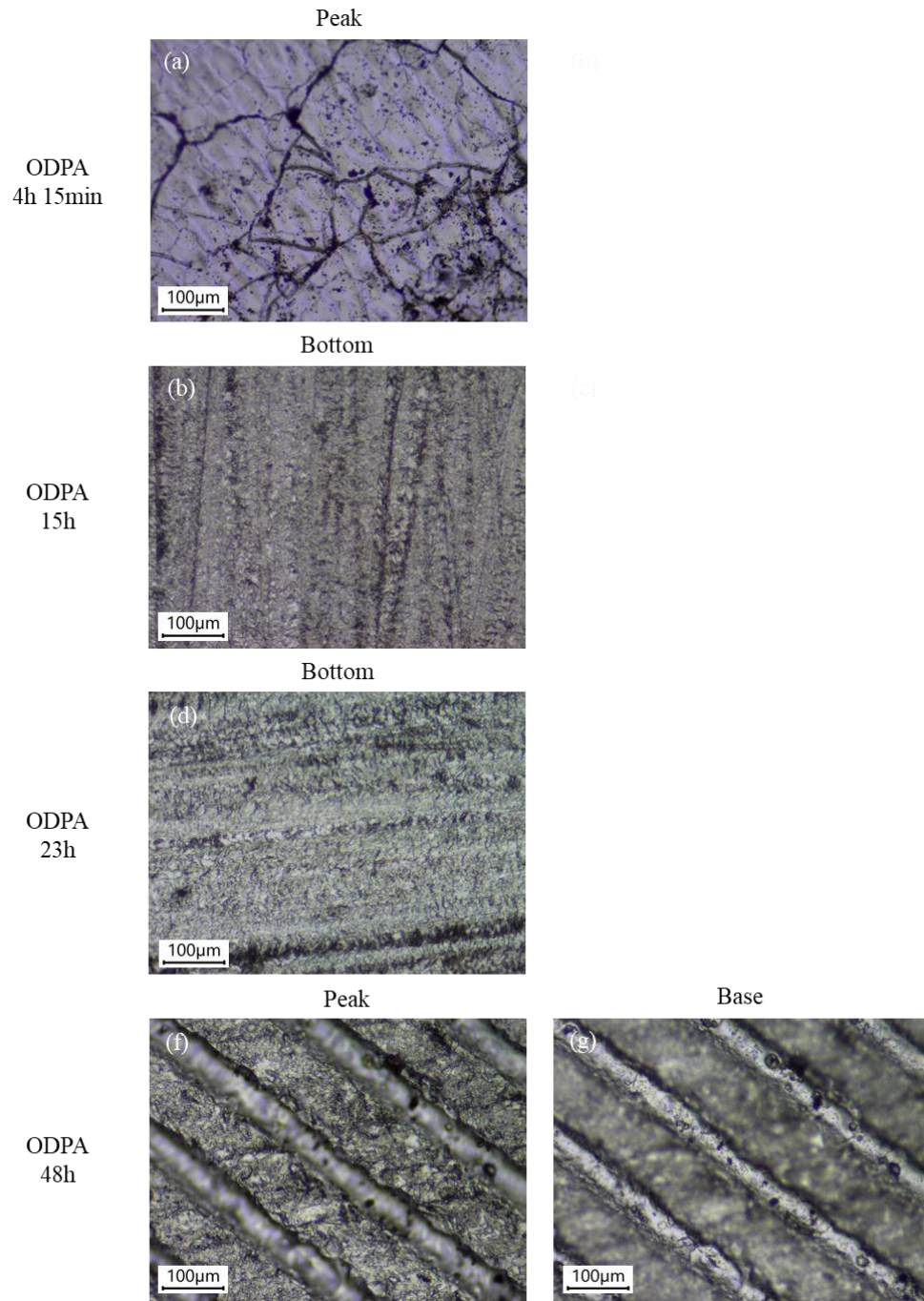


Figure 3.16 10X magnification images of the Al_2O_3 -deposited samples dip coated with ODPA for different time periods (High Temp Resin/ODPA/ Al_2O_3).

After the deposition of Al_2O_3 on the samples coated with DDT, film formation and cracking was only observed on the samples coated for 4h 15min and 23h, as shown in Figure 3.17 (a) and 3,17 (d), whereas film formation was not clearly observed on the samples dip coated for 15h and 48h. Hence these results for DDT are inconsistent, i.e., film formation was observed on the sample coated for 23h while no film formation was observed on the sample coated for 15h. Since DDT desorbs or decomposes at around 110 °C, DDT only prevented film growth at 70 °C . Also, further testing is needed to determine the efficiency of DDT against Al_2O_3 formation after dip coating for 15h, since there is a possibility of formation of multilayers of SAM on the surface of the sample due to undesired conditions.

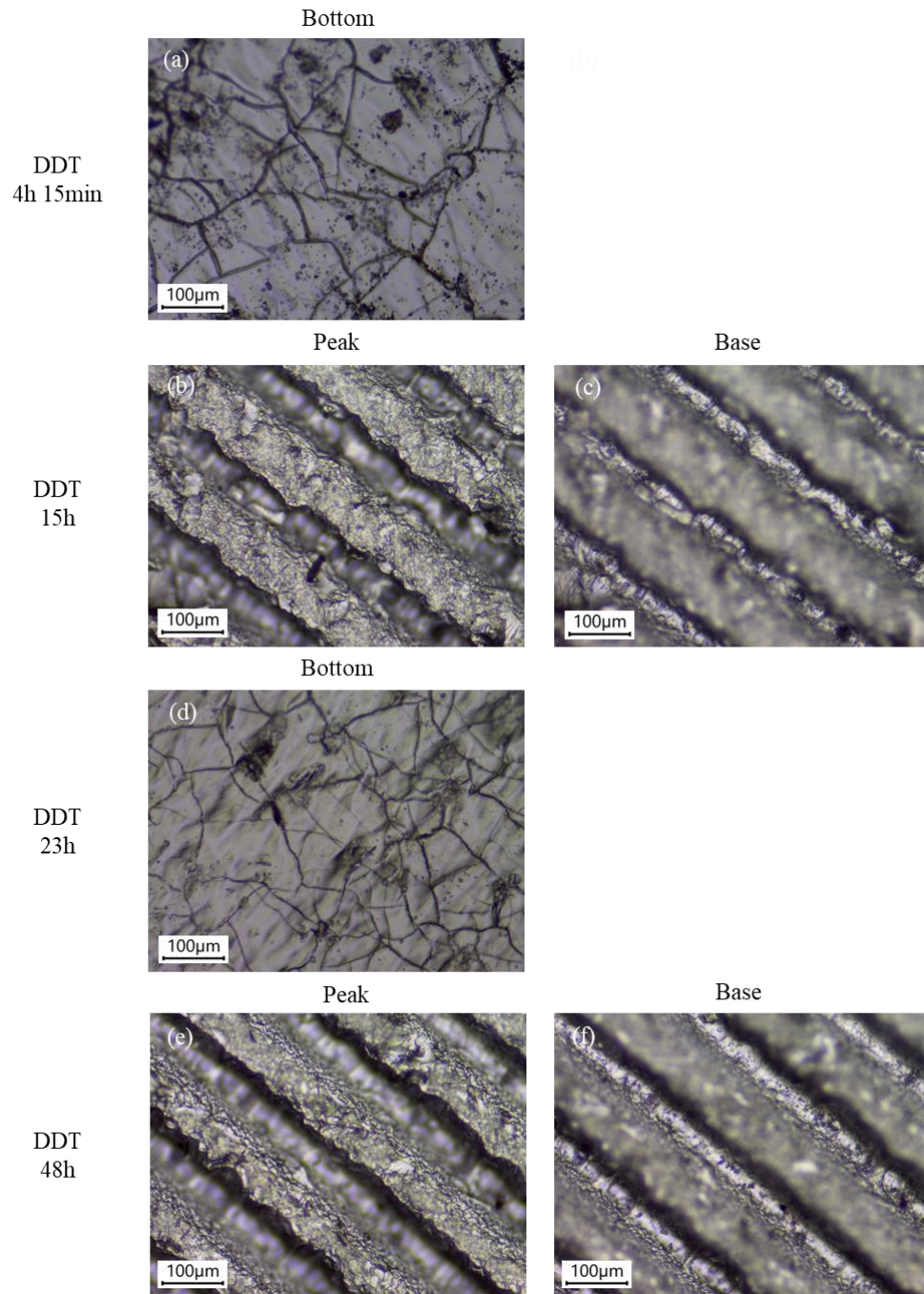


Figure 3.17 10X magnification images of the Al_2O_3 -deposited samples dip coated with DDT for different time periods (High Temp Resin/DDT/ Al_2O_3).

In addition to this, film formation was observed on all PVP coated samples, as shown in Figure 3.18 (a)-(c). Since moisture sorption on PVP is expected to increase with decreasing temperature, this can be one of the reasons for film and crack formation on PVP coated samples at the lower temperature of 70 °C.

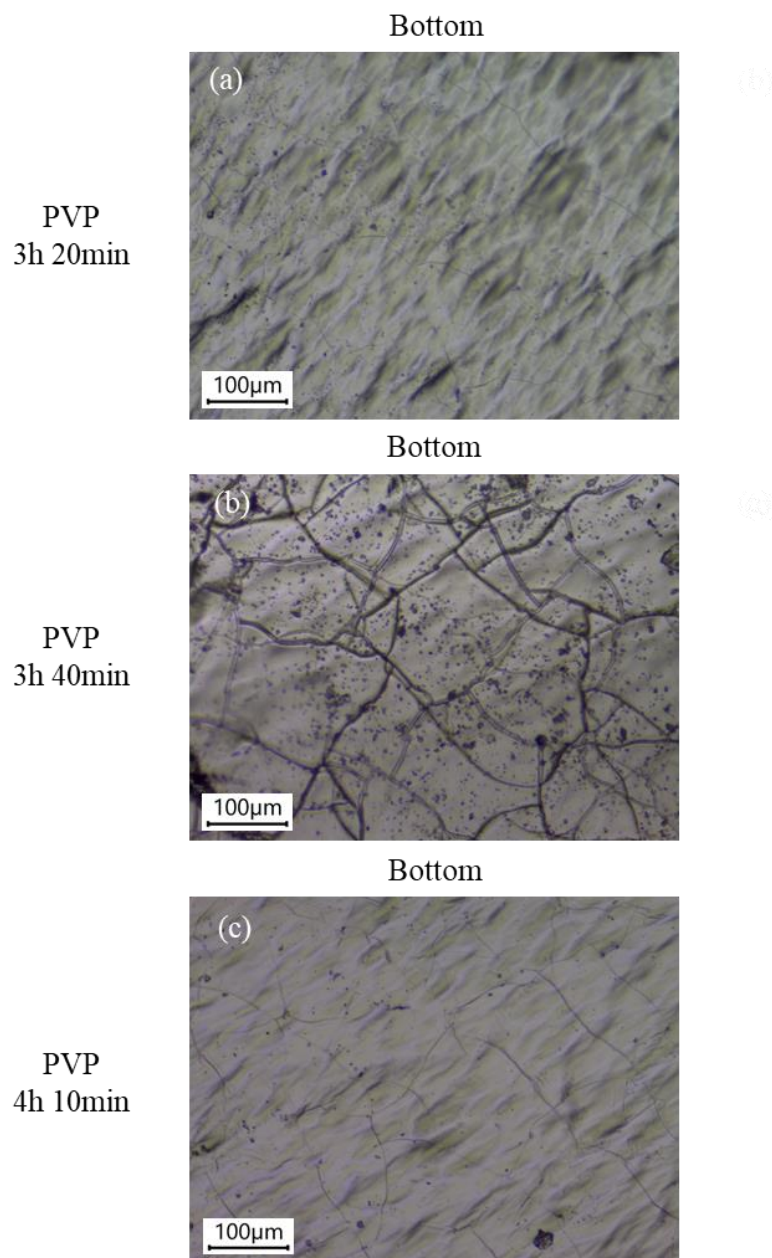


Figure 3.18 10X magnification images of the bottom face of the Al₂O₃-deposited samples dip coated with PVP for different time periods.

3.3.3 Deposition of Al_2O_3 with 3D printed reactors dip coated with growth inhibitors

From Sections 3.3.1 and 3.3.2, it can be concluded that no Al_2O_3 was present on the samples dip coated with PVP and ODPA after deposition at 100°C, whereas for deposition at 70°C, only ODPA worked effectively as a growth inhibitor on the High Temp Resin. Based on these initial results, PVP and ODPA were considered for dip coating an AP-SALD reactor head. However, since a lower dip coating time is preferred to prevent any warpage of the reactor head in the solvent, PVP was chosen because of its shorter dip coating period of approximately 4 hours and 10 minutes.

The objective of this work is to determine if dip coating the reactor head of an industrial-scale AP-SALD system can prevent or reduce powder formation on the reactor head. Currently, the system is used for coating plastics at low temperatures for sustainable food packaging applications. The temperature of the depositions is usually in the range between 50°C and 100°C.

From the Al_2O_3 depositions at 70°C, it was clear that PVP was unable to prevent the formation of Al_2O_3 after 500 cycles. Therefore, the initial goal was to determine if the PVP coating can prevent Al_2O_3 formation at a temperature of 100°C for a lower number of cycles (~200 cycles). For dip coating the reactor head with PVP, the PVP solution was prepared by dissolving ~0.25 wt.% PVP K-30 in diacetone alcohol and half of the reactor head was immersed in the solution for 4 hours and 10 minutes. Then the reactor head was removed from the solution, blow dried with nitrogen and a 200-cycle Al_2O_3 deposition was performed at 100 °C by collaborators Louis Delumeau and Tristan Grovu using the industrial-scale AP-SALD system. The reactor-substrate gap was maintained at 0.5 mm. The appearance of the reactor head after the deposition was performed is shown in Figure 3.19. After 200 cycles of Al_2O_3 deposition, powder formation was observed on both the coated and uncoated side.

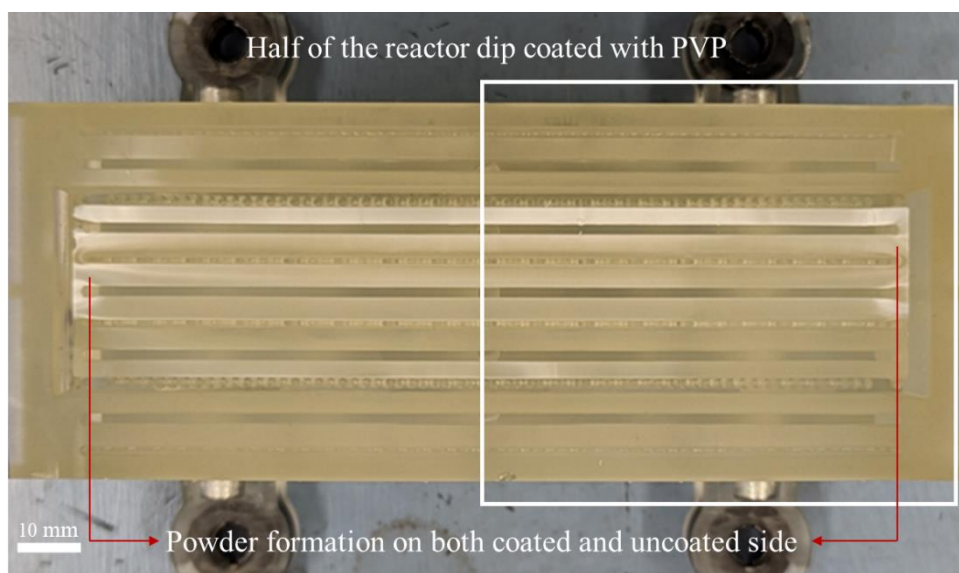


Figure 3.19 3D printed reactor head coated with PVP on the right side, after 200 cycles of Al_2O_3 deposition at 100 °C using the industrial scale AP-SALD system.

No significant difference between coated and uncoated sides can be observed. Initially, the powder formation was attributed to an insufficient concentration of PVP to properly coat all the surfaces. Therefore, for the next deposition, the concentration of PVP was increased to 1 wt. % PVP K30 in diacetone alcohol and a new 3D printed reactor head was immersed in the solution for 4 hours and 10 minutes. In this case, the deposition conditions were 100 °C and 500 cycles of deposition. It can be observed from Figure 3.20 that the powder formation on the coated side was similar or higher than the uncoated side. In this case, powder formation can be due to one of the following reasons:

- i) Since PVP is a hydrophilic polymer, the PVP coating with increased concentration on the coated side can adsorb moisture from the water co-reactant or the ambient atmosphere, which leads to more powder formation on the coated side,
- ii) The reactor-substrate gap maintained was 0.5 mm, which could lead to some CVD type reactions in the reactor-substrate gap.

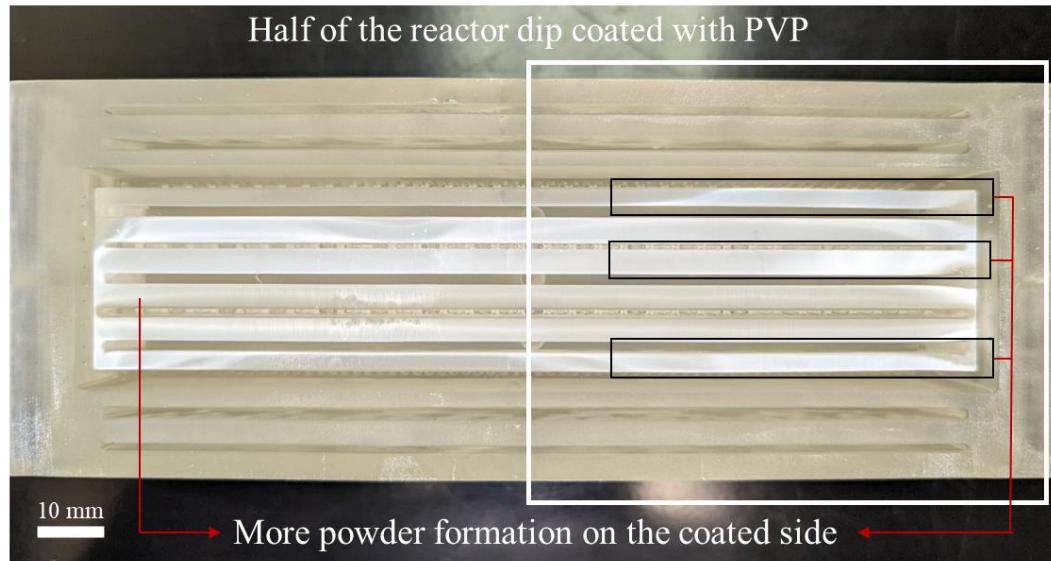


Figure 3.20 3D printed reactor head coated with PVP on the right side, after 500 cycles of Al_2O_3 deposition at 100 °C using the industrial scale AP-SALD system.

