Design of an Instrumented Microchannel Device for Characterization of Phase Change Nanofluids

by

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B.S., Mechanical Engineering (2008) Rutgers University

Submitted to the Department of Mechanical Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering at the Massachusetts Institute of Technology September 2010

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Abstract

As the energy needs of the world continue to grow, it becomes increasingly important to investigate alternative sources of energy. Solar energy is one of our most abundant sources of renewable energy, and researching ways to harness this energy is an area of great interest. While there are several different methods by which solar energy can be harnessed, including photovoltaics, low temperature collectors, and concentrated solar collectors, this investigation focuses on parabolic trough solar thermal power generation. Parabolic trough solar thermal power generation relies on parabolic shaped mirrors to concentrate sunlight on an array of pipes through which a heat transfer fluid flows. The heated fluid is subsequently used to drive a steam cycle to generate electricity.

Two of the main challenges facing parabolic trough solar thermal power generation are high temperature stability of heat transfer fluids and thermal storage methods. The current fluids used for heat transfer can only withstand temperatures of up to 400°C before undergoing thermal breakdown. The heat capacity of these fluids is also insufficient for them to act as an effective thermal storage mechanism during periods of low sunlight. This thesis explores a method of increasing the heat capacity of heat transfer fluids by introducing nanoscale phase change particles. A low temperature proof of concept is used to study nanosized particles of lauric acid which undergo phase change in water, which promises to increase the effective heat capacity by 16.4% using 10% volume fraction of particles. In order to characterize the heat transfer characteristics of the prepared phase change nanofluid, a heated microchannel was designed and fabricated. A microchannel with doped resistors as temperature sensors was microfabricated. The high temperature coefficient of resistance of doped silicon resistors allows for precise temperature measurements of 52.5 ohms/K. However, challenges with nanofluid stability and drift of the doped sensors limited further detailed investigations. This work is the first step towards developing nanofluids and characterization tools to demonstrate the feasibility of such fluids for parabolic trough solar thermal power generation.

Thesis Supervisor: Evelyn N. Wang
Title: Assistant Professor, Mechanical Engineering
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There are many people in my life whose help and support were instrumental in the completion of my thesis.

Professor Evelyn Wang has supported my work from beginning to end, especially when I needed it most. Her guidance and patience were invaluable.

The other students in the lab and my friends at MIT understand well the troubles that present themselves in the course of research. The presence of like-minded people to use as a sounding board for ideas was valuable in more ways than can be counted. Their advice, as well as the advice of post-docs Ryan Enright, Anand Veeraragavan, and Matt McCarthy led to solutions for challenges that I would likely have stumped me indefinitely without their input.

The MTL staff and their expertise made fabrication of my devices possible. I would have been lost without their advice.

Most importantly, my family supported me throughout the whole process. They may not have understood exactly what I was going through, but their words and thoughts helped me though the tough times.
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Chapter 1

1. Introduction

1.1 MOTIVATION

As our society becomes ever more dependent on electricity driven devices, it is very important to find sustainable sources of energy. The sun represents the largest source of renewable energy, with roughly 162,000 [1] terawatts of energy reaching the surface of the Earth every year. Even a small percentage of this could supply a large portion of the less than 20TW used worldwide each year. Currently, more than three quarters of the world’s energy needs are met through the burning of non-renewable fossil fuels. Without speculation as to the effects burning of such fossil fuels has on our climate, it is generally agreed upon that cleaner energy sources would be better for our environment. The ability to cleanly harness solar energy and reduce our dependence on fossil fuel would be a huge step towards achieving these goals. There are currently many different ways of utilizing the solar energy to meet our growing energy needs. Some of them, such as low temperature solar collectors, use the sun’s thermal energy to supply heat for domestic hot water purposes, while others such as photovoltaics convert the energy carried by the sun’s photons directly into electricity. Solar thermal power generation, which harvests solar energy to create steam to power electric generator, is a method capable of producing large amounts of electricity. This thesis will discuss the development and testing of new heat transfer fluids aimed at improving solar thermal power generation technology.
1.2 BACKGROUND

1.2.1 Low Temperature Solar Thermal Applications

For many years, solar energy has been used as a source of low temperature thermal energy. There are several different types of low temperature solar thermal energy collectors, most of them being very simple [2]. While low temperature solar thermal energy cannot be used for electricity generation, it can be readily used for the heating of domestic hot water or process heat for industrial facilities. The simplest and cheapest type of low temperature solar energy collector is the flat plate solar collector.

![Figure 1. Flat plate solar collector [1], and evacuated tube heat pipe solar collector [2].](image)

Flat plate solar collectors are stationary devices placed in areas of high sunlight in warm climates. The most rudimentary flat plate collector consists only of a flat black absorbing plate and a series of tubes through which either air or water is pumped. More advanced flat plate collectors have glazed glass covers that reduce re-radiation to the atmosphere and maximize the heat capture. Special coatings on the absorber surface and glass cover can further enhance the overall efficiency of the device. Some systems operate in an open loop, heating city water and...
storing it for later use, while other systems keep the heated water in a closed heating and storage loop. These systems transfer the stored heat to supply water by means of a heat exchanger, and often use a water/ethylene glycol mixture in the closed loop to prevent boiling of the water in the absorber tubes. Hot water from flat plate collector systems can achieve temperatures of up to 100°C. Operating temperatures are limited both by the method of collection and by conduction and convection losses to the environment. While the glazing on the glass cover of a flat plate collector helps mitigate radiation losses, there is no protection from conduction and convection of heat away from the glass surface.

Evacuated tube heat pipe type collectors, Figure 1, overcome the operational temperature limitations of flat plate collectors by introducing an insulating vacuum between the absorbing tube and the outside environment. Inside the absorbing tube is a small amount of fluid that absorbs the solar energy through evaporation. The vapor transfers its thermal energy to an external heat transfer fluid and returns to the liquid phase. The operating temperature of the heat pipe is set by choice of the working fluid and the internal pressure of the sealed pipe. As a result of the evacuated tube surrounding the heat pipe, evacuated tube solar collectors can achieve temperatures of up to 200°C without suffering appreciable heat losses to the environment.

1.2.2 High Temperature Solar Thermal Applications

High temperature solar thermal applications refer to those systems which are capable of producing high temperature and pressure steam for electricity generation or industrial processes. In order to generate these higher temperatures, it is necessary to use concentrating mirrors to increase the heat flux on a given area. High temperature systems include linear Fresnel reflectors, parabolic trough solar collectors, parabolic dish reflectors, and central receiver, in order of
increasing concentration factor. The concentration factor is directly correlated to the maximum possible operating temperature of each system.

Linear Fresnel reflectors, Figure 2, use a series of flat rectangular mirrors to focus sunlight on a pipe through which a heat transfer fluid flows.

Figure 2. Image of linear Fresnel solar collector (left) and parabolic trough installation (right).

Linear Fresnel collectors are very similar in principle to parabolic trough solar collectors, but they cannot achieve the same concentration ratios. For two systems of the same physical dimensions, the power output of a parabolic trough system will be greater than that of a linear Fresnel system. However, the linear Fresnel system does possess certain advantages. Construction of a linear Fresnel system is substantially simpler and less costly, owing largely to the flat mirrors that comprise the reflective surfaces. The flat mirrors are mounted low to the ground and do not require complex and expensive structures to track the sun.

Parabolic trough solar collectors operate on the same principle as linear Fresnel reflectors, but are much more refined. A long trough shaped parabolic mirror, seen in Figure 2, concentrates light onto the line that describes the focus of the parabola. Through the focus of the parabola runs a pipe covered in a special absorptive coating and surrounded by an evacuated glass tube. Parabolic mirrors are expensive to make and maintain, but they offer concentration
ratio advantages over non-focusing optics. Several different parabolic trough configurations are commercially available, with concentration ratios ranging from 50 to more than 80 [3]. Parabolic trough arrays are installed with the troughs running north to south, and track the sun as it crosses the sky from east to west.

Parabolic dish reflectors are parabolic mirrors with a heat collecting mechanism at the focus of the parabola. Figure 3 shows a parabolic dish reflector with a Stirling engine located at its focal point. Other choices for power generating element are photovoltaics or microturbines.

![Parabolic dish solar concentrator with Stirling engine generator (left) and power tower generating station (right) [1]](image)

Although the point focus of the parabolic dish can achieve much higher concentration ratios than the parabolic trough collectors, the total output of a parabolic dish reflector is limited due to size limitations of the parabolic mirror. Parabolic dish reflectors must track the sun on both axes in order to maintain the high concentration ratio. Concentration ratios can reach as much as 2000, and operating temperatures exceed 1500°C.

Central receiver systems, also known as power towers, are analogous to parabolic dish reflection systems in the same way the linear Fresnel systems relate to parabolic trough
installations. Although central receivers like the one in Figure 3 cannot achieve concentration ratios as high as a parabolic dish reflector, they still reach concentration ratios of up to 1500.

A central receiver system consists of many mirrors mounted on the ground and angled such that they reflect light to a receiver atop a tower. Like the parabolic dish system, these individual mirrors much track the sun on both axes to keep the sun’s rays focused on the central receiving unit. Molten salt is passed through the receiver, collecting the energy at a temperature of 550°C to drive a steam cycle and generate electricity. The advantage of a central receiver system is that it can achieve high concentration ratios but can be built much larger than a parabolic dish system due to the smaller size of the mirrors it uses. Table 1 compares the discussed solar thermal collection technologies.

<table>
<thead>
<tr>
<th>Collector Type</th>
<th>Concentration Ratio</th>
<th>Operating Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat plate</td>
<td>1:1</td>
<td>100°C</td>
</tr>
<tr>
<td>Evacuated tube</td>
<td>1:1</td>
<td>200°C</td>
</tr>
<tr>
<td>Linear Fresnel</td>
<td>60:1</td>
<td>300°C</td>
</tr>
<tr>
<td>Parabolic trough</td>
<td>80:1</td>
<td>400°C</td>
</tr>
<tr>
<td>Parabolic dish</td>
<td>2000:1</td>
<td>1500°C</td>
</tr>
<tr>
<td>Central Receiver</td>
<td>1500:1</td>
<td>550°C</td>
</tr>
</tbody>
</table>

1.2.3 Common Challenges Associated with Parabolic Trough Power Generation Systems

Parabolic trough solar thermal power generation is the lowest cost large-scale solar power generation technology currently available [3], but there is still significant room for improvement, most notably in the heat transfer fluid used for transferring the thermal energy from the
collectors to a steam cycle. A recent DOE call for research proposals seeks to address these concerns. Some of the metrics that are desired include a fluid that is stable to 500°C, has a freezing point below 80°C, and has a heat capacity between 2-5kJ/kg*K. Two of the challenges that any parabolic trough system must face are cold overnight temperatures and long periods without significant sunlight. Even in sunny areas, nighttime temperatures during the winter can drop to near freezing levels. Unlike power tower systems, whose fluid can drained by gravity alone, it is very difficult to remove the heat transfer fluid from the horizontal pipes of a parabolic trough system. As such, a suitable heat transfer fluid must have a freezing point low enough that overnight freezing is not a substantial risk. Also, during periods of low sunlight it would be advantageous for a parabolic trough system to be able to store sufficient thermal energy such that it can continue to generate electricity without additional input energy.

Figure 4. Two tank molten salt storage system [4].
The heat transfer fluid used in contemporary parabolic trough systems, Therminol VP1, is too expensive to be used as a thermal storage fluid. The current thermal storage method is a two tank molten salt system, pictured in Figure 4. In the two tank molten salt storage system, heat is collected by the parabolic trough array and carried by the heat transfer fluid to a heat exchanger. Heat is transferred from the heat transfer fluid to the molten salt and stored in a hot salt tank. In order to generate power, the molten salt must transfer the energy back to the heat transfer fluid before being stored in the cold salt tank. This method introduces two additional heat transfer steps that result in a loss of energy that would not be present if the heat transfer fluid itself could be used as a thermal storage mechanism. A heat transfer fluid with a higher heat capacity would obviate the need for a secondary storage fluid and result in greater energy capture.

1.3 THESIS OBJECTIVE AND OUTLINE

Phase change nanofluids may have advantages when used in heat transfer applications, specifically parabolic trough solar thermal power generation. The energy required to overcome the latent heat of phase change nanoparticles seeded in a carrier fluid acts to increase the effective heat capacity of the fluid, allowing similar masses nanofluid to remove more heat than their pure fluid counterparts. The phase change may also introduce other effects on the heat transfer characteristics of the fluid which are not obvious without testing. In order to determine the feasibility of phase change nanofluids as a heat transfer fluid for solar thermal power generation, candidate materials for phase change nanofluids are identified and characterized. To test the heat transfer characteristics of fabricated nanofluids, an instrumented microchannel device is developed and fabricated. The main focuses of this thesis are outlined below:
In Chapter 1, the challenges in current parabolic trough solar thermal power generation systems were discussed and phase change nanofluids were introduced as a potential solution to some of these challenges.

In Chapter 2, current and potential heat transfer fluids for use in solar thermal power generation are considered. A candidate phase change nanofluid is identified.

In Chapter 3, the design and fabrication of the instrumented microchannel device are described in detail.

In Chapter 4, an experimental setup for measuring the heat transfer characteristics of nanofluids using the microchannel device is presented. Challenges in the instrumentation and use of the device are also discussed.

