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Development of a High-Pressure Spatial Chemical Vapor Deposition Tool for Growth of Functional Materials

By

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Development of a High-Pressure Spatial Chemical Vapor Deposition tool for Growth of Functional Materials

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ABSTRACT

Development of next generation devices for high power, high frequency emitters, high efficiency electrical power conversion, and short wavelength (UV) emitters requires further development of the group III-N material system. Of particular challenge is the incorporation of indium (In) into the ternary or quaternary system (AlGaInN) due to its low decomposition temperature. In-containing films require reduced growth temperatures as compared to gallium or aluminum-containing films. To address this challenge, a new tool is proposed which can operate at elevated pressures up to 100 atm to increase the associated decomposition temperature. The proposed High-Pressure Spatial Chemical Vapor Deposition (HPS-CVD) reactor will permit high-quality growth of the complete solid solution of GaN-InN and AlN-InN at temperatures of at least 1000 °C, which opens the door for comprehensive bandgap engineering of device. CVD growth at elevated pressures faces multiple fluid dynamical, thermal, and mechanical challenges. To address these, computational fluid dynamics (CFD) techniques were carried out to analyze the fluid/thermal phenomena in this new CVD reactor design. The impact of rector design, chamber height, system pressure, inlet flow rate, and rotational speed were investigated and discussed. Flow instabilities arising from the heated and rotating susceptor have been minimized. Growth rates are anticipated to be enhanced by approximately a factor of 10 compared to an existing super-atmospheric horizontal MOCVD reactor design.
1 Introduction

1.1 Motivation

Light emitting diodes (LEDs) are regarded as the ideal light sources for displays because of their high brightness, durability, and minimal power consumption. After the development of the blue LED, LEDs can now act as a source of white light for general illumination with unprecedented efficiency (Figure 1-1). LEDs provide a considerable positive impact on energy consumption and the environment. Currently, roughly 22% of the electricity generated in the United States is dedicated to lighting applications. It has been computed that if all conventional white light sources in the world were converted to energy-efficient LED light sources, energy consumption could be reduced by around 1,000 TWh/yr – the equivalent of about 230 typical 500-MW coal plants – and greenhouse gas emissions by approximately 200 million tons [1].

Figure 1-1. Historical development of the most common white-light sources and improvements in their ability to produce white light efficiently [2].
An LED is a p-n junction semiconductor created by sandwiching an active, light emitting layer between an n-type and p-type layer (Figure 1-2). The n-type and p-type layers have abundance of electrons, which are negatively charged and mobile, and holes, which are positively charged and mobile, respectively. The energy difference between top of the valence band and the bottom of the conduction band (high- and low-energy electron state) is called the bandgap [3]. When the LED is forward-biased, electrons from the n-type layer and holes from p-type flow into and recombine in the active layer thereby emitting photons.

Figure 1-2. Schematic view of a double-heterostructure (DH) light emitting diode (LED) [3].

A single LED produces light of a particular wavelength with a narrow spectrum. To achieve white light using LEDs, this limitation can be addressed using different methods, some of which are presented in Figure 1-3.a. Although these solutions are inexpensive, most commercially accepted methods to produce white light LEDs, have low attainable efficacy and color-rendering index (CRI) values as compared to ideal white light.
CRI is a quantitative measure to determine how colors observed under LED emissions compare to an ideal white light source. Figure 1-3.b demonstrates the spectra for two phosphor-based white LEDs with different CRI values and sunlight.

Figure 1-3. a) Two dominant ways to produce inexpensive white light based on LEDs, b) comparison of the spectrum of ideal sunlight with two LED-based white-light sources [2].

Another solution is to produce the white light LED by combining three LEDs with blue, green, and red emitting color of light as presented in Figure 1-4, this can lead to higher CRI values and efficacy. Researchers [4,5] in the early 1990s developed high performance bright red and amber AlInGaP LEDs. Akasaki [6] and Nakamura [7] presented blue LEDs. However, a primary element of this solution, which is having a highly efficient green LED, is unavailable with current technology. Currently, LEDs with lower wavelength (below green) with significant efficiencies are not achievable. Group III-N material systems are a promising material to overcome these challenges, specially InGaN material system. InGaN/GaN LEDs can cover a wide range of emission wavelengths, from UV to infrared, by varying the indium content in the quantum well [8]. However, high In-content (> 30%) films are hard to achieve, for reasons discussed later in this chapter.
Figure 1-4. Schematic view of a white light LED produced by a combination of red, green, and blue LEDs.

Nowadays, III–nitrides and the III–phosphides are the most common materials system used for visible light LEDs. As demonstrated in Figure 1-5, both materials systems have low external quantum efficiency (EQE) in the green-yellow range of the visible spectrum. The lack of high efficacy LED in the green-yellow range is known as the green gap problem [9]. The external quantum efficiency of GaN-based yellow LEDs was reported to be only 26.7% (at 20 A/cm²) [10].
Figure 1-5. External quantum efficiency (EQE) of different commercial nitride and phosphide LEDs, demonstrating the “green gap” problem [9].

Many compound semiconductor systems have been investigated to address the green gap problem. A semiconductor with a bandgap in the range of 2.17 (yellow) to 2.48 (green) eV is required to use in the active region. Figure 1-6.a demonstrates the band gap energy and lattice constants for binary and ternary semiconductor systems in the group III-V material systems. Although these material systems can cover the UV-IR spectrum, many combinations of these binary systems are extremely difficult to grow because of their lattice mismatch of more than 2% leading to high dislocation density and hence low quality films [11]. As presented in Figure 1-6.b, the bandgap energy of AlGaInN compounds varies from 0.7 eV for pure InN to 3.4 eV for GaN and up to 6.2 eV for AlN [12–14]. This wurtzite crystal structure taken on by these materials not only has a direct band gap, leading to higher quantum efficiencies, but also is characterized by properties such as excellent
thermal conductivity (1.3 W cm\(^{-1}\) K\(^{-1}\) for GaN versus 0.55 W cm\(^{-1}\) K\(^{-1}\) for GaAs [14]),
physical and chemical stability, which are equally important for practical applications and
minimal toxicity [13,14].

![Figure 1-6. a) Band gap as a function of lattice constant for III–V compounds and
their ternary alloys [15], b) bandgap energy and relative wavelength of nitride-based
semiconductors [16].](image)

1.2 MOCVD growth of group III-nitrides

GaN was first grown by Juza and Hahn [17] in 1930s by passing ammonia over
gallium metal forming GaN needles. Grimmeiss et al. [18] employed the same method in
1959 and could synthesize small GaN crystals. Maruska and Tietjen [19] could successfully
grow GaN on sapphire using the hydride vapor phase epitaxy (HVPE) technique in 1969.