Therefore, ODPA was selected for dip coating, but only the samples dip coated for 23h or longer showed successful inhibition against 500 cycles of Al_2O_3 deposition at 70 °C in Figure 3.14. In order to determine if the 3D printed part is compatible with the long dip coating time, as the samples begin to absorb the solvent after some time, a lab-scale 3D printed reactor was immersed in the 1mM ODPA solution prepared using toluene and maintained at 50 °C. After approximately 6 hours, the reactor head warped and broke.

In order to determine if shorter ODPA dip coating times can prevent powder formation, an industrial-scale reactor head was dip coated for 20 minutes in the ODPA solution prepared with toluene at 50 °C. After 20 minutes, the reactor was taken out of the solution, blow dried with nitrogen and Al_2O_3 was deposited by Louis Delumeau using the industrial scale AP-SALD system for 200 cycles. It can be observed in Figure 3.21 that less powder was formed on the coated side when compared to the uncoated side. However, only some areas showed no powder formation. The reason behind this may be due to uneven distribution of ODPA atoms due to shorter dip coating times, as it can take up to 48 hours for a complete uniform monolayer to form.

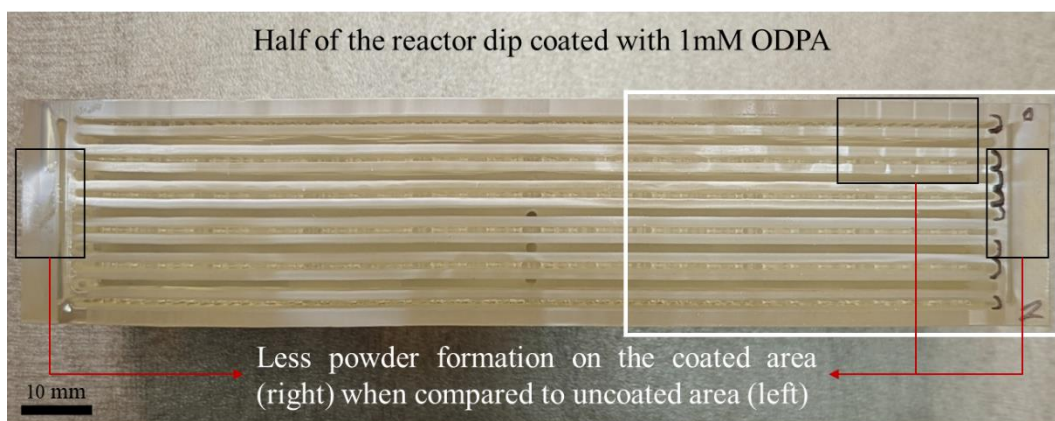


Figure 3.21 3D printed reactor head coated with ODPA on the right side, after 200 cycles of Al_2O_3 deposition at 70 °C using the industrial scale AP-SALD system.

In order to determine if increasing the concentration of ODPA and dip coating times would improve the Al_2O_3 growth inhibition, 10mM ODPA solution was prepared in toluene at 50 °C and another reactor head for the industrial-scale AP-SALD system was dip coated for 3h 30min. The reactor head was removed from the solution and blow dried under nitrogen. Then, the reactor head was used to deposit Al_2O_3 at 100 °C. After deposition of Al_2O_3 at 100°C for 250 cycles, less powder formation on the uncoated side as compared to the coated side can be observed, as shown in Figure 3.22.

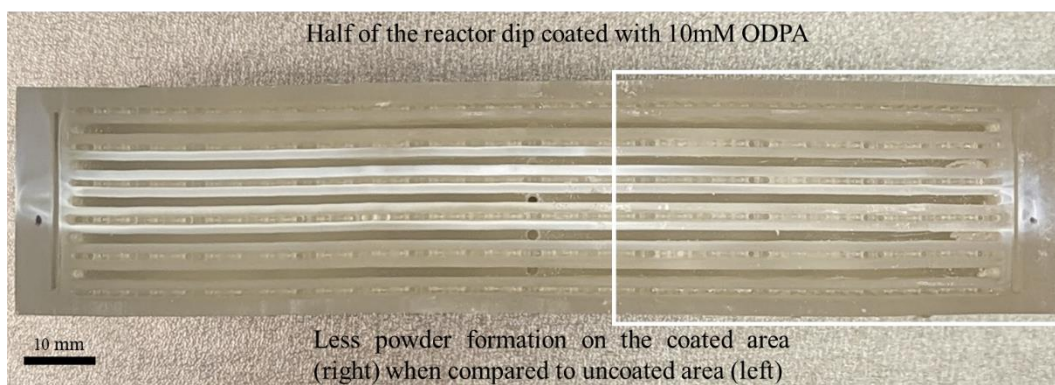


Figure 3.22 3D printed reactor head coated with ODPA on the right side, after 250 cycles of Al_2O_3 deposition at 100 °C using the industrial scale AP-SALD system.

3.3.4 Deposition of ZnO on 3D printed samples coated with growth inhibitors

Similar to the Al_2O_3 depositions, the growth inhibitors were tested to identify potential inhibitors to prevent ZnO formation on the High Temp Resin. As for Al_2O_3 , the 3D printed samples coated with ZnO at 100°C and 50°C were characterized using an optical microscope. In the case of ZnO, no visible difference between the uncoated sample and ZnO-deposited samples without inhibitor was observed using the optical microscope. All the microscope images of the samples after ZnO deposition are included in appendix A and B. For instance, an uncoated sample on which no inhibitor is present is shown in Figure 3.23. Figure 3.23 (a) and (b) are the microscopic images of the uncoated sample before ZnO deposition, whereas the uncoated sample after ZnO deposition at 100°C is shown in 3.23 (c) and (d).

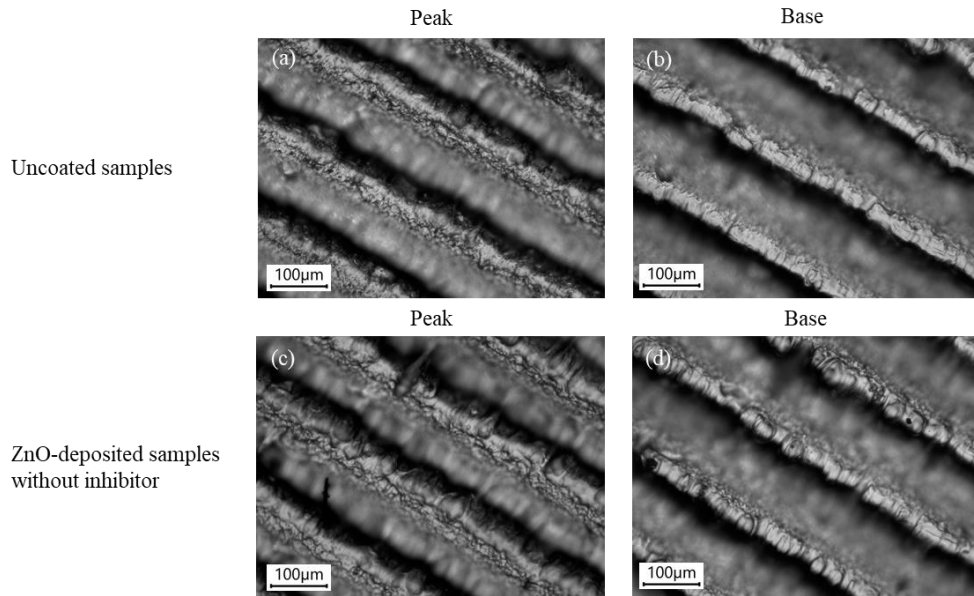


Figure 3.23 10X magnification images of uncoated samples and ZnO-deposited samples without inhibitor.

Since no clear difference was observed by optical microscopy, the samples coated with growth inhibitors on which ZnO was deposited were only characterized using SEM-EDX to determine the presence of zinc on them.

3.3.4.1 EDX analysis of samples after deposition of ZnO at 100°C

For the purpose of EDX analysis, only the samples dip coated with growth inhibitors for the highest time periods were analyzed and compared with the sample without any inhibitor. Figure 3.24 shows

the SEM images of the samples after ZnO deposition along with the area analyzed by EDX. The sample with no inhibitor is shown in Figure 3.24 (a), whereas the samples coated with PMMA, PVP, ODPA and DDT are shown in Figure 3.24 (b), 3.24 (c), 3.24 (d) and 3.24 (e), respectively.

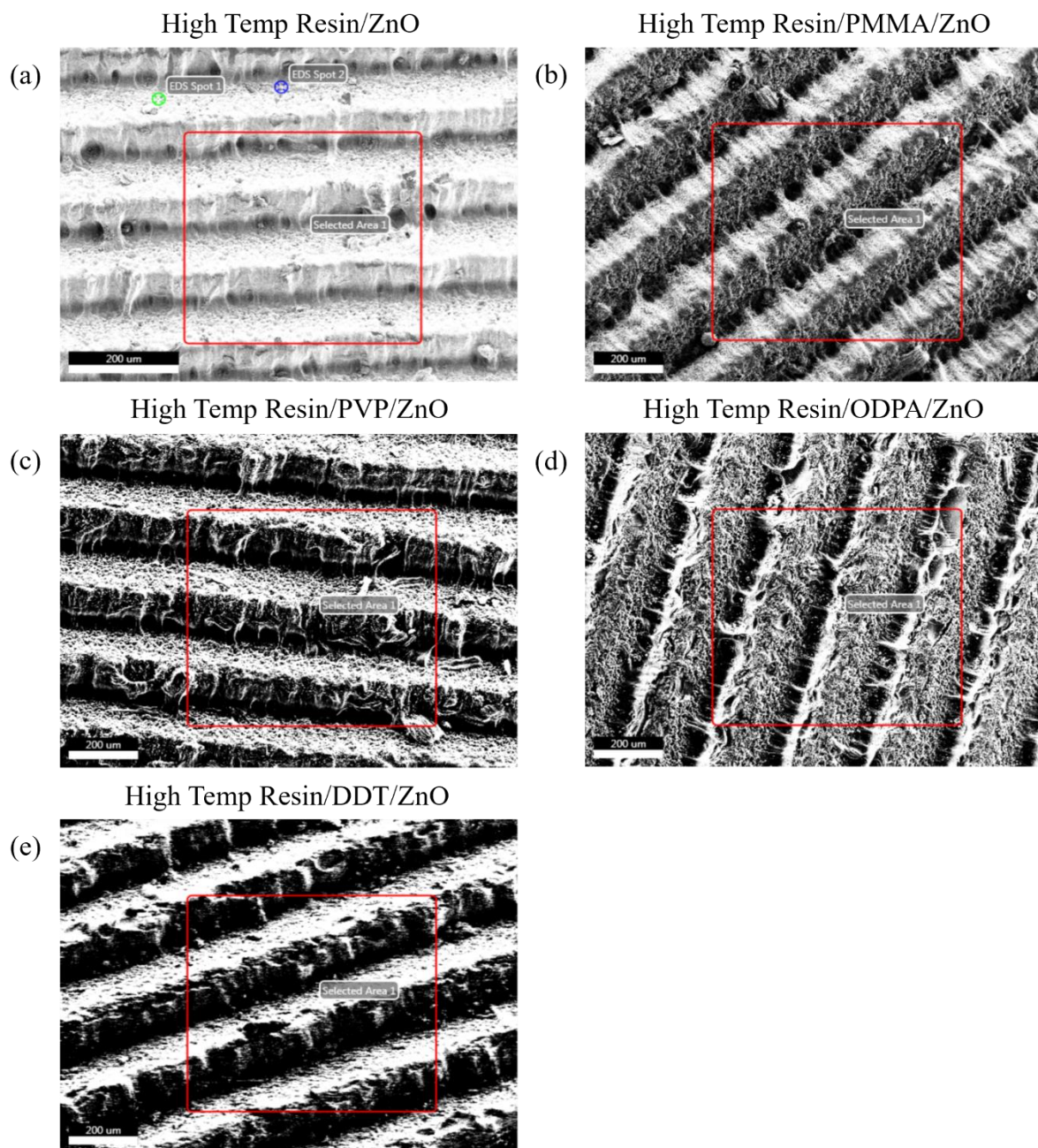


Figure 3.24 SEM images after ZnO deposited at 100 °C on (a) sample without any inhibitor and samples dip coated with (b) PMMA, (c) PVP, (d) ODPA, and (e) DDT.

The EDX spectra of all five samples are shown in Figure 3.25. Zinc peaks were observed on all the samples. In this case, it can be observed that the zinc peaks are lower on ODPa and PVP coated sample when compared to PMMA and DDT coated sample, indicating better inhibition against ZnO deposition.

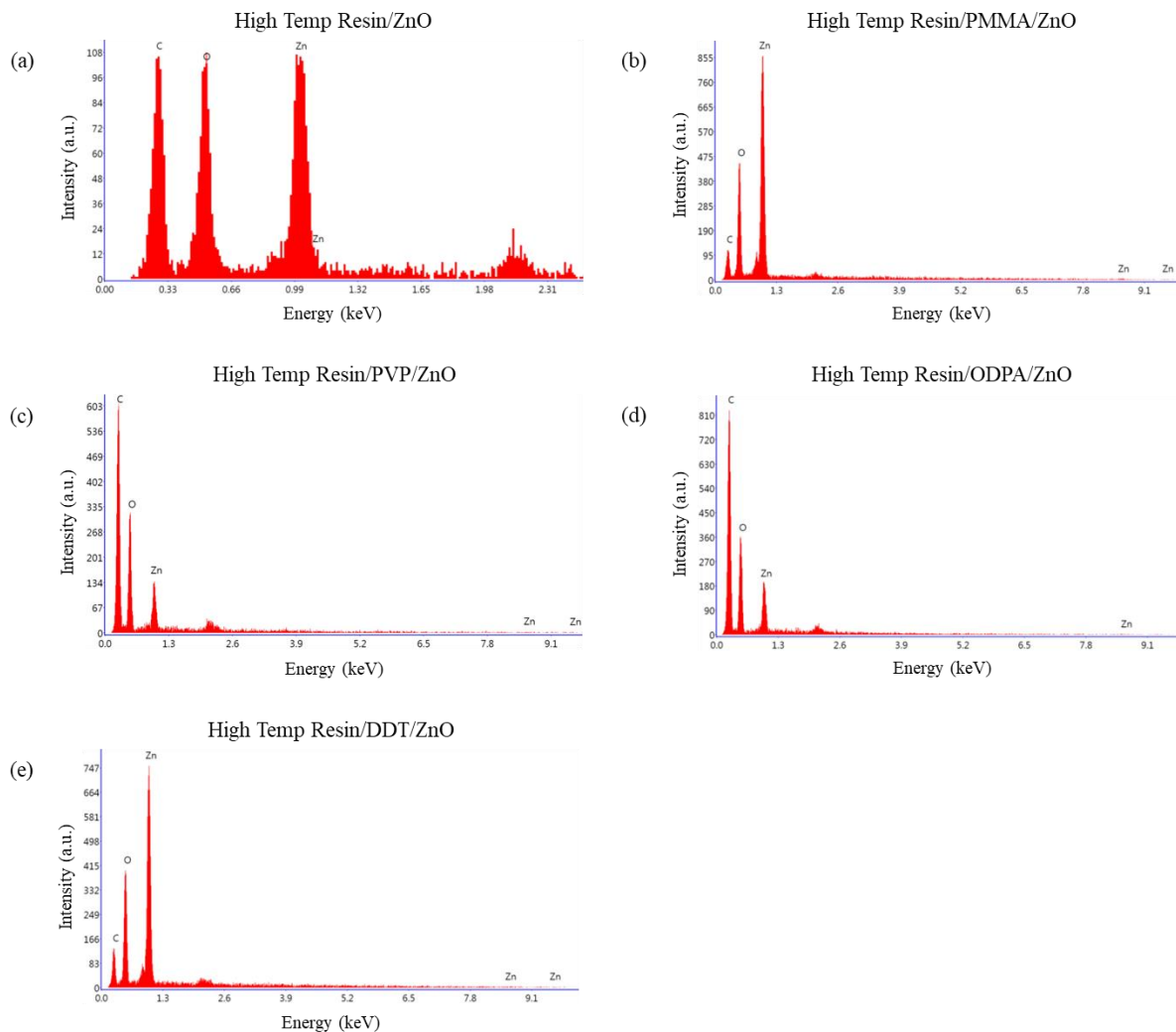


Figure 3.25 EDX spectra of the ZnO-deposited samples (a) without inhibitor, and dip coated with (b) PMMA, (c) PVP, (d) ODPa and (e) DDT. Note: Results generated from the system software using a Zeiss Ultra Plus FESEM coupled with an EDAX EDS detector.

3.3.4.2 EDX analysis of samples after deposition of ZnO at 50°C

In the same manner as the previous section, after the deposition of ZnO at 50°C, samples dip coated with inhibitors for the highest time periods were analysed by EDX and compared to a ZnO-deposited sample without inhibitor. Figure 3.26 shows SEM images along with the area analyzed by EDX.

