Thermal Characterization of Liquid Samples with Three-Dimensional On-Chip Micro Calorimeter

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THERMAL CHARACTERIZATION OF LIQUID SAMPLES WITH THREE-DIMENSIONAL ON-CHIP MICRO CALORIMETER

by

Hye Jeong Bak, B.S.

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ABSTRACT
THERMAL CHARACTERIZATION OF LIQUID SAMPLES WITH THREE-DIMENSIONAL ON-CHIP MICRO CALORIMETER

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Marquette University, 2014

This thesis presents a three dimensional on-chip microfabricated calorimeter (μ-calorimeter) to extract thermal diffusivity and specific heat capacity of liquid samples. These thermal properties are used to understand thermal reaction behavior, obtain information of stability for reactant molecules, and characterize a material. Thermally characterized solvents can be utilized to investigate a solute.

The μ-calorimeter introduced in this work has 3D wafer-scale structure. The μ-calorimeter consists of a reaction chamber, a nickel heater, and a resistance temperature detector (RTD) sensor. The reaction chamber enables analysis of 200 nl liquid samples. Also, its enclosed structure prevents liquid sample evaporation during an experiment. The heater and the sensor are integrated on the top and bottom sides of the reaction chamber. The heat flux travels directly through a liquid sample from the heater to the sensor with this configuration.

The heat penetration time measurement and thermal wave analysis (TWA) are used to measure thermal diffusivity and specific heat respectively. The heat penetration time measurement is the method that measures the heat penetration time through the liquid sample. Depending on the thermal diffusivity of the liquid sample and the heat flux distance, the heat penetration time alters. Since the geometry of the chamber is known, measuring heat penetration time allows detection of the thermal diffusivity of the liquid sample. The TWA is an AC calorimetry method. When an AC voltage of angular frequency, \( \omega \), is given to the heater, heat is generated by Joule heating at \( 2\omega \) frequency. The heat capacitance of the sample can be extracted by measuring this \( 2\omega \) component from the heater.

Based on the experimental work of μ-calorimeter, a new measurement system for thermal analysis is introduced. The new system is available to minimize the distance between heater and sensor and facilitate user friendly operation.
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1 INTRODUCTION

1.1 Objective of Research

The goal of this thesis is to extract the thermal properties specific heat and thermal diffusivity from liquid samples by using an on-chip micro-fabricated calorimeter (μ-calorimeter). The thermal properties are used to characterize a material, understand thermal reaction behavior, and obtain stability information for reactant molecules. In biochemical science, endothermic or exothermic heat is generated during the biological processes due to internal chemical reactions such as interactions, biological molecular reactions, and structural transitions. Knowing characteristics of heat capacity can allow us to measure complicated biological systems [1].

Calorimetry is the dominant method for observing phase changes, chemical reactions, and heat capacity in thermal analysis. It is capable of conducting the thermal analysis for wide range of temperature accurately and observing different state samples like gases, liquids, and solids [2]. Calorimeters, which are apparatuses for conducting calorimetry, have been developed in various designs to test different types of samples.

A calorimeter measures the amount of heat change caused by physical (phase transition) or chemical (enthalpy) reactions. The temperature change induced by the heat change corresponds with enthalpy in chemical reactions. Phase transition is detected when the phase or state of matter changes due to heat transfer. Thermodynamic information such as specific heat, melting point, free energy, and glass transition can be
experimentally extracted using functional relationships between temperature and enthalpy [1][3].

The following chapter provides an overview of calorimetry and categorizes various types of calorimeters according to their operation methods, construction principle, and experimental methods. The problems of conventional calorimeters and the advantages of on-chip μ-calorimeter will be discussed.

1.2 Calorimetry

Calorimeters have been used for more than 200 years since being invented by Antoine Lavoisier in 1783 [2][4]. Since then, numerous types of calorimeters have been produced and refined. In biochemistry, almost all biological and chemical phenomena, such as DNA denaturation, binding reaction, and catalyzed reaction, involve an exchange of heat. This motivated the improvement of calorimeter designs for the biological field. Observing biological interactions is challenging due to the lack of the biosample amount and the minute quantity of released or absorbed heat. These limiting conditions require increasing the sensitivity of the device and reducing the sample consumption.

As microfabrication and nanofabrication techniques have been developed, these techniques have been widely used to minimize the size of the calorimetric sensor. Microfabricated calorimeters can detect less than a microjoule of thermal energy. Furthermore, micro-fabricated devices have achieved high sensitivity, low power consumption, portability, parallel operation, and small characteristic dimensions [5]. Also, highly
developed silicon processing techniques and the minimized size of the device have allowed for mass production and reduced manufacturing costs.

μ-fabricated calorimeters have been developed in many different designs to be applied in diverse field of study such as thermochemistry, biomedical research, energy physics, and the pharmaceutical industry [5][6][7][8]. Because of the abundance of the calorimeter designs it is very difficult to classify them. In 1984, Hemminger and Höhne suggested classification methods using calorimeters’ modes of operation, construction principle, and experimental methods [5][2][9].

1.2.1 Modes of Operation

The modes of operation of conventional calorimeters are differentiated by surroundings. Therefore, it is necessary to know the distinction between surroundings and the measuring system in calorimetry. The measuring system is enveloped by the surroundings. The surroundings have to be perfectly sealed off from the outer world to prevent disturbances and measurement errors. The measuring system includes the boundary which is affected by the sample reaction. Let the temperature of the measuring system be $T_M$. $T_S$ is the temperature of the surroundings.

In isothermal operation, the calorimetric system and the surroundings have the same constant temperature ($T_M = T_S = \text{constant}$). The isothermal state used in the system has an infinitesimally small thermal resistance with the surroundings and infinite heat capacity. In practice, the term isothermal is not feasible in calorimetry. Without any temperature changes, heat transport from the sample to the surrounding is impossible [9].
Isoperibol operation describes when the calorimeter is used in the condition that the temperature of the surroundings is constant, but the temperature of the calorimetric system is variable \( (T_M \neq \text{constant}, T_S = \text{constant}) \). The designation of the isoperibol operation introduced by Kubaschewski and Hultgren refers to uniform surroundings [9]. In isoperibol operation, the heat exchange depends on the temperature of the surroundings and measuring system. Used thermal resistance is defined by the temperature of the measuring system due to the constant temperature of the surroundings. To maintain the temperature of the surroundings, a temperature controller may be required.

Adiabatic operation is another mode of operation, in which heat exchange does not occur between the measuring system and the surroundings. Consequently, the temperature of the surroundings and the temperature of the measuring system are independent. This operation requires three conditions: the rapid reaction of the sample, the separation of the measuring system and the surroundings, and the identical temperatures of the measuring system and the surroundings \( (T_M(t) = T_S(t)) \) [9]. The rapid reaction reduces the quantity of heat that can leave or enter the system during measurement. Also, by using a thermal insulator between the measuring system and the surroundings, heat loss can be reduced. Although the adiabatic operation is the most ideal method in calorimetric investigation, perfect adiabatic operation is impossible in practice due to the lack of infinite thermal resistance. Therefore, instead of adiabatic operation, quasi-adiabatic operation is more widely used in practical experiments [2].

In scanning operations, the temperature of the surroundings or the measuring system is linearly changed. Scanning operations can be subdivided into scanning of
surroundings, adiabatic scanning, and isoperibol scanning. In the scanning of surroundings operation, heat is applied to the surroundings. The temperature of the measuring system is changed according to the equation.

\[ T_S = T_S(t) = T_{S_0} + \alpha t \]  

(1.1)

\( T_{S_0} \) is the initial temperature of the surroundings, \( \alpha \) is the heating rate, and \( t \) is time. The temperature of the measuring system depends on the temperature of the surroundings. In the adiabatic scanning operation, \( T_M(t) \) is equal to the \( T_S(t) \). The isoperibol scanning operation has the condition that \( T_M = T_M(t) \) and \( T_F \) is a constant [9].

The isothermal, isoperibol, and adiabatic operations are static operations. Scanning operations are classified as dynamic operations. All of these operation modes of calorimeters are based on an ideal state. In practice, it is impossible to satisfy the ideal condition. Therefore, we use the terms quasi-isothermal and quasi-adiabatic which are suitable with the result of real measurement [9].

1.2.2 Construction Principle

Calorimeters can be categorized as single calorimeters and twin calorimeters. Although the single calorimeter has been widely used due to its relatively simple fabrication process, the single calorimeter has a drawback. The single calorimeter, which contains a single reaction chamber, cannot detect the errors generated by the environment. In contrast with the single calorimeter, twin calorimeters can operate on a differential measurement system. This system uses two identical temperature sensors. One of the sensors is used as a reference and the other sensor is used for the sample measurement.
Therefore, the experiment can cancel out the errors due to the environment. Using this technique, we can detect the internal and external noise and transient fluctuations [2].

1.2.3 Experimental Methods

Dynamic experimental methods may be divided into several classes such as differential scanning calorimetry, adiabatic twin differential scanning calorimetry, heat pulse calorimetry, and AC calorimetry [10][11].

Differential scanning calorimeter (DSC) is the measurement method that uses a reference. The heat capacity of a reference sample should be well-defined over the wide range of temperature to be applied. When a sample and a reference are heated at the same rate, the required powers are proportional to their respective heat capacities. The thermal capacity of the sample is determined from the consumed power and sensitivity calibration. DSC is modulated in order to be combined with other measurement methods so that noise generated from environment can be eliminated.

The adiabatic twin differential scanning calorimeter is a more sensitive version of DSC. This method is conducted with DSC under adiabatic condition. This system consists of an adiabatic shield with two identical cells. One cell is for the sample solution and another cell is used for the reference solution. The temperature given to each cell must be identical. This method is mostly used for determining the heat capacity of biomolecules, since it has very high sensitivity. However, it has the same limitation that the adiabatic operation has, as introduced in section 1.2.1. Since only the adiabatic
condition can be analyzed theoretically, a quasi-adiabatic condition is applied to conduct the experiments.

In heat pulse calorimetry, current is applied for a few micro seconds to an electrical conductor, generating heat by Joule heating. This heat is conducted to the sample material. The time of flight from the conductor to the sample can be measured during the heat transfer [2]. The thermal properties of the sample can be extracted from the data. Using this method, the heating time and measuring times can be reduced. Heat losses are minimized due to short measuring time. However, the short measurement time is inappropriate for samples which require large equilibration times.