In Chapter 5, methods for improving the microchannel device and resolving challenges are outlined.
The current fluid used in solar thermal power generation is a eutectic mixture of biphenyl and diphenyl oxide known by the trade name of Therminol VP1 and produced by Solutia. This particular fluid has a relatively high heat capacity of about half that of water, and remains liquid between 12°C and 252°C. The liquid range can be extended to nearly 400°C by pressurizing the system to 10 atmospheres. VP1 is an excellent heat transfer fluid for this application because of its high heat capacity and low freezing point, Table 2.

<table>
<thead>
<tr>
<th>Table 2. Properties of Therminol VP1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density, 393°C</strong></td>
</tr>
<tr>
<td><strong>Freezing Point</strong></td>
</tr>
<tr>
<td><strong>Boiling Point, 1 atm</strong></td>
</tr>
<tr>
<td><strong>c_p, 293°C</strong></td>
</tr>
<tr>
<td><strong>c_p, 393°C</strong></td>
</tr>
<tr>
<td><strong>Viscosity, 393°C</strong></td>
</tr>
</tbody>
</table>

Fluids used in parabolic trough power generation systems must have good freezing protection because it is very difficult to drain the horizontal fluid carrying pipes. However, improvements upon VP1 would make parabolic trough solar thermal power generation a more viable solution. The two major improvements that would be the most valuable are an increase in heat capacity as well as an increase in the maximum operating temperature of the fluid. An increase in heat capacity with all other thermophysical properties held constant would result in a decrease in the
amount of fluid needed for a given heat flux, and also a decrease in pumping power. Increasing
the maximum operating temperature would allow the Rankine cycle to operate in a more
efficient regime, generating more electricity from the available energy. Potential solutions to
both of these problems were investigated.

2.1 IONIC LIQUIDS

Ionic liquids are a class of ionic compounds that are liquid at or near room temperature.
These liquids were investigated for their potential as a replacement heat transfer fluid for
parabolic trough solar thermal power generation systems. Initial reports suggested that ionic
liquids might possess both the low freezing point and high boiling/thermal breakdown point
desired for use in solar thermal power generation. The National Renewable Energy Laboratory
has done significant work investigating the properties of ionic liquids with specific application to
solar thermal power [5]. Although initial research suggested that ionic liquids might withstand
higher temperatures than the VP1, thermogravimetric analysis showed ionic liquids tested to date
do not show any substantial improvement, Table 3.

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Ionic liquid} & \text{Melting point, } ^\circ\text{C} & \text{Decomposition point, } ^\circ\text{C} & \text{Viscosity at } 25^\circ\text{C}, \text{ mPa s} & \text{Density at } 25^\circ\text{C}, \text{ kg m}^3 \\
\hline
[\text{C}_{4}\text{mim}][\text{PF}_6] & 34 & 390 & -- & -- \\
[\text{C}_{4}\text{mim}][\text{PF}_6] & -75 & 416 & -- & -- \\
[\text{C}_{4}\text{mim}][\text{PF}_6] & 4 & 390 & 312 & 1219 \\
[\text{C}_{4}\text{mim}][\text{BF}_4] & -77.5 & -- & -- & -- \\
[\text{C}_{4}\text{mim}][\text{BF}_4] & -- & -- & -- & -- \\
[\text{C}_{4}\text{mim}][\text{BF}_4] & -75 & 407 & 219 & 1119 \\
[\text{C}_{4}\text{mim}][\text{bivitriflylimide} ] & -89 & 402 & 54.5 & 1119 \\
\hline
\end{array}
\]
One method of increasing the heat capacity of a fluid is by incorporating encapsulated phase change materials into the carrier fluid. The additional energy absorbed by the latent heat of phase change results in a greater overall heat capacity. Commercially available phase change fluids typically encapsulate a fatty acid or paraffin material inside a polymer shell. Encapsulation of the phase change material circumvents the problem of agglomerating phase change material during phase transitions. However, commercially available encapsulated phase change materials are all tens of microns in size. Microsized particles tend to increase viscosity significantly and can crush each other during pumping, reducing the effectiveness of the system over time.

Fang et al devised a method for producing nanosized encapsulation phase change materials in an effort to improve on microencapsulated phase change materials. N-octodecane was encapsulated in polystyrene [7]. After experimenting with different polymerization techniques, Fang was successful in making 124nm average diameter nanocapsules that would withstand multiple freeze/thaw cycles shown in Figure 5.

![Figure 5. N-octadecane encapsulated in polymer shell [7].](image-url)
Samples were thermally cycled over 100 times and no degradation of performance or leakage of the n-octadecane was detected. Although the nanosized encapsulated phase change materials are a promising idea, the polymer coating would not be able to withstand the high operating temperatures of a solar thermal power generation system. In addition, a shell of any material reduces the effectiveness of adding phase change material to the carrier fluid. An optimal solution would be to introduce the phase change material with a minimum of extraneous substances, thus not diluting the effects of the phase change.

![Heat flux curves for pure n-octadecane and prepared nanoencapsulated n-octadecane](image)

**Figure 6. Heat flux curves for pure n-octadecane and prepared nanoencapsulated n-octadecane [7].**

The reduced effective latent heat of encapsulated phase change materials can be seen in the heat flux plot in Figure 6. Pure n-octadecane requires more than twice the heat flux to induce phase change as the same mass of encapsulated n-octadecane. This reduction in effective latent heat results in a similar increase in the amount of nanoparticles needed to introduce the same effective heat capacity increase. Additional nanoparticles can cause problems both in rapid increases in viscosity as particle loading fraction increases as well as additional difficulties maintaining a stable suspension.
2.3 PHASE CHANGE NANOFUIDS

A promising idea for increasing the effective heat capacity of heat transfer fluids is the incorporation of nanosized phase change material into the carrier fluid without an encapsulating shell. Yang et al were able to suspend indium nanoparticles in polyalphaolefin oil and observe the melting and freezing peaks through the use of a differential scanning calorimeter [8]. Figure 7 shows the indium nanoparticles of roughly 30nm in diameter. To fabricate the nanofluid, PAO is heated such that its temperature is greater than the melting point of indium. After addition of indium, the mixture is stirred for 2 hours using a magnetic stirrer, creating a microemulsion. The micron sized indium droplets are ruptured through the use of an ultrasonic disruptor for an additional two hours.

![TEM of indium nanoparticles in polyalphaolefin](image)

*Figure 7. TEM of indium nanoparticles in polyalphaolefin [8].*

Differential scanning calorimetry is subsequently used to characterize the thermophysical nature of the suspension in Figure 8. It is evident that melting occurs at the same temperature as pure indium, but there is some lag in the freezing point. The suspended indium does not return to the solid phase until nearly 40°C below its melting point. The difference in freezing and melting
temperature of the suspended phase change material must be accounted for in using phase change nanofluids for practical applications, as it establishes a minimum working range of temperatures.

![Heat flux curves for pure indium, PAO, and indium in PAO nanofluid [8].](image)

Figure 8. Heat flux curves for pure indium, PAO, and indium in PAO nanofluid [8].

The first step in developing a phase change nanofluid for use in parabolic trough solar thermal power generation was to develop a list of materials that melt within the 293°C to 393°C working range of current systems. A list of common materials satisfying this requirement can be found in the appendices. Two important things to watch for are an increase in the effective heat capacity over the working range of the fluid, and an increase in the volumetric energy storage capability. An increase in the effective heat capacity will reduce the required mass flow and fluid requirements. Increasing the energy storage per unit volume allows for smaller, easier to insulate storage vessels. As a benchmark, simple calculations were performed on a mixture of lead and VP1. Using published thermophysical data for both lead and VP1, it is possible to determine the effective heat capacity and energy stored per cubic meter of a mixture of the two materials. A MATLAB program, cp1kg2.m (Appendix 6.2.7) was written to calculate the thermophysical
properties of mixture of VP1 and a designated material over a given temperature range. The plot clearly illustrates the advantages and drawbacks that must be considered when choosing a suitable phase change material for integration with VP1, or another heat transfer fluid.

Since the lead has a relatively low latent heat and heat capacity compared to the heat capacity of the VP1 oil, Figure 9 shows that adding lead to VP1 steadily decreases the overall heat capacity of the suspension. However, the high density of the lead causes an increase of the volumetric energy storage capability. It is also apparent that the mass fraction of lead required to attain an appreciable benefit would be prohibitive. Excluding lead as a possible material helps establish guidelines for the sort of material needed. Since the heat capacity of the phase change material in its solid and liquid phases will likely be less than that of the VP1, a high latent heat will be
required in order to make up for this shortcoming. High density will also lend itself to increasing
the volumetric energy storage capabilities of the heat transfer fluid.

Using the calculation results from lead as a guideline, further investigation of candidate
phase change materials yielded a small group of eutectic mixtures of fluoride salts that seem to
show promise, listed in Table 4. Due to the strong interatomic forces that hold ionic compounds
together, they often have large heat capacities and correspondingly large latent heats of fusion.
However, these strong forces also mean that most pure salts have melting temperatures that are
well outside the working range of a parabolic trough solar thermal power generation system.
Forming eutectic mixtures of two or more salts can create substances that possess melting
temperatures lower than that of its individual components. In general, the more salts that are
involved in a eutectic, the more the melting point is decreased. Below is a short list of fluoride
salt eutectics that could potentially be used in solar thermal power generation.

<table>
<thead>
<tr>
<th>Salt (mol%)</th>
<th>Form. wt. (g/mol)</th>
<th>Melting pt. (°C)</th>
<th>Density (g/cm³)</th>
<th>700°C heat capacity (J/g°C)</th>
<th>Viscosity (cP)</th>
<th>Thermal cond. (W/cm°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF–NaF–KF (46.5–11.5–42)</td>
<td>41.2</td>
<td>454</td>
<td>Alkali–Fluorides (IA) 2.53–0.00073 × T</td>
<td>1.89</td>
<td>0.04 exp(4170/T)</td>
<td>0.006–0.01</td>
</tr>
<tr>
<td>NaF–ZrF₄ (50–50)</td>
<td>104.6</td>
<td>510</td>
<td>Alkali+ZrF₄ 3.79–0.00093 × T</td>
<td>1.17</td>
<td>0.071 exp(4168/T)</td>
<td>~/0.01</td>
</tr>
<tr>
<td>NaF–KF–ZrF₄ (10–48–42)</td>
<td>102.3</td>
<td>385</td>
<td>3.45–0.00089 × T (est.)</td>
<td>1.09 (est.)</td>
<td>0.001 exp(3171/T)</td>
<td>~/0.01</td>
</tr>
<tr>
<td>Li–NaF–ZrF₄ (42–29–29)</td>
<td>71.56</td>
<td>460</td>
<td>3.37–0.00083 × T (est.)</td>
<td>1.46 (est.)</td>
<td>0.0585 exp(4647/T)</td>
<td>~/0.01</td>
</tr>
<tr>
<td>NaF–NaBF₄ (8–92)</td>
<td>104.4</td>
<td>385</td>
<td>Fluoroborates 2.252–0.000711 × T</td>
<td>1.51</td>
<td>0.0877 exp(2240/T)</td>
<td>~/0.005</td>
</tr>
</tbody>
</table>

Although these salts were intended to be used as heat transfer fluids in high temperature systems
operating well above their melting points, they possess certain thermophysical characteristics
that lend themselves to use in our intended application. The melting point of the NaF-KF-ZrF₄
eutectic is very near to the upper end of the working range of a parabolic trough system. It is
readily apparent that this salt eutectic would be much more beneficial than lead because of its
much higher heat capacity or 1.09 kJ/kg. Since the heat capacity of the fluoride salts are much closer to the heat capacity of the oil, the latent heat does not have to make up for the loss in specific heat incurred by adding the fluoride salt. Using a working range of 293°C-393°C and a heat capacity of 410 kJ/kg for the eutectic mixture, the increase in energy storage density as a function of volume fraction can be calculated. The results in Figure 10 show that even a small volume fraction of 4% results in a 25% increase in the amount of energy that can be stored in a particular volume.

![Figure 10. Energy storage density of fluoride salt in VP1 nanofluid.](image)

Since the heat capacity of VP1 is highly dependent on temperature, it is not practical to plot the change in heat capacity as a function of increasing volume fractions of fluoride salts. Rather, it makes more sense to calculate an effective average specific heat. Effective average specific heat computes the total energy absorbed by the suspension and divides it by the temperature width of
the working range, resulting in a value that describes the behavior of the suspension as if it were a pure fluid with constant heat capacity.

\[ \text{Volume Fraction} \]

<table>
<thead>
<tr>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
<th>0.06</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
<td>2.8</td>
<td>2.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

**Figure 11. Effective specific heat of fluoride salt in VP1 nanofluid.**

Examining Figure 11, it is clear that the large latent heat of the fluoride salt mixture more than makes up for its shortcomings in the area of specific heat. Although the increases in heat capacity are not nearly as pronounced at low volume fractions as those of the energy storage density, the calculated results are still very promising. Due to the difficulties in fabricating stable nanofluids at any volume fraction, the ability to achieve increases in the desired parameters even at low volume fractions is a great advantage.

Although the VP1 will benefit from the addition of the fluoride salt mixture in terms of its thermophysical properties, testing at these high temperatures does present challenges. VP1 must be pressurized to nearly 10 atmospheres at a temperature of 393°C in order to remain in the
liquid phase. The high pressure, in tandem with the high temperatures, makes testing the characteristics of a fluoride salt-VP1 suspension extremely challenging. For this reason, it was determined that initial testing would be a test of a fluid at lower temperatures without a pressurization requirement. Though initial testing will be carried out at temperatures much closer to room temperature, special attention will be paid to the testing methods such that they might be used for higher temperature tests at a later time.