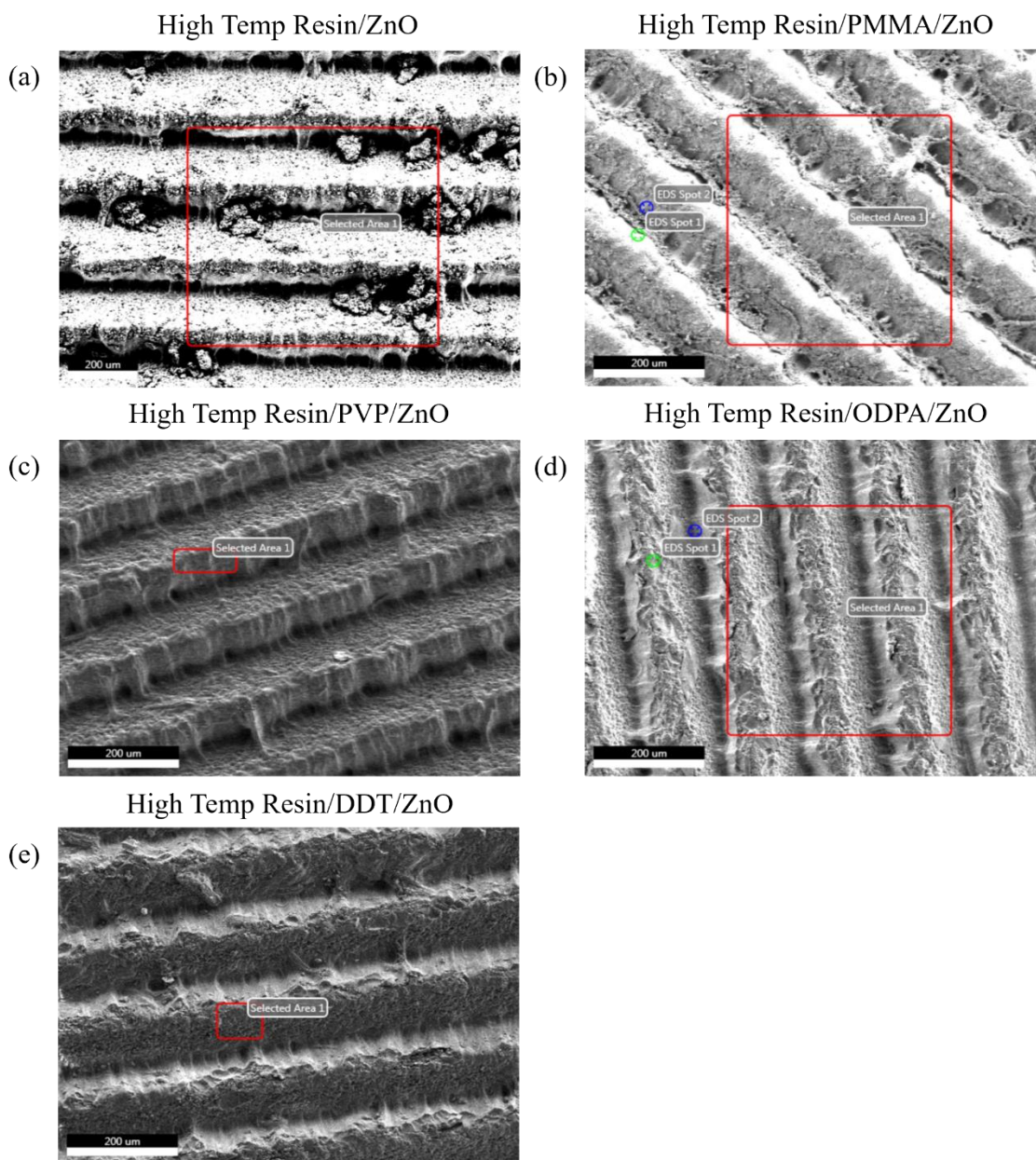


Figure 3.26 SEM images of ZnO deposited at 50 °C on High Temp Resin sample (a) without any inhibitor, and dip coated with (b) PMMA, (c) PVP, (d) ODPA, and (e) DDT.

The EDX spectra of all five samples are shown in Figure 3.27. From Figure 3.27 (c), (d) and (e), no Zn peaks were observed on the samples coated with PVP, ODPA, and DDT, whereas the percentage of zinc on the uncoated sample was significantly higher.

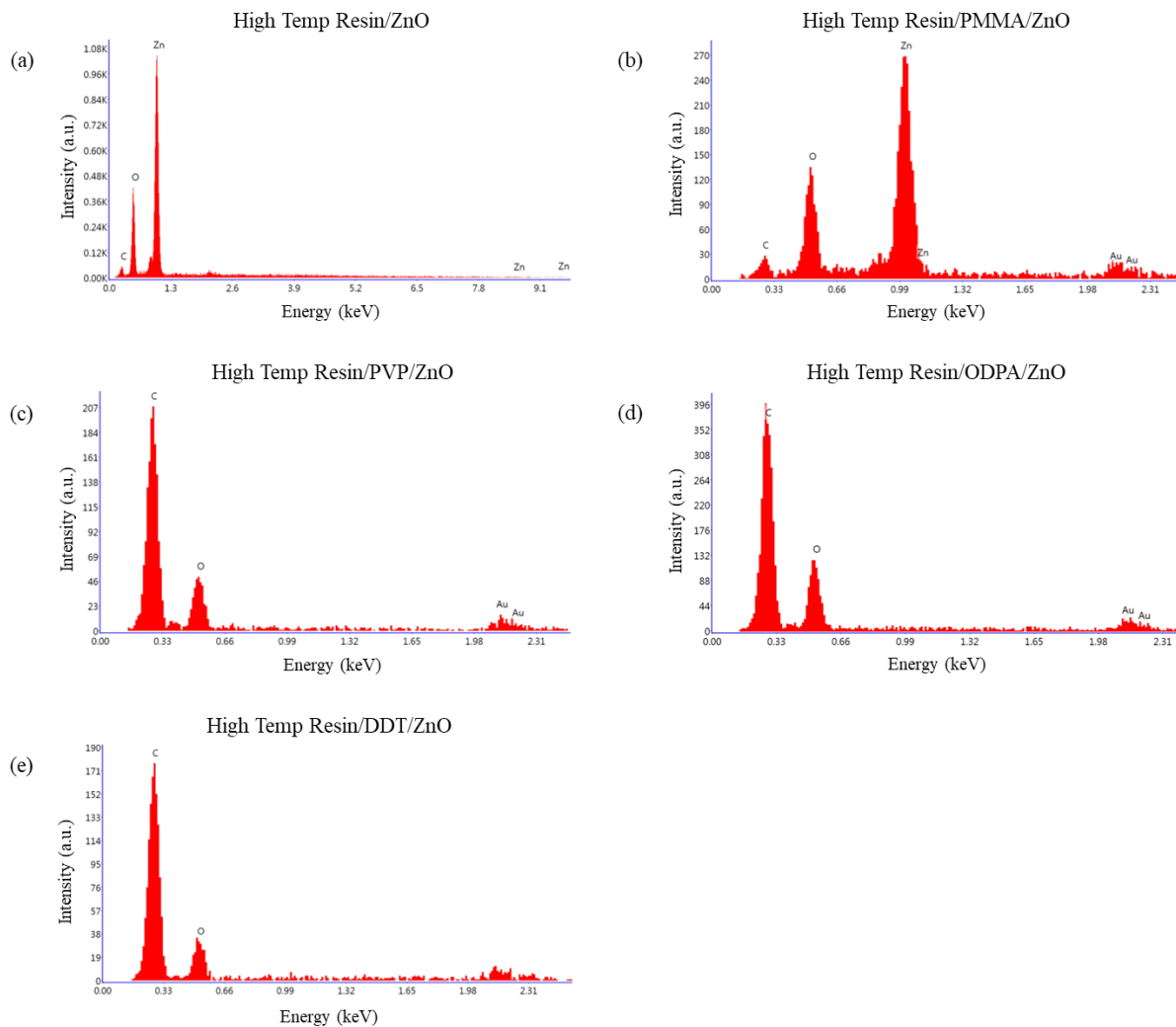


Figure 3.27 EDX-SEM analysis of the ZnO deposited samples (a) without inhibitor and coated with (b) PMMA, (c) PVP, (d) ODPA and (e) DDT. Note: Results generated from the system software using a Zeiss Ultra Plus FESEM coupled with an EDAX EDS detector.

3.4 Conclusion

In conclusion, several growth inhibitors were tested on 3D printed samples and 3D printed reactor heads to see if they could prevent the formation of alumina and zinc oxide. In the case of Al_2O_3 deposition, the growth inhibitors were tested at 70°C and 100°C for 500 deposition cycles. At 100°C, ODPA SAM and PVP growth inhibitors prevented Al_2O_3 formation; however, ODPA and DDT prevented Al_2O_3 formation after 500 cycles of deposition at 70°C.

These growth inhibitors were used to dip coat a 3D printed reactor head used in a commercial-scale AP-SALD system built at the University of Waterloo. During depositions at 100°C, powder formation was observed on the reactor head dip coated with PVP after 200 cycles. In addition to this, the powder formation increased with an increase in the PVP concentration. In the case of ODPA, significantly less powder formation was observed on the coated side of the reactor head compared to the uncoated side after 200 and 250 cycles at 70°C and 100°C, respectively. For deposition at 70°C, the concentration of ODPA was 1mM and the dip coating time was 20 minutes. Whereas, for the deposition at 100°C, the concentration was increased to 10 mM ODPA and the time for dip coating was increased to 3 hours and 30 minutes. It is to be noted that the dip coating times were shorter than the coating time that successfully prevented Al_2O_3 formation completely on the tested samples and the powder formation was reduced but not completely prevented. Since the inhibitors prevented film growth on the samples but could not completely prevent the powder formation on the reactor head, studying the flow of gases can help to better understand powder formation. Preliminary flow visualization attempts to study the gas flows in the reactor-substrate gap were unsuccessful but are discussed in Appendix C as a basis for future work.

In addition to this, the growth inhibitors were tested for ZnO deposition at 100°C and 50°C for 500 cycles. At 100°C, the nucleation of ZnO was delayed on samples coated with PVP and ODPA. For deposition of ZnO at 50°C, no zinc was observed on the samples coated with PVP, ODPA and DDT.

Chapter 4

Direct deposition of ZnO patterns with AP-SALD

Direct deposition of thin films over desired regions of a substrate using AP-SALD has been explored over the past few years, as discussed earlier in Section 2.3. With the help of 3D printing, reactor heads with channels that can deliver precursors to localized regions on the substrate can be fabricated and used to achieve direct selective deposition. In this work, reactor heads are designed, 3D printed and tested to deposit continuous strips of nanoscale thin films separated by a small distance between them, as well as narrow strips of thin films separated by larger distances. It is also shown that by mechanically adjusting the position of the reactor, the thin strips can be placed close to one another. Such thin-film patterns would be useful for high-throughput manufacturing of devices such as low-cost perovskite solar modules.

Jhi Yong Loke, a former master's student in our research group designed an AP-SALD reactor head to deposit thin films with thickness gradients, 3D printed it using a SLA 3D printer and successfully demonstrated nanoscale gradient thin film deposition using the lab-scale AP-SALD system [65]. The design of the reactor was further optimized by current PhD student, Denys Vidish. This 3D-printed AP-SALD reactor design was used as a starting point for this work. However, for the purpose of direct selective deposition, the design of the reactor channels needed to be modified to localize the precursors to the desired region of deposition.

4.1 Design and process guidelines for 3D printing

Some of the key parameters to be considered to model the design of the reactor and to ensure successful 3D printing with SLA 3D printers are as follows:

1) Build volume of the printer

The build volume of the Form 3 SLA 3D printer is $145 \times 145 \times 185 \text{ mm}^3$. The design of the reactor head must fit within this volume.

2) Resin for 3D printing the part

Formlabs offers a wide variety of resins ranging from standard prototyping materials to engineering materials. Depositions are performed using the AP-SALD system up to a maximum of 200 °C. Since the reactor is in close proximity to the heated stage, the parts

must be printed using a resin with high thermal stability. The High Temp Resin V2 has a heat deflection temperature of 238 °C and is ideal for this application.

3) Minimum wall thickness, distance between the walls and hole diameter

According to the Formlabs design guide for the Form 3 printer, the minimum wall thickness and hole diameter are 0.2 mm and 0.5 mm, respectively. In addition, the minimum distance between walls according to the Formlabs design community is 0.5 mm. Therefore, the part must be designed with these dimensional constraints in mind to avoid closing off of the features during printing.

4) Part orientation

The success of the print depends on the orientation of the part within the space of the build volume. This is a key parameter as it determines factors such as strength and quality of the print, supports required and time taken for printing the part, etc. Some orientation considerations for printing a part include how the uncured resin is drained, critical features to preserve, print time, warping etc.

After each layer is cured and solidified by the laser, resin which is not part of the cured layers adheres to the layer due to its viscous nature. This excess resin needs to be efficiently drained or removed to ensure the quality of the final printed part. When a part is oriented at an angle during the printing process, the excess resin is naturally drained away. Therefore, the model is oriented such that the channels and the gas inlets are facing towards the resin tank as shown in Figure 4.1.

5) Supports

Almost all parts or geometries to be 3D printed require some form of support. The support structures will leave marks on the surface when they are removed. The parts are oriented such that the supports are located away from critical features and surfaces where high quality and surface finish are crucial. Since the bottom surface of the reactor must have a high surface finish, this side is located on the other side of the supports during 3D printing as shown in Figure 4.1.

After printing and washing, the part needs to be cured under UV light. During this process, the part is heated and exposed to UV. If the model is not supported properly, it can lead to part warping.

6) Residual resin

After the part is printed, the part is transferred to a wash bath along with the build platform to wash off the excess resin from the 3D printed part. However, it is advised to not wash the high temp resin parts for more than 6 minutes since the part begins to absorb the solvent. Leftover resin in the channels of the reactor results in the formation of partially cured resin in undesired locations. Therefore, the part is washed, and a shim is used to manually remove the resin from the channels. The channels are then cleaned with the help of isopropanol and clean compressed air to avoid any residual resin.

7) Cure time and temperature

The curing time and temperature of the 3D printed parts depends on the type of the resin and the intended application. The parts are cured under UV light to achieve properties such as increased strength and stability. To achieve high thermal stability, it is recommended to cure the part at 80 °C for 2 hours. It must be noted that the part must be completely dry to avoid cracking of the part during curing.

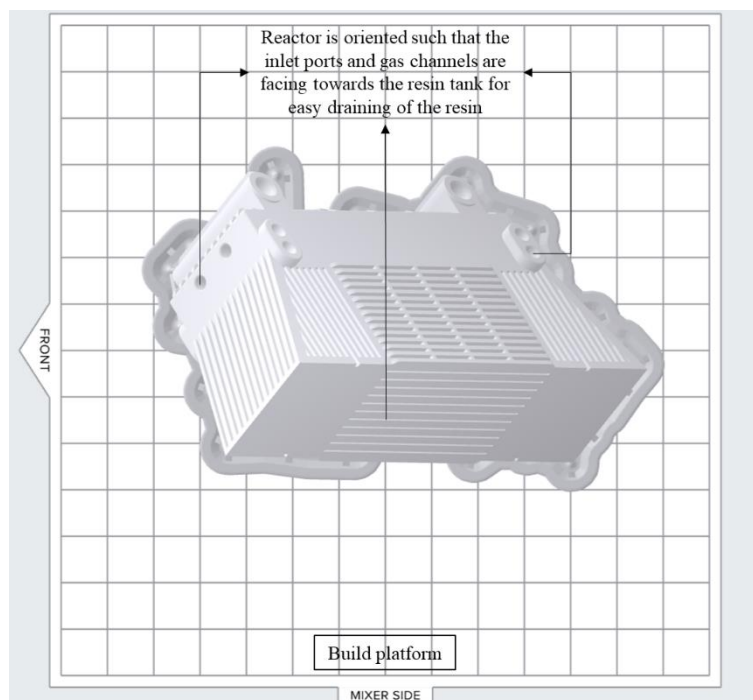


Figure 4.1 Orientation of the reactor head using preform software such that the inlets and channels are facing towards the resin tank (located opposite to the build platform) for easy draining of the resin from the channels. No supports on the bottom face near the channels to ensure a smooth surface.

4.2 Patterning reactor for depositing wide strips

4.2.1 Design of the reactor for depositing wide patterns

The channel configuration of the reactor to print patterns directly on the substrate is shown in Figure 4.2 (a). The channels follow an ENEAENEENE (E=Exhaust, N=Nitrogen, A=Precursor A and B=Precursor B or co-reactant) sequence and are divided into 4 regions separated by nitrogen channels, which are referred to as dividing channels (vertical channels in Figure 4.2). The channel dimensions are shown in Figure 4.2 (b). All the channels are 0.5 mm wide, whereas the dividing channels in the direction perpendicular to the precursor, exhaust and shielding channels were 0.45 mm wide. The channels adjacent to the dividing channels are at a distance of 0.2 mm on each side as shown in Figure 4.2 (b). The reactor modelled earlier by past students to print gradient thin films was modified with the channels and dimensions in Figure 4.2 (a) and 4.2 (b) as shown in Figure 4.2 (c) and 4.2 (d). Figure 4.2 (c) and 4.2 (d) show the gas flow paths and isometric view of the reactor head, respectively.

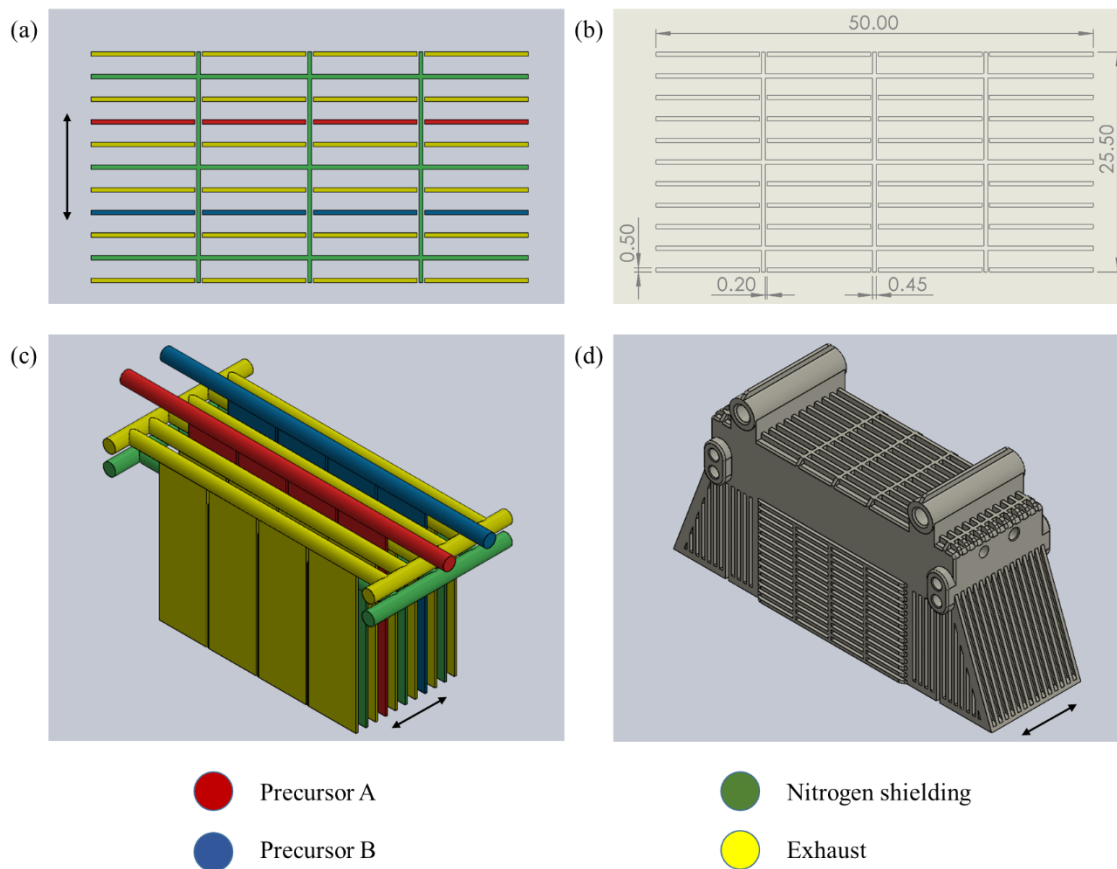


Figure 4.2 Design of the reactor to print wide patterns. (a) Location of each gas channel on the reactor head, (b) dimensions of the channels in mm (c) gas flow paths and (d) isometric view of the reactor. The arrow indicates the direction of substrate oscillation and the legend of each color corresponding to each channel is provided at the bottom.