The development of the nitride technology ultimately started in the mid-1980s by
the application of metal organic chemical vapor deposition (MOCVD) to the nitride
system. The use of low temperature AlN [20,21], and GaN [22] as buffer layers led to
growth of high quality GaN films with mirror-like surfaces despite a staggering 15% lattice
mismatch between the sapphire substrate and GaN. Another breakthrough was achieved by
Amano et al. [23] and Nakamura et al. [24] when they obtained p-type GaN films using
Mg as an acceptor impurity, a requirement to form an LED. The research was followed by the demonstration of the first III-nitride-system-based p-n junction LED [23]. Although Mg was a promising candidate as an effective acceptor impurity, a large concentration of dopants is required due to the relatively high ionization energy (between 150-250 meV in GaN). This limits the fraction of activated acceptors to ~1% at room temperature.

The MOCVD growth of the device's structure takes place in an ammonia atmosphere promoting the formation of electrically inactive Mg-H complexes within the GaN matrix. Nakamura et al. [24] explained the acceptor compensation mechanism by fabricating p-type GaN films using post-growth thermal annealing in the nitrogen atmosphere instead of ammonia. The formation of neutral Mg-H complexes was unambiguously identified as the dominant mechanism of acceptor compensation responsible for resistivity increases in p-type films grown in an ammonia atmosphere, which Neugebauer et al. [25] confirmed by theoretical calculations.

Further improvement of the MOCVD technique led to manufacturing of a high quality InGaN films designed to form the active region of a blue light emitting devices. Nakamura et al. [26] used a novel two-flow MOCVD reactor to grow an InGaN multiple quantum well (MQW) structure which emitted a strong band to band emission from UV to green, by increasing the In content of the InGaN quantum well. This was the starting point for mass production of blue and green LEDs with high efficiencies.

Growth of III-nitrides thin films by MOCVD occurs using conventional precursors such as trimethylgallium (TMGa), trimethylaluminium (TMAI), and trimethylindium (TMIn) for Ga, Al, and In, respectively. Hydrogen and nitrogen are the most common carrier gases, into which the precursors are diluted before entering the reactor chamber.
Atomic N is most often supplied with NH$_3$. Usually, precursors start to decompose around 450 °C, however ammonia does not decompose as easily as precursors at growth temperatures. Growth rates of approximated 1-2 µm/h have been achieved at 750-850°C for GaN via MOCVD [27]. Common MOCVD growth temperatures for GaN is 900-1000 °C, which are incompatible with high In-content In$_x$Ga$_{1-x}$N alloys. These films require growth temperature of 600-800 °C. As a matter of fact, this thermal stability problem was the primary motivation for our research.

Although group III-N material systems demonstrate promising properties to fulfill the requirement of next generation opto-electronic devices. There are still many difficulties to grow high quality InN and In-rich In$_{1-x}$Ga$_x$N material system, which are discussed in detail later in this chapter.

In$_{1-x}$Ga$_x$N ternary alloy is remarkably vital for many applications such as the development of high efficiency green LED devices. Pure InN was synthesized by Juza et al. [17] in the wurtzite crystal structure by using InF$_6$(NH$_4$)$_3$ in 1938. In 1972, Hovel and Cuomo [28] produced polycrystalline InN on silicon substrates, and Marasina et al. used CVD to grow the epitaxial layer of InN. Matsuoka et al. and Wakahara et al. then produced InN by the MOCVD process for the first time [29].

MacChesney et al. [30] demonstrated the high dissociation pressure of InN, as presented in Figure 1-7. High quality InN has not been produced by a traditional MOCVD process, because the low growth temperature is necessary to restrict the decomposition of InN. However, the low processing temperatures leads to poor cracking of ammonia as a nitrogen precursor and poor mobility of adatom on the surface [11]. Although increasing the temperature improves the NH$_3$ decomposition, it leads to InN thermal etching.
Based on Figure 1-7, it can be concluded that raising the MOCVD pressure should lead to higher achievable growth temperature. Indeed this was demonstrated by Dr. Dietz’s group as shown in Figure 1-8 demonstrates the potential of increasing the overall system pressure during the growth of InN and high-In content InGaN films. A linear dependence between growth temperature and system pressure is observed leading to the conclusion, based on extrapolation, that InN can be grown at ~ 1000 °C for system pressures of 70 atm. Growth at these pressures could open the possibility of stable growth of the full range of In-content InGaN alloys.
Figure 1-8. Increase in indium content in group-III nitride materials as a function of total system pressure in high pressure MOCVD system [11].

1.3 Existing Designs

Literature review suggests only two research groups have designed and built a super-atmospheric (> 2 atm) MOCVD reactor. Dr. Dietz’s group constructed a 1st generation of HPCVD reactor at North Carolina State University in 1996 and a 2nd generation at Georgia State University in 2001, shown schematically in Figure 1-9 [31–34]. Moreover, Dr. Stokes’s group at the University of North Carolina at Charlotte designed and built a vertical rotating-susceptor MOCVD chamber capable of growth pressures up to 2.5 atm, Figure 1-13 [35].
Figure 1-9. Schematic of 2nd generation HPCVD reactor designed by Dr. Dietz’s group [35].

Dr. Dietz’s group injected pressurized precursors, into a horizontal reactor with a constant cross-section and symmetric sapphire substrates arrangements in the upper and lower channel walls, see Figure 1-11 [11]. They performed pressure tests up to 120 bar, however, gas flow dynamics in their HPCVD reactor restricted the processing window of pressure ranges to only 15 bar, as shown in Figure 1-12. In addition, due to the increase of
pressure, the flow rate had to be reduced significantly to remain within the laminar flow regime directly leading to a reduction in growth rate (~200 nm/h) as showed in Figure 1-13, and low quality films [37]. Therefore, accessing the growth regime at super-atmospheric pressures brings significant challenges in maintaining laminar flow regimes to prevent gas phase pre-reactions while controlling precursors support through a reduced diffusion layer to the growth surface and optimizing the growth surface chemistry. To address these challenges, a new CVD reactor design is proposed which can operate at system pressures up to 100 atm.

Figure 1-11. Picture of 2nd generation HPCVD reactor designed by Dr. Dietz’s group reactor flow channel, which is 50 mm in width and 1 mm in height. The sapphire substrate is seen along the center axis of flow and is held in two α-Al₂O₃ plates. [11]
Figure 1-12. Laser light scattering analysis showing transition from laminar to turbulent flow conditions for GSU-HPCVD reactor.