AC calorimetry, introduced by Sulliivan and Seidel in 1968, is the most popular technique for measuring the thermal or physical properties of substances with high sensitivity. The basic principle of AC calorimetry is that an oscillating heat is applied to the sample. The temperature fluctuates in proportion to the supplied heat. Using the amplitude or the phase lag of this temperature, accurate thermal information of the sample can be extracted [12]. The amplitude of the temperature is inversely proportional to the specific heat of the sample. AC calorimetry can measure the thermal properties in low temperature change. One of the advantages of AC calorimetry is that it allows us to use the signal average technique. In micro/nano calorimetry, it is important to detect minute temperature changes while also considering noise. The signal average technique improves signal to noise ratio. Thus, it enhances not only sensitivity but also accuracy of the device performance.
1.3 On-chip Micro-fabricated Calorimeter

The configuration of the calorimeter has been improved by many researchers. Calorimeters are subdivided by into two categories depending on the designs of their reaction chambers. Reaction chambers can have either an open chamber structure by using a membrane, or the closed chamber structure with microfluidic channels. Both have advantages and disadvantages.

Zhuravlev et al introduced a calorimeter which contains an open reaction chamber [14]. Although the open chamber structure has relatively simple fabrication steps and convenience of placing a sample, it has crucial drawbacks. For example, placing samples is inaccurate since it requires the direct spotting method. Furthermore, evaporation of the sample hampers an accurate measurement.

In contrast, Lee et al developed a calorimeter with a closed reaction chamber using a glass cover. The heater and the thermopile are placed side by side [4]. This structure prevents evaporation of the sample. However, the large thermal mass of bulky encapsulating materials can reduce the sensitivity of the device. In general, the closed chamber design has a thermal insulation issue, since closed chamber calorimeters require additional material for sealing and integrated microfluidic channels. Typical microfluidic channels are generated by either polydimethylsiloxane (PDMS) or Si/SiO₂ etching. These calorimeters have a large heat capacity, thus reducing the sensitivity of the device due to absorbing heat from the sample. In addition, the parallel location of the heater and the sensor limits available thermal analysis methods due to fringing effects of heat flux.
Aiming to overcome these drawbacks, our μ-calorimeter is constructed with a suspended three-dimensional (3D) closed reaction chamber. The sealed reaction chamber prevents liquid sample vaporization and facilitates accurate experiments. The reaction chamber consists of thin, low stress Si$_x$N$_y$ film and polyamide thin film to reduce the thermal mass of the system. This minimized system thermal mass increases sensitivity of the device. Also, the reaction chamber is fully suspended from the other components of the device fully preventing an unexpected thermal link to handle wafer substrate.

The sensor and the heater are integrated on both sides of the chamber and one device includes two identical chambers. These features allow us to operate thermal wave analysis, time delay method, 3ω method, and differential scanning calorimetry [15].

1.4 Thesis Outline

In this thesis, a μ-fabricated calorimeter with a suspended thin film reaction chamber is applied to measure the thermal properties of liquid samples. Chapter 1 introduces the background concepts of calorimetry and heat transport phenomena. Chapter 2 details the unique three-dimensional design of the calorimeter. Chapter 3 describes the fabrication of the micro machined calorimeter. Chapter 4 discusses the process of device characterization such as calibrating the sensor and the heater as well as the AC and DC characterization of the calorimeter. In Chapter 5, the details of experimental methods and the thermal properties (specific heat, thermal conductivity, and thermal diffusivity) of liquid samples are presented. Finally, Chapter 6 summarizes the work and provides suggestions for future work.
2 MICRO-FABRICATED CALORIMETER DESIGN

This chapter elaborates on the background of heat transfer phenomena in micro-fabricated devices and the design of the μ-calorimeter. As mentioned in Chapters 1.2 and 1.3, various designs for calorimeters exist [2][9]. Therefore, it is essential to understand heat transfer phenomena and consider several factors such as the thermal properties of the materials, characteristics of the samples, and surrounding environment of the measurement system for either operation or design of the μ-calorimeter.

Conventional calorimeters have either open reaction chambers or closed reaction chambers and struggle with the evaporation of volatile liquid samples and large thermal mass respectively. The μ-calorimeter presented in this work consists of suspended 3-dimensional closed reaction chambers with an integrated heater and temperature sensor. The closed reaction chamber is constructed with a low stress silicon nitride film to minimize thermal mass. The heater and sensor are integrated on opposite sides of the reaction chamber. This configuration allows the device to perform various calorimetric measurements such as thermal wave analysis (TWA), differential scanning calorimetry (DSC), and 3-Ω technique [14][15]. Also, each die includes two reaction chambers which can be used for a differential calorimetric measurement.

2.2 Heat transfer phenomena

This section explains theoretical background of three critical heat transfer phenomena: convection, conduction, and radiation. Heat conduction occurs through the
transport of vibrational states. It does not include attendant transport of mass either by
diffusion or flow. Therefore, ideal heat conduction only occurs in solid materials. Heat
flow is generated by a temperature gradient. Consequently, the heat exchange due to heat
conduction cannot occur under isothermal conditions.

Heat exchange by convection is heat transport by flow in liquids and gases. The
flowing material absorbs heat at a higher temperature location and transfers it at a lower
temperature location. Convection can be classified into two categories. First, free
convection is the flow which is produced by a temperature field itself and generates
density differences. Second, forced convection is, as indicated in its name, a heat flow
which takes place due to stirring or pumping. This forced convection is mainly used for
heat transport in calorimeters.

All materials, including the substance in thermodynamic equilibrium, constantly
emit electromagnetic radiation. Heat radiation is electromagnetic radiation produced by
the thermal motion of particles. Heat radiation depends on the absolute temperature of the
body and of the surface structure. When a body absorbs heat radiation from other bodies,
the body emits radiation heat, having a zero energy balance. Heat transfer is heat
exchange at the boundary between two connected solid materials of different
temperatures. Therefore the heat flux in heat transfer can be defined by equation 2.4.

\[ \frac{dQ}{A} = w(T_2 - T_1) \]  \hspace{1cm} (2.4)

where \( w \) is the surface coefficient of heat transfer, \( dQ \) is the heat transfer rate, \( A \) is the
material of area, \( T_2 - T_1 \) is the temperature gradient. Therefore, the heat exchange between
the system and the sample can differ depending on the sample container.
In calorimetry, the heat transport phenomena entails heat losses due to heat leaks. Heat leaks describe when heat is transferred to the surroundings that cannot be detected by the measuring sensor. The adiabatic calorimeter and the differential scanning calorimeter may be used to reduce the errors from heat losses [9].

2.2.1 Conduction

Figure 2.3.1.1-1. One-dimensional conduction through a plane wall [2].

When a temperature gradient exists in a medium, heat always flows from the higher temperature area to the lower temperature area to generate heat flux. Based on this heat flow characteristic, the phenomenological law of heat conduction was proposed by Joseph Fourier, known as Fourier’s law of heat conduction. Figure 2.3.1.1-1 shows the one-dimensional heat flow across the wall to define this law. A is the surface area and L
is the thickness of the wall. When \( x = 0 \), temperature is defined as \( T_1 \) and temperature \( T_2 \) is at \( x = L \).

Fourier’s law of heat conduction in a homogeneous material describes how heat transferred by conduction is proportional to the negative of the temperature gradient \( \frac{dT}{dx} \) multiplied by the area.

\[
\dot{Q} \propto -A \cdot \frac{dT}{dx} \tag{2.5}
\]

\[
q = \frac{\dot{Q}}{A} \propto -\frac{dT}{dx} \tag{2.6}
\]

where \( \dot{Q} \) is heat flow or the heat transfer rate, \( q \) is heat flux or heat flow per unit area which is perpendicular to the flow direction (W/m\(^2\)), \( T \) is the local temperature (K or °C), and \( x \) is the coordinate in the flow direction (m). The SI unit of thermal conductivity is watts per meter Kelvin (W/mK). Thermal conductivity is the quantity of heat transmitted.

In steady state conditions, heat flows straightly through an isotropic medium.

Using a constant of proportionality \( k \), the equation 2.5 and 2.6 are redefined as equations 2.7 and 2.8.

\[
\dot{Q} = -kA \frac{dT}{dx} \tag{2.7}
\]

\[
q = \frac{\dot{Q}}{A} = -k \frac{dT}{dx} \tag{2.8}
\]

\[
\int_{x=0}^{x=L} \frac{\dot{Q}}{A} \, dx = -\int_{T_1}^{T_2} k \, dT \tag{2.9}
\]

\[
\frac{\dot{Q}}{A} L = -k(T_1 - T_2) \tag{2.10}
\]

\[
\dot{Q} = \frac{kA}{L} (T_1 - T_2) = \frac{(T_1 - T_2)}{L/kA} \tag{2.11}
\]

where \( k \) is thermal conductivity of the substance (W/m-K) and \( A \) is the area of the material. Fourier’s equation is defined in the one-dimensional case when thermal
conductivity has a constant value. The thermal conductivity is dependent upon the microscopic structure of the substance.

The equation 2.11 can be described by Ohm’s law to define a thermal resistance. The temperature difference, $\Delta T$, is analogous to the voltage change. The heat flow $\dot{Q}$ is similar with current flow in electrical domain. The thermal resistance, $R$, is proportional to $L/kA$ which can be compared to electric resistance. Therefore, equation 2.11 can be rewritten as equation 2.12

$$\dot{Q} = \frac{\Delta T}{R}, \quad R = \frac{L}{kA}$$  \hspace{1cm} (2.12)

Figure 2.3.1-2. Thermal resistance in thermal circuit [2].

2.2.2 Convection

Convection occurs when heat transfer from a surface to a moving fluid. When the fluid receives heat energy, its molecules starts to scatter and separate from each other, which reduces the density of the fluid. Due to buoyancy forces, the hotter fluid transfers to the cooler, less dense fluid. The heat transfer rate by convection between the surface and the fluid can be described by Newton’s law of cooling.

$$\dot{Q} = h_c A (T_{\text{sur}} - T_{\text{env}}) = h_c A \Delta T_{(t)}$$  \hspace{1cm} (2.13)

$$\dot{q} = h_c (T_{\text{sur}} - T_{\text{env}})$$  \hspace{1cm} (2.14)

$$R_c = \frac{1}{h_c A}$$  \hspace{1cm} (2.15)
where $h_c$ is the convection heat transfer coefficient (W/m$^2$K), $A$ is the surface area of the transferred heat, $T_{\text{sur}}$ is the temperature of the surface, $T_{\text{env}}$ is the environment temperature, and $T_{(t)}$ is the time dependent thermal gradient. The convection heat transfer can be expressed as the thermal resistance which defined in equation 2.15.