The model was then 3D printed using a Formlabs Form 3 3D printer using High Temp Resin according to the guidelines mentioned in section 4.1.1. Figure 4.3 shows a reactor on the build platform of the Form 3 3D printer after a successful print.

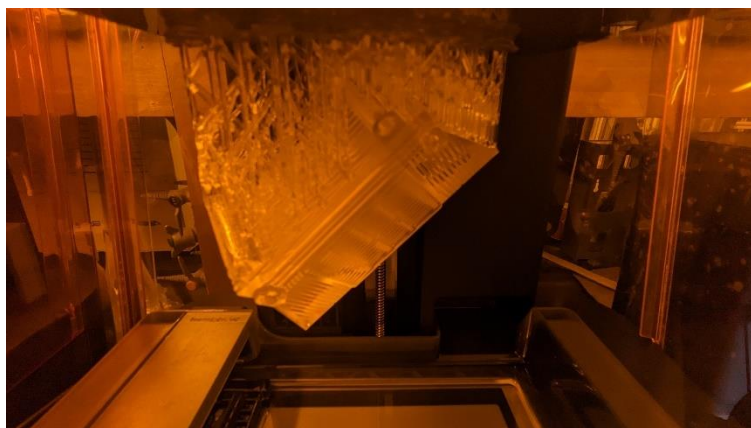


Figure 4.3 Reactor head 3D printed using a Formlabs form 3 3D printer.

The initial design for the patterning reactor was tested by depositing zinc oxide using the Functional Nanomaterials Group's lab-scale AP-SALD system. For the deposition of zinc oxide, nitrogen gas was bubbled through the diethylzinc precursor at 40 sccm and combined with a 200 sccm nitrogen carrier flow. Water was bubbled at 45 sccm and combined with a 200 sccm nitrogen carrier flow. The nitrogen-curtain flow rates were varied between 900, 1100 and 1300 sccm. A reactor-substrate spacing of 100 μm was used. The substrate was heated to 100°C and oscillated at a speed of 30 mm/s for 500 cycles. After deposition of zinc oxide, the films were characterized by ellipsometry using a Filmsense FS-1 ellipsometer.

4.2.2 Results and discussion

Figure 4.4 shows pictures of the ZnO films produced on 70 mm by 70 mm by 1.1 mm glass substrates (top) and ellipsometry measurements across the entire width of the samples (from left to right end) to determine their thickness (bottom).

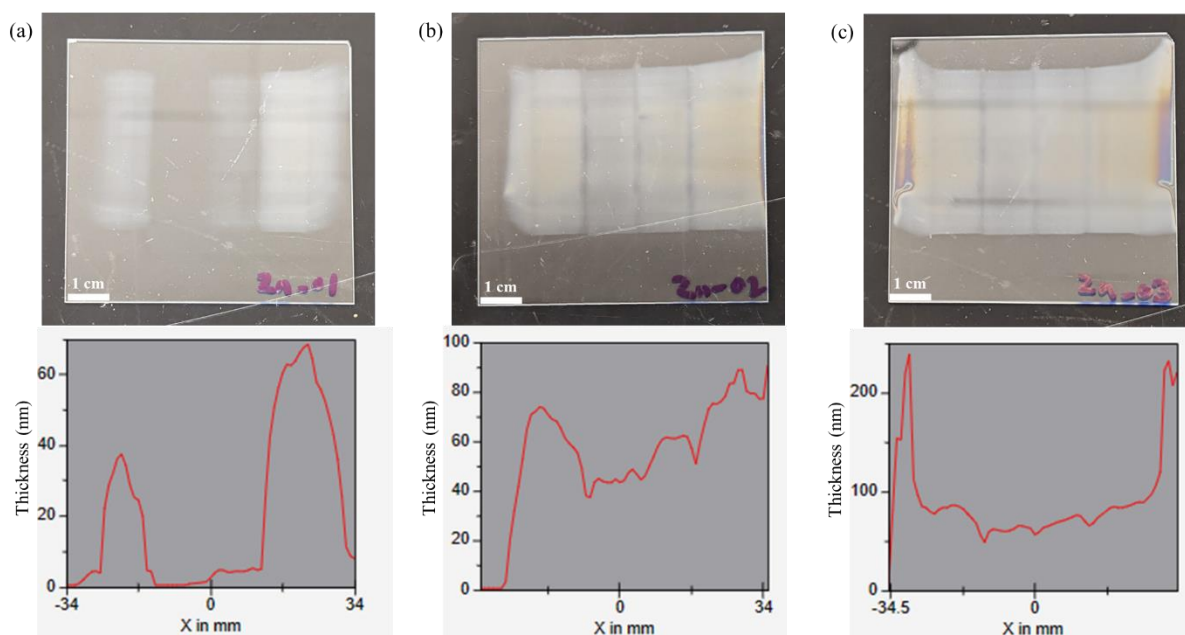


Figure 4.4 Pattern deposition on samples (top) and ellipsometry measurement across the substrate showing the measured film thickness (bottom) of the ZnO films deposited using the patterned reactor with different nitrogen-curtain flow rates (a) 900 sccm, (b) 1100 sccm, and (c) 1300 sccm.

After the deposition of zinc oxide on the samples shown in Figure 4.4 (a), (b) and (c), a clear pattern can be observed on the samples 4.4 (b) and (c). However, upon measuring the thickness of the sample with ellipsometry, film formation was also observed in the gaps. The thickness of the film deposited in the gap was approximately half the thickness of the film deposited in the other areas. The reason for this could be due to ineffective precursor isolation by the nitrogen channels located along the direction of oscillation, or precursor getting carried away from the precursor channel located at 0.2 mm on either side of the dividing channel and reacting with oxidant.

4.3 Patterning reactor for depositing narrow strips

4.3.1 Design of the reactor

In order to deposit narrow patterns, a reactor head was designed, as shown in Figure 4.5. Figure 4.5 (a) and 4.5 (b) shows the position of the gas outlets on the reactor head and the dimensions of the channels, respectively. The gas flow paths on the reactor are shown in Figure 4.5 (c) and the isometric view of the reactor is shown in Figure 4.5 (d). The metal precursor channel is 0.5 mm wide, and the adjacent exhaust channel is at a distance of 1 mm on each side. Therefore, the width of the deposited film can

be between 2.5 mm to 3.5 mm (dimensions of the exhaust channel). The channels in the middle (represented in grey) were not used in this deposition process.

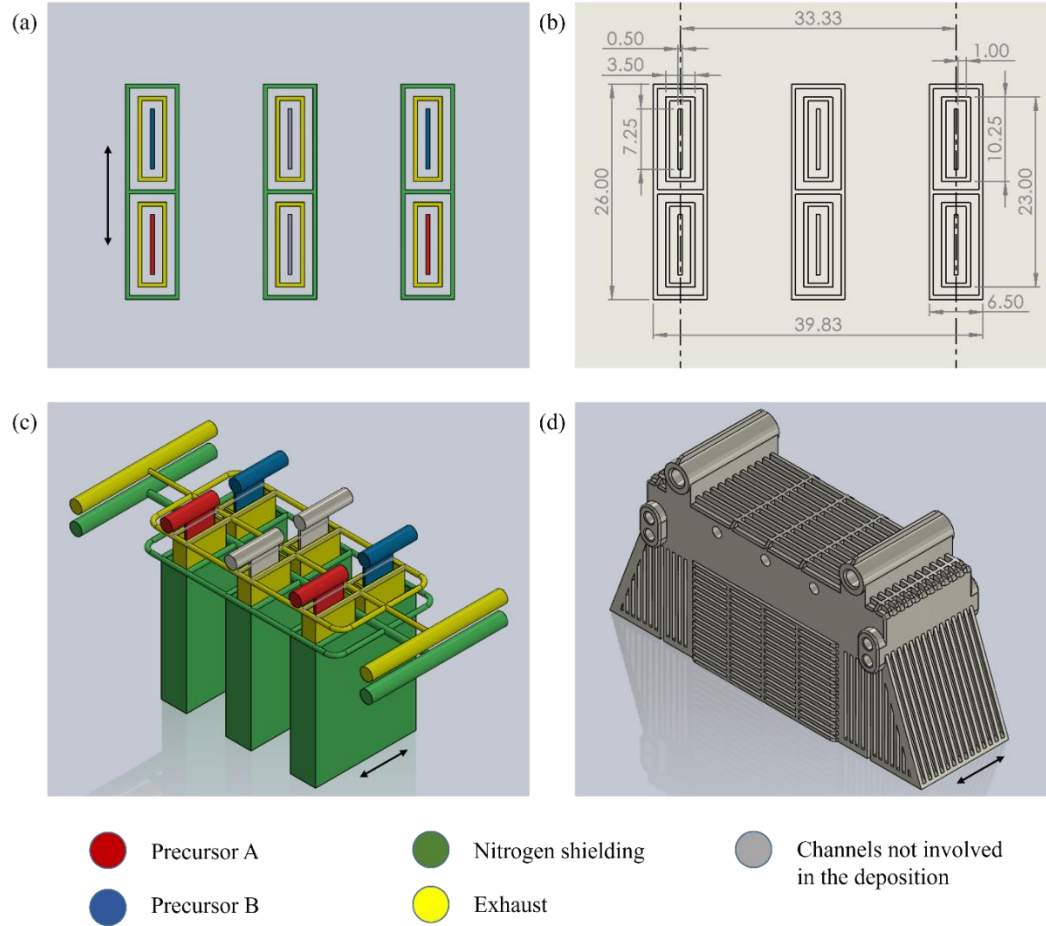


Figure 4.5 Design of the reactor to print narrow patterns. (a) Location of each gas channel on the reactor head viewed from the top, (b) dimensions of the channels in mm (c) gas flow paths and (d) isometric view of the reactor. The arrow indicates the direction of substrate oscillation and the legend of each color corresponding to each channel is provided at the bottom.

4.3.2 Deposition of closely-spaced strips by moving the substrate by a slight offset

The closest distance between two adjacent deposited strips is limited by the type of fabrication method used for fabricating the reactor. To overcome this, the reactor or the substrate can be manually offset (moved) by a small distance relative to the other to deposit closely-spaced strips of film.

A schematic of this method is described in Figure 4.6. After the first deposition, two strips are formed on the substrate as shown in orange in Figure 4.6 (a). As shown in Figure 4.6 (b), the substrate is then

offset by a small distance towards the left and the deposition is performed again, to form two more strips at locations close to the previously deposited strips. Theoretically, according to the dimensions of the reactor from 4.5 (b), if the offset distance is 4 mm, the strips should be located at a distance of 500 μm adjacent to the strips from the previous deposition.

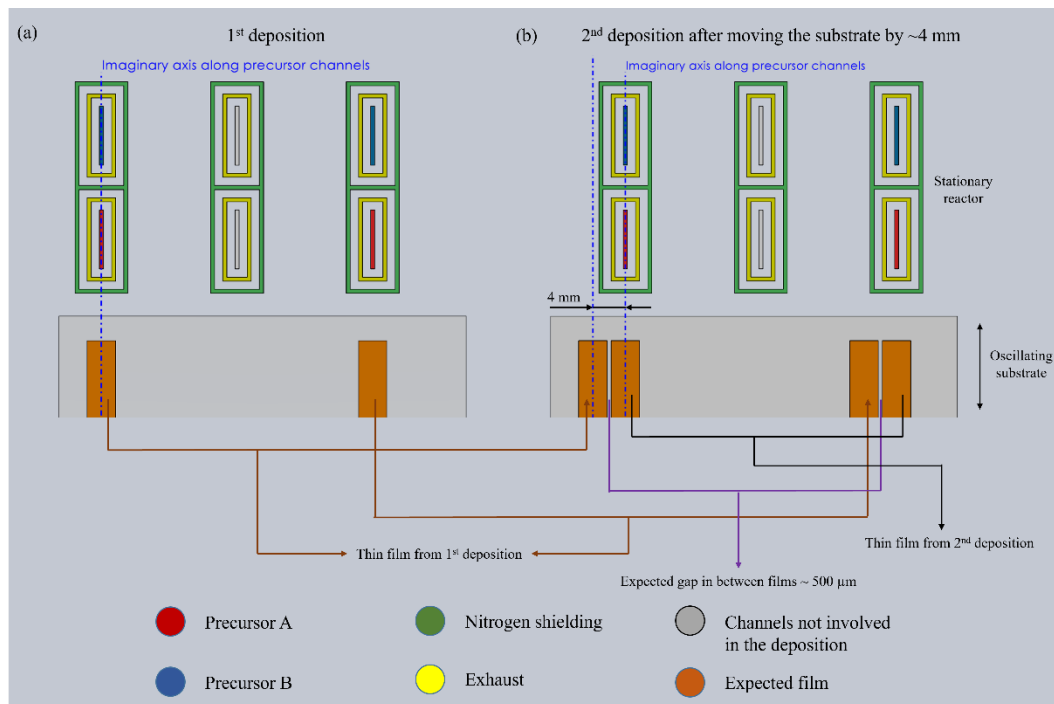


Figure 4.6 A schematic of the top view of the deposition process where the reactor is held stationary, and the substrate oscillates below the reactor. Precursors are supplied only to the channels at the left and right ends of the reactor head. (a) 1st deposition creates two thin strips of films on the substrate. (b) The substrate is moved to the left by a small offset distance of 4 mm and the deposition is performed again. Two more thin strips are deposited close to the strips deposited in the 1st deposition, resulting in films separated by a small gap. The arrow indicates the direction of substrate oscillation and a color legend corresponding to each channel is provided at the bottom.

The reactor head was tested by depositing zinc oxide using the lab scale AP-SALD system at the University of Waterloo. For the depositions of zinc oxide, nitrogen gas was bubbled through the diethylzinc precursor at 23 sccm and combined with a 127 sccm nitrogen carrier flow. Water was bubbled at 45 sccm and combined with a 255 sccm nitrogen carrier flow. The total flow rate from the nitrogen shielding channels was 2000 sccm. The substrate was heated to 70°C and oscillated at a speed of 30 mm/s for 150 cycles.

4.3.3 Results and discussion

Two halves of a Si/SiO₂ substrate were placed at the opposite ends of the reactor head below the precursor channels and the depositions were performed. Only the sample placed below the channels at the left end are discussed below.

The film formed on the substrate placed at the left end is shown in Figure 4.7. The width of the strip formed was approximately 5 mm, and the nitrogen channel surrounding the film was between 5.5 mm and 6.5 mm. The dimensions of the reactor superimposed on the deposited film is shown in Figure 4.8.

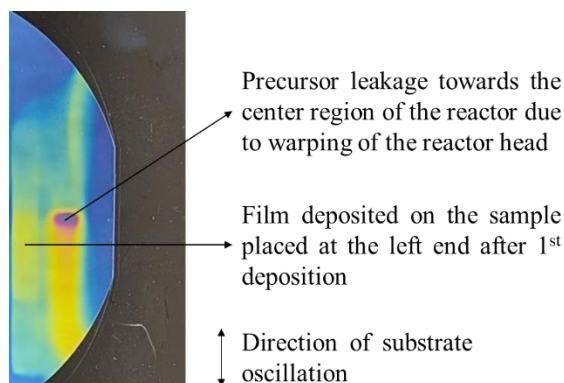


Figure 4.7 Film formed on the sample placed at the left end after 1st deposition.

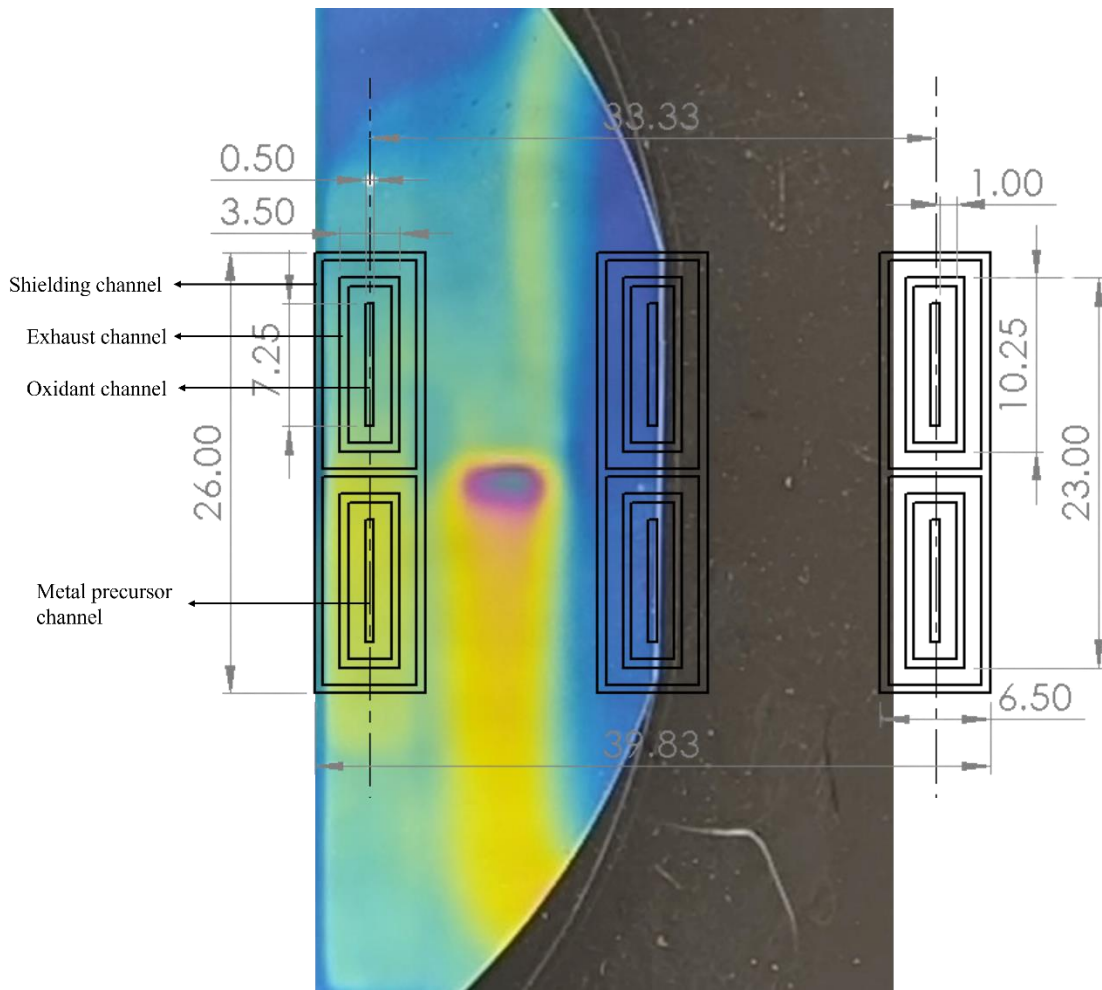


Figure 4.8 Channels of the reactor superimposed on the sample after 1st deposition.