Figure 1-13. InN growth rate as a function of HPCVD reactor, designed by Dr. Dietz’s group, pressure [37].

They could grow of InGaN on GaN substrate with approximately 0.14 μm/hr growth rate. No other literature were found about the InGaN composition or quality of thin film which they grew with vertical rotating-susceptor MOCVD reactor.
1.4 Principles of MOCVD

MOCVD is the most common technique for large scale semiconductor materials production. This technique has several advantages over other growth methods such as lower production cost, uniform growth, flexibility in precursor selection, and a wide range of processing conditions. Although MOCVD is the most popular method to grow group III-nitrides, there are many challenges to grow high quality indium rich Ga$_x$In$_{1-x}$N. MOCVD technique is a complex growth process integrating several disciplines, such as mass transport, heat transfer, kinetics, thermodynamics, and chemistry, which are summarized in Figure 1-14. Basic MOCVD principles will be discussed further in the next sections.

![Diagram showing the chemical vapor deposition process](image)

Figure 1-14. Basic principles involved in Chemical Vapor Deposition process [38].

1.4.1 MOCVD growth Processes

The MOCVD process is a non-equilibrium growth method in which the precursors are transferred via carrier gas to a heated surface, typically a atomically smooth single
crystal surface. They react on the heated substrate and their deposition results in epitaxial growth of the desired material as a thin film. The carrier gas then carries away byproducts of the reactions. The MOCVD reaction can be generally summarized as follows:

\[ R_3M(g) + EH_3 \rightarrow ME(s) + 3RH(g) \]

where R is an organic radical, M is a metal, and E is a nonmetal. The organometallic sources for group III are typically liquid trimethylgallium and trimethylaluminum or solid trimethylindium under processing conditions. Precursors are volatilized and commonly delivered to reactor via flow of carrier gas such as nitrogen (N\(_2\)) or argon (Ar) in bubbler, as shown in Figure 1-15.

![Bubbler setup of precursor materials](image)

Figure 1-15. Bubbler setup of precursor materials [39].

The MOCVD process for group III-V materials consists of homogeneous and heterogeneous reactions. Precursor molecules will transfer from the bubbler to the reactor via carrier gas (H\(_2\) or N\(_2\)). Once they reach the heated zone in the reactor, they can go through desired, or undesired, gas phase reactions. Undesired reactions include
decomposition or adduct formation in the gas phase. While for desired reactions, precursors will diffuse through the boundary layer to reach the substrate and adsorb onto the surface. The adsorbed species may decompose or desorb if the temperature is too high relative to the precursor’s bond strength, a common problem for indium precursors at high temperatures. When precursors decompose, adatoms will diffuse on the surface to incorporate into the film and create a new crystal bond. Gaseous byproducts diffuse through the boundary layer away from the growth surface until they are swept away by the carrier gas to the exhaust [40], demonstrated in Figure 1-16.

Figure 1-16. Schematic of growth steps in MOCVD process.

Thermodynamics defines the driving force for the growth process by determining which direction the reaction will occur and hence if growth will occur. Kinetics determines the rate of reactions, and hydrodynamics regulates the mass transport of source materials via carrier gas to the growing interface, reaction uniformity at the surface, and temperature distribution [40]. As presented in Figure 1-17, three growth regimes can be for MOCVD
growth of a material: kinetically limited, mass transport limited, and thermodynamically limited regimes.

![Schematic of the qualitative temperature dependence on the growth rate in MOCVD process.](image)

Figure 1-17. Schematic of the qualitative temperature dependence on the growth rate in MOCVD process.

1. **Kinetically limited regime:** due to low temperature, surface reactions are slower than mass transport and are limiting the growth rate. The atomic landscape of the deposition surface (crystallographic termination and availability of atomic steps and kink site) make a significant contribution to the growth rate. The growth rate as a function of temperature can be defined by an Arrhenius equation:

   \[ k = Ae^{\frac{-E_a}{RT}} \]

   where \( k \) is the rate constant, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature. This regime is undesired because the growth rates in kinetically limited regime have radical changes relative to temperature changes and kinetics of one element is different with another element.
2. **Mass transport limited regime**: gas diffusion through the boundary layer is slower than surface kinetics, making mass transport the limiting step. Since mass diffusion has a weak dependency on temperature, the growth rate is approximately constant and determined by the concentration of precursors in the gas stream. This regime is desired for growth of materials because growth rate is controlled by concentration of source materials in the gas flow.

3. **Thermodynamically limited regime**: at high temperatures the growth rate drops due to depletion of the reactants caused by an increase in desorption rate, gas phase reactions leading to loss of precursor, deposition on the reactor walls, and decomposition of the growing film.

InN is typically grown at the boundary between mass and thermodynamically limited regime. By increasing the pressure, growth temperature can increase which leads to grow InN in mass transport limited regime. To better understand the process parameters in MOCVD growth, it is crucial to find the optimal parameter window for the growth of high quality thin films with a maximum growth rate.

1.5 **MOCVD hydrodynamics**

In recent years, advanced CFD modeling technique has been used to design and optimize the performance of MOCVD reactors [41–48]. The reaction chamber flow conditions and temperature determine the film quality, uniformity, and deposition rate in most CVD processes. CVD reaction flow characterization studies have become essential for the improvement of the semiconductor manufacturing process [49]. The CVD reactor design success depends on the ability to achieve a stable and vortex-free flow pattern at
optimal operating conditions to reach growth uniformity and the maximum deposition rate by preventing adduct formation and loss of precursors [50–52]. The most essential prerequisite for designing a CVD reactor is to achieve a uniform boundary layer across the substrate to enable controlled growth and compositional uniformity, while operating in the mass transport limited region.

CVD reactors are commonly classified into two general designs: horizontal or vertical reactors, illustrated in Figure 1-18. Horizontal reactor designs are favorable due to their simple design, however uniform growth in horizontal reactors is hard to achieve. A vertical showerhead reactor results in more uniform deposition on the wafer due to more control in flow pattern compared to horizontal reactors [53]. Vertical CVDs with a rotating susceptor involves complex flow dynamics driven by interactions between buoyancy forces (natural convection), wafer carrier rotation, and forced convection. This type of reactor has been studied intensively theoretically and experimentally during the last two decades [54–62]. For example, Evans [54] used numerical solutions of the Navier-Stokes equations and mixed convection parameter (Gr/Re$^{3/2}$) to demonstrate that increasing the inlet fluid velocity effectively reduced gas vortex.
Figure 1-18. Schematic view of two common design of CVD reactors: a) horizontal and b) vertical showerhead reactor.