Lower temperature testing requires an investigation of phase change materials that melt at more manageable temperatures. The most obvious choices for a carrier fluid are water or some form of oil. It makes the most sense to use VP1 for any oil based nanofluids as it is the heat transfer fluid in a parabolic trough system, unless the VP1 is for some reason incompatible for the chosen phase change material. Two materials were initially tested as potential lower temperature phase change materials: HITEC solar salt and HITEC XL. These two salts are eutectic mixtures of salts in much the same way that the fluoride salts that are intended for use in the higher temperature system, and are used in solar power tower systems as the primary heat transfer fluid.

HITEC and HITEC XL were candidate phase change materials because of their melting point and similarity to the proposed high temperature fluoride salts. HITEC solar salt melts at 220°C, and HITEC XL melts at 147°C. First attempts with both salts began by heating a small amount of VP1 in an open beaker on a hot plate. Once the VP1 oil reached a temperature above the salt’s melting temperature (monitored by thermocouple), a small amount of the salt was added. Addition of the salt lowered the boiling point of the VP1 to approximately 140°C, no longer high enough to melt either of the salts. One theory was that the extremely jagged structure of the salt was providing nucleation sites for boiling of the oil. In order to test this hypothesis,
salt was melted first, and oil was then added on top of the already melted salt. Unfortunately, one of the components present in both salts is a very strong oxidizer, and does not react favorably with the oil. The salt causes the 252°C boiling point of the VP1 synthetic oil to be significantly reduced. The reduction is enough such that the maximum temperature of the boiling oil is no longer sufficient to melt the salt. As such, the HITEC/HITEC XL and VP1 mixtures are no longer a viable option as a low temperature phase change nanofluid.

Paraffins and fatty acids are often used as phase change materials for the purposes of energy storage, and were the next class of materials investigated as candidates for a low temperature phase change nanofluid. Below, Table 5 and Table 6 list paraffins, fatty acids, and their properties. It has been reported that paraffins do not have sharp melting points, and possess a ‘melting range’, it was decided that fatty acids would be more appropriate for low temperature testing. Due to a combination of pricing, availability, and thermophysical properties, lauric acid was selected as the first fatty acid material for testing as a phase change material. Following the same procedure as was followed for the HITEC salts, it quickly became apparent that the lauric acid was soluble in the VP1. As a result, lauric acid and VP1 are not appropriate as components of a phase change nanofluid.
Table 5. Potential Organic Compounds [10]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature (°C)</th>
<th>Heat of fusion (kJ/kg)</th>
<th>Thermal conductivity (W/m K)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl-sulfoxide (DMS)</td>
<td>16.5 [28]</td>
<td>85.7 [28]</td>
<td>n.a.</td>
<td>1009 (solid and liquid) [28]</td>
</tr>
<tr>
<td>Paraffin C₁₈–C₃₄</td>
<td>22–24 [1]</td>
<td>189 [1]</td>
<td>0.21 (solid) [1]</td>
<td>1232 (solid, 4 °C) [4,11]</td>
</tr>
<tr>
<td>Paraffin C₁₈</td>
<td>28 [1]</td>
<td>244 [1]</td>
<td>0.148 (liquid, 40 °C) [30]</td>
<td>0.900 (solid, 20 °C) [1]</td>
</tr>
<tr>
<td>Paraffin C₂₀–C₃₄</td>
<td>27.5 [30]</td>
<td>243.5 [30]</td>
<td>0.15 (solid) [1]</td>
<td>0.814 (solid, 20 °C) [1]</td>
</tr>
<tr>
<td>Paraffin C₁₆–C₂₅</td>
<td>42–44 [1]</td>
<td>189 [1]</td>
<td>0.21 (solid) [1]</td>
<td>0.765 (liquid, 70 °C) [1]</td>
</tr>
<tr>
<td>Paraffin C₂₀–C₃₃</td>
<td>48–50 [1]</td>
<td>189 [1]</td>
<td>0.21 (solid) [1]</td>
<td>0.769 (liquid, 70 °C) [1]</td>
</tr>
<tr>
<td>Paraffin C₂₂–C₄₅</td>
<td>58–60 [1]</td>
<td>189 [1]</td>
<td>0.21 (solid) [1]</td>
<td>0.912 (solid, 20 °C) [1]</td>
</tr>
<tr>
<td>Paraffin wax</td>
<td>64 [4,11]</td>
<td>173.6 [4,11]</td>
<td>0.167 (liquid, 63.5 °C) [4,11]</td>
<td>0.795 (liquid, 70 °C) [1]</td>
</tr>
<tr>
<td>Paraffin C₂₄–C₄₀</td>
<td>66 [4,11]</td>
<td>190.0 [4,11]</td>
<td>0.176 (liquid, 63.5 °C) [4,11]</td>
<td>0.820 (solid, 20 °C) [1]</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>80 [4,11]</td>
<td>147.7 [4,11]</td>
<td>0.132 (liquid, 83.8 °C) [4,11]</td>
<td>976 (liquid, 84 °C) [4,11]</td>
</tr>
<tr>
<td>Erythritol</td>
<td>118.0 [31]</td>
<td>339.8 [31]</td>
<td>0.326 (liquid, 140 °C) [31]</td>
<td>1300 (liquid, 140 °C) [31]</td>
</tr>
<tr>
<td>Trans-1,4-polybutadiene (TPB)</td>
<td>145 [33]</td>
<td>144 [33]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a.: not available.
Table 6. Candidate Fatty Acids for Use as a Low Temperature Phase Change Material [10]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature (°C)</th>
<th>Heat of fusion (kJ/kg)</th>
<th>Thermal conductivity (W/m K)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl palmiate</td>
<td>11 [34]</td>
<td>95–100 [34]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Isopropyl stearate</td>
<td>14–18 [34]</td>
<td>140–142 [34]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Caprylamic acid</td>
<td>16 [4,11]</td>
<td>148.5 [4,11]</td>
<td>0.149 (liquid, 38.6 °C) [4,11]</td>
<td>901 (liquid, 30 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.148 (liquid, 20 °C) [1]</td>
<td>981 (solid, 13 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1033 (solid, 10 °C) [1]</td>
</tr>
<tr>
<td>Dimethyl sabacate</td>
<td>21 [34]</td>
<td>120–135 [34]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.154 (liquid, 61.2 °C) [11]</td>
<td>1018 (solid, 1 °C) [11]</td>
</tr>
<tr>
<td>Vinyl stearate</td>
<td>27–29 [34]</td>
<td>122 [34]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Capric acid</td>
<td>32 [4,11]</td>
<td>152.7 [4,11]</td>
<td>0.153 (liquid, 38.5 °C) [4,11]</td>
<td>878 (liquid, 45 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.149 (liquid, 40 °C) [1]</td>
<td>1004 (solid, 24 °C) [4,11]</td>
</tr>
<tr>
<td>Methyl-12 hydroxy-stearate</td>
<td>42–43 [34]</td>
<td>120–126 [34]</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>49–51 [37]</td>
<td>204.5 [37]</td>
<td>n.a.</td>
<td>861 (liquid, 55 °C) [11]</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>64 [4,11]</td>
<td>185.4 [4,11]</td>
<td>0.162 (liquid, 68.4 °C) [4,11]</td>
<td>850 (liquid, 65 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td>61 [38,39]</td>
<td>203.4 [38,39]</td>
<td>0.159 (liquid, 80.1 °C) [11]</td>
<td>847 (liquid, 80 °C) [1]</td>
</tr>
<tr>
<td></td>
<td>63 [1]</td>
<td>187 [1]</td>
<td>0.165 (liquid, 80 °C) [1]</td>
<td>989 (solid, 24 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td>60–61 [39,40]</td>
<td>186.5 [39,40]</td>
<td></td>
<td>965 (solid, 24 °C) [4,11]</td>
</tr>
<tr>
<td></td>
<td>70 [1]</td>
<td>203 [1]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% in weight; n.a.: not available.

While it is evident that lauric acid and VP1 will not work as a phase change nanofluid, water can be used as the carrier fluid since the melting point of lauric acid is between 42°C and 44°C. Since the heat transfer mechanisms of a low temperature phase change nanofluid are the same as those in a high temperature fluid, a low temperature proof of concept will validate the additional efforts needed to overcome the difficulties that come with operating VP1 at high temperature and
pressure. To create the lauric acid in water nanofluid (LANF), water is first heated to 70°C and the desired amount of lauric acid is added. Once the lauric acid has completely melted, the mixture is stirred with a magnetic stirrer for 2 hours using a combination hot plate/magnetic stirrer shown in Figure 12.

Figure 12. Combination hot plate and magnetic stirrer.

The resulting microemulsion is milky in color as a result of light diffusion from the microsized particles. To further reduce the size of the particles, an 500W Vibra-Cell ultrasonic disruptor manufactured by Sonics & Materials Inc. seen in Figure 13 applies high level shear to the suspension.
The suspension remains on the hot plate throughout the disruption to prevent the particles from agglomerating before they have had sufficient time to be broken apart into smaller particles.

After 2 hours of ultrasonic disruption, the heat source is removed with the disruptor still on and the lauric acid and water mixture is allowed to cool. The disrupted suspension is now clear, suggesting that the particles are no longer large enough to diffuse the ambient light and cause a
cloudy appearance. Nanoemulsion status was verified through the use of dynamic light scattering (DLS). A DLS instrument from Malvern Instruments verifies a particle size distribution centered about 57nm shown in Figure 14.

![Figure 14. DLS characterization of LANF without high pressure homogenization.](image1)

Although it is unnecessary to further reduce the size of the particles, another Malvern instrument was tested as an alternate method of reducing the particle size after the 2 hour stirring step. A high pressure homogenizer forces the fluid through a microfluidic channel at high pressure, which generates enormous shear forces on the small lauric acid particles.

![Figure 15. DLS characterization of LANF with high pressure homogenization.](image2)
DLS analysis of the fluid after high pressure homogenization showed an even smaller particle size distribution, peaking at 13nm in Figure 15. Although the high pressure homogenizer does result in smaller lauric acid particles, the ultrasonic disruptor produces small enough particles for the present application.

Within an hour, the disrupted lauric acid phase could be seen agglomerating and separating to the top of the water. In order to combat this separation, the effects of adding the surfactants NaDDBS and SDS were tested. Guidelines from Islam were followed concerning the proper amounts of surfactant that should be added. Surfactant in the amount of ten times the mass of the lauric acid present was added to the suspension. Based purely on the separation rates of the suspensions post-disruption, SDS was the better surfactant choice. An important note is that no surfactant could be identified that would be usable at the higher temperatures at which a solar thermal power generation system operates. Lack of a suitable surfactant could prove problematic with respect to developing high temperature phase change nanofluids.

In order to characterize the heat capacity of the fabricated nanofluids, a differential scanning calorimeter was purchased. Before settling on the PolyDSC from Mettler Toledo, DSC units from Neztsch Thermal Analysis, Mettler Toledo, and TA Instruments were evaluated. The Polymer DSC of Mettler Toledo was compared to the Q200 of TA Instruments and the DSC 200 F3 Maia of Neztsch Thermal Analysis. Samples of VP1 sent to all three manufacturers revealed that each of the three units were more than capable of measuring the heat capacity to the degree of accuracy that is necessary. The standard method for calculating the specific heat capacity of a material using a DSC is detailed in ASTM method 1269-05. Although a standard method for the measurement of specific heat capacity exists, the method cannot guarantee better than ten percent error. The difficulties arising in the measurement of specific heat capacity stem from the need to
simultaneously measure both temperature and heat flux to a great degree of accuracy. More common applications of a DSC include identifying temperatures at which phase changes or crystal transitions occur. Phase changes and crystal transitions can be identified by a large peak or drop in the amount of heat flux required to heat the material. While it is necessary to measure heat flux in these applications, the amount of heat flux is not important, merely the temperature at which the transition occurs. When greater temperature accuracy is desired, very small heat fluxes and temperature ramps of less than $5^\circ$C/minute are used to allow the entire system to thermally equilibrate. If greater accuracy of heat flux measurement is desired, fast temperature ramps of greater than $20^\circ$C/minute must be used. In measuring heat capacity, the ASTM1269-05 method requires a temperature ramp rate of 10-20°C/minute in an effort to balance the need for both heat flux and temperature measurements. Data gathered from all three manufacturers showed much better performance. The Netzsch DSC 200 was ruled out due to pricing reasons. Both TA Instruments and Mettler Toledo were able to offer refrigeration units with their DSCs for comparable prices. The refrigeration units enable DSC measurements to be taken at temperatures as low as $-40^\circ$C, greatly expanding the range of temperatures at which the machine is useful. Ultimately, the Mettler Toledo PolyDSC was selected to meet the DSC needs of the project.