### 2.2.3 Radiation

All matter at a finite temperature contains electromagnetic radiation. Radiation is the thermal energy from either electromagnetic waves or photons. The amount of emitted radiation is defined using blackbody radiation. Blackbody is an object that perfectly emits and absorbs radiation. The surface of sun and earth are known as approximate blackbodies. The amount of radiant energy emitted from the surface of blackbody is given by equation 2.16, the Stefan-Boltzmann law.

$$\dot{Q} = \sigma A T^4$$  \hspace{1cm} (2.16)

where $\dot{Q}$ is radiation heat transfer rate (W), $\sigma$ is Stefan-Boltzmann constant ($5.67 \times 10^{-8}$ W/m$^2$-K$^4$), and $T$ is absolute surface temperature (K). According to the Stefan-Boltzmann law, all objects emit radiation as long as their temperature is greater than 0 K and the generated heat rate is proportional to the fourth power of the absolute temperature. The quantity of energy and radiation heat varies depends on the absolute temperature and characteristics of the surface.

Whereas the radiation heat transfer rate is independent of the surroundings, a net radiation heat transfer is defined by the difference of the surface temperature of two blackbodies. The net rate of radiant heat transfer is defined by equation 2.17.
\[ \dot{Q} = \dot{Q}_1 - \dot{Q}_2 = \sigma A_1 T_1^4 - \sigma A_1 T_2^4 = \sigma A_1 (T_1^4 - T_2^4) \]  \tag{2.17}

Where \( \dot{Q}_1 \) describes radiant heat emitted from the surface \( A_1 \) and \( \dot{Q}_2 \) is incident radiant heat on surface \( A_1 \). Each has temperature \( T_1 \) and \( T_2 \) respectively.

A true blackbody does not exist in the real world. In contrast, a real body emits radiation lower than a blackbody. The term “gray body” is defined to compensate for real conditions. The gray body emits radiant heat that is proportional to that of a blackbody at the same temperature. The radiation is emitted at a rate of \( \varepsilon \sigma A_1 T_1^4 \) at surface \( A_1 \) and temperature \( T_1 \). The net rate of heat transfer between the gray body and the blackbody’s surrounding is given below

\[ \dot{Q} = \dot{Q}_1 - \dot{Q}_2 = \varepsilon \sigma A_1 T_1^4 - \alpha \sigma A_1 T_2^4 = \varepsilon \sigma A_1 (T_1^4 - T_2^4) \]  \tag{2.18}

where \( T_1 \) is the temperature of the gray body, \( T_2 \) is the temperature of the surroundings, \( \varepsilon \) is emittance or emissivity, and \( \alpha \) is absorptance or absorptivity.

Thermal resistance, \( R_r \), in radiation, can be derived from equation 2.18 by selecting \( T_2 \) as a reference temperature.

\[ \dot{Q} = \varepsilon \sigma A_1 (T_1^4 - T_2^4) = \frac{(T_1 - T_2,r)}{R_r} \]  \tag{2.19}

\[ R_r = \frac{(T_1 - T_2,r)}{\varepsilon \sigma A_1 (T_1^4 - T_2^4)} \]  \tag{2.20}

Since heat exchange takes place in every calorimeter, understanding the thermal transfer phenomena conduction, convection, and radiation, is of major importance for operating and designing calorimeters [9]. An accurate calorimeter will not have heat leak due to the heat transfer from thermal components to the surroundings or silicon handle. Also, the heater and the temperature sensor need to have an efficient contact with the liquid samples to measure heat transfer from heater to the sample.
2.2 Device Design Consideration

The design of this μ-fabricated calorimetric device is based on the intended application of characterizing the thermal properties of biochemical liquid samples as well as the potential application of investigating DNA denaturalization. Sensitivity is a determining factor to consider in designing the device. The μ-calorimeter includes a closed reaction chamber to prevent sample evaporation. The two major drawbacks of the closed chamber are that it has relatively high thermal mass due to the construction material used and the thermal link from the chamber to the substrate. High thermal mass and heat leak lower the sensitivity of the device. To increase the device sensitivity, the reaction chamber needs to have a small thermal mass.

Biochemistry is the field of studying macromolecules systems [10]. The device dimension, therefore, needs to be small to reduce the volume of samples. The micro/nano scale device is suitable for the study of biomacromolecules and the development of new drugs. The minimized dimension of the device prevents superfluous sample consumption. Also, the small volume of the sample can reduce the error which can occur due to convection and increases in device sensitivity.

The measurement system requires quasi-adiabatic conditions, which dictate that the system be thermally isolated from the environment and the reaction chamber and substrate be sufficiently thermally isolated. These conditions minimize the noise or errors from the surroundings of the system and prevent heat sink to the substrate. As liquid samples require highly reliable sample handling, samples should be able to be loaded easily and accurately.
2.3 Device Structure

The device includes two identical reaction chambers. The micromachined chambers are able to contain only 200 nl of liquid samples. Each chamber is connected with two microfluidic inlets and one microfluidic outlet. On the top and bottom sides of the chamber, honeycombed shape resistors are integrated as a heater and a sensor. The dimension of the silicon die is 20 mm x 15 mm. The optical images of the device are shown in Figure 2.1-1.

Figure 2.2-1. Pictures of the μ-Calorimeter before polyimide bonding. (a) Shows the front side of the device, (b) is the close-up view of the front twin chambers. (c) is the reverse side of the device, (d) shows zoomed in shot of the reverse side of chambers.
2.3.1 3-Dimensional Chamber design

The μ-fabricated chamber is able to operate within the range from few microliters to few nanoliters. Crucially, sample evaporation entails measurement errors in the small scale of liquid samples. The fully enclosed structure of the reaction chamber is suitable to study the small volume of liquid samples, since it is able to secure sample evaporation [4]. The cross section view of the 3-dimensional enclosed reaction chamber is shown in Figure 2.2.1-1. The reaction chamber has the truncated pyramid shape due to its fabrication method. The details of its fabrication method will be discussed in the next chapter.

![Diagram of the reaction chamber](image)

Figure 2.2.1-1. The thin film suspended μ-calorimeter reaction chamber. (a) is a perspective view of the reaction chamber. (b) shows the cross sectional view.
Conventional encapsulating chambers are a few millimeters thick [5][16]. In contrast, our closed reaction chamber is constructed of a low-stress silicon nitride membrane ($\text{Si}_x\text{N}_y$) and a thin polymide film. The bottom side of the reaction chamber is connected with inlets and outlets of the device. The thin polymide film seals microfluidic channels and the underside of the chamber. Also, the reaction chamber is fully suspended by tethers from the silicon frame and surrounded by a thermal insulator, air. The thermal mass of the reaction chamber is about 3 orders of magnitude smaller than the conventional bulky enclosed chambers. Thermal mass is directly related to the temperature detection sensitivity. As a result, device sensitivity is increased.

2.3.2 Sensor and Heater Design

In μ-fabricated calorimeters, thermocouples and Resistance Temperature Detectors (RTDs) have been widely used as temperature sensing methods. Both devices have their own advantages and disadvantages. Thermocouples are inexpensive and can measure a wide range of temperatures. However, their limitations in accuracy hamper the application of biosensors, which require high sensitivity. In contrast, the RTDs are standard temperature measurement sensors due to their sensitivity, stability, high accuracy, linearity, reproducibility, and less complicated fabrication [17][18][19].
<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature Range (°C)</th>
<th>α at 20 °C (Ω°C)</th>
<th>Resistivity at 20 °C (Ω-cm)</th>
<th>Thermal Conductivity (W/m-k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>-200 to 800</td>
<td>0.00392</td>
<td>10.6 x 10^{-6}</td>
<td>69.1</td>
</tr>
<tr>
<td>Nickel</td>
<td>-100 to 260</td>
<td>0.00618</td>
<td>6.4 x 10^{-6}</td>
<td>60.7</td>
</tr>
<tr>
<td>Nichrome</td>
<td>-100 to 204</td>
<td>0.00518</td>
<td>110 x 10^{-6}</td>
<td>11.3</td>
</tr>
<tr>
<td>Copper</td>
<td>-50 to 250</td>
<td>0.00393</td>
<td>1.7 x 10^{-6}</td>
<td>388</td>
</tr>
</tbody>
</table>

Table 2.3.2-1 Comparison of the different types of metals [1].

The RTDs used in this work as temperature sensors operate based on the principle that changing the resistance of a pure metal is related to temperature change. Platinum, nickel, cooper, and nickel-iron are commonly used materials for RTDs. The characteristics of RTDs are specified by their materials. Table 2.3.2-1 shows a comparison of RTD properties depending on material. α is the temperature coefficient of resistance (TCR). It distinguishes the sensitivity of the device and the slope of the R versus T curve. Platinum is the most popular RTD material because of its wide temperature range and stability. The platinum thin-film RTD can measure the temperature range within -200 °C to 800 °C. The operation temperature range of nickel is -100 °C to 206 °C. This range is narrower than the platinum RTD but the temperature range is adequate for observing most biochemical reactions [1]. Our calorimeter design utilizes nickel as a RTD because nickel has a higher TCR and needs a lower evaporation temperature to be deposited compared to platinum.

The standard operation principle of nickel RTD is based on the relationship between the temperature and the resistance which is defined by the Callendar-Van Dusen equation shown in (2.1) [2].

\[
R(T) = R_0(1 + AT + BT^2 + CT^3 + DT^4 + ET^5 + FT^6)
\]  

(2.1)
where \( R(T) \) is the resistance (\( \Omega \)) of the RTD at temperature \( T \) (°C), \( R_0 \) is the resistance of the RTD at 0 °C, \( A = 5.485 \times 10^{-3} \), \( B = 6.65 \times 10^{-6} \), \( C = 0 \), \( D = 2.805 \times 10^{-11} \), \( E = 0 \), and \( F = -2 \times 10^{-17} \).

Since the values of \( B, D, \) and \( F \) have relatively higher order than \( A \), we may neglect those values and use linear approximation to simplify the equation without entailing significant errors. For the \( \mu \)-calorimeter, the equation defining the relationship between sensor resistance and temperature is approximated as shown in (2.2) and (2.3).

\[
R(T) = R_{rm}(1 + \alpha \Delta T) \quad (2.2)
\]

\[
\Delta T = T - T_{rm} \quad (2.3)
\]

where \( R(T) \) is the sensor resistance (\( \Omega \)) at temperature \( T \) (°C), \( R_0 \) is the sensor resistance (\( \Omega \)) at \( T = T_{rm} \), \( \alpha \) is the TCR (°C\(^{-1}\)), \( T_{rm} \) is room temperature (°C), and \( T \) is the temperature when heat is applied to the sensor (°C).