It is seen in Figure 4.8 that a significant amount of ZnO was also deposited in the area outside of the nitrogen shielding. This was attributed to some warping of the reactor. The reactor-substrate gap was likely higher at the center of the reactor due to the warping, causing some precursor to leak towards the center of the reactor.

Though leakage was observed on one side, the deposition appears to form a sharp deposition edge on the other. This can be used to deposit closely spaced features by the offset method explained in section 4.3.2.

Therefore, after the first deposition, the substrate was rotated by 180° and placed below the same channels at the left end by a slight offset distance, as shown in Figure 4.9 (b). 150 cycles of ZnO deposition were performed again on the sample using the conditions mentioned in section 4.3.2.

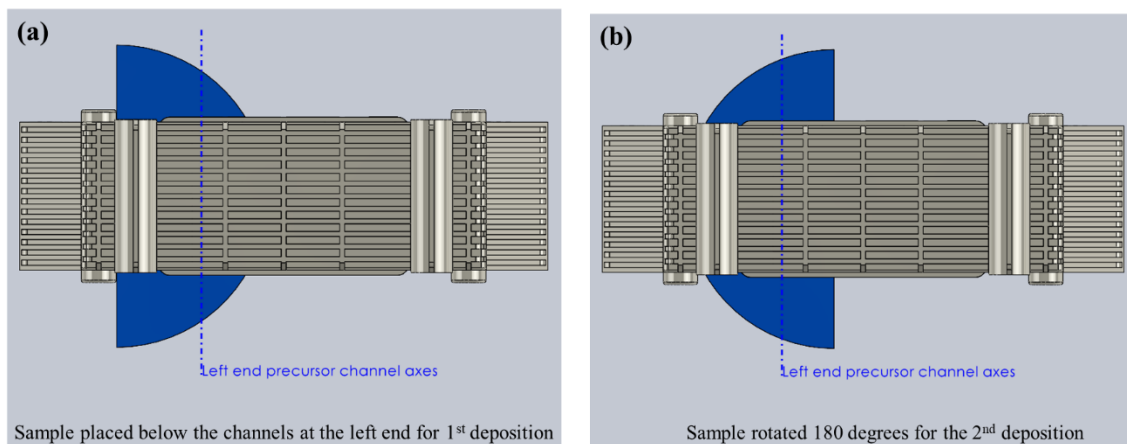


Figure 4.9 Positioning of the sample at the channels below the left end of the reactor head for (a) first deposition and (b) second deposition.

Figure 4.10 shows an image of the sample after the two depositions. Figure 4.11 shows the location of the reactor superimposed on the film deposited after the 2nd deposition. Precursor leakage was observed on the substrate along the same region towards the right, similar to the 1st deposition (Figure 4.7) due to the warping of the reactor head. Nonetheless, it is seen that a pattern consisting of strips separated by a distance of approximately 0.5 mm was produced.

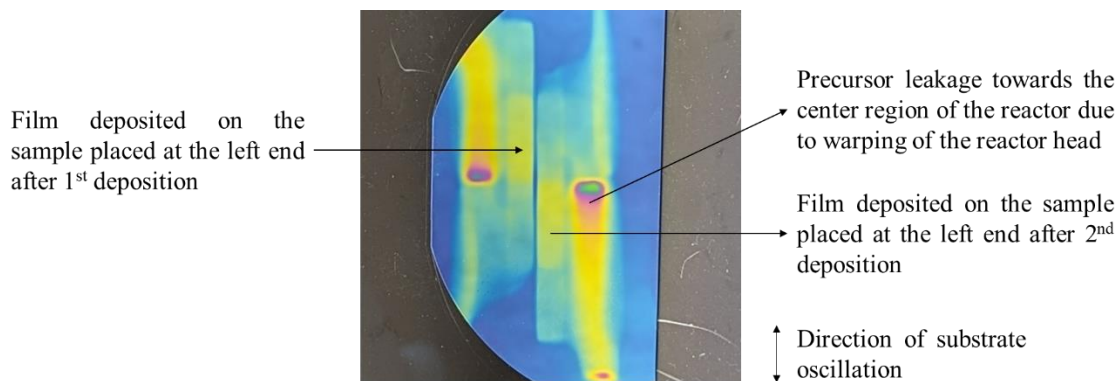


Figure 4.10 Film deposited on the sample after two depositions

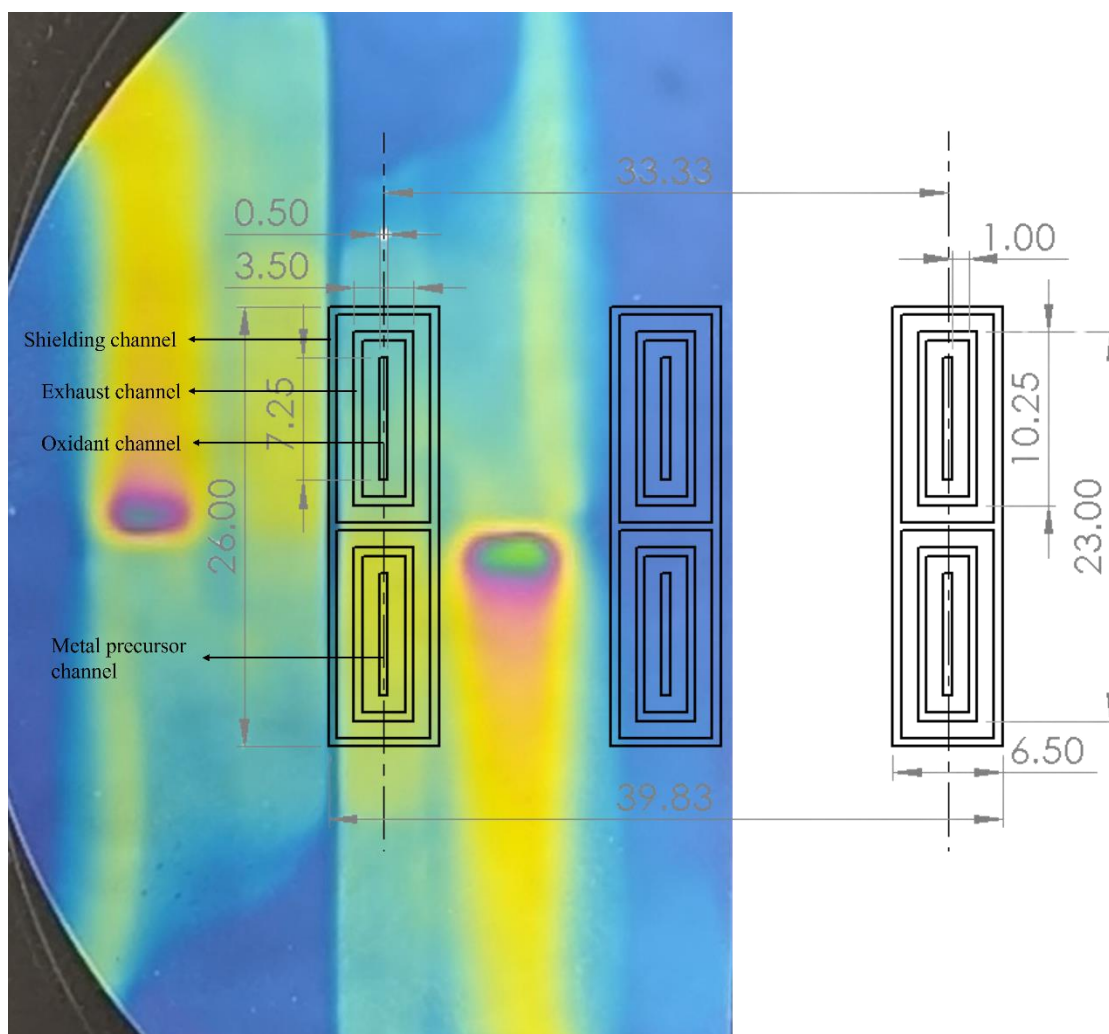


Figure 4.11 Channels of the reactor superimposed on the sample after 2nd deposition.

The sample was analyzed using EDX to determine if any zinc oxide was present in the region in between the two deposition regions. Spots inside and outside the deposition region were analyzed, as indicated in Figure 4.12.

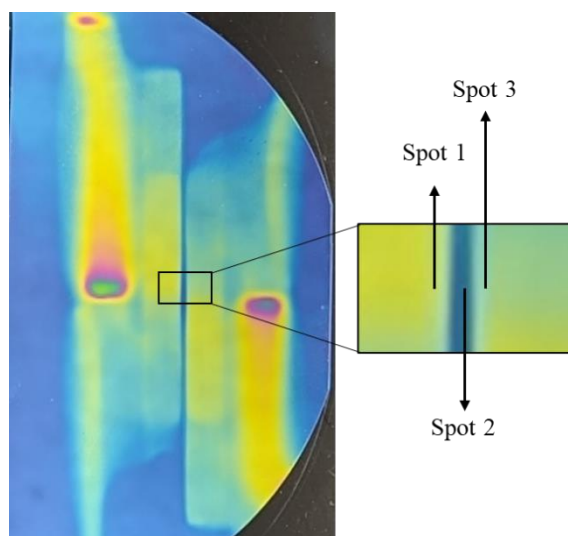


Figure 4.12 Part of sample used for EDX analysis. Spots 1, 2 and 3 are the analyzed spots.

The EDX results are presented in Figure 4.13 and the zinc content at each spot is tabulated in Table 4.1. It is seen that while a strong zinc signal is observed inside the ZnO deposition areas, only a trace amount of zinc is detectable in between the two deposition areas.

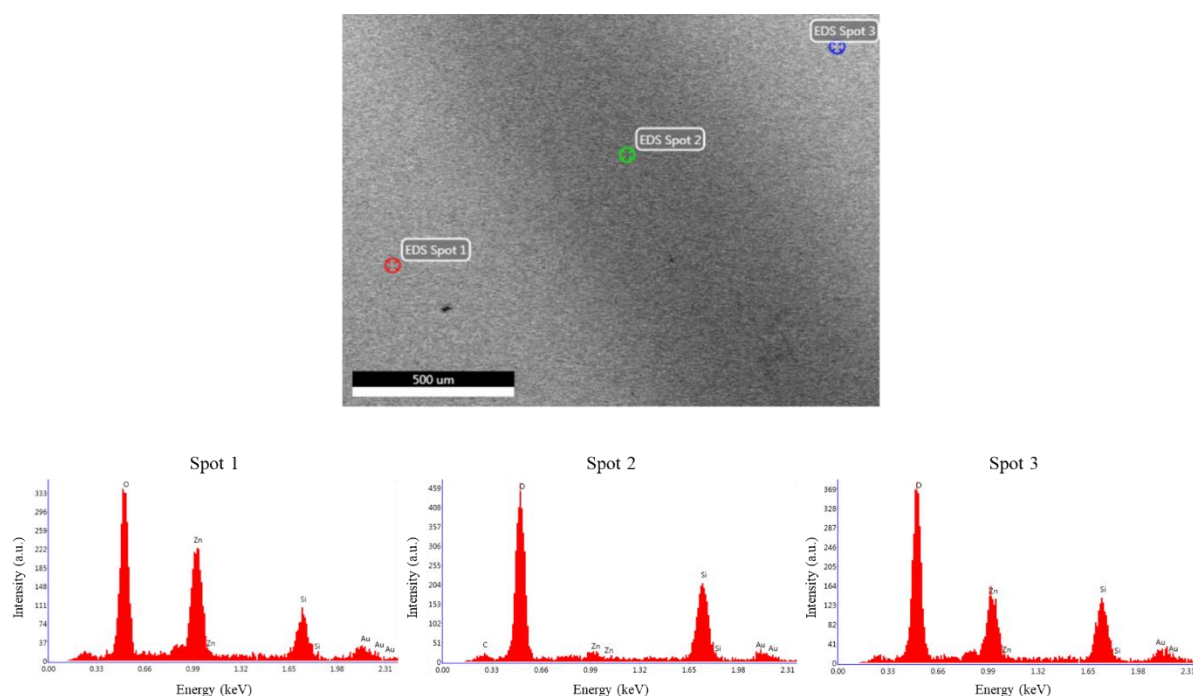


Figure 4.13 SEM image of the gap region (top) and EDX spectra at various spots (bottom). Note: Results generated from the system software using a Zeiss Ultra Plus FESEM coupled with an EDAX EDS detector.

Table 4.1 Elemental composition at different spots on the sample

	Element	Weight %	Atomic %
Spot 1	Zn L	35.62	16.82
Spot 2	Zn L	2.32	0.81
Spot 3	Zn L	24.43	10.76

4.4 Conclusion

In conclusion, two AP-SALD reactor heads were designed, 3D printed and tested for direct selective deposition of zinc oxide. Zinc oxide was deposited using the first reactor that can deposit wide patterns separated by a small gap between the patterns. Film growth was observed in the gaps where film formation was undesired. Moreover, the thickness of the film deposited along the separation gaps was significant, almost half the thickness of the film formed in other areas. Then a second reactor that can print narrower patterns was fabricated and the ability to deposit closely spaced patterns by moving the substrate by a slight offset distance relative to the reactor was tested. Using this method, it was shown that another thin film pattern can be deposited approximately 0.5 mm from the adjacent pattern. However, film growth was observed along the gap in between the patterns due to precursor leakage. Therefore, to deposit patterns separated by a small distance, the offset distance and nitrogen shielding must be carefully controlled and optimized to avoid leakage of the precursors, so that no film growth can take place at the region of separation in between.

Using 3D printing, reactor heads with sophisticated channel designs that cannot be fabricated using conventional manufacturing can be fabricated to deposit thin films at desired regions on a substrate by localizing the AP-SALD precursors at those regions. The distance between two adjacent strips deposited simultaneously is limited by the fabrication method selected, SLA in this case; however mechanical offsetting of subsequent depositions enables patterns with closely spaced features.

Chapter 5

Conclusion and future work

In conclusion, the first objective of this research was to develop methods to prevent or minimize powder formation in AP-SALD systems through comprehensive testing of growth inhibitors on 3D-printed samples and then reactor heads made from the same printer resin. It was found that ODPA and PVP effectively prevented alumina formation during deposition cycles at 100 °C. While ODPA demonstrated success in preventing alumina even at 70°C, PVP proved effective only at 100°C. Moreover, since DDT molecules decomposes and desorbs around 110 °C, it only prevented film growth on the samples at 70°C. For ZnO deposition at 100°C, the amount of zinc on the samples coated with ODPA and PVP was significantly lower. However, for ZnO deposition at 50°C, no zinc was present on samples coated with ODPA, PVP and DDT. The application of these inhibitors through dip coating a 3D-printed reactor head and depositing alumina using a commercial-scale AP-SALD system further revealed valuable insights. Due to the hygroscopic nature of PVP, the PVP-coated reactor heads exhibited powder formation after 200 cycles at 100°C and the intensity of the powder was more with an increased PVP concentration. On the other hand, ODPA-coated reactor heads demonstrated slightly reduced powder formation, especially at shorter dip coating times. It is to be noted that the coating time was lower than the coating time that successfully prevented the formation of alumina completely.

Challenges persisted as the inhibitors, while effectively preventing film growth on samples, could not entirely eliminate powder formation on the reactor head, prompting the need for a deeper understanding of gas flows. In an effort to gain insights on the dynamics of gases within the reactor-substrate gap and understand their impact on powder formation, preliminary flow visualization experiments were conducted using smoke as the tracer. Unfortunately, these attempts faced challenges, primarily attributed to the condensation of smoke which hindered the success of the visualization technique.

In the second objective, two uniquely designed AP-SALD reactor heads were developed to selectively deposit zinc oxide patterns on silicon substrates. Wide patterns (strips) separated by small gaps can be deposited with the first reactor, but film growth with significant film thickness in the undesired gaps highlighted a challenge. Further optimization of the gas flows and nitrogen curtains would be required to eliminate deposition in the gaps. Subsequently, a second reactor capable of printing narrower patterns was fabricated, showcasing the ability to deposit closely spaced patterns with a slight offset distance. This reactor revealed a promising observation of a clear film edge on one side of the pattern. However,

a notable challenge arose from reactor warping, leading to undesired film deposition on the opposite side of the pattern. In this method, successful deposition of patterns was demonstrated with minimal material extending beyond the desired area. To address this issue, further experiments are warranted to identify the optimum design or process parameters that can effectively prevent precursor leakage. Additionally, maintaining the reactor at a stable position and temperature is imperative to prevent reactor warping, which can contribute to precursor leakage. These refinements are crucial for ensuring the precision and reliability of the selective deposition process.

5.1 Future work

Firstly, the future work on AS-ALD revolves around testing various chemical coatings against ALD precursor nucleation. Only a few growth inhibitors have been reported in the literature for Al_2O_3 and ZnO depositions using TMA and DEZ as the precursors. Further research on stable and non-reactive materials such as fluoropolymers is required to prevent ALD precursor nucleation for a sufficient number of cycles in order to prevent powder formation on the AP-SALD reactor head. In addition to this, recent work on AS-ALD includes vapor-phase-delivery inhibitors, that can regenerate the quality of the degraded inhibitor layers. Such inhibitors can be integrated with the AP-SALD system to coat the reactors at regular intervals of time.

For the patterning strategies discussed in Chapter 4, instead of manually offsetting the reactor to produce closely spaced deposition areas, the substrate could be oscillated between two different reactors positioned such that the axes of their metal channels are separated by a small offset distance. This type of fabrication could be suitable for high-throughput applications. Moreover, with the help of 3D printing and careful design considerations, reactors with complex channels can be designed such that the precursors are delivered at different locations of the reactor head, such that the strips are deposited close to each other. In addition to this, recent interest has grown in the process of AS-ALD using small molecule inhibitors. Microchannels could be included in an AP-SALD reactor head that deliver SMIs on the substrate at desired locations to achieve area-selective spatial ALD.