To verify that the nanofluid behaved as expected, the Mettler Toledo DSC unit was used to provide heat flux data for a 10% volume fraction suspension of lauric acid in water, displayed in Figure 16.
Heat flux data matched the expected behavior of a phase change nanofluid. Since the heat capacity of both the solid and liquid lauric acid was less than that of water, it was expected that the calculated heat capacity would be less than that of pure water for those regions outside the melting regime. Inside the melting regime, there was a peak in heat flux and therefore calculated specific heat capacity. For the right range of working temperatures, the specific heat capacity peak resulting from the latent heat of melting can overcome the reduced specific heat capacity observed outside the melting regime. For example, take a 10% by volume suspension of lauric acid in water. A 10% volume fraction of lauric acid in water corresponds to an 8.9% by mass suspension. If we take the heat capacity of water as a constant 4.182 kJ/kg*K, and that of the lauric acid as 2.0 kJ/kg*K, the heat capacity of the nanofluid is 3.988 kJ/kg*K. This represents a 0.194 kJ/kg*K or 4.6% decrease compared to that of pure water. However, the latent heat of
lauric acid is 178 kJ/kg. As long as the nanofluid is exposed to a working range of temperatures in which the lauric acid melts, the system will benefit from 15.8 kJ of energy absorbed by the lauric acid during the phase change, provided the working range is less than 81.7 K. However, the advantage of the phase change nanofluid is greatest when the working range is small.

An investigation of different types of fluids for potential use as a heat transfer fluid in a solar thermal power generation facility revealed a promising idea in phase change nanofluids. Although phase change nanofluids cannot address the challenge of increasing the temperature stability of the heat transfer fluid, they can serve to increase the heat storage capability of the heat transfer fluid. However, there still exist some challenges to this approach. While it has been shown that nanoparticles can be observed to change phase while suspended in a carrier fluid, the heat transfer characteristics of a phase change nanofluid in a flow situation remain to be characterized. Also, nanofluid stability and fabrication method challenges must be addressed in order to make phase change nanofluids feasible in a large scale system.
Chapter 3

3. Design and Fabrication

In addition to using DSC measurements to characterize the specific heat capacity of fabricated fluids, it is necessary to observe the behavior of the phase change nanofluids in a non-static situation. As a result, a microchannel device was envisioned for the testing of phase change nanofluid heat transfer characteristics. The two main choices in the experimental design were those of scale and temperature measurement methodology. As detailed in the previous chapter, there are many issues with fabricating large volumes of nanofluids. It is difficult to make more than 100s of mL of nanofluid at a time, and the process is very time consuming. A macro-scale setup, even a closed-loop system that recycled the fluid through the test section many times would require a prohibitively large volume of fluid. Potential agglomeration issues would further complicate the use of a macro-scale system. Agglomerated and solidified PCM could potentially build up in the test section or other areas of the experimental setup and contaminate measurements. As a result, it becomes apparent that a disposable test cell capable of performing measurements on a small volume of fluid would be extremely beneficial for testing purposes. For this reason, a microfluidic device was chosen as the appropriate method for testing. This microfluidic device must be capable of both heating the flowing fluid as well as measuring its temperature precisely. Since our device must map the temperature profile of a substance undergoing phase change, during which the temperature is nearly static, it is necessary to have the capability to measure temperature to within 0.1K. The method of temperature measurement is the second major design choice.
There are many different ways to measure temperature in an experimental setting. The most common method of temperature measurement is the thermocouple, which is cheaply available in different configurations for the measurement of different temperature ranges. However, thermocouples are easily ruled out for our application as they cannot be relied upon to measure temperature to a level of precision any less than 1K. A common technique used to measure temperature in microfluidic devices is the use of platinum resistance thermometers. Compared to other metals, platinum has one of the highest temperature coefficients of resistance of patternable materials (3.92*10^{-3} Ω/K), which makes it a very good thermometer material for many applications. However, the most common microfluidic application in which platinum was used as a thermometer dealt with temperature differences measured in tens of degrees [11]. These differences were more than two orders of magnitude greater than the 0.1K necessary for our application. Although platinum is often used in larger scale resistance temperature detectors to measure temperature, the small scale that our device requires makes this approach prohibitive. In order to accommodate enough thermometers to create a detailed temperature profile of the fluid in the channel, they must have extremely small dimensions. These geometric restrictions and the limitations of metal deposition technology result in patterned resistors with high resistance. Typical platinum RTDs have a base resistance of just 100 Ω. At this resistance level, a 0.1K measurement requires a multimeter to accurately register a resistance change of 0.03 Ω, or 0.03% of the full scale measurement. While a very small proportion of the original measurement, this is still within the range of many common laboratory multimeters. However, the dimensional and technological restrictions that we are presented with would result in resistors in the 100 kΩ range. A 0.1K temperature measurement would still require the measurement of a 0.03 Ω resistance measurement, which is a much smaller portion of the full scale measurement.
Doped silicon resistors provide a solution to this problem, as they can have a temperature coefficient of resistance much higher than that of platinum, and they can be patterned directly into a silicon wafer. For this reason, doped silicon resistors became the chosen method of temperature measurement. Since doped silicon resistors obviously require a silicon substrate, it was determined that microfluidic channels would be etched into the silicon, as opposed to using PDMS or glass.

3.1 MICROCHANNEL DESIGN AND DIMENSIONS

Although the flow in a full scale parabolic trough solar thermal power generation system is highly turbulent, with a Reynolds number of nearly 60000, numbers such as these are not practical in a microfluidic system. For this reason, Reynolds numbers for the microfluidic flow cell were not chosen to reflect those of the full scale system. Reynolds numbers were set low so as to reduce the volume of required nanofluid and keep heating power requirements to a minimum. The channel design and dimensions were structured around a Reynolds number of 25. A channel etched into silicon will be roughly rectangular; and in order to simplify heat transfer calculations for the purpose of mathematical simulation, a high aspect ratio rectangular shape was selected. The channel width is 2mm, and its depth is 50 μm, giving it an overall aspect ratio of 40:1.

![Figure 17. Schematic of microchannel device. Depth is 50 μm measured into the page.](image-url)
This high aspect ratio allows it to be treated as two infinite parallel plates for the purposes of heat transfer calculations. At an aspect ratio greater than 8:1, the Nusselt number of a 3 dimensional channel becomes very nearly the same as the Nusselt number of two infinite parallel plates.

The length of the channel needed to be sufficiently long so that the test section is well beyond both the thermal and hydrodynamic entrance length of the microchannel. With the described dimensions, the rectangular microchannel has a hydraulic diameter of 9.756e-5m. The hydrodynamic entrance length can be described by the equation \( L_h = 0.05 \text{Re} D_h \), such that the hydrodynamic entrance length for the microchannel is 122 \( \mu \text{m} \). The thermal entrance length can be calculated by \( L_t = 0.033 \text{Re} \text{Pr} D_h \), putting the thermal entrance length at 563 \( \mu \text{m} \). Given these entrance lengths, it is clear that even a channel of a few millimeters in length would be enough to obtain a meaningful test section. At this point, the determination of the length of the channel became a decision based on the dimensions of the thermometers and ease of wiring. Based on dimensional and geometric placement of thermometers, the overall channel length was determined to be 3.5 cm. This length provides sufficient length between thermometers to allow easy wiring and help to mitigate thermal saturation of the channel by conduction axially through the silicon. At either end of the channel is a 1 cm by 1 cm reservoir at the same depth as the microchannel. This allows fluid from the inlet sufficient time to settle before entering the channel. In terms of heating the channel, the design condition was to provide sufficient power to raise the temperature of pure water 10K between the inlet and the outlet. This would ensure sufficient power to melt the PCM within the confines of the test section. Given this requirement, and a Reynolds number of 25, the heat input requirement can be calculated. Assuming that the heat generator can be approximated as a source of constant heat flux along the entire floor of the
channel, the needed heat can be calculated using $P = m c_p \Delta T$. The mass flow rate can be determined from the Reynolds number of 25 and the properties of water at 323K, which is approximately the proposed operational temperature of the channel. Relating the mass flow rate to the Reynolds number gives a value of $1.40 \times 10^{-5}$ kg/s. This corresponds to a volume flow rate of 0.85 mL/min, which would allow for a test of many minutes with only a small batch of nanofluid. Given the mass flow rate, the input power required to heat the fluid becomes 0.586 W.

Heat will be provided to the microchannel by a patterned aluminum heater on the back side of the device. The aluminum heater is designed to provide a 1.2 W of heat in order to guarantee that the microchannel has the necessary power to heat the fluid in the channel. Due to contact lithography limitations, the maximum thickness of Al that can be patterned onto the silicon wafer is 1 μm. Based on observations from other heaters used for similar applications, the heater is a series of 50 μm wide Al lines running back and forth along the length of the channel, with a spacing of 50 μm between each of the lines. The first Al line begins 200 μm outside of the channel to provide the most uniform heat flux possible. A 300 μm gap between lines is placed along the centerline of the channel to allow room for the incorporation of thermometers. These design specifications result in twenty-two 50 μm wide Al lines running the length of the 3.5cm channel for a total resistor length of 0.7718m. The resistivity of Al is $2.7 \times 10^{-8} \ \Omega\cdot m$ for a total resistance of $416.772 \ \Omega$. At this resistance 54 mA of current will be sufficient to supply 1.2 W of power to the device. With such small resistors, it is important to make sure that the electromigration limit of Al is not exceeded, as this could severely shorten the effective operational life of the heater. Below current densities of $1 \times 10^5 \ A/cm^2$, the effects of electromigration in Al are negligible. The current density of the Al heater at the design loading is below this threshold value and electromigration is not expected to be a problem.
3.2 THERMOMETER DESIGN

Once it was determined that doped resistors would be the best way to measure temperature of the fluid as it traversed the channel, the parameters by which the resistive thermometers would be formed needed to be optimized. A method of calculating the resistance per square of doped silicon resistors was presented in Reggiani et al [12]. Below are the relevant constants necessary for the resistance calculation.

**Table 7. Constants and Mobilities for Evaluation of Doped Resistors**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (T_n = T/300K) )</td>
<td></td>
</tr>
<tr>
<td>( \mu_{max} ) (cm(^2)/Vsec)</td>
<td>470.5</td>
</tr>
<tr>
<td>( c )</td>
<td>0.0</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>2.16</td>
</tr>
<tr>
<td>( \mu_{0d} ) (cm(^2)/Vsec)</td>
<td>90.0( T_n^{-1.3} )</td>
</tr>
<tr>
<td>( \mu_{0a} ) (cm(^2)/Vsec)</td>
<td>44.0( T_n^{-0.7} )</td>
</tr>
<tr>
<td>( \mu_{1d} ) (cm(^2)/Vsec)</td>
<td>28.2( T_n^{-2.0} )</td>
</tr>
<tr>
<td>( \mu_{1a} ) (cm(^2)/Vsec)</td>
<td>28.2( T_n^{-1.8} )</td>
</tr>
<tr>
<td>( C_{r1} ) (cm(^3))</td>
<td>1.30( 10^{18} T_n^{2.2} )</td>
</tr>
<tr>
<td>( C_{r2} ) (cm(^3))</td>
<td>2.45( 10^{17} T_n^{3.1} )</td>
</tr>
<tr>
<td>( C_{s1} ) (cm(^3))</td>
<td>1.1( 10^{18} T_n^{6.2} )</td>
</tr>
<tr>
<td>( C_{s2} ) (cm(^3))</td>
<td>6.10( 10^{20} )</td>
</tr>
<tr>
<td>( \alpha_{1} )</td>
<td>0.77</td>
</tr>
<tr>
<td>( \alpha_{2} )</td>
<td>0.719</td>
</tr>
</tbody>
</table>
The following steps, implemented in MATLAB, allow the resistance to be calculated as a function of both the implantation dosage as well as the temperature. First,

$$E_g = 1.170 - \frac{(4.730 \cdot 10^{-4} \cdot T^2)}{T + 636}$$

is used to calculate the electron band gap, $E_g$, of the silicon wafer as a function of the ambient temperature, $T$. The intrinsic ion concentration, $n_i$, is calculated as

$$n_i = \left(2.4 \cdot 10^{31} \cdot T^3 \cdot e^{8.617 \cdot 10^{-3} \cdot T} \right)^{0.5},$$

and the p and n type ion concentrations are calculated by:

$$p = \frac{n_{con}}{2} + \left(\frac{n_{con}}{2}^2 + n_i^2\right)^{0.5}, \text{ and } n = \frac{n_i^2}{p},$$

where $n_{con}$ is the dopant concentration, calculated by

$$n_{con} = 10^{-0.0724 \cdot \log(dose) + 2.831 \cdot \log(dose) - 6.907}.$$

In this case, the doping ion is boron, whose dosage, dose, is measured in ions/cm$^2$. The function describing $n_{con}$ is a fit derived from the tsuprem4 simulation of the particular doping and annealing recipe used in the fabrication of the doped resistors on the microfluidic device. For low dopant concentrations below about $10^{22}$,

$$N_D = n,$$

$$N_A = p.$$

$N_D$ is donor concentration, and $N_A$ is acceptor concentration. Final dopant concentrations in the resistors for the microfluidic flow cell do not exceed $7 \cdot 10^{18}$, so the above approximation remains appropriate for this application. Bulk, $\mu_b$, and lattice, $\mu_L$, mobilities are calculated by
\[
\mu_b = \mu_0 + \frac{\mu_L - \mu_0}{1 + \left(\frac{N_D}{C_{r1}}\right)^{\gamma_1} + \left(\frac{N_A}{C_{r2}}\right)^{\gamma_2}} + \frac{\mu_1}{1 + \left(\frac{N_D}{C_{s1}} + \frac{N_A}{C_{s2}}\right)^{-2}}, \text{ and}
\]

\[
\mu_L = \mu_{\text{max}} * T_n^{-\gamma + c + 7}, \text{ respectively.}
\]

\(\mu_{\text{max}}\) is the lattice mobility at room temperature, and \(c\) is a correction factor for the slope of \(T_n\).

\[
\mu_0 = \frac{\mu_{0d} * N_D + \mu_{0a} * N_A}{N_D + N_A} \quad \text{and} \quad \mu_1 = \frac{\mu_{1d} * N_D + \mu_{1a} * N_A}{N_D + N_A}
\]

are weighted averages of the limiting values for donor and acceptor concentrations. Once the bulk mobility is calculated, the first approximation for the resistivity, \(\rho_{\text{MATLAB}}\), of the doped sensors can be calculated using

\[
\rho_{\text{MATLAB}} = \frac{0.01}{1.602 \cdot 10^{-19} \cdot (\mu_b * n + \mu_b * p)} \Omega \cdot \text{cm}.
\]

While this calculation is very close, it does not quite match the numbers from \textsc{tsuprem4}, a widely used program for modeling migration of ions. Though any calculation or simulation is only a guess, results from \textsc{tsuprem4} are generally accepted as valid. However, \textsc{tsuprem4} only reports resistivity data for room temperature. Since \textsc{tsuprem4} is the only way to calculate the necessary junction depth to determine the resistance per square of the doped thermometers, the MATLAB data for room temperature resistivity values was fit to the \textsc{tsuprem4} data and this adjustment was applied to the rest of the resistivity measurements.

\[
\rho_{\text{tau}} = 10^{1.062 * \log(\rho_{\text{MATLAB}})^{1.00} + 0.596}
\]

The depth of the junction can be calculated as a function of the \(n_{\text{con}}\) using a fit based on the \textsc{tsuprem4} simulation.

\[
\text{depth} = 10^{0.02334 * \log(n_{\text{con}})^{2} - 0.862 * \log(n_{\text{con}})^{-1.652}} \text{ m}
\]
Finally, the resistance per square, $R_{\text{square}}$, can be determined by dividing the resistivity calculated using the tsuprem4 adjustment by the calculated junction depth.

$$R_{\text{square}} = \frac{\rho_{\text{cu}}}{\text{depth} \times 100} \Omega/\text{square}$$

By solving this set of equations for multiple temperature values, resistance can be determined for a multitude of temperature values. These values allow a calculation of an average temperature coefficient of resistance for a particular temperature range of interest.