The heater operates by Joule heating in that thermal energy is transferred from the electrical current when it is passing through a resistance. While the thermal microfluidic systems utilize several other heating methods such as microwave heating [20][22][23], preheated liquids [24][25], and chemical reactions [26]. Joule heating can operate in a wide temperature range with stable heating and has relatively better control than other methods.

Both heater and sensor have a symmetric serpentine design. The serpentine resistor pattern has several advantages. First, it provides maximum electrical resistance in the limited spatial extent. Second, the resistor can be symmetrically distributed on the surface. Finally, the sensor can measure the average temperature from uniform heat flux generated by the heater. Both sensor and heater resistances is in the 1k-4k Ω range.
3 DEVICE FABRICATION

In general, micro-fabrication includes deposition, lithography, and etching processes on a silicon wafer. This chapter will give an overview of fabrication techniques. Based on these fabrication techniques, the details of the μ-calorimeter fabrication process will be introduced. The μ-calorimeter fabrication processes fall into three main parts: thermal components, the reaction chamber, and metallization.

3.1.1 Use of Silicon Wafer

Silicon is widely used as a substrate and structural material due to its intrinsic stability, flatness, integration feasibility, and excellent machinability [27]. Because of this feature, silicon is capable to be combined with various coatings and thin films and used as a substrate for micromachining application. Silicon can be utilized in a wide temperature range without stress because of its very low thermal expansion coefficient. Although it may be a high cost material per unit area compared to other substrate materials such as ceramics, plastic, or glass, this cost is offset by the capability of micromachining with silicon.

The definite advantage of silicon as a base structural material is it is well characterized for micromachining [27]. Due to its single-diamond structure, silicon has a very unique wet etching profile. Atom-packing density of {111} planes are higher than other planes. This high packing density hampers etching processes and reduces etching speed. Anisotropic wet etching by using potassium hydroxide (KOH) etchant is possible
due to this unique structure of silicon. In addition, well-known etch stop techniques have led to silicon becoming the major material for bulk micromachining.

3.1.2 Thin Film Deposition

These devices, developed by micro-fabrication, generally contain many layers above the silicon wafer. These layers are deposited by implementing several deposition techniques. Deposition methods can be chosen by considering two matters. First, the quality of deposited films needs to be considered. The quality indicates composition, defect density, contamination class, and mechanical and electrical properties. It also shows stability and low stress of deposited films. The second matter is uniformity of the layer thickness. The deposited layer should have a certain thickness along a substrate, from wafer to wafer, and different topographies. Non-uniform thickness of layers causes electrical resistance change and mechanical defects [28].

3.1.2.1 Chemical Vapor Deposition

Deposition techniques can be classified into two groups: chemical vapor deposition (CVD) and physical vapor deposition (PVD) [28]. Both methods are performed in deposition chambers and deposited materials are delivered as gas phases to the wafer surface to form a thin film. CVD is based on chemical reactions. When a reactant gas is introduced into a chamber, the surface of the substrate, which is supplied energy, chemically reacts with the gas and generates a thin film. CVD has been primarily
used for silicon and dielectric deposition. Compared to PVD, CVD has better step coverage and higher quality films. CVD is subdivided into Atmospheric Pressure CVD (APCVD), Low-Pressure CVD (LPCVD), and Plasma-Enhanced CVD (PECVD).

APCVD is the simplest CVD process. It uses an atmospheric deposition chamber. Although APCVD is not the common process today due to the increase use of LPCVD and PECVD, the basic deposition steps of CVD is based on APCVD [28]. The CVD deposition process has 7 steps:

A) Gaseous reactants are transported by forced convection to the deposition region.

B) By diffusion force, reactants from the main gas stream are transported to the wafer surface. This step is known as the mass transfer.

C) Reactants are absorbed into the wafer surface.

D) The surface reacts with the reactants.

E) After the surface processes C and D, byproducts are desorbed from the surface.

F) Byproducts are diffused back to the main gas stream.

G) By forced convection, byproducts are transported away from the deposition region.

Relative to APCVD, LPCVD is conducted under a lower pressure atmosphere in the 0.25 to 2.0 torr range and a higher operating temperature (300 °C - 600 °C). Low pressure in the system increases the diffusivity and enhances the thin film growth velocity. LPCVD requires the gaseous reactant to exist long enough in the chamber to react and deposit each substrate surface to cover local topographical features.
In some specific cases, the high temperature process is not available when substrate layers include a material which has a low melting temperature. APCVD and LPCVD may operate at low temperatures (< 400°C). The deposition rate exponentially decreases according to the Arrhenius equation and the deposited film has low quality. PECVD was developed to be applied in this circumstance [28]. PECVD uses not only a thermal source but also a plasma source to provide the energy for the chemical reaction occurred during the deposition. Plasma, a highly ionized gas, supplies additional energy to reactant gases instead of using higher thermal energy. The operation temperature range of PECVD deposition is 200-350°C.

3.1.2.2 Physical Vapor Deposition

In PVD, the gas phase atoms physically condense on the surface and form a thin film. In general, PVD is used for metal deposition. The PVD process requires very low pressure. Since the constituent atoms physically transport onto the substrate surface, the space between the surface and the constituent source should not be disturbed by particles. The average distance that a particle can move without collision is defined as the mean free path. PVD uses either evaporation or sputtering methods.

In the evaporation processes, the source materials are heated in a vacuum chamber (<10⁻⁵ torr). The source atoms are heated up, evaporated, and deposited onto the target surface. Two types of heaters are used for evaporation: the resistance type and e-beam heater. The resistance type heater uses a tungsten filament which heats up when given a current. E-beam heater uses kinetic energy to transfer thermal energy. A
generated high energy electron beam is focused onto the source material and evaporates it. The deposited film thickness is monitored by a quartz crystal microbalance (QCM) that measures a mass per unit area by measuring the frequency change of a quartz crystal resonator. A quartz crystal oscillates at its resonance frequency, which is dependent on the thickness of mass of the deposited film onto the crystal. QCM requires the deposited material information such as Z-factor: the ratio of a real gas volume to an ideal gas volume.

Compared to evaporation, the vacuum requirement for sputtering is less crucial (<0.1 torr). For sputtering, a source material, a substrate, and an inert gas are placed in a vacuum chamber. The inert gas becomes plasma state by the power source and the ions are accelerated to the source material. Then, the gaseous source material collides with argon plasma. This provides pressure or energy to the target material (the coating material) and the ionized target material condenses on the substrate. Although the deposition condition of sputtering is simpler than evaporation, significant contamination is allowed. However, availability of high purity gas sources enables its use in deposition.

### 3.1.3 Photolithography

Photolithography is the technique that transfers a pattern onto the surface of a silicon wafer. Photolithography is normally limited to a two-dimensional process. However, the rapid and continuous growth of photolithography techniques has allowed for a wider range topography process [27]. The steps for photolithography are listed below [27].
A) Surface cleaning
B) Barrier layer deposition
C) Spin coating with photoresist (PR)
D) Soft baking
E) Mask alignment
F) Exposure
G) Development
H) Hard Baking
I) Post process cleaning

Before printing any pattern on the wafer surface, cleaning the wafer is very important. Contaminants on the surface may be caused by the atmosphere, wafer handling, process equipment, or solvent chemicals. Contaminants on the wafer can be dust, particles, or bacteria [27]. The wafer is rinsed with deionized (DI) water before any processes are conducted. If the wafer is visibly contaminated, it can be cleaned by soaking in a piranha solution. Piranha solution is the mixture of sulfuric acid (H$_2$SO$_4$) and hydrogen peroxide (H$_2$O$_2$) with a ratio of 1 to 3.

The materials for a barrier layer are chosen regarding a final function or the operating temperature of the device, or as a diffusion barrier material. Usually, silicon dioxide is used as the barrier layer, but silicon nitride (Si$_x$N$_y$), polysilicon, and metals are also often used [27]. Once the wafer is ready for the photoresist spinning, adhesion
promoters such as 1,1,1,3,3,3-hexamethyldisilazane (HDMS) or trichlorophenylsilane (TCPS) are coated onto it after removing all remaining H₂O by heating.

PR is a mixture of a polymer (base resin), a sensitizer, and a casting solvent. When the polymer is exposed to radiation, it changes structure and reacts with the developing solution. The solvent provides fluidity and allows for the use of the spinning process. The chemical reactions are controlled by sensitizers. PRs are classified into two types according to the etched area after exposure: positive resists and negative resists. For negative PRs, the illuminated area of the thin PR film remains after exposure. In contrast, the illuminated area is etched away in the case of positive PRs. Once the wafer is placed on a spinner, PR is dropped on it by a pipette and uniformly spin coated onto the wafer. The film thickness depends on the spinner rotational speed and the resist viscosity. After PR is coated on the wafer, the solvent of PR is evaporated by soft baking, also known as prebaking, and becomes dense.

The desired pattern stencils on the wafer from the mask. To print accurate patterns on the wafer, alignment of the mask to the substrate has to be precise. The mask is flat glass with a chromium pattern layer covered to absorb the radiation. The mask physically contacts the wafer, is proximately aligned, or uses projection systems. The contact masks, also referred to as hard contact, stamps the image on the wafer with a 1:1 ratio. This method is a relatively inexpensive process and widely used in R&D, although the mask or the wafer surface may be damaged from the direct contact. The proximity aligner prevents surface damage from direct contact, but is not commonly used due to its poor resolution. Very Large Scale Integration (VLSI) lithography utilizes projection systems. The projection system uses the projection printing method and has high resolution
compared to other methods. In this system, imaging optics are placed between the mask and the wafer. The minimum feature size is defined by the practical limiting resolution \( R \), given by equation 3.1.

\[
R = \frac{k_1 \lambda}{NA}
\]  

(3.1)

where \( k_1 \) is an experimentally determined coefficient that depends on PR parameters and process condition, \( \lambda \) is the wavelength of the light source, and \( NA \) is the numerical aperture of the lens. A larger \( NA \) value means the lens can accept the light source in a wider incidence angle. Once the PR coated wafer is exposed to ultra violet light (UV light), the PR is photopolymerized and etched by the development solution (developer).

The Postbaking or hard baking step eliminates residual developing solvents as well as anneals the film. The firm film endures subsequent etching steps. Postbaking can be unnecessary for some processes that require the soft PR film, such as metal lift off patterning. The last step is PR removing and post process cleaning. The PR is etched out by a 1165 stripper which contains n-methyl-2-pyrrolideon. Also, oxygen plasma etching is used to remove organic polymer contaminants.