Finally, apart from smoke visualization, there are a wide variety of other flow visualization techniques that can be employed for studying the flow pattern of the gases in the reactor-substrate gap, such as particle image velocimetry, laser induced fluorescence etc. Since the gap is typically less than 500 microns, microscale flow visualization techniques would be useful.

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Appendix A

Effect of dip coating High Temp Resin 3D printed parts against ZnO deposition at 100°C

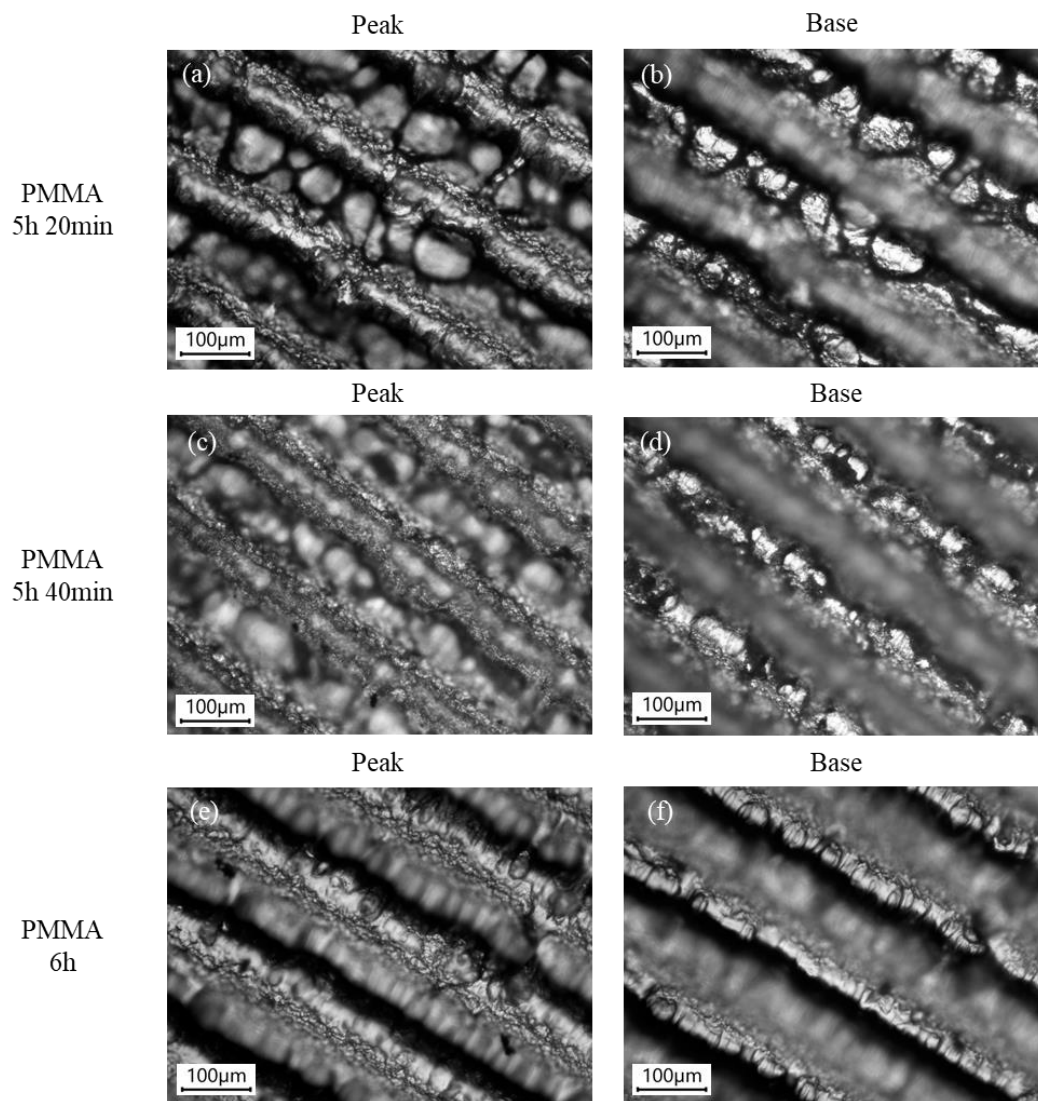


Figure A.1 10X magnification images of the ZnO-deposited samples dip coated with PMMA (High Temp Resin/PMMA/ZnO) for different time periods.

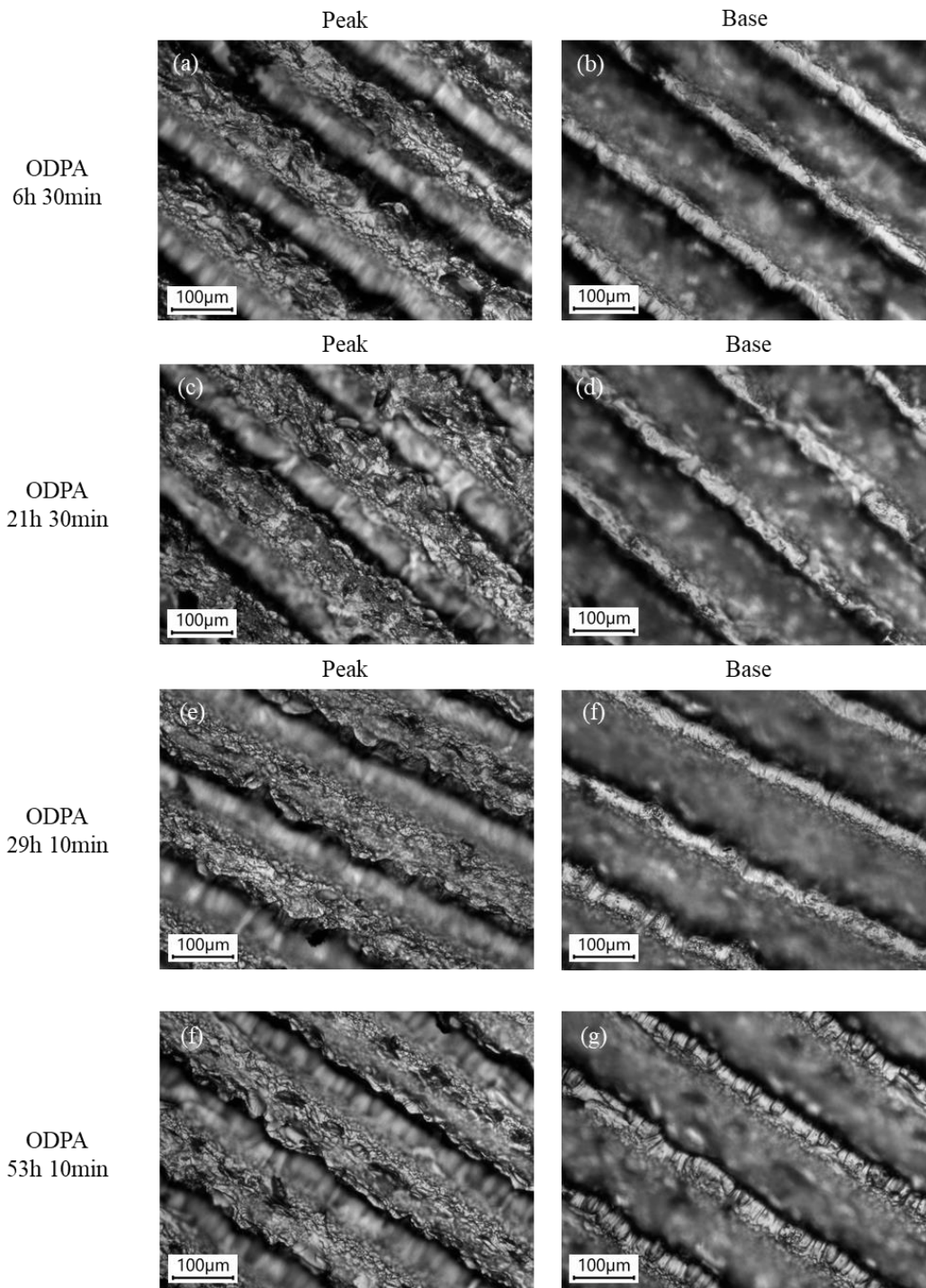


Figure A.2 10X magnification images of the ZnO-deposited samples dip coated with ODPA (High Temp Resin/ODPA/ZnO) for different time periods.

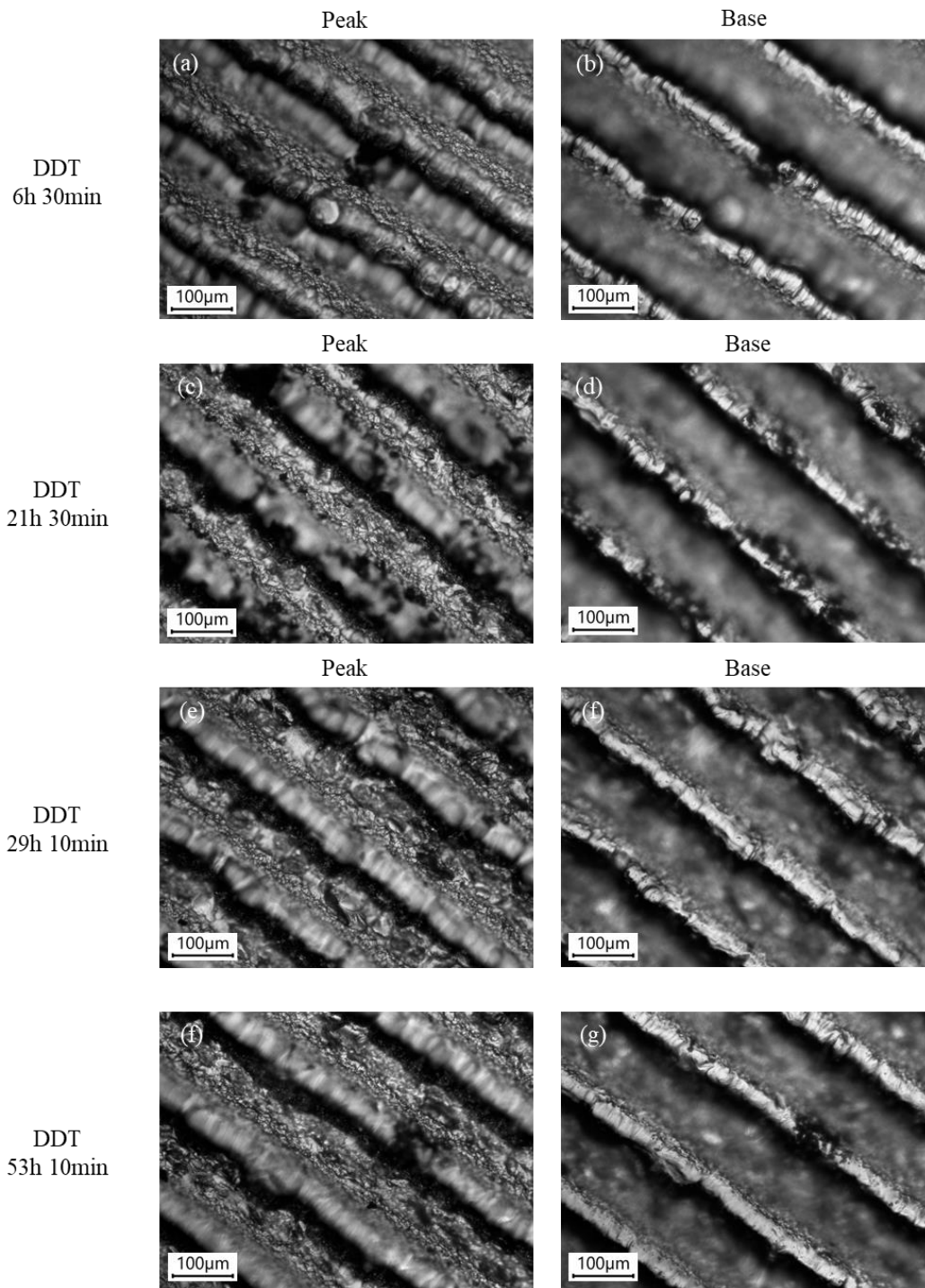


Figure A.3 10X magnification images of the ZnO-deposited samples dip coated with DDT (High Temp Resin/DDT/ZnO) for different time periods.

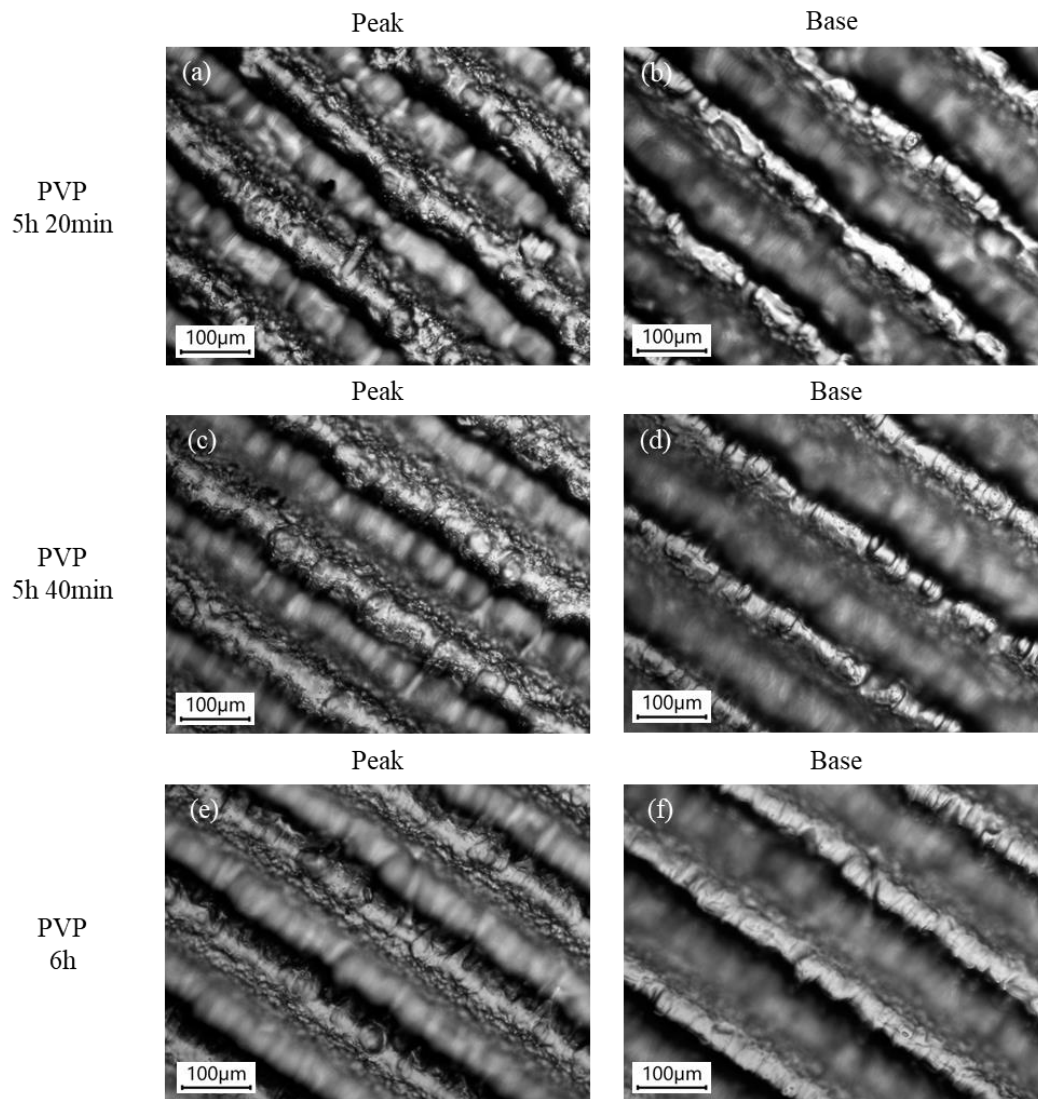


Figure A.4 10X magnification images of the ZnO-deposited samples dip coated with PVP (High Temp Resin/PVP/ZnO) for different time periods.

Appendix B

Effect of dip coating High Temp Resin 3D printed parts against ZnO deposition at 50°C

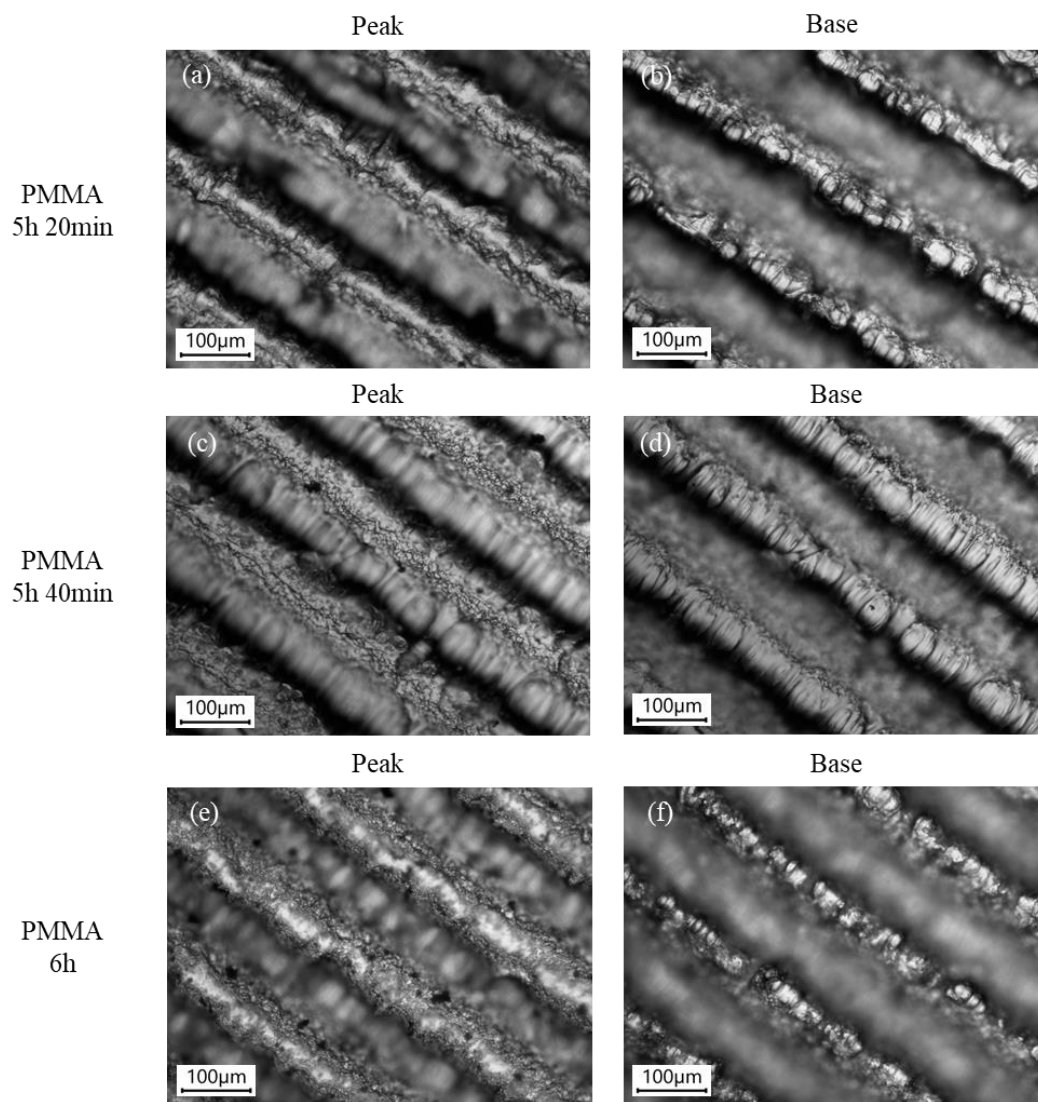


Figure B.1 10X magnification images of the ZnO-deposited samples dip coated with PMMA (High Temp Resin/PMMA/ZnO) for different time periods.

