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MODELING, FABRICATION AND CHARACTERIZATION OF A BIO-MICRO THERMOELECTRIC DEVICE FOR HIGHLY LOCALIZED TEMPERATURE CONTROL

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

By
Aparna Prabhakar
B.E., Visveswaraya Technological University, India, 2003
August 2006
Dedicated to my parents

“They gave me life and taught me to love”
Acknowledgements

The dictionary defines graduation as the successful completion of a program of study, but, for me it means a lot more. To me, it is an accomplishment of a cherished dream, a first step towards progressing onto a new threshold in life. I have no idea what future holds in store for me, but I do know that I have a lot of people to thank for getting me till here.

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Abstract

There is an ever expanding interaction between the fields of micro-electromechanical systems (MEMS) and biology to develop devices to monitor, control and act on living systems. Particularly in the field of cryobiology, there is a need to monitor and control temperature at the cellular level. An important step towards achieving this aim is to fabricate an array of microscale thermoelectric actuators. As a first step for towards achieving such localized control of temperatures in cells and tissues, an array of individually addressable micro-thermoelectric coolers (µTECs) were modeled, characterized, and fabricated. Prefabrication experimentation and modeling were carried out to understand the behavior of the device. Two mathematical models, the lumped parameter model and finite element model, were used to identify important device parameters and dimensions. The organization of the proposed device was an array of 4 x 4 microscale (~10 µm) thermoelectric actuators, each of which was separated by a distance of 50 µm center-to-center and dimensioned so that each µTEC could measure or modulate the temperature in the neighborhood of a single cell. The prefabrication experiments showed that it was feasible to produce the TECs required for fabrication of the device through electrodeposition. Bismuth-telluride was electrodeposited to form the n-type and p-type leg elements of µTEC and the deposition was achieved by varying the cathodic potential. Hence, the material deposition development could focus on a single material system, yielding both n-type, and p-type pellets of TEC. The prototype devices were successfully fabricated with a modified multi-step LIGA (Lithographie, Galvanof ormung and Abformung) technique wherein a patterned positive photoresist and photomasks defined the geometry of the device. This enables high-density wiring required for the device.
In future, these µTECs will be embedded in Polymethylmethacrylate (PMMA) matrix to improve insulation. An artificial tissue (AT) system composed of Normal Human Dermal Fibroblat (NHDF) cells from stem cells will be grown on the device for experimentation wherein a PMMA sheet will act as an interface between the cooler and the embedded cells. The thermoelectric micro device thus developed will result in the unique capability of temperature manipulation and control on cellular scales (micrometers).
Chapter 1

Introduction

1.1 Motivation

Cryopreservation refers to storage of living organisms or tissues at ultra low temperatures, below -80 °C, such that it can be revived and restored to same living state as it was before being stored. Currently, only very simplistic organisms and small samples have been successfully recovered after cryopreservation. Should preservation of large and complex systems be accomplished, the benefits to medicine and science would be enormous. But before effectually doing so, it is essential to gain better understanding of the various underlying mechanisms involved, the most important of which is the role of temperature after freezing.

It is well known that at temperatures below 123 K, no changes of biological importance occur, and biological time stops in its tracks; the reason for this being that as temperature decreases below a certain point, the rates of all chemical reactions and biophysical processes will become too slow to affect cell survival. However, in cooling to these stages of ‘suspended animation’, cells and tissues are exposed to a range of dangerously low temperatures. This exposure occurs both in cooling to and thawing from storage temperatures. It is in these intermediate phases of cooling and re-warming that the phenomenon of “thermal shock” occurs. This sets up the possibility of unusual mechanical stress due to expansion and contraction of cell membranes thereby contributing towards cell death. There is no exact knowledge of either when this phenomenon occurs or why it occurs and the effects of the same on the biological system.
One way of doing acquiring better knowledge of this phenomenon would be to modulate temperature changes on the cellular level and study the subsequent physio-chemical changes that occur. As a first step towards modulating temperature changes at cellular level, arrays of individually addressable micro-thermo-electric-coolers (µTECs) were modeled, fabricated and characterized.