### 3.1.4 Etching

Etching is the technique for removing materials from the surface. The deposited film on the wafer is selectively removed by etching and only desired patterns are left on the wafer surface. If the designed structure is complex and requires multiple layers, the etching process is conducted sequentially. The ability of an etching system is decided by two criteria: selectivity and directionality. When the etching system has good selectivity,
it will etch only the selected layer. The underlying material will be damaged by poor selectivity of the etching system. Directionality refers to how well side etching is controlled. An ideal anisotropic etching provides a vertical side wall because the layer is etched, not laterally, but only vertically. In contrast, an isotropic etch occurs in all direction and produces round side walls. Figure 3.1.4-1 shows how the cases of poor directionality and selectivity in an etching profile compare with the ideal etching profile.

3.1.4.1 Wet Etching

The names of etching methods, wet and dry etchings, come from the etching environment. Wet etching utilizes a liquid etchant. The wafers are immersed in the liquid etchant and the exposed area is etched by chemical reactions. In wet etching, chemical processes are dominant rather than physical processes. Wet etching is well-established, inexpensive, and relatively simple. Also, since wet etches are based on chemical reactions, they have high selectivity. The selectivity, $S$, is defined by the ratio of the etch rates of two different layers

$$S = \frac{r_1}{r_2}$$

(3.2)

where $r_1$ is the etch rate of the layer being etched and $r_2$ is the etch rate of masking layer. When the etching process has the high selectivity ($S \gg 1$), this etch process has good selectivity for material 1 over material 2. Although it has high selectivity as well as many other advantages, wet etching may not be an appropriate method for some device fabrications that require more vertical wall structures and a small line width because the undercut generated from wet etching may entail crucial structural defects.
Hydrofluoric acid (HF) and Buffered Oxide Etch (BOE) are the common etchants for etching silicon dioxide (SiO$_2$). The chemical reaction formula is described in equation (3.3)

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$$  \hspace{1cm} (3.3)

Most of wet etching processes produce water soluble byproducts or gases. In the case of HF etch, H$_2$SiF$_6$ is produced as a byproduct. BOE is the etchant that ammonium fluoride (NH$_4$F) adds to the HF etchant. Buffering agents are often used to change the characteristics of the etch solution, such as etch rate. In BOE, added NH$_4$F prevents the fluoride ion exhaustion and reduces the etch rate of PR. The slower etch rate can be useful for some cases due to the convenience of the etching control.

Most wet etch etchants have the isotropic etching directionality. However, some wet etchants are very dependent on the orientation of crystalline materials and have the anisotropic etching characteristic. The representative anisotropic wet etchant is potassium hydroxide (KOH). Silicon, a single crystal material, has a very atomically dense structure in $<$111$>$ direction and is more time consuming to etch. The etch rates, therefore, vary with crystal direction. Figure 3.1.4.1-2 shows the cross section of an anisotropic wet etch
outcome on silicon wafer. KOH etching has not only the directionality and selectivity characteristics, but the etch also stops almost automatically when it reaches another layer’s surface,

![Figure 3.1.4- 2. KOH etching profile.](image)

### 3.1.4.2 Dry Etching

Dry etching is the dominant method used in industry due to mass production. Dry etching or plasma etching could have supplanted wet etching because of its good directionality. Directional etching can minimize underetching and etch bias which is suitable for more complex and smaller device fabrication. Plasma etching systems are based on both the reactive chemical components and the ionic components. The fundamental dry etching system is constructed in a low pressure atmosphere chamber. A high electric field is applied across two electrodes and plasma is generated by creating free electrons and positive ions.

Dry etching is subdivided by its mechanisms: chemical etching, physical etching or sputtering, and ion-enhanced etching. Chemical etching utilizes free radical reactions.
A free radical is an atom that is neutral and has incomplete bonding. Due to its incomplete bonding, a free radical is very unstable and has high reactivity. In the chamber, these free radicals chemically react with free electrons in the plasma and generate fluorine. Equation 3.4 describes this process.

\[ e^- + CF_4 \rightarrow CF_3 + F + e^- \]  
\[ 4F + Si \rightarrow SiF_4 \]  

Equation 3.5

Fluorine reacts with the surface of silicon substrate and produces \( SiF_4 \) as a byproduct. Since the chemical etching mechanism is based on chemical reactions, it has similar directionality, isotropic, characteristic as wet etching.

Physical etching systems exploits the ions in the plasma. The voltage drop between the plasma and electrodes generate an electric field across the sheaths in the chamber. The ions are accelerated toward the wafer and the silicon wafer is etched by this kinetic energy. Physical etching is much more directional than chemical etching due to the directionality of the electric field from the plasma to the wafer surface. In many cases, ionic and reactive chemical atoms are combined to be used. Ion-enhanced etching is based on this synergetic effect. Using this mechanism, directional and selective etching can be achieved. Reactive Ion Etching (RIE) is one of the plasma etching equipment that based on ion-enhanced etching mechanism.

### 3.2 Micro-Calorimeter Fabrication

The \( \mu \)-calorimeter device introduced in this work is fabricated on a 300 \( \mu \)m thick silicon wafer (100). Silicon dioxide (\( SiO_2 \)) layers and low-stress silicon nitride (\( Si_xN_y \))
layers are deposited on the both sides of silicon wafer by thermal growth and LPCVD respectively. The device fabrication processes mainly pass through three steps: thermal components integration, the reaction chamber and micro-fluidic construction, and metal deposition for electrical contact with the device sealing.

### 3.2.1 Thermal Component Fabrication

Printing patterns on 3D structures is challenging, especially when they are constructed with minimized wall thickness. In this work, a self-shadow masking process is used to place the thermal components: the heater and the sensor, on the reaction chamber. This novel metal patterning process resolves the lithographic difficulties with the 3D structure of the microfabricated reaction chamber. The simplified process flow is shown in figure 3.2.1-1.

![Figure 3.2.1-1. The simplified thermal components fabrication flow. (a) is the front view after PR spinning. (b) is after PR etching, (c) is after the silicon nitride layer etching, (d) ](image)

Figure 3.2.1-1. The simplified thermal components fabrication flow. (a) is the front view after PR spinning. (b) is after PR etching, (c) is after the silicon nitride layer etching, (d)
is the silicon oxide etched front view, and (e) is isotropic etched silicon wafer configuration.

After the PR is deposited on the wafer using PR spinning, serpentine grooves with honeycomb outer shapes are printed on the wafer surface by photolithography. The serpentine structure window as shown in figure 3.2.1-1 (b) on the PR layer allows the silicon nitride (Si$_x$N$_y$) to be etched away as the same serpentine honeycomb pattern on PR. Silicon dioxide (SiO$_2$) is etched with the same pattern. Figure 3.2.1-2 shows the top view of the serpentine pattern after Si$_x$N$_y$ and the SiO$_2$ layer is etched. RIE is used to etch the Si$_x$N$_y$ and SiO$_2$ is etched by BOE (6:1). PR is removed after RIE using the piranha solution.

![Figure 3.2.1-2](image)

**Figure 3.2.1-2.** The top view of the serpentine patterns on the wafer surface after SiO$_2$ Etching.

The next step is silicon isotropic etching as shown in figure 3.2.1-1 (e). The silicon layer surface is etched by poly etch. Poly etch uses HNO$_3$:H$_2$O:HF (+ CH$_3$COOH) wet chemical etchants and creates undercut. Generated undercut in this step will provide
the base structure to form the Si$_x$N$_y$ hang over configurations. The same processes are applied on the other side of the wafer to form both the heater and the sensor on each side of the wafer. Top and bottom patterns are aligned by the double sided mask aligner. An integrated self-shadow mask in a blanket metal evaporation process will be applied in the final step of the metal evaporation process to complete the isolated thermal component integration. The details of the final step will be elaborated on in section 3.3.3: electrical contact and device preparation.

3.2.2 Chamber and Micro-fluidic Channel Fabrication

μ-calorimeters require two conditions to effectively operate. First, the experiment system with the μ-calorimeter needs to be conducted under quasi-adiabatic conditions. The reaction chamber should be thermally isolated from ambient conditions as well as the device frame. Second, the reaction chamber structure should be built minimizing thermal mass. To reduce the thermal mass, the reaction chamber consists of a Si$_x$N$_y$ thin film and a thin polymide film. In addition, the reaction chamber is fully suspended from the silicon frame, minimizing the thermal link from the reaction chamber to the silicon handle and substantially reducing heat loss to the substrate by thermal conduction.
Figure 3.2.2-1. (a) is the bottom view of after patterning microfluidic channels and the reaction chambers. (b) show the configuration of after the first KOH wet etching. (c) is the view of after Si$_x$N$_y$ film deposition.
The reaction chamber fabrication utilizes an anisotropic chemical wet etching for 3D micromachining. After the isotropic silicon etching of thermal components, the 0.5μm thickness low-stress Si$_x$N$_y$ film is deposited by LPCVD to cover exposed silicon. Second, the reaction chamber and the microfluidic channels are printed on the bottom side of the substrate surface. Figure 3.2.2-1 (a) shows the bottom view of the substrate after the second step of the reaction chamber fabrication, using the same processes as thermal components fabrication except for the silicon wet etching. The third step is KOH anisotropic etching and creates the truncated pyramid shape. It provides the base structure of the reaction chamber. Then, another 0.5μm thickness Si$_x$N$_y$ layer deposition using LPCVD. This process creates the walls of the reaction chambers with the Si$_x$N$_y$ layer. Lastly, another KOH wet etching is provided on the top side of the wafer surface to isolate the reaction chamber from the silicon handle. Figure 3.2.2-2 shows the configuration of the device after the second KOH etching. This last step is to fully suspend the reaction chambers structure by thin tethers from the handle.

Figure 3.2.2-2. The top view of the twin chambers after second KOH chemical etching.
3.3.3 Electrical Contact and Polyimide bonding

Using the integrated self-shadow mask in a blanket metal evaporation, 30-70 nm thick nickel is deposited by evaporation on both sides of the substrate. Figure 3.3.3-1 shows the cross sectional view after metallization. Nickel layers are disconnected due to the Si$_{x}$N$_{y}$ over hang. The inlets and outlets must be opened since they are initially blocked by the silicon nitride thin film. Once the inlets and outlets are opened, the back side of the device is sealed with a 25 μm polyimide film using a silicon adhesive (50 μm). Figure 3.3.3-2 shows the device after the final step of the fabrication.