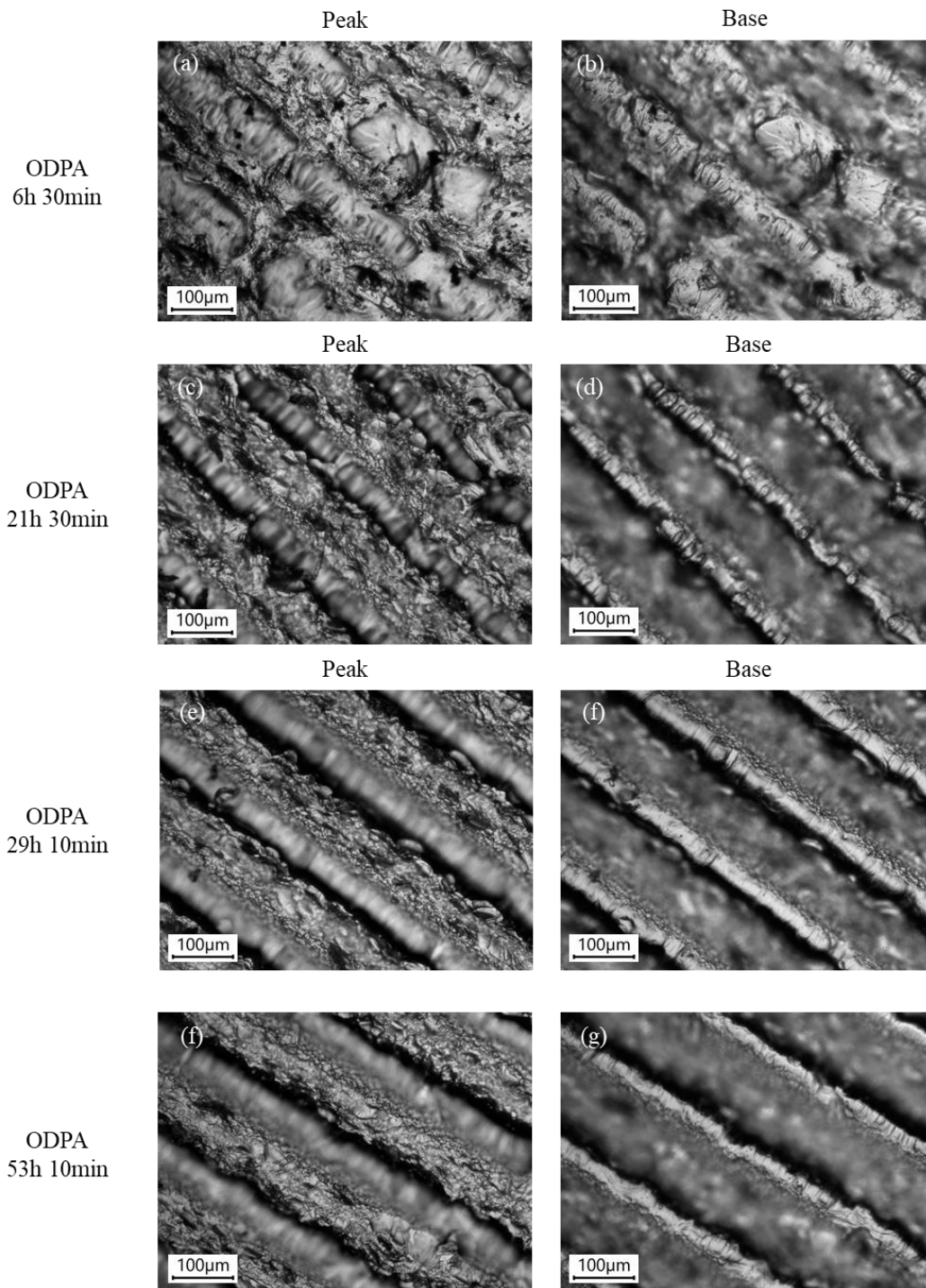


Figure B.2 10X magnification images of the ZnO-deposited samples dip coated with ODPA (High Temp Resin/ODPA/ZnO) for different time periods.

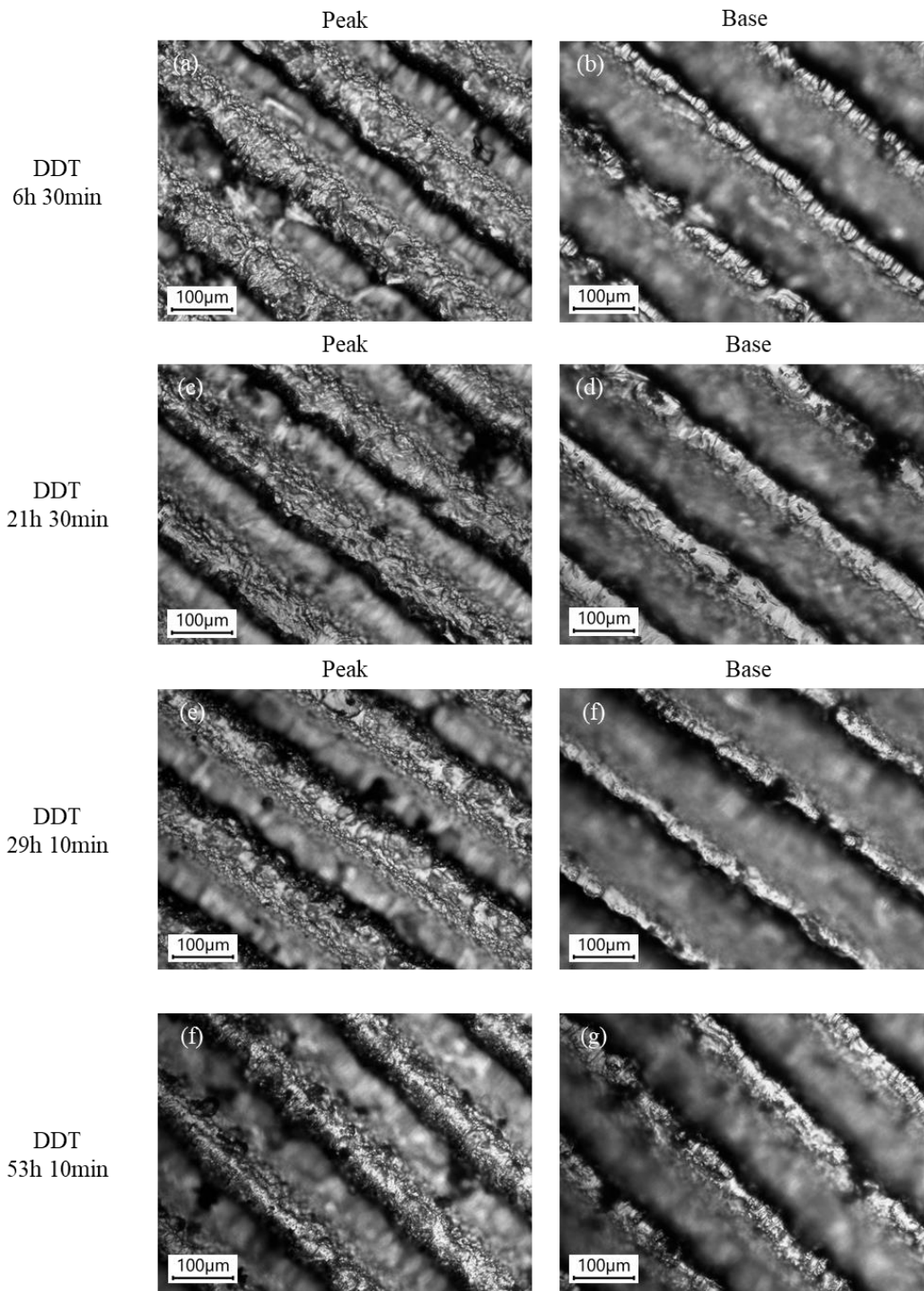


Figure B.3 10X magnification images of the ZnO-deposited samples dip coated with DDT (High Temp Resin/DDT/ZnO) for different time periods.

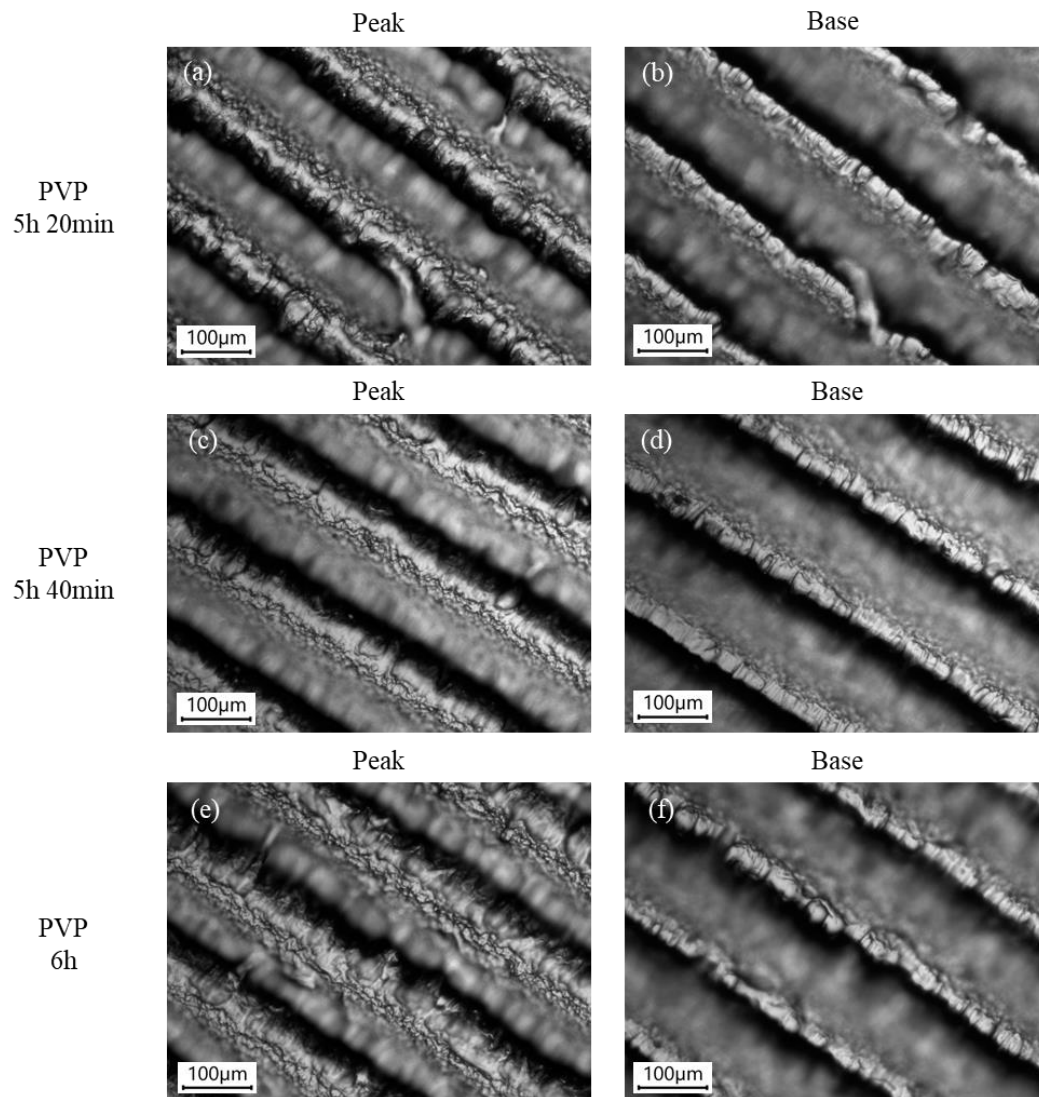


Figure B.4 10X magnification images of the ZnO-deposited samples dip coated with PVP (High Temp Resin/PVP/ZnO) for different time periods.

Appendix C

Flow visualization of gases in the reactor head-substrate gap of an AP-SALD system

C.1 Overview

As described earlier in section 2.4, the precursor channels should be well isolated to avoid precursor intermixing and must also be isolated from the ambient. When a metal precursor comes in contact with the oxidant either from the oxidant channel or the surrounding atmosphere, it leads to powder formation. Also, inefficient isolation of precursors can cause intermixing of gases, leading to CVD type reaction. As a result, a non-uniform thin film is deposited on the substrate.

Moreover, powder formation can be detrimental to the system. The powder can accumulate along the bottom surface of the reactor head and the reactor channels. This can affect the flow of gases in the reactor-substrate gap and affect uniformity of the deposited thin film. In addition to this, the powder accumulates along the exhaust channels, exhaust line and exhaust filter. This could lead to a pressure drop along the exhaust channel and the rate of removal of excess precursor and byproducts may drop to a lower rate causing further powder formation.

Finally, the powder can also end up in the deposited film, affecting film quality. Therefore, methods to prevent intermixing of gases and ensure effective removal of excess precursors, byproducts, and powders are crucial. The aim of this work is to use flow visualization techniques to determine the flow patterns of the gases flowing from the metal precursor and oxidant channels to verify effective gas isolation and removal. In this study, smoke flow visualization is tested because it is simple, cost effective, easy to setup and does not involve complex data reduction and analysis steps.

C.2 Initial smoke visualization setup

C.2.1 Experimental method

A schematic of the flow visualization setup is shown in Figure C.1. A fog machine was used to generate smoke required for flow visualization. The fog machine used here was a Hurricane 1200 from Chauvet DJ. In this type of fog machine, the fog fluid is heated to a vapor state by pumping the fog fluid through a heated steel tube with a small inner diameter. When the vapor enters the ambient atmosphere, a dense cloud of smoke is generated due to its condensation. The water-based fog fluid was purchased from

Chauvet DJ. Commonly, fog fluids are made using a deionized water-propylene glycol mixture. The fog machine can generate smoke at a maximum continuous rate of 18000 cfm. A controller was used to program the smoke machine to produce the required amount of smoke either continuously or at regular time intervals.

The fog machine was connected to the smoke chamber (also known as “plenum”), as shown in Figure C.1, to store the smoke. With the help of flowmeters, as shown in Figures C.1 and C.2, the nitrogen flowrate through metal precursor, nitrogen shielding, and oxidant precursor lines were adjusted. Separate inlets were provided for each channel (metal precursor, oxidant precursor, nitrogen shielding and exhaust) on the reactor head. Therefore, the tubes from the metal, oxidant, and shielding flowmeters were connected to the respective manifolds to split the flow. Tubes from the manifold outlets were connected to the respective channels on the reactor head. A diaphragm pump from ULVAC technologies, Inc. (DA-20B) was connected to the smoke chamber to remove any excess smoke present in the chamber.

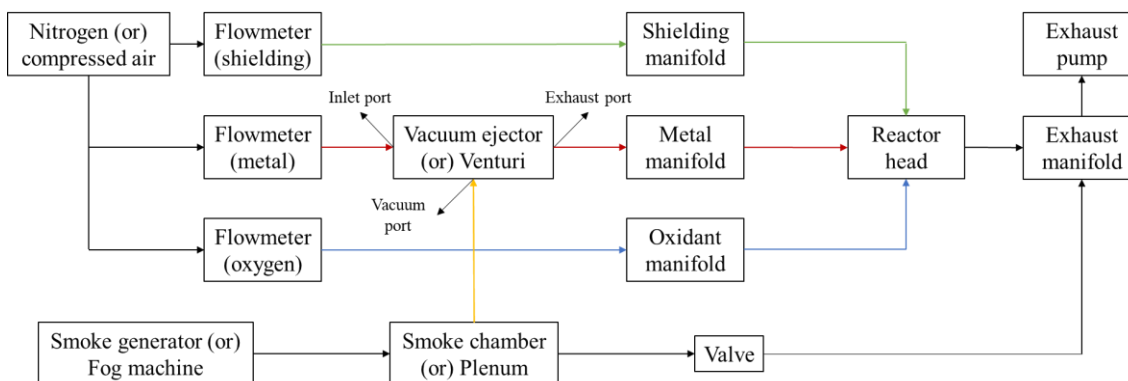


Figure C.1 Schematic of the flow visualization setup using smoke.