The establishment of a method for calculating a temperature coefficient of resistance as a function of the implant dosage allows for optimization of the resistance thermometers. Although it might seem more appropriate to plot resistance per square as a function of implanted ion concentration, it is more useful to employ a function of implant dosage because this is the only parameter that can be actively controlled.

![Figure 18. Resistance/square as a function of the logarithm of implant dosage in ions/cm².](image-url)
A log plot of the resistance per square against the log of implant dosage in Figure 18 shows a one way trend of decreasing resistance versus increasing implant dosage. This makes physical sense, as the increased presence of ions in the silicon substrate would tend to increase the ability of the silicon to conduct electrons. The selected dosage value must yield a resistance that is within the range of laboratory measurement equipment.

![Graph](image)

**Figure 19.** Temperature coefficient of doped resistors as defined by implant dosage.

More important than the overall resistance value is the temperature coefficient of resistance. As implant dosage decreases in Figure 19, the temperature coefficient of resistance increases substantially. It is obvious that a higher temperature coefficient of resistance is valuable to our measurements, but a more useful metric is the relationship between temperature coefficient of resistance and the overall resistance per square of the doped resistor. In short, the greatest benefit is achieved with the highest ratio of temperature coefficient of resistance to full scale resistance.
method, as described earlier in the discussion of temperature measurement methodology.

The ratio of temperature coefficient as a function of implant dosage has a clear peak at $2.1 \times 10^{12}$ ions/cm$^2$, visible in Figure 20. However, the native ion concentration of the silicon is on the order of $10^{15}$ ions/cm$^3$. If the doped concentration of ions does not exceed this value by at least 2 orders of magnitude, an electrical junction will not be formed between the doped region and the rest of the wafer. Electrically, the doped region and the silicon surrounding it will not differ. This requirement places a lower limit of approximately $5 \times 10^{12}$ ions/cm$^2$. Since the lowest possible dosage yields the best ratio, $5 \times 10^{12}$ ions/cm$^2$ was chosen as the implant dosage for the doped resistors. Following the calculation procedure detailed above, an implant dosage of $5 \times 10^{12}$ ions/cm$^2$ would yield a room temperature resistance of 11.874 k$\Omega$/square and a temperature coefficient of resistance of 52.5 $\Omega$/square*K.

Figure 20. Ratio of temperature coefficient to total resistance of doped resistors.
3.3 **FABRICATION**

The microfluidic flow cell was fabricated at MIT in the Microtechnologies Laboratory (MTL). The entire process was composed of more than thirty steps and used six different masks. Much of the process was adapted from a process used for a similar application in [13] and [14].

![Figure 21. L-edit mask overlay.](image)

Figure 21 is an overlay of the six masks, showing the seven devices contained on each wafer.

Initially, each wafer would only yield 5 devices, but were redesigned to produce seven devices.
when it was determined that the space between devices was more than enough to hold the anodically bonded pyrex in place. Masks were designed using L-Edit software, and were etched onto chrome on glass masks.

The first mask used contains the alignment marks, Figure 22. These alignment marks were etched into what will be referred to as the back side of the wafer. The mask, pictured below, was completely covered in chrome save for the alignment marks themselves.

![Figure 22. Alignment marks mask.](image)

The etching of the alignment marks began by first placing the wafers to be etched into the hexamethyldisilazane (HMDS) treatment oven, Figure 23a. The HMDS process is a batch
process, and up to 25 wafers can be placed into a metal carriage before placing them in the HMDS treatment oven.

![Figure 23. Alignment marks photolithography and etching.](image)

This process helps dehydrate the wafers and coats them with a layer of HMDS to help the photoresist adhere to the wafer. Once the roughly half-hour HMDS process is completed, 1 μm OCG-825 photoresist is spun coat onto the wafers, Figure 23b. Applying photoresist is a serial process and must be handled one wafer at a time. The quality of the photoresist coating is highly dependent on how well the wafer is centered on the spinning chuck before the photoresist is applied. If the wafer is off-center, the photoresist will be uneven and create problems later on in the etching process. Photoresist is dispensed onto the center of the wafer for 9 seconds while the wafer spins at 500 rpm. The wafer spins at 750 rpm for 6 seconds to spread the photoresist before spinning at 3000 rpm for 30 seconds to thin the coating to 1 μm. Immediately following
the spin-coating of photoresist onto the wafers, they were placed into a plastic cassette
photoresist side up as to prevent gravity from causing the photoresist to flow to one side of the
wafer. The plastic cassette was placed into the pre-bake oven at 95°C for 30 minutes and then
allowed to cool. The pre-bake process partially sets the photoresist so it is no longer free-
flowing. After the wafers have cooled to room temperature, they are exposed using the EV-LC.
The alignment mark mask is first mounted to the EV-LC, and the wafer is exposed. Exposed
wafers are one by one soaked for 50 seconds in a developer solution that washes away the
exposed regions of photoresist, Figure 23c. After a spin-rinse-dry cycle, the wafers are post-
baked at 120°C for 30 minutes. Post-baked wafers are ready for etching in the STS2 plasma
etching machine. Using the alignmark recipe, the alignment marks are etched into the wafers one
by one, Figure 23d. While only one wafer can be in the plasma chamber at a time, two wafers
can be loaded into the carousel in the loading area of the machine. Since the alignment marks do
not need to be etched very deep, the alignmark recipe only etches for about 30 seconds, and uses
no passivation step. Once the alignment marks are etched, the wafers are ready to begin the
process of etching the channels into the wafers. However, the photoresist must first be removed
from the etched wafers. Removal of photoresist is accomplished by soaking the wafers in a
mixture of sulfuric acid and hydrogen peroxide known as piranha. Using the acid hood, a quartz
container is filled partially with hydrogen peroxide, and then with three times more sulfuric acid.
The wafers are placed in a plastic cassette and soaked in the piranha for 15 minutes before being
placed in the dump-rinser. The quartz container must be aspirated of the piranha and then rinsed
and aspirated three time in order to clean away any remnants of the corrosive mixture. After the
acid hood station is properly cleaned, the wafers are put through a spin-rinse-dry cycle.
Following the SRD cycle, the wafers are put through the asher for 25 minutes to remove any
remaining organics before proceeding to the next photolithography step. It is recommended that wafers be processed for photolithography within 24 hours of ashing to ensure no organic buildup. At this point photolithography for the channels can begin.

The second mask, Figure 24, is similar to the first in that it is completely covered in chrome save for the shape of the 7 channels and the cross-shaped alignment marks.

![Figure 24. Reservoir and channel mask.](image)

The beginning of the second major phase, Figure 25, of processing in the MTL is very similar to that of the first phase. The wafers are processed in the HDMS batch-wise, Figure 25a, and then
spun coat with 1 μm of OCG-825 photoresist, Figure 25b. At this point the process begins to differ from the alignment mark step.

In exposing the photoresist with the alignment mark mask, no alignment of the wafer to the mask was required, because there were no features already on the wafer. At this point, the channels must be matched up to the appropriate location by use of the cross shaped alignment marks, depicted in Figure 26. Alignment was achieved by a technique known as front-to-back alignment. The alignment marks reside on the backside of the wafer, while the channels much be etched into the front side of the wafer. This type of alignment takes slightly longer than a transparent topside alignment. Once the mask is secured to the EV-LC and the optics below the mask are focused on the alignment marks on the mask, a green cross is superimposed digitally on the computer screen at the location of the alignment marks of the mask. These digital green crosses are aligned to the cross shaped alignment marks on the backside of the wafer and the top
side of the wafer is subsequently exposed. Exposed wafers are then developed and post-baked, Figure 25c.

![Cross shaped alignment marks on microchannel mask (left) and alignment mark mask (right).](image)

The etch process is once again carried out in the STS2 plasma etching machine, but requires a slightly more involved recipe. In a deeper etch, the STS2 cycles back and forth between etch and passivation steps. The etch step etches into the wafer, and the passivation step coats the sidewalls of the etched trench to ensure a more vertical etch. However, before etching the entire 50 μm depth of the channels, the etch rate of these particular wafers must be determined. After a 5 minute etch of one wafer using the jbetch recipe, the Nanospec machine is used to characterize the depth of the etched trench, and it is determined that the wafer is etching at almost exactly 2 μm per minute. The partially etched wafer is etched for another 15 minutes, and all other wafers in the process stack are etched for 25 minutes to obtain the desired 50 μm deep channels and reservoirs. The wafers are then put through the piranha process and the asher to remove the photoresist and prepare them for the next step in the process.
The next portion of the fabrication begins the process of patterning the doped resistors. The mask used for this portion of the process, Figure 27, contains 7 sets of 15 small voids that will become the resistors for measuring temperature.

![Doped resistor mask](image)

**Figure 27. Doped resistor mask.**

Before photolithography for this portion of the process proceeds a protective layer of oxide must first be grown on the wafers. In order to ensure the best quality oxide growth, the wafers must again be cleaned in the piranha solution and then cleaned at the RCA station. The RCA clean involves two separate baths that remove any metal ions and strips the wafers of any natural oxide growth. After the RCA clean, the wafers must be transferred to the A2 tube furnace within 4 hours.
After engaging the furnace, which typically idles at 600°C, the wafers are placed in a quartz boat and inserted into the furnace tube. The furnace temperature is then ramped to 950°C before starting the oxygen flow. The dry oxidation process to grow 250Å of oxide takes approximately 45 minutes. After 45 minutes, the oxygen flow is stopped and the furnace temperature is reduced to 600°C so the wafers can be removed. The wafers are now ready for photolithography.

Figure 28. Photolithography and doping of resistors.

Identical to the beginning of the two previous photolithography steps, the wafers are first put through the HMDS and spun-coat with 1 μm of OCG-825, a-b in Figure 28. This time a transparent alignment step can be used on the EV-LC because the alignment marks and the resistors are both on the back side of the wafer. The optics on the upper portion of the EV-LC are first focused on the chrome alignment marks on the mask. Since the area immediately surrounding the alignment marks is free of chrome, these marks shown in Figure 29 can be matched with the corresponding marks on the back side of the wafer. Each wafer is then exposed and developed. At this point, the wafers are ready for ion implantation, Figure 28c, but the MTL lacks the equipment to perform this operation on site. The wafers are boxed and shipped to
Innovion where Boron ions are implanted into the wafers at a dosage level of $5 \times 10^{12}$ ions/cm$^2$ and an accelerating voltage of 40 keV.

![Alignment marks for dopant mask.](image)

After receiving the wafers back from Innovion, the photoresist is removed with two ten minute piranha baths. To remove the 250Å oxide coating, the wafers are dipped in a 20:1 HF solution. The next step is to grow 2500Å of oxide to anneal and passivate the resistors, so the wafers must be put through the RCA clean again before going into the furnace. At this point it is relevant to mention that the 250Å oxide coating should not have been removed. The resistors should have been annealed with the protective oxide coating still on the wafers. A percentage of the implanted ions do not make it through the oxide coating, but will diffuse through the oxide into the silicon during the annealing process. For this reason, it is a better practice to anneal doped resistors prior to stripping of any oxide. Growth of 2500Å of oxide also uses the A2
furnace tube in the TRL and follows the same insertion and removal procedure as the previous oxidation step.

The much thicker 2500Å oxide coating uses a wet oxidation process rather than a dry oxidation. The addition of hydrogen gas to the furnace tube during the oxidation process causes the oxide growth to progress much faster. The oxidation step only takes about an hour, though additional
steps in the recipe bring the total process time not including insertion and removal to nearly two hours. After annealing and passivation, the resistors are fully formed, but the insulating oxide layer prevents electrical contact and must be etched away in order to form the electrical contacts.