![Figure 3.3.3- 1. The simplified side view after metallization.](image)

![Figure 3.3.3- 2. Top and bottom side views of the fabricated device. (a) shows the top side of the device. (b) is the bottoms side view of the device.](image)
3.3.4 Fabrication Flow Diagram

The details of fabrication processes are explained in previous sections. The following figures are the cross section views of the overall device fabrication steps. First, we start with the patterning of the heater and the temperature sensor. The second step is micromachining the 3D reaction chamber. KOH etching is conducted twice, both on the bottom and top surface. Finally, the nickel layer is deposited over the entire wafer surface for RTDs and electrical contact.
Figure 3.3.4-1. The process flow for the patterning the heater and the temperature sensor. (a) the wafer surface before the fabrication, (b) the Si$_x$N$_y$ film is etched by RIE, (c) the SiO$_2$ is etched by BOE isotropic wet etching. (d) the silicon substrate is etched using isotropic poly etch and undercut is created.
Figure 3.3.4-2. The process flow. (a) The cross section view of after patterning the heater and the temperature sensor, (i) shows the closeup view of the isotropic etch profile, (b) Si$_x$N$_y$ deposition by LPCVD, (ii) is the closeup configuration of (b), (c) shows after patterning the reaction chamber, (d) KOH etching, (e) Si$_x$N$_y$ deposition by LPCVD to create the walls of reaction chamber, (f) shows patterning for KOH etching to isolate the reaction chamber from the silicon handle, (g) is the cross section view after metallization, and (iii) is its closeup view.
4 MICRO-FABRICATED CALORIMETER CHARACTERIZATION

The device calibration is conducted with the temperature sweep in a thermal bath and a step response measurement. Each calibration requires the specific interface between the device and the electrical source. This chapter elaborates the characterization of the μ-calorimetric device based on the results of this calibration.

4.1 RTD Calibration

As discussed in chapter 2.3.2, Sensor and Heater Design, resistance and temperature have a linear relationship in metal conductors that can be defined using the simplified Callendar-Van Dusen equation [1][2].

\[ R(T) = R_0(1+\alpha\Delta T) \]  

(4.1)

R(T) is the resistance (Ω) of the RTD at temperature T (°C), \( R_0 \) is the sensor resistance (Ω) at \( T = T_{\text{sensor}} \) or \( \Delta T = 0 \), \( \alpha \) is the thermal coefficient of resistance (TCR), and \( \Delta T \) is the temperature difference between the sensor and the ambient. The electrical resistance of the nickel film is in the range of 1-4 kΩ. These values vary depending on the thickness of the films (30-70 nm). Since the resistance of the RTD is known, TCR needs to be defined by calibration to observe the exact temperature change according to the change in the resistance. Characteristic parameters of the sensor such as the accuracy, thermal noise, and temperature resolution are also calculated from this experiment.
4.1.1 RTD Calibration Measurement Setup

The TCR of the nickel RTD is measured using a HAAKE thermal bath. The temperature inside the thermal bath sweeps from 10 °C to 50 °C with 5 °C increments per hour. To make electrical contact from the RTD to the test equipment, a 3D designed device holder is exploited. The interface setup flow is shown in Figure 4.1.1-2. When the device is mounted on the holder, the commercial RTD sensor (Pt 100) is also connected to the interface as a reference. The RTD is connected to a SourceMeter (Keithley 2400) and the resistance is recorded by 4 wire measurement by giving current source (1 mA). The device holder is placed inside the stainless steel vessel to protect the device from the underwater environment. The temperature of the HAAKE thermal bath is controlled by LabVIEW.

Figure 4.1.1- 1. The device connection with the test equipment for calibration
Figure 4.1.1-2. Interface set up for calibration. (a) shows the base of device calibration holder, (b) depicts when the device is placed, and (c) is the device holder after it assembled.

4.1.2 RTD Calibration Result

The resistance is ramped according to the temperature augmentation. The original data plot for the RTD sensor is shown in Figure 4.1.2-1. The temperature increases 5 °C per hour. Once calibration scanning is completed, the stabilized resistance values in each
temperature range are selected for sampling. The sampled data plot, as shown in Figure 4.1.2-2, is curved fitted to characterize the RTD sensor linearity.

Figure 4.1.2-1. The plotted original data for the RTD sensor calibration

Figure 4.1.2-2. The plotted sampled data for the RTD sensor calibration
From the linear fit of the sample data, we can observe that the RTD are extremely linear. A coefficient of determination ($R^2$) demonstrates quantitative linearity of the measured data. When $R^2$ value is closer to 1, the observed data has better linearity. The coefficient of determination, $R^2$, has 0.99 value which demonstrates the measured data fits well into the modeled linear plot.

The TCR of the heater and the sensor are calculated using two sampled points. Two sampled points are substituted into the simplified Callendar-Van Dusen equation. TCR value is determined by dividing these two equations. The measured TCR of the sensor is $2.55 \times 10^{-3} \, ^\circ\text{C}^{-1}$. Whereas the reported TCR of bulk nickel is $6 \times 10^{-3} \, ^\circ\text{C}^{-1}$ [29]. The TCR value is related with the mean free path of electrons in the film. The mean free path can be reduced due to the electrons scattering with phonon, impurity, surface boundary, and grain boundary [30]. The external surface boundary scattering causes a reduction of the mean free path of the deposited thin nickel film [16]. Figure 4.1.2-3 shows the simplified electron mean free path distribution in the metallic film. $A_b$ is the distribution of mean free path in the bulk material. It is determined by the scattering with phonon and impurity. $A_f$ is the reduced film mean free path. It is shorter than $A_b$ due to the scattering with phonon, impurity, and surface boundary [30].
Accuracy, thermal noise range, and temperature resolution represent criteria for describing device performance. These parameters are extracted from the RTD thermal calibration experimental results. The accuracy of the RTD is calculated using the reference value from a commercial RTD sensor (Pt-100). The temperature measured by the fabricated RTD sensor is compared to the measured temperature from the commercial RTD sensor. The temperature measuring efficiency between the reference value and the measured value demonstrates 2.36% accuracy.

The noise occurring in a laboratory situation can be generated by intrinsic and external noise sources [31]. External noise arising from the environment can be minimized by experimental design. Thermal noise, however, is inherent to the physical process. Because of this thermal noise, the resolution of the sensor is limited. When the voltage is across the terminals of a resistor, a noise voltage is generated because of thermal fluctuations from moving charge carriers in a resistor [32]. Johnson-Nyquist noise is defined as the mean square value of noise voltage shown in Equation 4.2.

\[
\overline{V_n} = 4k_B T R \Delta f
\]  

(4.2)
\[ R_{\text{Noise}} = \frac{\bar{V}_n}{I_{\text{Sensor}}} = \frac{\sqrt{4k_B R_{\text{rm}} T_{\text{rm}} \Delta f}}{I_{\text{Sensor}}} \]  

(4.3)

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature (K), \( R \) is the resistance (Ω), and \( \Delta f \) (28.5Hz) is frequency bandwidth determined by the measurement equipment, the SourceMeter. The noise resistance \( (R_{\text{Noise}}) \) is calculated by ohm’s law in Equation 4.3. \( I_{\text{Sensor}} \) is the current given at the sensor, \( T_{\text{rm}} \) is room temperature (K), and \( R_{\text{rm}} \) is the resistance at room temperature. Using the simplified Callendar-Van Dusen equation and the calculated \( R_{\text{Noise}} \), a thermal noise value of \( 8.16 \times 10^{-6} \) (Ω/\( \sqrt{(Hz)} \)) is determined.

The sensor resolution that minimizes detectable temperature change is determined using the root mean value of the sensor resistance in room temperature and the maximum resistance change. The resistance resolution converted to temperature resolution is 0.002 °C.

### 4.2 Step Response

A thermal circuit has analogous character to an electrical circuit. The thermal models such as thermal mass, heat flow, temperature, thermal resistance match a capacitor, a current, a voltage, and a resistor in electrical circuit. The system with the calorimeter and the loaded sample is modeled as a first order lumped circuit which as shown in Figure 4.2-1 [33]. The thermal parameters such as thermal mass, thermal resistance, and the equilibrium time constant are experimentally extracted using the step function response. At the heater, the heat pulse is generated by applying a 1 mA current. The sensor detects the heat traveling through the liquid sample by 4 wire measurement. This measurement uses two SourceMeters to generate and detect the heat source for the
heater and the sensor respectively. The differential equation in 4.4 of the circuit is derived by using nodal analysis.

\[ P_{\text{in}} R_t = \Delta T(t) + R_c C_t \frac{d\Delta T(t)}{dt} = \Delta T(t) + \frac{\tau d\Delta T(t)}{dt} \quad (4.4) \]

where \( P_{\text{in}} \) is input power (W), \( R_t \) is thermal resistance (K/W), \( C_t \) is thermal capacitance (J/K), \( \Delta T \) is charge in the reaction chamber temperature (K), and \( \tau \) is the time constant of the system.

Figure 4.2-1. The cross section view of the reaction chamber.
Figure 4.2- 2. The lumped modeled circuit. $P_{in}$ is the input power, $C_t$ is the thermal mass of the system which includes the calorimeter and the target sample, and the $R_{th}$ is the total thermal resistance of the $\mu$-calorimeter.

4.2.1 Step Response experiment Preparation

To prepare the device for the measurement, 4 layers of acrylic interfaces are used. The base layer aligns and supports the other layers. The second layer is the electrical interface to connect with the heater. The third layer is where the device is placed. 3 pieces of ion plate (~1mm) are adhered on the acrylic layer and placed behind where the microfluidic inlets and outlets sit. Once the device is set on this layer, the thin torus shape polydimethylsiloxane (PDMS) pieces are placed on the inlets and outlets of the device to prevent leakage when the liquid sample is injected. The fourth layer is the magnet aligner layer. Microfluidic inlets and outlets are connected with cylindrical magnets to tubes. The fourth layer aligns the magnets on the inlets and outlets of the device and the aluminum film pieces on third layer anchor the magnets. The magnetic interface facilitates easier sample handling and cleaning of the microfluidic channels. The fifth layer is the same as
the second layer, it electrically contacts the sensor to the measurement equipment. The device installation flow on the measurement jig is shown in Figure 4.2.1-1.