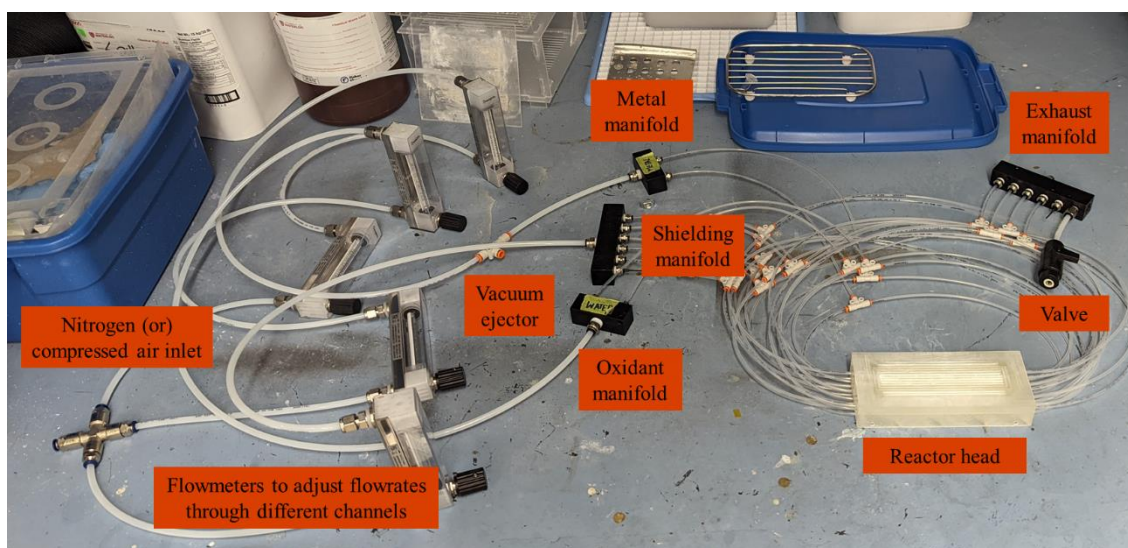


Figure C.2 Experimental flow visualization setup.

A vacuum ejector was used to bring smoke from the smoke chamber into one of the flow lines. The vacuum ejector consists of three ports, an inlet, an exhaust (outlet), and a vacuum port. As the gas flows from the inlet to the exhaust port, a vacuum is generated at the vacuum port. The inlet, exhaust and vacuum ports were connected to the flowmeter, manifold, and smoke chamber, respectively, as shown in Figure C.1. The smoke mixes with nitrogen and is delivered to one of the manifolds (the metal manifold in Figure C.1). The vacuum ejector can be connected either to the metal precursor, oxidant or nitrogen shielding line to visualize the flow from these outlet channels on the reactor head. The reactor head was placed in an inverted position and a glass substrate was placed on top at a distance of 200 microns with the help of shims to image the flows in the reactor substrate gap from the top and the front as shown in Figure C.3.

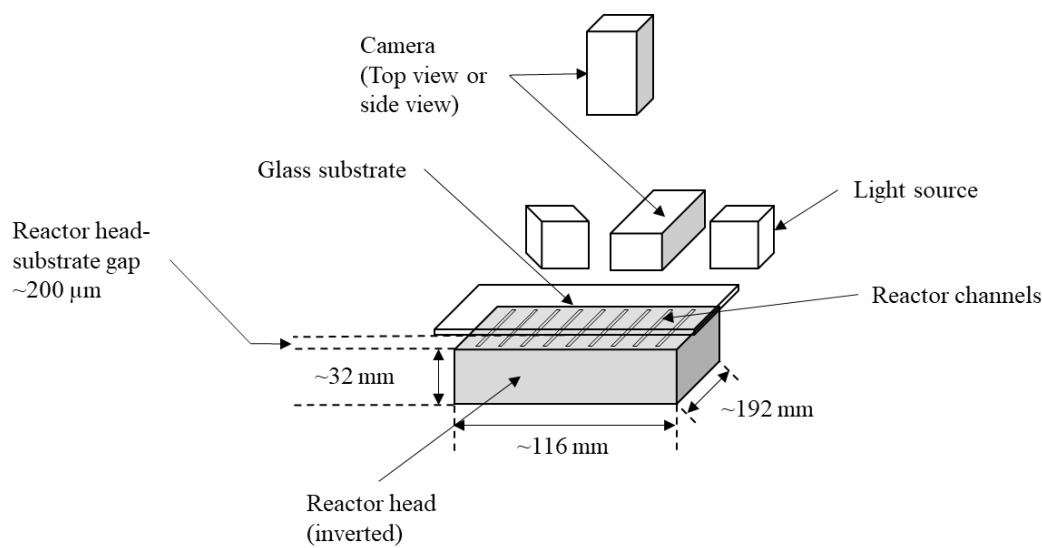


Figure C.3 Initial plan to image the flows in the reactor substrate gap from the front and the top.

C.2.2 Results and discussion

Initially, the smoke machine was directly connected to the metal manifold for testing, and when the smoke machine was operated at its maximum capacity, the smoke was visible along the metal precursor channels of the reactor. But the flow rate was very high since the smoke machine generates smoke at 18000 cfm. When the smoke machine was connected to the smoke chamber to allow control over the flow rate, most of the smoke started to condense along the chamber walls, as shown in Figure C.4. Similarly, the smoke was observed to condense on the substrate, resulting in fogging. In addition to this, when a vacuum ejector was used to draw the smoke from the plenum, the smoke began condensing along the tubes connecting the plenum to the vacuum port, exhaust port to the manifold and the manifold to the reactor head.

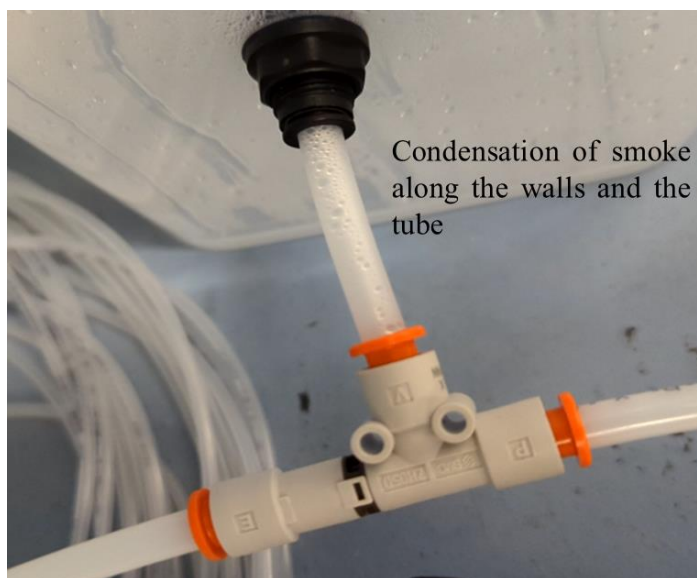


Figure C.4 Condensation of smoke along the walls of the smoke chamber and the tube connected to the vacuum port of the vacuum ejector.

To replicate flows used in the Functional Nanomaterial Group’s industrial-scale AP-SALD system, the flowrates in Table C.1 were set using the respective flowmeters. When the vacuum ejector was connected along the metal precursor and oxidant lines, no smoke was observed along the channels of the reactor head. When the vacuum ejector was connected along the nitrogen shielding line, the smoke was barely visible along the shielding channels of the reactor head. The smoke was clearly visible only when the flowrate was nearly 9000 sccm.

Table C.1 Flowrates of different flowmeters

Flowmeter	Flow rate
Nitrogen shielding	6500 sccm
Metal bubbler	70 sccm
Metal carrier	200 sccm
Water bubbler	70 sccm
Water carrier	1000 sccm

The amount of smoke carried by the nitrogen leaving the exhaust port of the vacuum ejector depends on the flowrate at the inlet. At higher flow rates, a higher vacuum is generated, and more smoke is carried. Moreover, most of the smoke condensed along the tubes due to the low temperature of the compressed air or nitrogen. In addition to this, when the reactor was placed in an inverted position, the build-up of the residual condensed liquid with a slightly high viscosity on the reactor caused clogging after operating for a short time. Therefore, methods to avoid condensation of the smoke become crucial for smoke visualization.

C.3 Various methods tested to avoid condensation of smoke

In order to prevent condensation of the smoke along the tubes and the reactor head channels, several methods were tested. These included:

- a) Reducing the length of the tubing and eliminating the manifold to split the flows
- b) Heating the tubes carrying the smoke to the reactor head with heating sleeves
- c) Using high flowrates to carry more smoke and controlling the flowrate downstream with a rotameter
- d) Using a condensation trap to remove the condensed liquid
- e) Using high density fog fluid
- f) Using a vacuum ejector that can generate higher vacuum at lower flowrates
- g) Using incense and an ultrasonic atomizer to generate smoke and mist for flow visualization
- h) Using an electronic atomizer to generate a smaller amount of smoke required for the flow visualization

All the above methods were tested for the metal channel. All the methods tried are illustrated in Figure C.5 and C.6. Detailed explanation of the methods and their effects are discussed in Section C.3.1. While performing these experiments, the reactor was placed on top of the substrate such that the channels are facing downwards to avoid residue build-up on the reactor head. The reactor was cleaned at constant intervals to avoid clogging due to residue formation.

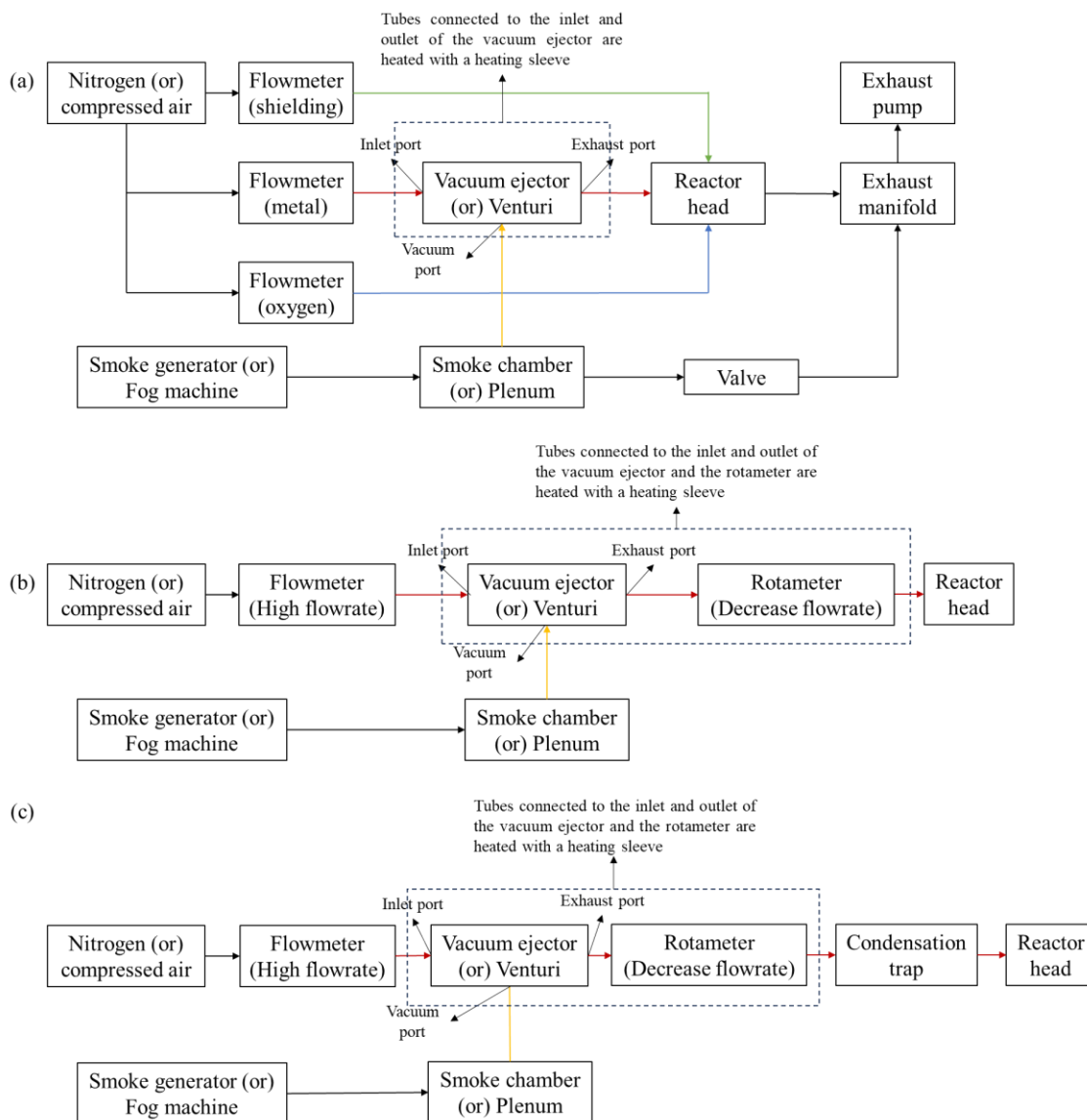


Figure C.5 Various techniques employed to control condensation of smoke generated using the fog machine. (a) Setup without manifolds and the addition of a heating sleeve. (b) A high flowrate generates a higher vacuum pressure to carry more smoke and the flow is controlled downstream using a rotameter. (c) A condensation trap removes the condensate before the smoke enters the reactor head.

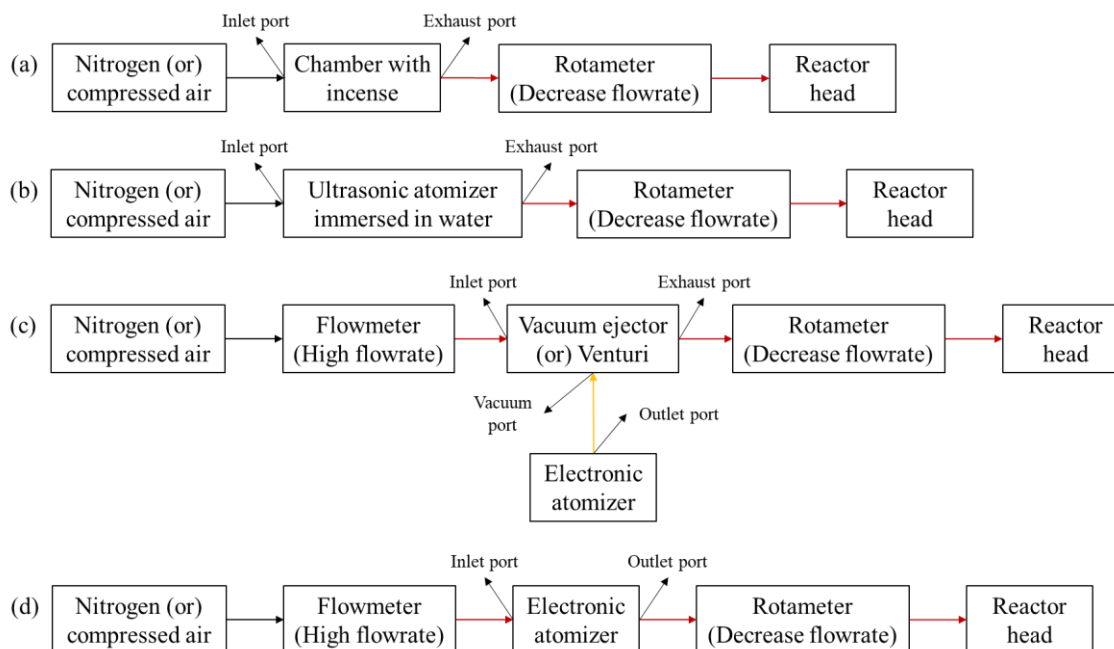


Figure C.6 Alternate methods for flow visualization using (a) incense, (b) ultrasonic atomizer, (c) and (d) electronic atomizer. The smoke can be produced either by creating a vacuum at the outlet of the atomizer or by passing nitrogen or compressed air through the inlet of the atomizer.

C.3.1 Experimental setup and observation

Figure C.5 (a) shows the schematic of the updated setup with a modified reactor head that eliminates the need for a manifold and heating of the line carrying the smoke to the reactor head. However, due to the low flowrate set on the metal flowmeters, the vacuum generated was insufficient to draw smoke from the smoke chamber, so no smoke was observed along the metal channels of the reactor head.

Therefore, a higher flowrate was used to create a higher vacuum pressure to carry more smoke from the plenum and the flow was decreased downstream with the help of a rotameter, as shown in Figure C.5 (b). No smoke was observed in this case along the metal channel, since the smoke began condensing along the channels on the reactor head leading to the formation of liquid residue. As shown in Figure C.5 (c), a condensation trap was placed downstream to the rotameter to remove the condensed liquid from entering the reactor head. As the nitrogen-smoke mixture passed through the condensation trap, all the smoke in the mixture condensed in the condensation trap and therefore, no smoke was observed along the metal channel.

A high-density fog fluid was purchased from Chauvet DJ that can produce thicker clouds of smoke when compared to the regular fog fluid. This was used to produce dense smoke using the smoke machine; however, using this type of smoke fluid led to the formation of more condensate in the tubes and channels and left more residue on the reactor head. As described earlier, the vacuum generated at a lower flow rate was insufficient to carry the smoke from the smoke chamber. Therefore, instead of using a higher flow rate to carry the smoke from the smoke chamber and decreasing the flow rate using a rotameter downstream, a similar type of vacuum ejector that can generate a higher vacuum to carry more smoke from the chamber was tested. However, this method also resulted in condensation of the smoke along the tubes. The higher concentration of the smoke resulted in increased concentration of the condensed liquid along the channels.

As all the above-mentioned methods did not facilitate flow visualization, incense and an ultrasonic atomizer were used to generate smoke and mist and study the flow along the metal channel. A chamber consisting of an inlet and outlet was filled with incense or water. The smoke was generated by burning incense and the mist was generated by immersing the ultrasonic atomizer in water. Nitrogen at high pressure was used to drive the smoke or mist in the chamber to the reactor head, as shown in Figure C.6 (a) and (b). The rotameter was set to the desired flow rate mentioned in Table C.1. In this case, smoke and mist was observed along the metal channel. However, it was only barely visible.

Finally, an electronic atomizer that can generate smoke by heating a very small amount of glycol was used to determine if generating a limited amount of smoke can prevent condensation. To generate smoke using the atomizer, high density fog fluid and glycerin were tested. Figure C.6 (c) and (d) describe the schematic of the setup for generating smoke using an electronic atomizer. In Figure C.6 (c), the high vacuum generated at the vacuum port of the venturi nozzle draws the smoke from the outlet port of the atomizer. In Figure C.6 (d), smoke was generated at the outlet port of the atomizer by passing nitrogen through the inlet port. In both cases, the condensation of smoke was observed when either glycerin or high-density fog fluid was used.

C.4 Conclusion

In conclusion, various experimental arrangements for smoke visualization were tested on the commercial-scale AP-SALD reactor head. However, these approaches were not suitable for examining the gas flow from the metal and oxidant channels of the reactor head, particularly at lower flowrates. The smoke condenses along the tubes and the channels of the reactor head. The observed issue may

arise due to the nature of the smoke fluid, which consists of a glycol-water mixture that can condense when it comes into contact with surfaces, leaving behind a residue. In addition to this, the low temperatures of the compressed air or nitrogen can cause the smoke to condense. Other possible advanced flow visualization techniques that can be used to study the flow patterns of gases from the metal and oxidant channels are listed in Chapter 5.