1.2 Approach
A prototype device consisting of a 4 x 4 array of µTECs was fabricated using a modified multi-step LIGA (Lithographie, Galvaniformung and Abformung) technique. The micro devices were separated by 50 µm center-to-center and dimensioned so that each device could measure or modulate the temperature in the neighborhood of a single cell. Mathematical models were used to identify important device parameters and dimensions. The resultant configurations were fabricated in a four mask process. The n-type and p-type leg elements of each individual µTEC were electrodeposited alloys of bismuth-telluride, Bi-Te. In parallel with the device fabrication, the relationships among the deposition potential, and the thermoelectric properties of Bi-Te films electrodeposited from a solution containing 10 mM Bi2O3, 10 mM TeO2 were also investigated. The device was successfully produced thereby opening the way to new prototyping with optimized steps in the processes. A second generation device will consist of a 100 x 100 array of µTECs, where the TEC films fabricated and characterized here, can be patterned to achieve optimal device characteristics.

1.3 Thesis Outline
The rest of the thesis is outlined as follows. Chapter 2 will present a brief overview of some of the main concepts involved including the three thermoelectric effects, operational and design theories of TECs and a general understanding of the various fabrication techniques
used. Chapter 3 will present the various methodologies used to identify the optimal layout of
the proposed μTEC device. The preliminary lumped 1-D parameter model and 3-D finite
element model (FEM) development and the corresponding model results will be discussed in
detail. In Chapter 4, the electrodeposition technique adopted to deposit n-type and p-type Bi-
Te elements will be discussed. It will focus extensively on the Rota-Hull technique used to
obtain the electrodeposition characteristics of Bi-Te the current densities ranging from 0.2 to
13.88 mA/cm².

The microfabrication techniques and the various photolithography steps involved in
device fabrication will be included in Chapter 5. The major challenges encountered in
fabrication of the prototype device and method and the results from characterization of the Bi-
Te elements will be described and discussed here. Lastly, Chapter 6 will present the
conclusions, and future work.
Chapter 2
Background and Significance

2.1 Introduction

The ability to control the temperature locally promises to pave the way to many new applications chief amongst which are low temperature banking of artificial and native tissues and organs. Localized control of temperature at the cellular level can be achieved by fabrication of a µTEC. The precise temperature control and spot cooling features of the proposed µTEC device make it an ideal choice for enabling temperature modulation of individual cells embedded in an extracellular matrix. However, to fully understand the working of such a µTEC some understanding of the science of thermoelectricity is required. The following sections provide a brief overview of some of the main concepts, which when combined together, provide a reasonable basis for an advanced understanding of the capabilities and limitations of the proposed device.

2.2 Thermoelectric Phenomenology

Thermoelectricity, as its name suggests, is characterized by simultaneous effects of both thermal and electrical phenomenon. To truly understand this phenomenon it is essential to start with the most fundamental concept of electricity and eventually move on to the principle behind operation of TECs with the emphasis on the concepts involved rather than the equations employed.

2.2.1 Fundamentals of Electricity

In order to understand the technology it is essential to understand the relationship between the flow of electricity and the existence of charge carriers. The charge carriers can be
defined as the physical component of a material that allows it to conduct electricity. According to electron theory, electricity is caused by the movement of electrons in a circuit. This occurs whenever there is a continuous conductive path across an applied voltage with the voltage providing an electromotive force which sets the electrons in motion causing a current to flow.

In a semiconductor material the movement of charge is facilitated by both electrons and holes. The semiconductors in general can be distinguished into two types, n-type (electron dominated) and p-type (holes dominated) based on the majority carriers. These majority carriers enable the flow of current. In essence, if these charge carriers can be forced to move, voltage and current flow can be created. One way to enable motion of charge carriers is a heat flux, which allows the charge carrier to carry electric charge. However, there are just three mechanisms by which such a coupling can be realized. The three effects, the Seebeck, Peltier and Thomson effects are the basis of thermoelectricity. All of these effects are closely related; the knowledge of the Seebeck coefficient as a function of temperature allows the calculation of the Peltier and Thomson coefficients\(^2,1\).