The mask that outlines the contact pads will open two 150 μm squares, one at each end of the rectangular shaped resistor. For future designs, it would be advantageous to design the oxide holes to be slightly smaller than the width of the doped region. A slight difference in dimensions between the doped regions and the contact windows would prevent small alignment errors from allowing the electrical contact with non-doped regions of the silicon.

Photolithography for the contact pads also utilizes a top side transparent alignment and is identical in practice to that of the ion implantation photolithography. Post photolithography, a 6:1 HF solution in the acid hood station is used to etch holes through the insulating oxide layer. Two processing mistakes were made in this step, almost resulting in a loss of the wafers. The first mistake was using a mixture of just hydrofluoric acid and water, rather than a prepared buffered oxide etch. The BOE mixture etches in a much slower and controlled fashion, which is important for precise processing. The other mistake was placing all the wafers into the etchant solution at the same time. The etch rate first should have been checked by using a single wafer, so that any mistakes would only result in the potential loss of one wafer from the process stack. Unfortunately the strong acid solution quickly removed portions of the photoresist and completely stripped away large patches of oxide. Whereas the intended result was to open small holes directly over the doped resistors, Figure 31c, the result was a splotchy removal of large portions of oxide, Figure 31d.
Luckily, the wafers were not completely ruined. Two options for fixing this issue were growing a new oxide coating on the wafers, or using a chemical vapor deposition process to deposit oxide on the backside of the wafers. CVD was chosen as the appropriate solution, because the high temperature oxide growth in a furnace tube could cause the implanted ions to diffuse further into the wafer and change the characteristics of the resistors, an undesirable result. Before CVD processing, the remaining patchy photoresist and oxide on the wafers is removed by dipping them first in piranha and then in a strong HF solution for a few minutes, Figure 32a-b. The process to replace the oxide will include a CVD deposition and then a thermal anneal of the oxide to improve its strength and resistance to etching. Since the thermal anneal requires the use of the furnace tube, an RCA clean in TRL must be done prior to the deposition of oxide in the
Immediately following the RCA clean, a 3000Å oxide layer is deposited on the backside of the wafers using the DVCD in the ICL, Figure 32c.

![Diagram showing the process](image)

**Figure 32. Removal of remaining oxide and deposition/etching of new oxide layer.**

One difference to note is that the DCVD only deposits oxide on one side of the wafer, whereas oxide growth results in an oxide layer on both sides of the wafer. These wafers are then annealed in the A2 tube furnace in the TRL at 900°C for 30 minutes. The 900°C temperature should not diffuse the implanted ions to any appreciable extent because it is sufficiently below the temperature at which the resistors were initially annealed. Differing from previous furnace steps, this is a purely thermal process, and no oxygen is flowed through the furnace tube during the process. Once the oxide has been deposited and annealed, the photolithography steps for the etching of contact windows in the oxide are repeated, Figure 32d. This time, however, a BOE
etchant is used to create the holes in the oxide. The BOE etchant etches thermal oxide at around 1000Å per minute, taking just over 3 minutes to etch through the oxide and open windows through to the silicon. For reference, the BOE etchant would have etched the non-thermal oxide at 1 μm per minute. The extremely fast etch rate of non-thermal oxide could have resulted in problems similar to those in the last oxide etch attempt, justifying the annealing step prior to etching.

Figure 33. Aluminum heater and contact pad mask.

Following the opening of holes in the oxide, Al heaters and contact pads must be patterned on the backside of the wafer via the mask in Figure 33. First, the Endura machine in
the ICL is used to deposit a 1 μm thickness layer of Al on the backside of each wafer, Figure 34a-b. While the machine only handles one wafer in the processing chamber at a time, all wafers in the process stack can be loaded into the load lock at left until Al deposition on all wafers has been completed. The wafers are now prepared to undergo photolithography to establish the patterns that will be the electrical system for the devices. The mask for this step differs from the previous masks in that it is largely clear save for the areas that will retain the aluminum layer. Photolithography for the Al etch step is procedurally the same as the other top-side transparent alignments, but a lack of foresight in the design of the mask for this part of the process made alignment difficult, Figure 34c-d. Previous masks had a small window surrounding the alignment marks had a series of squares surrounding the alignment marks that indicated in which direction the alignment marks lay. However, these marks were not surrounded by any larger markers and were quite difficult to find. Post photolithography, the unneeded aluminum must be etched away using a standard aluminum wet etchant in the acid hood, Figure 34e. Given the etch rate of the aluminum etchant, removal of the aluminum should have taken approximately 90 seconds. However, it was over 15 minutes before the aluminum was completely etched. Possible reasons for the slow etch rate could have been old etchant or etching at a less than optimal temperature. The etchant recommends a process temperature of 50°C, but the TRL acid hood lacks the ability to closely regulate the temperature of an etchant so the etch was carried out at room temperature. To proceed to the next step in the process, the photoresist must be removed from the wafers. However, the wafers can no longer be put in a piranha solution because it would attack the metal and destroy the contacts and heaters. The photoresist is instead removed by ashing for one hour.
The functional portions of the flow cell are now nearly complete. However, analysis of the resistors on a probe station shows that the aluminum does not have good contact with the doped regions of the wafer. This lack of electrical contact is common and is the reason for the next step in the process. Wafers are processed in the A3 furnace tube at 400°C for 45 minutes under a flow of hydrogen and nitrogen gas, known as a forming gas anneal. The forming gas anneal causes the aluminum contacts to grow into the silicon, enhancing the electrical contact with the doped regions. Post-forming gas anneal measurements on the probe station show much better electrical response. To ensure that the resistors respond to changes in temperature as necessary for measurements, one wafer is removed from the MTL to be tested on a probe station equipped with a hot plate. In heating from room temperature to approximately 150°C, a resistance change of nearly 10 Ω/K is observed, confirming the required sensitivity to temperature. Following confirmation of the resistivity response to temperature, processing in the
MTL can be resumed. In order to protect the electrical contacts from stray connections or
damage due to incidental physical contact, it is useful to deposit an insulating oxide layer over
the entire wafer. Once again, the DVCD in the ICL is used to deposit an oxide layer on the
wafers. As before, portions of this oxide layer must be removed to establish electrical contact
with the patterned heaters and contact pads. The same mask as was previously used to open
contact windows is reused for this purpose. This particular mask was specifically designed such
that it could be rotated 180° and reused for the second oxide etch. Photolithography for this step
is identical, but a dry etch must be used instead of a wet etch due to the critical nature of this
portion of the process. A wet etch could easily and very rapidly remove the aluminum contacts
that were deposited on the wafers.

The rainbow machine in the ICL is capable of performing the etch necessary to remove
the oxide over the electrical contact pads without risking removal of the contact pads themselves.
Like many of the other processing tools used, the machine actively processes just one wafer at a
time, but will load wafers automatically from a cassette. Use of the rainbow proved problematic
due to the etched channels on the front side of the wafers. The etched channels often caused
errors when the wafers were handled by a vacuum chuck within the machine. As long as the
wafers were loaded with the channel pointed in a specific direction, the machine would begin
processing the wafers properly. However, an error message would always be triggered when a
wafer was moved from the processing chamber to the vacuum chuck at the exit of the machine.
Due to this problem, the research specialist in charge of the rainbow was forced to manually
override the error as each wafer was processed. After processing in the rainbow, photoresist was
again removed with one hour in the asher.
The final mask, Figure 35, outlines the inlet and outlet holes for the channels, as well as the areas of silicon that are being removed to thermally isolate the channel. These areas were initially solid but were changed to a more standard ‘halo’ shape to achieve better results. Etching of smaller areas can result in shorter processing times and generate less heat. These areas will be etched through the entire wafer.

![Figure 35. Mask for thermal isolation and inlet/outlet hole etch.](image)

Photolithography for this step is slightly different from prior photolithography because of the amount of material that will be removed. Figure 36 diagrams this portion of the process. Though the photoresist does not etch as fast as the targeted areas, some amount of photoresist is removed during any etching process. Since the through etch will require the removal of 2000Å of
oxide followed by an etch of 625 \( \mu \text{m} \) of silicon, 1 \( \mu \text{m} \) of OCG-825 is not nearly enough photoresist. For this process, it is necessary to use a 10 \( \mu \text{m} \) coating of AZP. As with OCG-825, the wafers are first processed in the HMDS oven and then moved to the spin-coating station. AZP uses slightly different spreading and spin times, but the spin-coating process is largely the same. After spin coating wafers are pre-baked at 95°C and then moved to the EV-LC. The biggest difference in the photolithography of a thick resist coating comes in the exposure and development phase. Rather than a simple 3 second exposure, the thicker resist requires four 5 second exposures. Developing times are also much longer, taking as much as 5 minutes to remove the developed resist. Post-baked wafers are transported to the ICL for oxide etching. The protective oxide layer must first be removed by the rainbow before the STS can etch through the silicon wafer. Once again, Eric Lim patiently waited for each wafer to be processed as he needed to manually override the errors returned by the vacuum chucks. Once the oxide layer above the areas to be etched in the STS machine have been removed, the wafer must be mounted on a handle before the final etch step. Figure 36a-d shows the steps used to open inlet/outlet holes and thermally isolate the microchannel. Deep etches and etches that go through the entire wafer will release pieces of silicon and also carry the risk of shattering a wafer inside the machine. In order to protect the machine from loose pieces of silicon, wafers are mounted on pyrex, quartz, or another wafer. A quartz wafer is spun coat with a ‘bulls-eye’ pattern of AZP photoresist and the wafer to be etched is placed on top. The photoresist will act as a glue to hold the two wafers together. A 30 minute bake at 95°C helps establish the bond between the two wafers. The attached wafers can now be etched in the STS1 plasma etching machine.
Figure 36. Photolithography and etching of inlet/outlet holes and thermal isolation tabs.

The through etch uses the aggressive etch recipe mit56. Just as was done for the etching of the channels, the etch rate must first be determined with a short preliminary etch. A 25 minute etch and subsequent metrology using the Nanospec shows the etch rate to be 2.23 μm per minute. Etching through the wafer in its entirety should take just under 5 hours from start to finish. However, it was discovered that the etch rate of this particular machine was very non-uniform. As a result of the way the plasma etching machine is designed, the outer portions of the wafer etch faster than the inner portions. However, even after 5 hours of etching, not even the outer portions of the wafer had been etched completely through. From this point, the wafer was etched one hour at a time and progress was checked after each hour. Kapton tape was placed
over the outer regions of the wafer as they etched through to prevent overetching of the features. Total etching time approached nearly 12 hours, more than double the calculated time from the initial etch rate estimate. More evidence of the nonuniformity of etch rate was seen upon attempting to etch a second wafer. After 7 hours of etching the photoresist had been completely removed and large portions of the wafer had been significantly etched. Future etches must be closely watched for completion, as the etch rate calculations are not reliable.

After the through etch, the quartz wafer handle must be removed from the processed wafer before continuing. Removal of the handle is achieved by soaking overnight in acetone. Ultrasonication can help speed this process. It is important to note that the wafer is ‘red’ after the through etch step and careful consideration must be taken to only use ‘red’ labeled hardware for handling the wafer. The final processing step is anodically bonding a 0.5mm borosilicate glass wafer to the wafer to seal the channels and act as a window to view the flow. During the anodic bonding process, a large voltage is applied across the two wafers, causing sodium ions to migrate from the borosilicate glass into the silicon wafer. The charge imbalance created by the migration of ions results in a strong attractive force which holds the two wafers together.

The bonded wafer now needs to be diced apart into the individual devices. Dicing is done using the diesaw in the ICL packaging area. Before cutting the wafer into pieces, it is mounted on a piece of flexible plastic with adhesive on one side. The plastic backing prevents the pieces of the wafer from being ejected by the saw as they are freed from one another and serves to prevent the saw from contacting the metal stage upon which the wafer sits. There are two modes in which the saw operates, A-mode and G-mode. A-mode can only be used for thinner cuts and takes only one pass. G-mode is used for thicker cuts such as bonded wafers and can make up to six passes for a single cut. It is important to choose the depth of each pass carefully, as a pass
that cuts very closely to the depth of an anodic bond or other junction of surfaces can cause the two surfaces to separate. Comparative to other structures, a single wafer bonded to a borosilicate glass wafer is not particularly thick and requires only two passes to complete each cut. Once the seven devices have been cut apart, they must be removed from the plastic backing. The adhesive on the plastic backing is sensitive to ultraviolet light, and after a 1 minute exposure using the EV-LC in the TRL the diced devices peel away easily.

The last step taken in the MTL is wire bonding from the contact pads on the back of each device to carefully designed printed circuit boards. A 16 contact PCB is glued along each side of the channel on the backside of the device. Gold wire bonds are then made between each of the contacts on the PCB and the contact pads on the device. While most of the contacts accept the wire bonds readily, some of them must be cleaned with ethanol and scratched with a pair of tweezers before wire bonds will stay attached. The apparent reluctance of some of the contact pads to accept the wire bonds is likely a result of aluminum’s tendency to readily oxidize in the atmosphere. Only one wire bond was made to each resistor contact pad, but several contacts were made to each of the heater’s contact pads because of the larger current they will have to carry. Once wire bonds are established, all work in the fabrication facilities is completed.