Disk rotation and impinging jet are two fluid flow mechanisms used to control uniformity of the boundary layer in vertical showerhead CVD reactors [63]. Figure 1-19.a represents the gas flow passing through a porous medium which acts as a gas distributor to achieve an axially uniform flow in the inlet. Inlet geometry is one of the most influential factors that determines the reactor performance. For instance, recirculating loops or eddies can be prevented by optimizing the angle of divergence. The goal is achieving laminar flow through the reactor without recirculating loops or eddies which leads to adduct formation, memory effects, and lack of control on thin film composition. Furthermore, the hydrodynamic boundary layer width, $\delta_w(h)$, in the inlet depends on gas viscosity, the height of the inlet (h), and inlet gas velocity. Figure 1-19.b shows that the vertical axially uniform flow profile above a heated substrate surface, demonstrates that the stagnation point flow geometry is a special case of an impinging jet for which the axial velocity is independent of radial position and a plane jet impinges vertically on the flat surface.
Figure 1-19. a) Schematic of a single wafer shower head CVD reactor, b) schematic of the fluid flow in a stagnation point configuration [64]

For a uniform boundary layer to be formed on top of a static substrate with the layer thickness ($\delta_s$) given as:

$$\delta_s = 5.83 \sqrt{\frac{\nu \ast h}{V}}$$

Where $\nu$ is the kinematic viscosity, $h$ is the height of the inlet, and $V$ is the inlet velocity.

CVD reactor performance is also affected by thermal convection. Free thermal convection can destabilize the gas flow as cold inlet gas impinges on the heated substrate in the CVD reactor. This effect can be reduced by operating at reduced pressure (sub-atm pressures), increasing the volume flow rate, or rotating of the substrate by dominating the forced thermal convection.

As a consequence, for the development of a high-pressure CVD reactor an increase in the volumetric flow rate and an increase in the substrate rotation are the most impactful choices to reduce the effect of thermal convection on the gas flow. This improves the uniformity of gas flow on top of the substrate and also radially, as it pumps out the reaction
byproducts from the surface. The resulting uniform boundary layer, as shown in Figure 1-20, with a thickness of $\delta_r$ forms on top of the rotating substrate and is given by:

$$\delta_r = 5.5 \sqrt{\frac{v}{\omega}}$$

where $\omega$ is the angular velocity of the rotating disk [63].

![Figure 1-20. A schematic of the boundary layer on a rotating-disk [65].](image)

The Richardson number (Ri) is a dimensionless parameter used to estimate the relative magnitude of buoyancy and forced convection. Sparrow et al.[66] presented that the dominant flow mechanism can be determined by the Richardson number which is the numerical value of the ratio of Grashof number (Gr) and Reynolds number (Re), as are given below:

$$Re = \frac{V \times D}{v} \quad Gr = \frac{g \times \beta \times \Delta T \times h^3}{v^2}$$

$$Ri = \frac{\text{Natural Convection}}{\text{Forced Convection}} = \frac{Gr}{Re^2}$$

Where D is the inlet diameter, g is the acceleration of gravity, $\beta$ is the thermal expansion coefficient of the gas, and $\Delta T$ is the difference between the gas inlet temperature
and substrate temperature. When $\text{Ri} \ll 1$ free convection can be neglected [64], therefore thermal effects on flow pattern are minimized. As Richardson number demonstrates, the height of inlet ($h$) is the most crucial variable in the CVD reactor design substrate to achieve a laminar flow pattern through the CVD reactor and needs to be minimized.
2 OBJECTIVES

2.1 Thesis Objective

This study investigates and optimizes the design of a newly proposed High-Pressure Spatial Chemical Vapor Phase tool (HPS-CVD) designed for epitaxial growth of materials at high pressure, in particular decomposition-limited materials.

The primary objective of this thesis is to analyze the transport phenomena in the proposed HPS-CVD reactor design and reducing flow instabilities arising from the heated and rotating substrate by revising the design. The effects of reactor design, chamber height, system pressure, inlet flow rate, and rotational speed were investigated to achieve a stable, vortex-free flow pattern which will lead to a uniform growth rate.
3 APPROACH

3.1 HPS-CVD Design

Accessing the growth regime at super-atmospheric pressures brings significant challenges to prevent gas phase pre-reactions while controlling precursors passing through a reduced diffusion layer to the growth surface and optimizing the growth surface chemistry. Gas phase reactions need to be suppressed while precursors reach the substrate surface though a diffusion layer in a controlled manner to optimize the growth surface chemistry. Hence, precursors are physically separated by separation barriers and have a separate path for each precursor prior to reaching the boundary layer. This prevents mixing of precursors and reduces the probability of gas-phase collisions. Moreover, researchers [67–69] have reported that separating gas inlets in CVD reactors may improve growth rate and film thickness uniformity. Therefore, each precursor is designed to have an individual chamber, separated by an adjustable mechanical barrier. The wafer is cyclically exposed to these chambers in a circular path, as shown in Figure 3-1. Moreover, the boundary layer thickness needs to be controlled by mechanical separating barriers. So, the boundary layer thickness doesn’t need to be controlled via rotational speed which would negatively impact the ability to control growth parameters.

Having separated chambers for each precursor enhances the capability of HPS-CVD reactor. Each chamber can be assigned to a specific precursor and precursors may change dynamically during the growth process. Since precursors are spatially separated and the nitrogen pressure is increased to high pressures, we are referring to the new design as High Pressure Spatial CVD (HPS-CVD) reactor.
3.2 Target Specifications

The HPS-CVD reactor design has the following target specifications:

1) Prevent gas phase pre-reactions by physically separating gas supply zones.

2) Substrate temperature must reach 1000 °C (for growth of InGaN alloys) with a target of up to 1400 °C (for high Al containing AlInGaN alloys).

3) Design reactor pressure needs to reach 100 atm.

4) Reactor wall temperatures are targeted to be lower than ~425 °C to:
   - reduce undesirable depositions on the wall
   - expand on materials selection window (use of ferrous alloys) and enable easier compliance of the guiding ASME Pressure Vessel Codes
   - reduce maintenance cost
increase ease of manufacturability

5) Gas flow rates are targeted to be on the order of 5 slm leading to a target 0.5 µm/min deposition rate. The primary motivation is the minimization of overall gas consumption.