2.2.2 Seebeck Coefficient

Fig. 2.1 shows a schematic of a conductor with an applied temperature gradient. The electrons or holes, will thermally diffuse from the hot end to the cold end, and carry their charge with them. This charge builds up on the cold end and creates an electric field inside the sample. When the current generated by this electric field cancels the flow due to thermal diffusion, equilibrium is reached\(^2,1\).
The Seebeck coefficient is the ratio between this electric field and its temperature gradient. It can be thought of as a measure of coupling between the thermal and electrical currents in a material as given by Equation 2.1:

$$E = \alpha(T) \nabla T$$  \hspace{1cm} (2.1)

where, $\alpha(T)$ is the Seebeck coefficient, $\nabla T$ is the temperature gradient and $E$ is the electric field.

### 2.2.3 Peltier Effect

Fig. 2.2 shows a current passing through a junction between the two different materials held at constant temperature. The electric current will drag along the thermal current, the magnitude and direction of which depends on the Seebeck coefficients.

Figure 2.1: Schematic representation of the Seebeck effect.

Figure 2.2: Schematic representation of the Peltier effect.
If the Seebeck coefficients are different, the thermal energy enters and leaves the junction at different rates, leading to either heat generation or heat absorption at the junction. If there are two semiconductor materials, a p-type and a n-type, heat will be carried towards the junction and power will be generated \(^{2.2-2.3}\). The Peltier coefficient is a property of the junction, dependent on both of the materials, and can be defined as the ratio of the power generated at the junction to the current flowing through it (Equation 2.2).

\[
\Pi_{xy} I = Power \ evolved \ at \ junction
\]  

(2.2)

where \( I \) is the current flowing through the materials, \( \Pi_{xy} \) is the Peltier coefficient when current is flowing from material x to material y.

### 2.2.4 Thomson Effect

To understand the Thomson effect, consider a material with a current flowing through it and a temperature gradient applied. The thermal energy is either generated or absorbed all along the sample, since the Seebeck coefficient, a temperature dependent parameter, is different at different places along the sample. The sample can be thought of as a series of many small Peltier junctions, each of which is either generating or absorbing heat \(^{2.4}\). The Thomson coefficient, \( \tau \), is the ratio of the power generated per unit volume in the sample to the applied current and temperature gradient (Equation 2.3).

\[
\tau \ I \ \nabla T = Power \ evolved \ per \ unit \ volume
\]  

(2.3)

where \( I \) is the current flowing through the material and \( \nabla T \) is the temperature gradient.

### 2.2.5 Thermodynamic Relationships Between the Coefficients

The existence of the thermodynamic relationships between the three thermoelectric coefficients is of great importance in the theory of thermoelectric refrigeration. These relationships are known as Kelvin relations and can be derived rigorously using irreversible
thermodynamics. Using absolute thermoelectric coefficients the relationships are shown in Equations 2.4-2.5:

$$\tau = T \frac{d\alpha}{dT}$$ \hspace{1cm} (2.4)

$$\Pi = \alpha \ T$$ \hspace{1cm} (2.5)

The relationships have been proven experimentally as well as theoretically\textsuperscript{2,1-2,2}. Equation 2.5 is particularly important, since it enables the expression of the rate of Peltier cooling to the Seebeck coefficient, which is a material property.

2.3 Operational Theory of TECs

Amongst the three thermoelectric effects, TECs are based on the principle of the Peltier effect and typically use semiconductor materials which are optimized for Seebeck effect. The schematics demonstrated in Fig. 2.3 show the simplest possible examples. In Fig. 2.3a the n-type semiconductor with electrons as majority charge carriers is used to create the bulk of Peltier effect. With the DC voltage source connected as shown, the electrons will be repelled by the negative pole and attracted by the positive pole of the supply; this forces the electrons to flow in a clockwise direction. With the electrons flowing through the n-type material from bottom to top, heat is absorbed at the bottom junction, and actively transferred to the top junction. Similarly in a p-type material where holes dominate, heat is drawn towards the negative pole of the power supply and away from the positive pole of the power supply (Fig. 2.3b). Whenever an electrical conductor is generated between two different temperatures, the conductor transfers thermal energy from the warmer to the colder side. Furthermore, the physical process of transferring this heat also tends to move electrical charge
carriers within the conductor in same direction as the heat flow. This charge carrier movement can be used to generate the electrical current, if the circuit is effectively completed.