Figure 4.2.1-1. (a) The jig base layer. (b) The electrical connection for the heater. (c) The device seating part with metal pieces. (d) shows the device placed on (c). (e) The magnet aligning layer. (f) is configuration after magnets are placed. (g) The electrical connection for the sensor
4.2.2 Step Response Result

When a step input power is applied into the system at time $t = 0$, the temperature of the system exponentially increases as shown in Equation 4.5 which is derived from Equation 4.4.

$$\Delta T(t) = P_{in} R_t \cdot [1 - e^{-t/\tau}]$$

(4.5)

According to the Equation 4.2 and the Figure 4.2.2-1, thermal parameters such as the time constant, thermal resistance, and thermal capacitance can be extracted. The time constant is the required time for the step response to reach 63% of the steady state value ($\Delta T_{ss}$). Thermal resistance is determined by using the relationship with the steady state
temperature and the input power ($P_{in}$). The thermal capacitance is extracted from the initial slope of the step response. The equations to extract each thermal model parameter are described below.

\[
\Delta T(t = \tau) = \Delta T_{ss} \left[ 1 - e^{\left(-\frac{t}{\tau}\right)} \right] = \Delta T_{ss} \cdot 0.63 \tag{4.6}
\]

\[
R_t = \frac{\Delta T_{ss}}{P_{in}} \tag{4.7}
\]

\[
C_t = P_{in} \cdot \left[ \frac{d\Delta T}{dt} \Big|_{t=0} \right]^{-1} \tag{4.8}
\]

![Figure 4.2.2-1. The step response of the μ-calorimeter.](image)

From Equations 4.3-4.5 and the step response of the μ-calorimeter, the extracted values of the time constant, thermal resistance, and thermal capacitance are 1.33 sec,
58.87 K/W, and $6.63 \times 10^{-3}$ J/K respectively. The thermal model parameters are used to determine the thermal characteristic of the liquid sample thermal parameter.
5. EXPERIMENTAL METHODS AND RESULTS

The fabricated μ-calorimeter is able to carry out different calorimetry methods such as DC calorimetry, AC calorimetry (transient), and TWA in a single device due to its 3D machined suspended chamber. DSC can also potentially be performed using the twin chambers on a single device. The thermal properties of thermal diffusivity and specific heat capacity are measured with different methods and experimental setups. Deionized (DI) water, glycerol, and ionic liquid are used as liquid samples and literature values are used to compare to the measured values. Both experiments are performed in quasi-adiabatic conditions. The stationary setup of measurement prevents external flow.

5.1 Measurement of Thermal Diffusivity

The heat penetration time measurement method is used to measure the thermal diffusivity of liquid samples [2]. The principle of heat penetration time measurement is based on measuring the travel time of heat from one place of the sample to another place of the sample. This penetration time or the delay time \(t_d\) is expressed in Equation 5.1 [2].

\[
t_d = \left[ \frac{L^2}{\left(\frac{16}{\pi}\right) \cdot \alpha} \right]
\]

where \(L\) is the distance that heat travels through the liquid sample and \(\alpha\) is the thermal diffusivity of the sample. Figure 5.1-1 shows the schematic of heat flux flow in the reaction chamber. Using the integrated sensor and heater with opposite side planes of the
reaction chamber, thermal diffusivity of the liquid sample can be measured by the heat penetration time measurement method.

Figure 5.1-1. Cross sectional view of the reaction chamber during the thermal diffusivity measurement. The generated heat flux from the heater diffuses to the sensor through the liquid sample.

The layer thickness of the sample that the heat flux traveled converges to the thickness of the wafer, which is approximately 300 ± 5 μm. The correction parameter (p) for the device thickness is calibrated by the result of DI-water thermal diffusivity. The known thermal diffusivity [15] and measured thermal diffusivity of DI-water are used for calibration. From the fitting calibration, the heat penetration time can be expressed as equation 5.2.

\[
t_d = \frac{(L \times p)^2}{\left(\frac{16}{\pi}\right)\alpha}
\]  (5.2)
In the time delay thermal diffusivity measurement, the calorimetric device which contains the liquid sample is placed in a thermally isolated enclosure. This minimizes the error or effect from the environment and satisfies quasi-adiabatic condition. To set up the measurement, the heater, the SourceMeter is connected with the heater to apply current source. A 1 mA rectangular pulse signal generates the heat according to Joule heating from the heater.
The sensor, the SourceMeter (Keithley 2400) and a current preamplifier (Stanford SR570) are connected with the RTD sensor. The current preamplifier is used to amplify the signal and increase the detection limit as well as the resolution. The operation principle of the current preamplifier is based on an offset and a gain. The preamplifier reads current and has a voltage output. Once the offset current value (1 mA) is configured, a fixed amount of voltage is given to the RTD sensor and this voltage is adjusted to be 1 mA, the same as the offset current. If the offset is less than 1 mA, the sensor signal noise increases. In contrast, if the offset is higher than 1 mA, the sensor temperature is affected and hampering its ability to sense the heat from the heater. Since the current flowing through the sensor and the preamplifier offset current have the same value, the voltage output is infinitely closer to zero. Adjusting the voltage output to be 0 V prevents overload at the preamplifier when heat is applied.

When heat is generated from the heater, the liquid sample temperature increases, raising the RTD sensor resistance. As the amount voltage given at the RTD sensor is fixed, the current flow through the sensor decreases according to the resistance increase. The current preamplifier converts current input to voltage output and amplifies the output. The ratio of amplified signal to original signal is defined by the gain. In this measurement, 1 V/nA is selected. Therefore, a 1 nA change from the input or the RTD sensor gives 1 V change at the output. The outputs from the heater and the sensor are read by an oscilloscope (Agilent DSOX 2024A) and the experiment is controlled by a LabVIEW program.
From the DI-water sample, the correction factor (p) was found to be 0.89. This parameter defines the effective heat travel distance to be 270 μm. Using Equation 5.2 and the correction parameter, the thermal diffusivity of glycerol is calculated \(9.94 \times 10^{-8} \text{ m}^2/\text{s}\). The reported glycerol diffusivity is \(9.22 \times 10^{-8} \text{ m}^2/\text{s}\) [34]. The measured thermal diffusivity of glycerol, therefore, has less than an 8% error, which shows good agreement with the reported literature value.

### 5.2 Measurement of Specific heat capacity

The specific heat of the samples is measured with TWA as introduced by Garden et al [1]. The heat capacity of the sample is in inverse proportion to the amplitude of the temperature oscillations under two conditions. First, the temperature of the sample has to
be homogeneous. Second, the sample and the system containing the sample needs to be under quasi-adiabatic condition satisfying Equation 5.3 [1].

\[ \tau_{\text{int}} \ll \frac{1}{\omega} \ll \tau \]  

(5.3)

where \( \tau_{\text{int}} \) is the heat diffusion time into the sample, \( \omega \) is the angular frequency of the temperature oscillations, and \( \tau \) is the thermal relaxation time of the liquid sample. The measurement time has to be longer than the diffusion time, since heat cannot be measured before the heat is delivered. Also, the heat needs to be measured before it diffuses into the ambient environment, which requires measurement time to be shorter than relaxation time.

The frequency in Equation 5.3 is determined by the normalized \( \omega \cdot \delta T_{\text{ac}} \) value where \( \delta T_{\text{ac}} \) is the amplitude of the oscillating temperature in the sample. The experiment conducted in the frequency range of 0.01 Hz to 0.1 Hz with 0.005 Hz increment. \( \omega \cdot \delta T_{\text{ac}} \) for each frequency is normalized by dividing the maximum \( \omega \cdot \delta T_{\text{ac}} \).

The measurement setup to measure the frequency in Equation 5.3 and specific heat is shown is Figure 5.2-1. The heater is given a sinusoidal voltage signal from the function generator (3325A Synthesizer/Function Generator). The SourceMeter is used to monitor the signal from the heater. When the AC signal applies to the heater, power dissipation occurs due to Joule heating as defined by Equation 5.4:

\[ P = I_h^2 \cdot R_h, \]  

(5.4)

where \( I_h \) is the current passing through the heater and \( R_h \) is the heater resistance. The alternating current at the heater is described in Equation 5.5 [35].

\[ I_h(t) = I_{h,0}\cos(\omega t) \]  

(5.5)
where $I_{h,0}$ is the peak amplitude of alternating current and $\omega$ is the angular frequency of the heater. Assuming the resistance change is negligible compared to the current amplitude, the power is proportional to the heat generated from the heater and can be rewritten:

$$P = \frac{1}{2} I_{h,0}^2 \cdot R_{h,0} (1 + \cos(2\omega t)), \quad (5.6)$$

where $R_{h,0}$ is the peak resistance amplitude.

Figure 5.2-1. The experimental setup for thermal wave analysis (TWA) block diagram.
The SourceMeter (Keithley 2400) is connected to the sensor to give the current source. A lock-In amplifier (Stanford Research Systems SRS830) is used to detect the signal from the sensor. The lock-In amplifier is based on a phase sensitive detection technique. The phase sensitive detector (PSD) requires the reference frequency, which is the signal from the function generator in this measurement. The average product of two sinusoidal signals is zero due to its orthogonality unless their frequencies are exactly same. The voltage signals from the sensor and the reference are shown in Equation 5.7

\[ V_{\text{sig}} = V_{\text{sig},0} \sin(\omega_{\text{sig}} t + \theta_{\text{sig}}) \]
\[ V_{\text{ref}} = V_{\text{ref},0} \sin(\omega_{\text{ref}} t + \theta_{\text{ref}}) \]

where \( V_{\text{sig},0} \) and \( V_{\text{ref},0} \) are the amplitude of the signal output and the reference respectively. Using product and sum trigonometric identities, the product of the voltage outputs from the sensor and the reference is calculated as in Equation 5.8.

\[ V_{\text{PSD1}} = V_{\text{sig}} \times V_{\text{ref}} \]
\[ V_{\text{PSD1}} = V_{\text{sig},0} \sin(\omega_{\text{sig}} t + \theta_{\text{sig}}) \cdot V_{\text{ref},0} \sin(\omega_{\text{ref}} t + \theta_{\text{ref}}) \]
\[ = \frac{1}{2} V_{\text{sig},0} V_{\text{ref},0} [\cos((\omega_{\text{sig}} - \omega_{\text{ref}}) t + (\theta_{\text{sig}} - \theta_{\text{ref}}))] \]
\[ - \cos((\omega_{\text{sig}} + \omega_{\text{ref}}) t + (\theta_{\text{sig}} + \theta_{\text{ref}}))] \]

The outputs of PSD are two AC signals, one the difference frequency \((\omega_{\text{sig}} - \omega_{\text{ref}})\), the other the sum frequency \((\omega_{\text{sig}} + \omega_{\text{ref}})\). When the output signal passes through the low pass filter, nothing can pass unless \( \omega_{\text{sig}} \) and \( \omega_{\text{ref}} \) are equal. Therefore, the AC signal is removed and the reference voltage is eliminated by division. The filtered output of PSD is
\[ V_{PSD1} = \frac{1}{2} V_{sig,0} V_{ref,0} \cos(\theta_{sig} - \theta_{ref}) \]