6) Rotational speeds of the substrate carrier needs to below 1000 rpm, though ideally variable to allow for its optimization during the growth of thin films. It is desired to be as low as possible to avoid substantial wear and tear on the parts.

7) Process window, as determined by the combination of substrate temperature, gas flow rates, and system pressure, should be maximized to ease synthesis materials.

8) The system should allow for multiple wafer growth in parallel to provide a pathway for commercialization.

9) The number of gas chambers should be optimized to allow for the growth of at least ternary nitrides with both p- and n-type dopants. The ultimate target would include eight source chambers for cation sources (B, Ga, In, and Al), two chambers for anion sources (N), and two dopant sources (Mg and Si).
4 METHODS

Design of the HPS-CVD reactor is more complicated than a regular CVD reactor due to higher pressures resulting in easier onset of turbulent flow formation, increase of gas phase reactions, increased mechanical design complexity, and increased complexity of control systems. Computational fluid dynamics (CFD) models are a crucial first step to develop a basic understanding of the transport phenomena in HPS-CVD reactor design process and predict viability of the tool.

Substantial CFD modeling occurred and as part of this thesis a variety of reactor geometries were investigated. Process parameters and how they affected the flow pattern and heat transfer phenomena in the HPS-CVD reactor were explored.

4.1 Geometry Approach

For 3D geometry design, SolidWorks software was used. It is an industrial grade computer-aided design (CAD) program for engineering applications and can be interfaced with COMSOL Multiphysics platform which allows for directly importing 3D CAD designs to the CFD modeling platform.

4.2 Modeling Approach

For computational fluid dynamics (CFD) modeling, COMSOL Multiphysics software was used. COMSOL is a cross-platform finite element analysis, solver and multiphysics simulation software. COMSOL Multiphysics platform allows coupling of heat transfer (conduction, convection, and radiation) and fluid flow (K-ω model) physics [70]. Surface reaction physics can be added in the future to investigate the effects of
momentum, heat, and mass transport within the HPS-CVD reactor. Although COMSOL Multiphysics is a user-friendly platform, due to the complexity of the HPS-CVD geometry no mathematical approach to validate simulation results was found. It would therefore be necessary to build a prototype for validation of modeling results.

The following conditions were selected for CFD and heat transfer simulations:

➢ Boundary Conditions:
  
  o For fluid (turbulent) flow (K-ω model) physics:
    
    ▪ Inlet: Set flow velocity at the inlet plane.
    ▪ Outlet: Set pressure difference at exhaust plane.
    ▪ Rotating Wall: Sliding wall condition with rotational speed.
  
  o For heat transfer:
    
    ▪ Set a constant temperature (1000 to 1373 K) boundary condition at the substrate surface and define that surface as a radiation source to ambient.
    ▪ Initially, other walls defined as thermally insulated walls. Later, cooling will be assigned leading to a constant temperature wall condition.

➢ Mesh:
  
  o Unstructured mesh with boundary layer mesh applied (approximately 5.9×10⁻⁴ m³ volume size). For each geometry, there were approximately 7 million mesh elements.

➢ Typical simulation conditions:
  
  o Inlet Gas pure N₂, H₂, or NH₃
- Total system pressure: 1, 10, or 100 atm
- Substrate T: 1000 to 1373 K

Typically, each simulation takes up to 30 hours to be solved on our computing computer (Intel Xeon CPU E5-2609 v4 @1.70 GHz, 16 cores, 128 GB RAM). The computational time depends on the complexity of the geometry and size of the applied mesh.

Initially, symmetry conditions were used to reduce the computational time to approximately 6 hours, however in later designs because of the complexity of the geometry, symmetry conditions couldn’t be applied.

In order to evaluate our design, the following parameters calculated by CFD simulation where investigated:

- The appearance of vortices in velocity streamlines
- Temperature distribution throughout the chamber
- Residence time and overall flowrates of the gases within the chambers
- Boundary layer thickness
- Pressure difference between inlet and outlet
5 RESULTS AND DISCUSSION

The initial design concepts materialized into a particular system designs, as presented in Figure 5-1, and further revised over the course of the research. A 2-inch wafer size was selected as a substrate size, which is a standard wafer size for research level work and associated fabs exist for further processing of these materials. A symbiotic relationship between CFD simulation results and design modifications lead to several modified design configurations and summarized in the following sections. 15 design iterations were studied which are categorized in four generations with major modifications applied between each generation. All designs in a specific category (“generation”) pursue a particular design guideline or philosophy, while minor revisions track as continual increases in version # starting with the very first design proposal. Table 1 summarizes this information while subchapters discuss in more detail.
Table 1. Detailed information on the four design generations and their characteristics.

<table>
<thead>
<tr>
<th>Categories</th>
<th>System Design Version #</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st generation</td>
<td>V.1 - V.6</td>
<td>- Introduce individual source gases separately into chamber</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Modify inlet path to specific gas properties to ensure laminar exit flow into chamber</td>
</tr>
<tr>
<td>2nd generation</td>
<td>V.7 - V.8.4</td>
<td>- Swap inlet and outlet direction and position</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Find minimum height of chamber</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Separate path for each gas to prevent pre-reactions</td>
</tr>
<tr>
<td>3rd generation</td>
<td>V.9.1 - V.9.4</td>
<td>- Spiral shape, curved separation barrier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Design for manufacturability</td>
</tr>
<tr>
<td>4th generation</td>
<td>V.10 - V.15.2</td>
<td>- Circular outlet outside</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Reduce thickness of separation barrier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Reduce rotating disk diameter</td>
</tr>
</tbody>
</table>

5.1 First generation designs

The first generation design was based on the conceptual design, in which individual source gases are introduced into the reactor chamber individually in a horizontal channel. The channel optimized the flow such that they are able to flow in a laminar fashion over the surface of the substrate, Figure 5-1. Although the inlet path was modified to ensure
laminar exit flow for each specific gas, the biggest challenge was achieving a laminar flow regime inside the reactor.

Adjustable separation barriers were implemented to control boundary layer thickness for the growth of different materials and ease the maintenance and replacement of barriers. Besides, the capability of an increasing number of chambers was considered in the first design. Seven individual chambers are necessary for the growth of ternary nitrides and InGaN alloy corresponding to precursors (Ga, In, and Al) and doping materials (like B, N, Mg, and Si).

Figure 5-1. First generation design of HPS-CVD reactor, which represents six horizontal inlets and six vertical outlets for each specific source gas.