![Diagram](image)

**Figure 2.3:** Images from left to right are (a) a single n-type semiconductor element connected across a voltmeter (b) a p-type semiconductor element connected across a voltmeter.

However, if the conductor which completes the circuit is identical to the first conductor, if both conductors are either n-type or p-type, the flow of the thermal energy will create a potential for equal charge carrier movement in both conductors. Also, the potential for current flow in one conductor will oppose that in the other conductor, resulting in no net current flow. Two different elements, an n-type and p-type, are employed as a couple to facilitate a simple TEC (Fig. 2.4).

![Diagram](image)

**Figure 2.4:** Schematic diagram of a typical TEC. The n- and p-type elements are configured thermally in parallel, but electrically in a series circuit.
This configuration derives its basis from the electron theory which states that the concentration of electrons in any two materials is, in general, different at the same temperature\textsuperscript{2.5-2.6}. If two different metals are then placed in contact the electrons will diffuse from that metal in which the concentration of electrons is large (n-type) to that in which it is small (p-type). This diffusion will continue until the electrical field set up by the motion of electrons away from their compensating positive charges is sufficient to balance the difference of pressure due to the difference of concentration. This produces a temperature difference or application of a voltage, the Peltier effect, and forms the basis of operation for a simple TE cooler. In Fig. 2.4, the holes in the p-type element are repelled by the positive potential and attracted by the negative pole; the electrons in the n-type element are likewise repelled by the negative potential and attracted by the positive pole of the voltage supply. In the metal interconnects, the electrons are the charge carriers and when the electrons reach the p-type material, they simply flow through the holes. The electrons flow continuously from the negative pole of the voltage supply through the n-type element, through the metal interconnect, through the p-type element and back to the positive pole of the supply. However, due to the use of two different kinds of semiconductors, n-type and p-type, the charge carrier and heat all flow in the same direction through the TEC legs. The TEC consists of alternate n- and p-type semiconductor thermo-elements, which are connected in parallel thermally and electrically in series with metal connecting strips, sandwiched between two electrically insulating but thermally conducting plates. When an electric current is passed through such a device, heat is absorbed at one end and rejected at the other end allowing the TEC to act as a cooler.
2.4 Design Theory for TECs

2.4.1 Conventional Design Theory

The operation of the TEC can also be described mathematically and device performance can be calculated using the conventional design theory. This is done by considering an idealized TEC obtained by making the following assumptions: (1) TEC elements have zero electrical resistance (2) the branches are of height \( h_p \) and \( h_n \) and of cross-sectional area \( A_p \) and \( A_n \) where in general, the ratios \( h_p/A_p \) and \( h_n/A_n \) are different from one another (Fig. 2.5); (3) steady-state current is unaffected by the shape of the branches; (4) Heat is transferred from the heat source to heat sink solely by conduction along the branches; (5) the heat is pumped from the source at an absolute temperature, \( T_i \) to the heat sink at temperature \( T_2 \) by means of the Peltier effect.

2.4.1.1 Cooling Power

It is important to note that the Peltier and Seebeck effects depend on bulk rather than the surface properties of the materials. When an electric current flows through a conductor it transports heat. Due to the Peltier effect, the heat liberated or absorbed due to passage of current in the given conductor is different from the heat transported in another conductor. In
the two branches, the heat transported from the source to the sink is modeled by Equations 2.6 and 2.7:

\[ q_p = \alpha_p I \left( T - \kappa_p A_p \frac{dT}{dx} \right) \]  
\[ q_n = \alpha_n I \left( T - \kappa_n A_n \frac{dT}{dx} \right) \]  

where \( \alpha \) is the absolute Seebeck coefficient, \( \kappa \) is the thermal conductivity, \( T \) the absolute temperature, and \( \frac{dT}{dx} \) is the temperature gradient along the elements. The subscripts \( p \) and \( n \) signify p-type and n-type semiconductors. The Peltier coefficient is given by \( \alpha T \) (Equation 2.5).