3.4 SUMMARY

Fabrication of the microchannel device encompassed five major phases of processing: channel and reservoir etching, ion implantation, patterning of electrical connections, inlet/outlet hole and thermal isolation etches, and final production steps. Execution of the fabrication process raised several points for future improvements. During the ion implantation phase, the 250Å protective oxide coating was stripped from the wafer after ion implantation but before annealing.
of the resistors. It was later discovered that many of the implanted ions may be removed by removing this oxide layer prior to resistor annealing and passivation. In fabrication of future devices, no oxide layer should be removed until after the resistors have been annealed. Several difficulties related to the patterning of electrical connections also presented themselves. First, a hand prepared hydrofluoric acid and water mixture was used to create contact windows in the oxide layer covering the doped resistors which resulted in overetching of the oxide layer. A prepared buffered oxide etchant would have been more appropriate due to its much slower etch rate. Additionally, the contact windows to be etched into the oxide for the purpose of making electrical contact with the doped regions were identically sized to the doped regions themselves. In this case, even the slightest imperfection in alignment allows electrical connection to be made with the bare silicon surrounding the doped resistors. Oxide etch masks should be remade such that there is at least a 5 μm margin between the edge of the contact windows and the outer edge of the doped area. Patterning of aluminum heaters also resulted in unforeseen problems. When deposited aluminum is rapidly cooled, cracks can occur. Thin lines of aluminum such as those in the heater design of the microchannel device are especially susceptible to this type of damage. Cracking resulted in breaks of the majority of the patterned heaters. If patterned heaters are to be used, they must be redesigned such that their geometry resists damage. Finally, close attention must be paid to the etch step that creates the inlet and outlet holes and thermally isolate the microchannel. The particular plasma etching machine that is available for etching all the way through a wafer displays significant non-uniformity with respect to its etch rate and therefore must be monitored so as to not over-etch and damage wafers.
4. Experimental Setup and Testing

4.1 DESIGN

The experimental setup revolves around the dimensions and requirements of the fabricated microfluidic flow cell. The main components of the experimental setup are the: microfluidic flow cell, cell mount, syringe pump, temperature controlled bath, multimeter and switch, and data logging software. The most important component, the microfluidic cell, has dimensions of 15mm by 60mm.

The cell mount was designed around the microchannel dimensions.

![Clamping block with gasket (left) and mounting disk (right).](image)

Figure 37. Clamping block with gasket (left) and mounting disk (right).

The cell mount serves the dual purpose of holding the microfluidic cell in a fixed position during testing as well as allowing the device to be viewed on the inverted microscope. Though it is unlikely that the nanoparticle melting will be visible on the microscope, the ability to view the channel under magnification could prove useful for troubleshooting problems in the channel.
Potential issues include nanoparticle agglomeration and boiling or bubble formation in the carrier fluid. The cell mount, Figure 37, was machined from a 5mm thick, 108mm diameter stainless steel disk. A 55mm by 42mm rectangular hole was machined in the center of the steel disk and slots were cut for the flow cell to sit in. Special care was taken in designing the mounting device such that there would be sufficient clearance between the back side of the mount and the microscope objectives. A thin soft rubber gasket was placed underneath the glass portion of the cell to protect the cell from cracking when it is secured to the mounting disk with the clamping blocks. The clamping blocks, Figure 37, were machined from plastic and are the primary means by which fluid is delivered to the flow cell. A rubber gasket sits in a shallow machined groove in the clamping block to create a seal with the device. Four 1-72 machine screws attach the clamping blocks to threaded holes drilled in the mounting disk.

Figure 38. Top and bottom views of ProEngineer schematic of microchannel device.

Printed circuit boards were already attached to the devices at this point, but they were designed around the constraints provided by the device and the cell mount. Given the 15 thermometers and accompanying heater it was necessary to have 32 electrical contacts between the two circuit boards. Each board has 16 contacts in a span of 30.5mm as to prevent contact with the channel or
reservoirs. These contacts fan out to a width of 40.5mm to accommodate the mandatory 0.1" pin spacing dictated by the PCB fabrication process. Contacts are gold plated to ensure strong bond when wire bonded. Further wiring was then soldered to the nickel plated contact pins.

Figure 39. Top and bottom views of test assembly schematic.

Figure 40. Fabricated microchannel devices.
The wiring soldered to the nickel plated pins was routed to a solderless breadboard to make easy connections. From the solderless breadboard, connections were made to a Keithley 7000 Series switch with a 7011-S 40 channel switch. Switching between channels can be prescribed by programming directly from control panel of the switch, or remotely through a GPIB connection. The 7011-S series switch has 4 independent banks of 10 two-pole connections for a total of 40 channels. Each bank can output separately, or can be linked to a single output. To accommodate the 15 resistors, two of the 10 channel banks were linked together to a single output which is then connected to the input of a Keithley 2001 Series Multimeter. Both the switch and the multimeter are daisy-chain connected to a computer. A LabVIEW program controls both channel switching and logging of resistance measurements.

In order to ensure that target resistance changes could be measured, careful selection of a multimeter and switch combination was required. The average calculated temperature coefficient of resistance for a temperature range of 300-350K and a dopant dosage of $5 \times 10^{12}$ ions/cm$^2$ is 52.5$\Omega$/K. The total resistance of the single square resistors is calculated as 11.874k$\Omega$ at 300K. Since the desired temperature resolution is 0.1K, the multimeter must be capable of reliably measuring a 5.25$\Omega$ change in resistance with a full scale measurement of 11.874k$\Omega$. The Keithley 7 ½ digit multimeter has several different resistance ranges, each with different error tolerances. Between 300K and 350K thermometer resistance measurements are expected to fall between 11.874k$\Omega$ and 14.499k$\Omega$, placing the measurement in the 20k$\Omega$ range. The adjacent ranges are 2k$\Omega$ and 200k$\Omega$, so all measurements will fall clearly within a single range. When measuring a resistance between 2k$\Omega$ and 20k$\Omega$, the Keithley 2001 7 ½ digit multimeter, Figure
41, uses a test current of up to 89μA.

Figure 41. Keithley 2001 Series 7 1/2 Digit Multimeter.

For up to 2 years, the instrument is designed to give a reading within ±(80ppm reading + 4.5ppm range). Taking the maximum likely resistance value of 14.499kΩ and the range of 20kΩ, this yields an accuracy of ±1.25Ω. If the machine is regularly calibrated, it can be expected have an accuracy of ±0.80Ω within 1 year of calibration, and ±0.54Ω within 90 days of calibration. The maximum error that can be expected from the digital multimeter represents a temperature difference of just 0.024K, acceptably below the desired temperature resolution. The other major electrical component needed for the setup was some sort of switching device to cycle between the 15 thermometers. Other than the requisite number of connections, switching requirements are not particularly demanding. Fluid temperatures within the microchannel device and therefore
temperature measurements should read steady state during operation, meaning that switching speed is not of paramount importance. To meet switching needs, the Keithley 7001 Series switch mainframe with 7011-S switch card was selected, Figure 42.

Figure 42. Keithley 7001 Series Switch System with 7011-S switch card.

The 7011-S card can handle 40 2-pole measurements in four banks, and the 7001 switch can cycle through channels at a rate of 130/second. The maximum channel scan rate is much higher than necessary, but will be useful for any transient measurements.

Equally important as the electrical side of the setup, the fluid portion of the setup begins with a Harvard 2000 series syringe pump. The syringe pump can supply fluid at a rate anywhere between 0.0001 μL per minute to 220 mL per minute. From the syringe pump, the fluid flows through a length of tubing to the input port on the clamping block of the cell mount. A length of
the tube between the output of the syringe pump and the input of the microfluidic device is submerged in the temperature controlled bath in.

Figure 43. Lauda RE207 heated/refrigerated circulator.

The temperature controlled bath can be heated or cooled to whatever temperature is desired, and maintains temperature uniformity within the bath of 0.001K. By setting the bath to a temperature just below the melting point of the phase change material in the fluid to be tested, the fluid is ensured to enter the microfluidic device on the verge of melting, allowing the largest portion possible of the test section to be devoted to the melting regime of the nanofluid. The temperature
controlled bath is also used as a calibration device for the on chip thermometers. Figure 44 shows a rough schematic of the experimental setup.

4.2 ALTERATIONS AND CHALLENGES

As a result of certain difficulties with the microfluidic device, several changes were made to the experimental setup. The first issue that needed to be addressed was a problem with the patterned aluminum heaters. Of the first five devices that were fabricated, only one of them had a heater which yielded the intended resistance of approximately 500Ω. Two of the devices read
heater resistances of 40-50 MΩ, and two of them read resistances in the GΩ range. The most likely explanation is cracking of the aluminum due to residual thermal stresses. Thin patterned lines of aluminum can crack if they cool too fast after deposition or annealing. For future devices, thicker aluminum lines should be used to help protect against cracking of the heaters. As a substitute heat source, a solar simulator can be used. The solar simulator is capable of producing heat fluxes at intensities up to 10 times that of the sun, depending on how close to the lamp the device is placed. The solar simulator can be used to heat the device from either the front or the back, though heating from the front is advised to avoid directly heating the resistive thermometers. Another possible heating option is the use of Kapton heaters, which would also have to be affixed to the glass cover on the front of the devices. Kapton heaters are available in a variety of powers and geometries and can be purchased with adhesive backings to attach directly to the microchannel device. While both of these options could provide the necessary power to heat a phase change nanofluid, they both make observation of the microchannel device during operation with the use of the inverted microscope impossible. For this reason, it would be useful to develop a resistive heater geometry that resists cracking during the fabrication process.

A second issue which requires investigation is drift of the doped resistor measurements. Since each resistor on each device is likely to react slightly differently to changes in temperature, it was necessary to calibrate the thermometers prior to experimentation. In order to calibrate the thermometers, the device was wired to the switch and multimeter system, placed in a watertight plastic bag, and submerged in the temperature controlled bath. By monitoring resistance readings as the temperature of the bath is adjusted, it should have been possible to create a temperature-resistance curve for each of the thermometers. Using these curves, resistance measurements during experiments can be translated to accurate temperature profiles for evaluating the thermo
physical and heat transfer characteristics of the experimental fluid. However, calibration attempts
of the microfluidic devices revealed substantial drift in the resistance measurements. Placed in
the bath at 25°C, a slow fluctuation of roughly 0.5 kΩ was observed.

![Graph showing resistance drift with constant temperature of 25°C.](image)

**Figure 45. Resistance drift with constant temperature of 25°C.**

The fluctuation was slow and steady, progressing in one direction or the other at a rate of several
Ω per second, which made the possibility of a poor electrical connection unlikely. A poor
electrical connection would likely result in a jumpy measurement, quickly changing between the
true resistance value and a very large or overflow value. No discernable pattern or identifiable
frequency of the oscillation could be determined. Raising the temperature of the bath did
increase the resistance measurements as expected, but it was not possible to reliably determine
the temperature coefficient of resistance due to the fluctuation in the measurements. However, it
was possible to take time averaged resistance measurements with a known bath temperature to
obtain an approximate measure of the temperature response of the doped resistors. The temperature of the bath was increased in increments of 5°C from 25°C to 70°C. At each temperature resistance readings were recorded every minute for an hour and averaged. By recording resistances for a period of one hour, it was possible to average the result of several up and down resistance fluctuations. The averaged results in Figure 46 show an average temperature coefficient of resistance of 88.9Ω/K.

![Graph showing resistance vs. temperature](image)

**Figure 46. Time averaged resistance measurements with increasing temperature.**

Based on the approximated temperature coefficient of resistance of 88.9Ω/K, a 0.5kΩ variation represents greater than a 5K temperature difference, more than times greater than the degree of accuracy required for experimentation. It is interesting to note that the approximate temperature coefficient of 88.9Ω/K is much greater than the expected temperature coefficient of resistance, 52.5Ω. However, stripping of the 250Å protective oxide layer may have removed some of the
implanted ions before they could diffuse into the silicon and lowered the effective ion implantation dosage. The ion implantation dosage that would result in a resistance of 13.44 kΩ at 25°C would result in a temperature coefficient of resistance of 61.7Ω/K, as calculated by the MATLAB code. This is still lower than the approximated temperature coefficient of resistance, suggesting that the MATLAB calculations may under predict temperature coefficient of resistance.

A first thought regarding the source of the resistance change was ohmic heating resulting from continued application of the multimeter test current. A resistance reading was taken quickly and the circuit was then opened to allow any heat generated in the resistor to dissipate. Repeated trials of this nature unfortunately did not yield consistent resistance readings. Another possibility investigated was interference due to the large number of closely positioned wires. A 1kΩ resistor was added to the test assembly and tested alongside the doped resistors on the device, but no fluctuation of resistance was observed. The variation in measured resistance may be a result of the low doping concentration or a misalignment of the mask used to etch contact windows in the oxide layer covering the resistors. However, neither of these can be easily tested without further iterations of fabrication.
5. Conclusions and Future Work

Our preliminary estimates suggest that phase change nanofluids are promising for application to parabolic trough solar thermal power generation. However, through the work in this thesis, we found that there are many challenges that need to be solved in the fabrication and testing to further this research. Fabrication of nanofluids of any sort is still a process that is best suited for small batches, and the introduction of phase change nanoparticles only serves to complicate the process. In order for phase change nanofluids to become practical for a large scale application, mass production techniques need to be developed. Stability of nanofluids also remains a challenge. Phase change nanofluids with sufficient stability to be used in laboratory testing after their fabrication were developed with the aid of surfactants, but even these would eventually separated if given sufficient time. In addition, no surfactants that are viable at the temperatures required by solar thermal power generation systems are commercially available. Also, surfactants were minimally helpful in mitigating agglomeration of phase change materials upon multiple freeze/thaw cycles. For phase change nanofluids to be practical in any situation, long term stability and agglomeration prevention are a must. Additional investigation into methods and mechanisms for nanofluid and nanoemulsion stability could prove to be very valuable.