CFD modeling was performed using for three different gases (N₂, H₂, or NH₃) separately at three different reactor pressures (1, 10, or 100 atm). Figure 5-2 presents the velocity streamlines of CFD modeling result for hydrogen gas at 1 atm. Streamlines are curves that are instantaneously tangent to the velocity vector of the flow, which present the direction that a massless element will travel at any point in time in fluid. It demonstrates that vortices appeared at the entrance point, despite the existence of laminar flow pattern.
throughout the inlet channel. To respond to this problem, the introductory angle of the inlet was changed to reduce turbulence caused by the inlet gas introduction. Gas was introduced more tangentially to the circumference of the wafer to prevent vortices formation at the entrance, as it is shown in Figure 5-3. Three different angles, up to 40 degree relative to yz plane, were investigated and it was found that turbulent vortices caused by inlet gas introduction was eliminated with the maximum introductory angle (40 degree) as presented in Figure 5-4. Larger scale vortices in the chamber independent of the gas inlets were still present though.

Figure 5-2. CFD modeling result of a 3rd design that demonstrated laminar flow in the inlets and appearance of vortices at the entrance of gases to the chamber.
Figure 5-3. a) Gas cavity of 3\textsuperscript{rd} design with inlets normal to the outer surface of the chamber, b) gas cavity of 5\textsuperscript{th} design with inlets that hold a 40° angle with their tangency line.

Figure 5-4. CFD modeling result of a 5\textsuperscript{th} design, which doesn’t show vortices at the entrance because of changing the angle of the inlet to introduce the gas tangency, but circulation vortices are be identified.

For the next step, the effect of chamber height on turbulent vortices in the reactor chamber was investigated. As Figure 5-5 presents, by reducing the height of the chamber from 1 inch to 0.3 inches, vortices were significantly reduced, which is in accordance with
literature studies on conventional vertical CVD reactors [71–73]. In addition, we studied reactor designs with vertical inlets and outlets, Figure 5-6, which did not show promising results (Figure 5-7).

Figure 5-5. CFD modeling result of a 5th design with smaller height chambers which prevents the appearance of circulation vortices.

Figure 5-6. Gas cavity of 6th generation design of HPS-CVD reactor, which represents 6 vertical inlets and 6 vertical outlets for each specific source gas.
Figure 5-7. CFD modeling result of a 6th design which didn’t show promising flow patterns.

First generation designs showed that the source gas could communicate to the next neighboring chamber via the boundary layer, inlet gas could enter the chamber with a laminar flow pattern, and the height difference between the growth surface and top of the chamber is plays a crucial role in generating vortices in the chamber.

Figure 5-8. CFD modeling result of a 5th design, which demonstrates that fresh source gas doesn’t cover the whole substrate surface.
Although first generation was promising, still suffered from turbulent flow in the chamber and new source gases do not distribute evenly on top of the wafer and do not cover the entire surface of the wafer (Figure 5-8). This is thought to be due to the gas is fighting the centrifugal force. These shortcomings need to be addressed in the next generation design.

5.2 Second Generation designs

This design was a conceptual exploration to provide deeper insight into fluid dynamic trends for the system. To accomplish this, the inlet and outlet flow directions were swapped (Figure 5-9). In doing so, the nature of the centrifugal force helps the source gas to distribute on the growth surface and push the byproducts out into the exhausts (outlets). Additionally, a separated channel was created for each gas to have a reservoir on top of the boundary layer. The impact of chamber height was also investigated.

The effect of chamber height on turbulent flow pattern generation was investigated by increasing the chamber height from 0.2 inch to 1.5 inch (Figure 5-10). Moreover, the inlet channel was tapered to a trapezoid shape with the smaller base on the outer side to introduce gas on top of the rotating disk with the same linear velocity.

All simulations were calculated for the worst case scenario, fluid dynamically speaking, which is associated with nitrogen gas at 100 atm pressure as observed by our modeling results and predicted by previous studies [74].
Figure 5-9. Gas cavity of 8.1 design of HPS-CVD reactor, which represents four separate pathways, each has a vertical inlet and a horizontal outlet.

Figure 5-10. Gas cavity of 8.3 design of HPS-CVD reactor with an extra box on top of the horizontal pathway to investigate the effect of height of pathway on the flow pattern.

CFD modeling studies revealed that laminar flow could be obtained in a chamber with 0.2 inch height (Figure 5-11) unlike a 1.5 inch height (Figure 5-12). Nevertheless, source gases go directly to exhaust without transferring to the next chamber. This means the precursors will not mix well enough in the boundary layer to yield uniform growth.
CFD modeling results for design with twisted inlets (Figure 5-13 and Figure 5-14) demonstrated that source gases can communicate to the neighboring chamber via the boundary layer. Although successful flow patterns was obtained (Figure 5-14), this design is complex questioning its manufacturability.

A direct relationship between increasing the chamber’s height and appearance of vortices was observed. Although laminar flow can be easily obtained in small height chamber HPS-CVD reactor design, the small height difference between substrate and roof of the chamber leads to an increase in temperature of the roof walls and potentially unwanted depositions on them, which may clog the boundary layer pathway and increase the maintenance period or otherwise impact laminar flow of the gases. Furthermore, an increase in wall temperatures results in a decrease in mechanical properties and possibly reduce corrosion resistance.

Figure 5-11. CFD modeling result of 8.1 design which represents a promising laminar flow pattern.
Figure 5-12. CFD modeling result of 8.3 design with a box which demonstrates the appearance of vortices on top of the wafer.

Figure 5-13. Gas cavity of 8.4 design of HPS-CVD reactor which has a twist in the shape of the pathways.
Figure 5-14. CFD modeling result of the 8.4 design of HPS-CVD reactor which shows a laminar flow pattern through whole the chamber.

5.3 Third Generation design

The third generation designs drew motivation from the previous generation, was designed to be more manufacturable. Spiral shape, curved separation barriers were introduced to ensure the source gas have the same exposure time over the wafer surface and to accommodate for the increased tangential velocity of the gases as it radially transverses the disc (Figure 5-15). A 5 to 10 degree draft was applied to the top of the chamber to reduce the height in the outer shell to accommodate for the increase in overall volume of the chamber as a function of radius. The effect of shape and relative position of inlet and outlet were also investigated.
Figure 5-15. Gas cavity of four CAD designs of 3rd generation design of HPS-CVD reactor.

Figure 5-16 presents the 9.4 design of HPS-CVD reactor, which demonstrated the most promising results among previous generations. This design included six vertically tailored inlets and six horizontal outlets which are tangent to the circumference of wafers. A 5° draft was applied to the top surface of the chamber.