The rate of heat generation per unit length within each branch, due to the Joule effect is given by \( I^2/A\sigma \), where \( \sigma \) is the electrical conductivity. This heat generation implies that the temperature gradient is nonlinear and gives Equations 2.8 and 2.9:

\[ -\kappa_p A_p \frac{d^2T}{dx^2} = \frac{I^2}{A_p \sigma_p} \]  
\[ -\kappa_n A_n \frac{d^2T}{dx^2} = \frac{I^2}{A_n \sigma_n} \]  

Setting the boundary conditions so that

\[ T = T_c \quad @ \quad x = 0 \]  
\[ T = T_h \quad @ \quad x = h_p \text{ or } h_n \]  

Equations 2.8 and 2.9 are combined with Equations 2.6 and 2.8 to obtain the heat flow at \( x = 0 \) (Equations 2.12-2.13),

\[ q_p = \alpha_p I \left( T - \frac{\kappa_p A_p}{h_p} (T_h - T_c) \right) - \frac{I^2 h_p}{2A_p \sigma_p} \]
\[ q_n = \alpha_n I T - \frac{\kappa_n A_n}{h_n} (T_h - T_c) - \frac{I^2 h_n}{2 A_n \sigma_n} \]  

(2.13)

where, \( T_c \) is the cold side temperature while \( T_h \) is the temperature at the hot side of the TEC.

Adding, \( q_p \) and \( q_n \) at \( x = 0 \), the cooling power \( Q \) at the heat source can be given by Equation 2.14:

\[ Q = (\alpha_p - \alpha_n) I T_c - \frac{1}{2} I^2 R - k_{TE} (T_h - T_c) \]  

(2.14)

where the electrical resistance, \( R \) and thermal conductance, \( k_{TE} \) of the two branches are

\[ R = \frac{h_p}{A_p \sigma_p} + \frac{h_p}{A_n \sigma_n} \]  

(2.15)

\[ k_{TE} = \kappa_p \frac{A_p}{h_p} + \kappa_n \frac{A_n}{h_n} \]  

(2.16)

The equations were derived by applying the simplifying assumption that the TEC material parameters \( \alpha, \kappa \) and \( \sigma \) are invariant with temperature\(^{2.8}\).

2.4.2.2 Figure of Merit

When Equation 2.14 is inspected, it can be seen that the Peltier cooling term \( (\alpha_p - \alpha_n) I T_c \) varies linearly with the electrical current \( I \), while the Joule heating term \( I^2 R/2 \) varies as the square of the current. There must be a particular current \( I \) at which the cooling power reaches its maximum value. This current is found by setting \( dQ/dI = 0 \) and finding the maximum current \( I_{max} \) given in Equation 2.17:

\[ I_{max} = \frac{(\alpha_p - \alpha_n) T_c}{R} \]  

(2.17)

However, although the current is a major limiting characteristic in the final operation of the TEC, the overall thermoelectric performance is limited by its figure of merit, \( Z \), given by Equation 2.18:
\[ Z = \frac{(\alpha_p - \alpha_n)^2}{K_{1e}R} \]  

(2.18)

Since \( Z \) includes terms that involve the relative dimensions of the TEC elements, it is not a characteristic of a pair of materials but, rather, of a particular couple. Therefore, for a given pair of elements the highest \( Z \) is reached when the product \( \kappa R \) is minimized. The condition is shown in Equation 2.19:

\[ \frac{h_n A_p}{h_p A_n} = \left( \frac{\kappa_n \sigma_n}{\kappa_p \sigma_p} \right)^{1/2} \]  

(2.19)

If Equation 2.19 is satisfied, the figure of merit takes the form shown in Equation 2.20:

\[ Z = \frac{(\alpha_p - \alpha_n)^2}{\left[ \left( \kappa_p / \sigma_p \right)^{1/2} + \left( \kappa_n / \sigma_n \right)^{1/2} \right]^2} \]  

(2.20)

To achieve the best thermoelectric performance it is essential for the designed TEC to satisfy Equation 2.17 and choose materials with the highest figure of merit. This conventional design theory outlines the basic analytical formulae for thermoelectric design and forms the basis for all the further design and optimization techniques developed for TEC.