(5.9)

\[ V_{PSD1} \cong V_{sig,0} \cos(\theta_{sig} - \theta_{ref}) \]

To obtain the amplitude of the PSD output, the phase is adjusted by using a second PSD which is the reference signal with a 90° shift.

\[ V_{PSD2} = \frac{1}{2} V_{sig,0} V_{ref,0} \sin(\theta_{sig} - \theta_{ref}) \]

(5.10)

\[ V_{PSD2} \cong V_{sig,0} \sin(\theta_{sig} - \theta_{ref}) \]

When \( V_{PSD1} \) and \( V_{PSD2} \) are \( X \) and \( Y \) respectively, the magnitude and the phase of the signal are obtained using the quantities \( R \) and \( \theta \) [35].

\[ R = V_{sig,0} = (X^2 + Y^2)^{1/2} \]

(5.11)

\[ \theta = (\theta_{sig} - \theta_{ref}) = \tan^{-1}(Y/X) \]

The current given by the SourceMeter at the sensor is constant. The alternating resistance due to the heat from the heater is shown in Equation 5.12

\[ R = R_{s,0}(1 + \alpha_s \Delta T_{DC} + \alpha_s |\Delta T_{AC}| \cos(2\omega t + \phi)) \] [36]

(5.12)

where \( R_{s,0} \) is the sensor resistance at room temperature, \( \alpha_s \) is the temperature coefficient of resistance (TCR) of the sensor, \( \Delta T_{DC} \) and \( \Delta T_{AC} \) are DC and peak AC temperature rises respectively, and \( \Phi \) is phase lag. The resulting voltage at the sensor, therefore, can be obtained by multiplying the constant input current by the sensor resistance.

\[ V_{sensor} = I_{sensor} \cdot R_{s,0}(1 + \alpha_s \Delta T_{DC} + \alpha_s |\Delta T_{AC}| \cos(2\omega t + \phi)) \]

(5.13)

The \( 2\omega \) component of heat is used to measure this work.

From the function generator, alternating voltage, which has an amplitude of 3 \( V_{pp} \) peak to peak is applied within the frequency range of 0.01 Hz to 0.1 Hz with a 0.005 Hz
increment. At the sensor, the 0.1 mA DC source is given to measure the temperature change according to the frequency sweep by the SourceMeter. The lock-in amplifier measures the output from the sensor. The measurement is controlled by the LabVIEW program. The experimental result finds the frequency which satisfies the quasi-adiabatic condition as shown in Figure 5.2-2. The graph of the normalized $T_{ac}$ and a 1% error lines is used to detect the suitable frequency for the TWA method [1].

![Normalized T_{ac} vs Frequency](image)

Figure 5.2-2. The normalized value of the measured $T_{ac}$ for different liquid samples. The 1% error line is shown with the dotted line. The frequency range within the error line satisfies the quasi-adiabatic condition.

The specific heat, $C_p$, is given by Equation 5.14 with measured AC temperature from the sensor [1].
\[ C_p = \frac{C_0 P_{in}}{2\omega m \partial T_{AC}} \]  \hspace{1cm} (5.14)

where \( P_{in} \) is the input power given at the heater, \( \omega \) is the thermal wave frequency from the heater, \( m \) is the mass of the liquid sample, \( \partial T_{AC} \) is the amplitude of the oscillating temperature, and \( C_0 \) is the calibration factor of the input power (0.712). The input power calibration factor is used to reduce the measurement error due to heat loss. The result of the DI-water sample experiment is used to determine the input power calibration factor. The input power is calculated by dividing the heater resistance value into the square of the given voltage root mean square (rms) value at the heater (\(3/\sqrt{2} \) V). \( \omega \) in the Equation 5.3 is found from Figure 5.2-3, which is the frequency satisfying the quasi-adiabatic condition. Each sample has a different frequency value. The amplitude of the oscillating temperature is calculated using the peak amplitude resistance from the sensor, the sensor resistance at the room temperature, and the TCR.

The specific heat of DI-water was measured to be 3.93 J/gK. This value shows good agreement (~5% error) with the reported literature value of 4.179 J/gK [15]. The heat capacity of different Ionic liquids was measured for the first time. 4 types of ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide ([EMIM][Tf2N]), 1-buthyl-3-methylimidazoliumhexafluorophosphate ([BMIM][PF6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM][PF6]), and 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF6]), have measured specific heats of 2.75, 2.83, 0.86, 2.55 J/g K, respectively. From the specific heat measurement, the feasibility of the TWA method with the fabricated \( \mu \)-calorimeter is demonstrated with different liquid samples. The measurement errors, which are less than 10% in all cases,
may occur due to the heat loss to the ambient or due to the parameters, which may only be suitable for large volume of samples.
6. New Automatic Measurement System

Although the μ-calorimeter showed good performance for measuring thermal properties of liquid samples, it has one drawback. The distance between the heater and the sensor is fixed by the wafer thickness and may limit the flexibility of the thermal components configuration. Also, the device interface is complicated. To overcome these drawbacks, the new thermal measurement system is introduced.

Figure 6.1- 1. (a) The serpentine patterned resistor device. (b) The electrical interface between the device and the experimental equipment.
A device used in this system includes 10 membranes. 4 of them, which are placed at the center of the device, are integrated with serpentine patterned resistors to be used as a heater or a sensor. The others membranes are able to use to inject liquid samples. The device design is intended to align with another device by facing each other as the heater and the sensor respectively. The device has rectangular shape with $2 \times 1.5$ cm dimension and device resistors are located at the edge of the square shape. This unique structure design allows the heater and the sensor devices to be aligned with the perpendicular angle to the X-Y plane. Also, electrical wiring bonding is made at the side edge of the device which doesn’t overlap with another device after alignment. The electrical interface is designed for wire bonding to the device, connecting to the experimental equipment, and placing on the motor system. Figure 6.1-1 depicts the device and its interface and Figure 6.1-2 shows the actual prototype of the motor system. The full system configuration is shown in Figure 6.2-3 and the system operation processes are shown in Figure 6.2-4.
The system is constructed based on 3 stepper motors which move toward the X, Y, and Z axes. The direction and speed of the stepper motors are controlled by KCam Router/Mill software. A microcontroller and a stepper motor driver send signals from KCam Route/Mill software to the motor. The X and Y axes motors are mounted together into the first subsystem. The first subsystem consists of a monitoring camera, a manual X-Y aligner, an extra pressure absorber constructed with spring supports, and an acrylic plane with a metal ball for leveling. The second subsystem consists with the Z motor and
a metal device interface holder. Once the sensor and the heater are aligned using an X-Y aligner or motors, the second subsystem adjusts the distance between the heater and the sensor by moving the Z-axis.

Figure 6.1-3. The full system configuration. A close up view of the inner square is shown in the process flow figure.
Figure 6.1-4. The new measurement system. (a) Device holders for a heater and a sensor are placed on the X-Y direction motor and Z direction motor. (b) shows loading a liquid sample on the device. (c) depicts the top and bottom device alignment before contact. (d) shows the configuration after contact.
When the device interfaces are placed on the two motor subsystems, the interface for the heater is tilted 90 degrees from X axis to Y axis compared to the sensor. Since the electrical contact wires for the device are located at the right and left edges of the device, electrical interference between the heater and the sensor is prevented with this aligned position. The distance between the heater and sensor is modified by the spacer between the devices. Figure 6.1-5 shows the top view configuration after alignment.

Figure 6.1-5. (a) The configuration after aligning the heater and the sensor device. (b) shows close up view of the single RTD sensor and the heater resistor and (c) is the optical image of (b).
7. CONCLUSION

This chapter summarizes the project by reviewing the μ-calorimeter design and device performance. Also, the new measurement system design is briefly reviewed. As future work, suggestions of additional work for the new design of thermal measurement system are presented.

7.1 Conclusions

This thesis introduced an on-chip micro-fabricated calorimeter (μ-calorimeter) for measuring thermal properties of liquid samples. The intended application of the μ-calorimeter is characterizing the thermal properties of biochemical liquid samples and has the potential application of investigating DNA denaturalization.

The μ-calorimeter is fabricated using a wafer scale 3D micromachining process which does not require additional off-chip bonding processes. The reaction chamber design has three essential features: a fully enclosed structure, suspension from the substrate handle, and a thin film structure. The enclosed chamber structure prevents liquid sample evaporation. Fully suspending the structure from the silicon handle minimizes the thermal link and reduces the heat loss from the sample. The thin film walls reduce the thermal mass of the system and increase the temperature measurement sensitivity.

The design of our μ-calorimeter device allows us to integrate the heater and the sensor on opposite planes of the 3D reaction chamber. The efficient coupling of the
thermal components (heater and sensor) and the reaction chamber provide accurate heat detection. Owing to the thermal components’ location, the measurement of both the thermal diffusivity and specific heat are conducted without changing the measurement setup.

The measured thermal diffusivity and specific heat of liquid samples by the heat penetration time measurement and thermal wave analysis showed repeatable performance and good agreement compared to the literature values (< 8%). The μ-calorimeter introduced in this work can not only conduct various measurements but also demonstrates potential possible use for testing other biochemical liquid samples, including a buffer with a DNA sample.

Measuring liquid sample thermal properties with the μ-calorimeter shows good performance and has a variety of uses in thermal analysis. However, it was has one limitation; the distance between the heater and the sensor is fixed. The new system can adjust the position of the sensor and the heater to X, Y, and Z axes. It allows us to place the heater and sensor extremely close to each other.

7.2 Future Work

A following list suggests more theoretical and experimental work to improve the performance of thermal analysis.

First, differential scanning calorimetry can be performed with the μ-calorimeter and the serpentine patterned resistor device. Both devices have symmetric design. Each temperature sensor, therefore, can be operated individually. Differential scanning
calorimetry is used to cancel out the errors occurring from the environment by comparison with a reference signal.

Second, the new system requires further investigation for sample handling. The sample droplet is placed by a pipette. Although this method is uncomplicated, it is difficult to accurately adjust an amount and a location of a sample. Injecting the liquid sample using capillary tube may be used to control the amount of sample more precisely and place a sample accurately.

Third, it is necessary to develop a method to investigate solvents. To reduce the sample evaporation, different shapes or materials of spacer can be used. Also, instead of using the liquid form of the sample, sample jellification could be used to prevent evaporation.
BIBLIOGRAPHY