Figure 5-17 shows one of the CFD modeling results demonstrating that nitrogen gas is more susceptible to creating turbulent flow regime above the underlying boundary layer, as was demonstrated by previous researches in different MOCVD reactors [74,75]. Although Figure 5-18 presents laminar flow through the chamber with negligible vortices, the source gas stays in a boundary layer for an extended period of time, which may cause a memory effect phenomenon throughout the chamber. Furthermore, the gases don’t cover the whole surface of the wafer in the first cycle probably leading to nonuniformity in the growing films. These problems were addressed by increasing the inlet velocity, as presented in Figure 5-19. In doing so, however, some vortices reappeared in the chamber.
Figure 5-16. Gas cavity of 9.4 design of HPS-CVD chamber with spiral shape chambers.

Figure 5-17. CFD modeling result of the 9.4 design of HPS-CVD reactor, comparing these CFD results demonstrate that nitrogen gas has worse flow pattern compare to hydrogen or ammonia gas.
Figure 5-18. CFD modeling result of the 9.4 design of HPS-CVD reactor, represent promising laminar flow pattern but the fresh gas source doesn’t fully cover the substrate surface and also takes a long time to leave the chamber.

Figure 5-19. CFD modeling result of the 9.4 design of HPS-CVD reactor, by increasing the inlet velocity to 0.05 m/s, two problems which present in Figure 5-18 are solved, but small vortices appeared.

Although the 9th design of HPS-CVD demonstrated a laminar flow pattern with negligible vortices relatively to previous design, the separation barriers between chambers are wide and may lead to unwanted deposition on them thereby roughening the channel.
This could lead to increased turbulence or complete disturbance of the boundary layer and hence should be eliminated. This needs to be addressed in the next generation designs.

5.4 Fourth generation design

The main motivation for this generation designs was to reduce the thickness of separation barriers, thereby decreasing the chance of unwanted depositions on the barrier walls. Moreover, the outlet shape design was modified as demonstrated in Figure 5-20. Vertical separation barriers’ walls with sharp corners were modified to curved shape spiral walls to navigate gas smoothly into the boundary layer to the neighboring chamber and the disk diameter was reduced from 6” to 5.5” to increase the gap between the rotating desk and chamber walls, Figure 5-21.

![Figure 5-20](image)

Figure 5-20. a) Gas cavity of 10th design of HPS-CVD chamber with spiral shape chambers with a thinner barrier, which has 6 vertical inlets and one circular outlet outside, b) cross-section view of 10 design gas cavity
Figure 5-21.  a) Gas cavity of 15.1 design of HPS-CVD chamber with curved spiral shape chambers, b) cross-section view of 15.1 design

CFD modeling studies with various inlet velocities demonstrated that gas recirculation markedly increased compared to the previous design. Figure 5-22.b presents flow pattern in 15.1 design of HPS-CVD chamber as an example of recirculation and turbulent flow in the reactor.

Figure 5-22. CFD modeling result of a) the 10th design, b) the 15.1 design of HPS-CVD reactor. Which demonstrate the effect of outlet shape on flow pattern.

This issue can be addressed by changing the exhaust shape to the frustum of a cone (Figure 5-23), which better navigates the boundary layer gas to the exhaust and improves
exhaust gas collection efficiency. CFD modeling results represented less recirculation vortecis after the exhaust shape modification, as presented in Figure 5-24.

Figure 5-23. Gas cavity of 15.2 design of HPS-CVD chamber with frustum of a cone shape exhaust.

Figure 5-24. CFD modeling result of the 15.2 design of HPS-CVD reactor.

Though CFD results looked promising, one gas streamline attracted our attention. It is highlighted with a red pointer in Figure 5-25. This gas streamline suddenly changes the pathway near the outlet surface and comes back into the chamber which cannot be physically justified. After extensive investigations, no explanation for this phenomenon was found leading to uncertainty on the validity of the simulation outcomes. Therefore,
and alternative approach was taken to simulate the system by moving a $k-\omega$ turbulence model with more accuracy boundary formulations.\(^1\)

\(^1\) *Difference between $k-\varepsilon$ and $k-\omega$:* In earlier CFD modeling, the $k-\varepsilon$ turbulence model was used. This model uses one of two equation turbulence models, meaning it includes two extra transport equations to demonstrate the turbulent properties of the flow. This allows two equation turbulence models to account for historical effects like convection and diffusion of turbulent energy. In the $k-\varepsilon$ turbulence model, turbulent kinetic energy, $k$, and turbulent dissipation rate, $\varepsilon$, values need to be specified which are rarely known exactly and may act as a source of uncertainty. Though this model does the second transport variable in the $k-\omega$ turbulence model is the specific dissipation, $\omega$, which is variable and determines the scale of the turbulence. Therefore, the $k-\omega$ turbulence model for CFD simulations was used instead of the $k-\varepsilon$ and a finer mesh was applied to improve the level of accuracy of CFD modeling results near walls and boundaries.
Figure 5-25. CFD modeling result of the 15.2 design of HPS-CVD reactor. A specific gas streamline was indicated by a red pointer which changes its pathway suddenly near the outlet surface.

In a next step, the effect of rotational speed and inlet velocity on the flow pattern was investigated to determine resilience of the system design and parameter space that can be accessed during growth. Figure 5-26 and Figure 5-27 represents gas flow patterns throughout the chamber when the rotational speed is increased from 100 to 800 rpm and inlet velocity reduces from 0.1 to 0.04 m/s, respectively. Simulation results suggest that for each rotational speed there is an optimum associated inlet velocity with the gas velocity value being closer to the average linear velocity of the rotating disk. This suggests more sophisticated controls may be required to ensure optimal performance for different growth regimes.
Figure 5-26. Velocity streamline of CFD modeling results of 15.2 design are presented to demonstrate effect of rotational speed a) 100rpm, b) 200 rpm, c) 400rpm.

Figure 5-27. Velocity streamline of CFD modeling results of 15.2 design are presented to demonstrate effect of inlet flow: a) 0.2 m/s, b) 0.1 m/s, and c) 0.05 m/s.

The fourth generation design demonstrated the most promising results among all generations. However, further dedicated studies are required to expand the operation window by modifying shape of separation barriers. In addition, all CFD simulations were studied one gas as the fluid, it is necessary to study the effect of having two or three different gases in different chambers of flow pattern in the reactor.