The final microfluidic flow cell revealed several shortcomings in the initial design and fabrication process that, if addressed, could result in a much more successful test platform. In order of the fabrication process, the first mistake made was stripping the protective 250Å oxide layer prior to annealing of the doped resistors. The 250Å oxide layer protects the silicon from being damaged by the bombardment of ions during the doping process, but it also prevents some
of the ions from penetrating into the silicon. By stripping the oxide prior to annealing, these embedded ions are prevented from diffusing into the silicon, reducing the intended ion concentration. Another alteration that could improve the quality of the resistors is a redesign of the mask that opens windows in the grown oxide layer so that electrical contact can be made with the thermometers. The doped regions were 150 μm by 450 μm, and the contact windows were a pair of 150 μm squares separated by a distance of 150 μm. Figure 47 shows the current and proposed geometries for the doped resistors and the oxide etch for contact windows.

![Figure 47. Current (top) and proposed (bottom) resistor and oxide etch geometry.](image)

Choosing contact windows that swept out an area identical to that of the resistors ensured that any error in alignment, no matter how small, would result in electrical contact between the deposited aluminum and the bare silicon. Future revisions of the design should place the edges of the contact windows no closer than 5 μm to the edges of the doped regions to provide a buffer zone protecting against imperfect alignments. The aluminum heaters patterned on the backside of the microfluidic cell also proved to be problematic, as many of the aluminum heaters were not functional. Wider aluminum heater lines might prevent breakage of the heaters during the
fabrication process. A test of several different aluminum heater designs should be conducted to determine the best geometry to reduce or eliminate the likelihood of thermal cracking and still provide the necessary heat input.

The most important problem presented by the microfluidic device was the unexplained drifting of thermometer resistance. Future investigation must resolve the drifting problem for the microfluidic cell to be a viable test platform. Without the capability to confidently and accurately measure temperature, it is impossible to determine the properties of a phase change nanofluid. By redesigning the mask for the etching of contact windows to the bare silicon to prevent contact between the aluminum electrical contacts and the non-doped regions of the wafer, the possible sources for resistor error are reduced. The current low dopant dosage used is another potential source of resistor error, and higher dopant dosages could potentially create more stable resistors. However, increasing the dopant concentration would also result in a lower temperature coefficient of resistance. In order to determine the best balance of doping level and temperature coefficient of resistance, several wafers must be doped at different dosages and tested for resistor stability. If higher dopant dosages result in sufficiently stable resistances to reliably measure the needed 0.1K temperatures differences, the lowest such dopant dosage that results in stable resists should be selected. Once stable resistors can be fabricated, devices can be calibrated and used as described previously. Failure of ion implantation dosage alternation to produce stable resistors would necessitate investigation into other possible reasons for the yet unexplained fluctuations in resistance. Lacking a final resolution to the drifting resistor problem would require exploration into other avenues for the measurement of temperature for testing of the phase change nanofluids.
# 6. Appendices

## 6.1 Process Flow

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Machine Name</th>
<th>Lab</th>
<th>Wafer</th>
<th>Au</th>
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<td>STS2</td>
<td>TRL</td>
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<td>Green</td>
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<td>Step</td>
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<td>Condition</td>
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<td>b. Pirahna (10 min)</td>
<td>a. Acid Hood</td>
<td>b. Acid Hood</td>
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<td>b. RCA Station</td>
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<td>12.</td>
<td>Oxidation</td>
<td>Wet 950 C 1hr (~2500A), Annealing and passivation of resistors</td>
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<td>Coater</td>
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<td></td>
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<td>UV exposure: EV1</td>
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<td>Develop:</td>
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<td>Silicon to glass slide, 1200V 250C</td>
<td>Evalig/Bond</td>
<td>TRL</td>
<td>Silicon</td>
</tr>
</tbody>
</table>
6.2 MATLAB CODE

6.2.1 Coeff_ressq.m

Coeff_ressq.m calculates temperature coefficient of resistance per square based for an input dose and temperature range.

```matlab
function coeff_ressq=tempcoeff_res(dose,temp)
    coeff_ressq=zeros(length(dose),3);
    for k=1:length(dose)
        ressquare=resistivity(dose(k),temp);
        coeff_ressq(k,1)=(ressquare(1)-ressquare(l))/(temp(1)-temp(l));
        coeff_ressq(k,2)=ressquare(1);
        coeff_ressq(k,3)=ressquare(l);
    end
```

6.2.2 Resistivity.m

Resistivity.m calculates the resistance per square of a doped region based on an input dose and temperature.

```matlab
function ressquare=resistivity(dose,temp)
    con=10.^con_dose(log10(dose));
    depth=10.^depth_con(log10(con));
    [matres,mu]=resistivityboron2(temp,con);
    tsures=10.^tu_mat(log10(matres.*100));
    ressquare=tsures./((depth.*100));
```

6.2.3 Con_dose.m

Con_dose.m calculates the base 10 logarithm of ion concentration as a function of the base 10 logarithm of the implant dosage. The log-log fit used to define this relationship is based on tsuprem4 simulations run using the recipe described in the process flow.

```matlab
function con=con_dose(dose)
%must input log10(dose), function will return log10(concentration)
p1 = -0.0724;
p2 = 2.831;
```
p3 = -6.907;
con=p1.*dose.^2 + p2.*dose + p3;

6.2.4 Depth_con.m

The depth of the junction is determined by relating the base 10 logarithms of depth and concentration arrived at by using the tsuprem4 simulation software.

function depth=depth_con(con)
depth=0.02334.*con.^2+-.6862.*con+1.652;

6.2.5 Resistivity_boron2.m

Resistivity_boron2.m calculates resistivity for an input temperature range and implant ion concentration based on the method described in Reggiani et al.

function [rescalc,mub] = resistivity_boron2(temp, ncon)

% check !

Eg=1.170-(4.730e-4.*temp.^2)/(temp+636); % check !!!!

ni=(2.4e31.*temp.^3.*exp(-1.*Eg./8.617e-5./temp)).^.5; % check !!!!

p=(ncon./2)+((ncon./2).^2+ni.^2).^5; % check !!!!

n=ni.*ni./p;

ND=n;
NA=p;

mu0=(mu0d.*ND+mu0a.*NA)./(ND+NA);
mul=(mu1d.*ND+mu1a.*NA)./(ND+NA);
\[
\mu_L = \mu_{\text{max}} \cdot \left(1 - \gamma \right) \\
\text{second} = \frac{\mu_{L} - \mu_0}{1 + \frac{\text{ND}}{\text{Cr1}} \cdot \alpha_1 + \frac{\text{NA}}{\text{Cr2}} \cdot \alpha_2} \\
\text{third} = \frac{\mu_{L}}{1 + \left(\frac{\text{ND}}{\text{Cs1} + \text{NA}}\right) \cdot \frac{\mu_{L}}{p}} \\
\mu_b = \frac{\mu_0 + \text{second} - \text{third}}{1 + \left(\frac{\text{ND}}{\text{Cs1} + \text{NA}}\right) \cdot \frac{\mu_{L}}{p}}
\]

**6.2.6 Tsu_mat.m**

Tsu_mat.m relates the base 10 logarithms of the MATLAB calculated resistivity values to those determined by a tsuprem4 simulation.

```matlab
function tsu = tsu_mat(mat)
    tsu = 1.062 * mat + .596;
```

**6.2.7 Cp1kg2.m**

Cp1kg2.m calculates the effective specific heat capacity and energy storage density of a phase change nanofluid for a given temperature range and prescribed PCM thermophysical properties with VP1 as the carrier fluid.

```matlab
function hpm3 = cp1kg2(cpdiscrete,Tlow,Thigh,latentheat,rhodiscrete)

%cpdiscrete is cp of discrete phase
%Tlow is low temp of cycle
%Thigh is high temp of cycle
%latent heat is latent heat of discrete phase (0 if no phase change)
%rhodiscrete is density of discrete phase

% sets up mf (mass fraction) and determines overall cp of mixture for a
% range of mass fractions and temperatures

mf = linspace(0,1);
cplkm = cpdiscrete.*ones(100,1).*mf + (cpvpl(linspace(Tlow,Thigh))).*(1-mf);

% size(cp1km)
%cp1km(1:10)

cplk = ones(100,1);
for k=1:100
    cplk(k) = trap(linspace(Tlow,Thigh),cplkm(:,k)) + mf(k) * latentheat;
end
```
%cplk

rhoThigh=ones(100,1);
for k=1:100
    rhoThigh(k) = 1/(mf(k)/rhodiscrete+(1-mf(k))/rhovpl(390));
end

hpm3=rhoThigh.*cplk;
phi=(mf./rhodiscrete)./(mf./rhodiscrete+(1-mf)./rhovpl(Tlow));
hpm3inc=hpm3./hpm3(1);
[AX,H1,H2]=plotyy(phi(1:20),hpm3(1:20),phi(1:20),cplk(1:20)./100);
set(get(AX(1), 'Ylabel'), 'String', 'Energy Stored per Cubic Meter C (kJ/m3)')
set(get(AX(2), 'Ylabel'), 'String', 'Effective Heat Capacity cp (kJ/kg*K)')
title('Thermophysical Properties of VP1 Mixture, 293-393C')
xlabel('Volume Fraction')
hold on
%plot(mf,hpm3(1)*1.1.*ones(100,1),mf,hpm3(1)*1.25.*ones(100,1),mf,hpm3(1)*1.5 .*ones(100,1))
figure(2)
plot(phi(1:50),hpm3inc(1:50))
xlabel('Volume Fraction')
ylabel('Increase in Energy Storage Density')
title('Increase in Energy Storage Density with Increasing Volume Fraction')
figure(3)
plot(phi(1:20),hpm3inc(1:20))
xlabel('Volume Fraction')
ylabel('Increase in Energy Storage Density')
title('Increase in Energy Storage Density with Increasing Volume Fraction')

figure(4)
plot(phi(1:20),cplk(1:20)./(Thigh-Tlow))
title('Effective Average Specific Heat')
xlabel('Volume Fraction')
ylabel('Specific Heat Capacity (kJ/kg*K)')

6.3 TSUPREM4 CODE

$ TSUPREM4 V 6.5.2 (on Solaris - thera, mtl-apps & cad)
$ Try out Hang's devices implanted in UTMARLOWE
$* Standard Settings

$Colors: 1=white, 2=red, 3=olive green, 4=blue, 5=light blue, 6=light purple

$* Setup

MESH DYSURF=0.001 DYL.SURF=0.06 DYL.ACTIVE=0.15 DYL.ACTIVE=0.01 + 
LY.BOT=10  DYL.BOT=10

INITIALIZE <100> Phosphor=1.0E15
$ INITIALIZE IN.FILE=post_annel

DEPOSIT OXIDE THICKNESS=0.0007

OPTION DEVICE=X

SELECT Z=LOG10(Boron)
PLOT.1D X.VAL=.1 line.typ=1 color=2  y.min=13 + 
y.max=22 left=-3.5 right=3

LABEL x=0.4 y=14 LABEL ="Initial" line=1

DEPOSIT oxide THICKNESS=0.025
IMPLANT  Boron DOSE = 5e12 ENERGY = 40 tilt=7

DIFFUSION TEMPERATURE=950 TIME = 60 wet

SELECT Z=LOG10(Boron)
PLOT.1D X.VAL=.1 line.typ=2 color=2 +
y.min=13 y.max=22 left=-3.5 right=3 +
^Clear ^axes symbol=1
LABEL x=0.4 y=13.5 LABEL ="Annealed" line=2

SELECT Z=LOG10(Phosphorus)
PLOT.1D X.VAL=.1 line.typ=2 color=4 +
y.min=13 y.max=22 left=-3.5 right=3 +
^Clear ^axes symbol=1

$SAVEFILE OUT.FILE=post_anneal

SELECT Z=DOPING
EXTRACT OUT.FILE=profile
FOREACH DEPTH (0 TO 2 STEP 0.01)
EXTRACT SILICON X=0.0 DISTANCE=@{DEPTH} Y.EXT VAL.EXT
EXTRACT WRITE
END
$EXTRACT CLOSE

SELECT Z=DOPING
EXTRACT SILICON X=0.0 VALUE=0.0 D.EXTRAC PREFIX="JUNCTION DEPTH=" SUFFIX=" um"
EXTRACT WRITE
EXTRACT CLOSE
SELECT Z=1.0
PRINT. 1D LAYERS X.V=0
SELECT Z=Boron
PRINT. 1D LAYERS X.V=0
SELECT Z=1.0
PRINT. 1D LAYERS X.V=0
SELECT Z=Phosphor
PRINT. 1D LAYERS X.V=0
ELECTRIC X=0.0 RESIST V="-2 " PLOT.REG=1 BIAS.REG=1

SELECT Z=DOPING
EXTRACT SILICON X=0.0 VALUE=0.0 D.EXTRAC PREFIX="JUNCTION DEPTH=" SUFFIX=" microns"
EXTRACT PRINT
SELECT Z=Boron
EXTRACT SILICON X=0.0 DISTANCE=0.0 VAL.EXTR PREFIX="SURFACE CONCENTRATION=" + SUFFIX=" /cm3"
EXTRACT PRINT
7. Bibliography