5.5 Growth Analysis

The HPS-CVD reactor design is anticipated to enhance the growth rate compared to the super-atmospheric horizontal MOCVD reactor designed by Dr. Dietz’s group [37]. This MOCVD reactor design [11] exhibited a reduction in growth rate at growth pressures
above 5 atm due to the onset of turbulence within the chamber. This presumably led to a loss of source material via pre-reaction of the precursors in the gas phase. The HPS-CVD reactor addresses these shortcomings by physically separating the precursors thereby controlling flow pattern throughout the chamber; thus, precursors premixing is primarily limited to the user-defined boundary layer and the time they reside within the boundary layer. The shorter residence time leads to fewer pre-reactions of the precursors and source material loss.

Figure 5-28 demonstrates the basic aspects of boundary later of developing fluid flow over a stationary substrate in Dietz’s horizontal MOCVD design. The thickness of boundary later is 0.04 inches equal to reactor height. Although the Reynolds number in their design is in laminar flow region, they couldn’t achieve the laminar flow pattern because of sharp corners in horizontal design. Long pathway for precursors to arrive at substrate surface and premixing of precursors throughout the channel lead to precursor loss and lower growth rate, as shown in Figure 1-13.

Figure 5-28. Growth of a boundary layer in Dietz’s horizontal MOCVD design.
Laminar flow patterns were achieved at higher pressures (up to 100 atm) in the third HPS-CVD design because good control of the thickness of the boundary layer via improved separation barriers. The thickness of the boundary layer was calculated using CFD modeling. Although the boundary layer thickness is constant below the separation barriers, it increases between separation barriers by 50% (0.1 to 0.15 inches).

Growth processes occur in the mass transport limited region and hence the growth rate is limited by the precursor concentration on top of the substrate, as they need to diffuse through the boundary layer. For diffusion calculations, the average value of the boundary layer of CFD modeling results was applied. As presented in Figure 5-29, the boundary layer thickness was taken to have an average value (0.1 inches) of the maximum and minimum of CFD results for diffusion calculations.

Figure 5-29. Schematic cross-section view of the HPS-CVD reactor, which represents the boundary layer thickness.

Theoretical predictions for this diffusion layer using Fick’s second law suggest that the TMGa gas precursor diffusion time through the boundary layer in the HPS-CVD with a 400 rpm rotational speed is at least five times shorter than the time the gas precursors need to travel to reach the substrate surface in Dietz’s MOCVD reactor after they are introduced. This should directly relate to an improvement in growth rate because the
growth rate is limited by precursor concentration at top of the substrate in the mass transport limited region. Existing super-atmospheric horizontal MOCVD reactor design [11] used pulsed precursors injection to reduce the premixing of precursors, though it doesn’t entirely eliminate them. Physical separation of the precursors provides a significant improvement and reduces the time that precursors have been exposed to each other before reaching the boundary layer.

To a further reduce of precursor premixing, surface related effects such as undesirable surface reactions or deposition which lead to loss of precursor which are further mitigated in the HPS-CVD design as compared to Dietz’s MOCVD design as the exposed surface area of mixed gases flow is reduced by a factor of four. This would further improve upon precursor availability for growth by decreasing undesirable surface reactions and hence precursor loss.

Based on these factors, it is crudely estimated that a growth rate enhancement of approximately 10x is achievable compared to the existing state of the art. This could suggest peak growth rates up to 4 μm/hr. This is comparable to existing atmospheric MOCVD reactors.
6 Conclusion

Computational fluid dynamics (CFD) modeling was carried out to optimize the design and analyze transport phenomena in a newly proposed vertical type High-Pressure Spatial Chemical Vapor Deposition (HPS-CVD) reactor, which is capable of growth up to 100 atm. The effects of reactor design, chamber height, system pressure, inlet flow rate, and rotational speed were investigated. It was found that by reducing the height of the chamber, the flow instabilities reduced significantly due to the suppression of the thermal and mass transfer boundary layers caused by the geometry of the reduced space. CFD modeling was also used to obtain the optimal HPS-CVD reactor design and growth parameters to minimize flow instabilities. Moreover, achievable growth rates are anticipated to be enhanced approximately by a factor of 10 as compared to current super-atmospheric horizontal MOCVD reactor design up to 4 μm/hr. Important to achieving this is the separation of source materials and controlling the thickness of the boundary layer via mechanically controlled separation barriers.
7 Future Work

Further dedicated studies are required to improve the 4\textsuperscript{th} generation design and investigate the temperature envelope throughout the chamber. Mass transport and gas phase kinetic reactions studies are needed to better understand achievable growth rates and interface roughness.

Upon satisfactory conclusion of the design phase, a prototype needs to be built and validated to the modeling results. Trail runs must be performed to provide confidence in observed model trends and to allow for further optimization and tailoring of the growth conditions in real time.
REFERENCES


[65] S. Imayama, P.H. Alfredsson, R.J. Lingwood, Experimental study of rotating-disk
https://doi.org/10.1017/jfm.2015.634.

https://doi.org/10.1063/1.1705928.


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- **Teaching Assistant** for “Solidification of Metals” 2012-2014
- **Engineer** in Gostare Tejarat Farasoo Co. 2014
  Assistant Manager of R&D and Manufacturing group, focusing on diecast and plastic injection mold design.
- **Summer Internship** Godaz Sanat Co., 320 hours. 2013
  Assistant Factory Manager in “GZ Co.”, Alloy Steel Casting Foundry.
- **Internship** Daghigh Rizan Paya Hadid Co., 200 hours. 2012
  Assistant production manager, Investment Casting Manufacturing Company.
- **Part-Time Intern** in Irmantech Sepahan Co. 2011-2012
  R&D group, job consisted of research on “IR Window” and “Design and construction of composite container”.
- **Internship** in Mana Ghete Sepahan Co. 2011-2012
  R&D group to Reverse Engineering from “Inconel Turbocharger” for manufacturing.
- **Member of executive council** in Shahid Ejei Cultural Convention 2007-2015
  (The NGO that does cultural activity, combination of citizenship learning, debate club, sport club, and scouting.)
- **Executive member of** in Cultural Convention of MATSE department at IUT 2010-2014
  Director of monthly scientific and cultural seminars in Materials Eng. department.

**Certificates & Memberships:**
- Member of The American Society of Mechanical Engineers 2016-Present
- Member of The Minerals, Metals and Materials Society 2016-Present
- Certificate of qualification in the 9th National Heat Treatment Competitions 2012
- Certificate of qualification in the 1st National Student Foundry Competitions 2012
- Certificate of participation in training workshop on Defects in Castings 2011