2.4.2 Optimization of TEC Performance

In conventional design theory it was assumed that the Seebeck coefficient, \( \alpha \), the thermal conductivity, \( \kappa \) and the electrical conductivity, \( \sigma \), of the TEC material were invariant with temperature. In practice this is never the case and numerical computation must be done for modeling, designing, and optimizing TECs using parameters measured over the temperature range in question. Based on this conventional design, a “temperature averaging” methodology was developed \(^{2.12-2.14}\) for TEC materials in an attempt to partially account for the effects ignored by the conventional design theory. Inaccuracies inherent in the
“temperature averaging” methodology were ameliorated by Yamanashi\textsuperscript{2,15, 2,17} and Chen and Schouten\textsuperscript{2,16} who derived dimensionless entropy equations that formed a closed form expression for the TEC with heat sinks. This dimensionless entropy model was later used to analyze the design variables of a TEC, serving as the basis for most of the design improvements for macro-TEC designs\textsuperscript{2,18-2,22}.

However, these mentioned design methodologies disregard the effect of the thermal and electrical contact resistances. The assumption of negligible thermal and electrical contact resistance is reasonable for macro TECs (>100 µm) but its inclusion is essential to accurately model µTECs\textsuperscript{2,23-2,25}. A recent model of µTEC performance accounts for contact resistances \textsuperscript{2,23}, but was not applicable when the object to be cooled or heated, a passive load, was comparable in size with the µTEC. In the present study these drawbacks were addressed and incorporated in the design of a cooler with a passive load of size comparable to the cooling device.

2.5 Thermoelectric Material Selection and Fabrication

The performance of a TEC material is estimated by its figure of merit, $Z$ and the dimensionless figure of merit given by the product of $Z$ and $T$, the operating temperature. The material with high $Z$ or $ZT$ shows high performance as TEC material. In order to obtain high performance material it is required to have large $\alpha$, small $\rho$ and low $\kappa$ (Equation 2.18). Up to the present the most efficient TEC materials remain the alloys of bismuth-telluride\textsuperscript{2,3} (Bi-Te)\textsuperscript{2,26}, which were selected for the fabrication of the p-n junction of the proposed µTECs.

However, the fabrication processes of the TEC materials affect the essential figure of merit. So, choosing the right process to suit the required performance and fabrication is necessary. Alloys of Bi-Te and its solid solution films have been fabricated by using a number
of techniques, such as sputtering\(^{2.27-2.28}\), metal-organic chemical vapor deposition\(^{2.29-2.30}\), molecular-beam epitaxy\(^{2.31-2.32}\), evaporation\(^{2.33}\) or electrodeposition\(^{2.34-2.37}\). The electrodeposition technique offers the lowest cost method for high-quality metal, alloy, and semiconductor films and makes it possible to control the particle growth rate via changing electrolyte, concentration, current density, and applied potential. This alleviates the problem of non-stoichiometry, making introduction of doping agents unnecessary. It is possible to modify the common carrier, the electrolyte solution, of Bi-Te alloy to give either n-type or p-type semiconductor material\(^{2.26}\). The n-type or p-type semiconductor can be achieved by adjusting the percentage of tellurium or bismuth; tellurium rich gives n-type, bismuth rich gives p-type, wherein Bi-Te with a stoichiometric composition ratio of Bi\(_2\)Te\(_3\) is electrically neutral.

### 2.6 Fabrication Methodology

Commercial TEC module technology is ill-suited for the development of miniaturized devices due to mechanical and manufacturing constraints for thermo-element dimensions (100-200 µm minimum device height and footprint area). This bulk fabrication technology makes integration with microelectronics difficult resulting in high packaging costs\(^{2.39}\). Furthermore, the reliability of packaged modules employing a TEC is usually limited by the reliability of the cooler itself\(^{2.40}\). A solution to these problems is to shift from bulk thermo-elements to integrated thin film coolers which make the fabrication of \(\mu\)TECs possible. The greatest advantage of the thin film coolers is the gain in cooling power density which is inversely proportional to the height of the thermo-elements. In addition, the thin film coolers can also be made in large quantities using well known integrated circuit batch fabrication methods resulting in lowered costs and greater reliability. The first commercial product with
microfabricated Bi$_2$Te$_3$ was presented by DTS$^{241}$. The n- and p-type TEC materials were deposited with a thickness of a few millimeters onto a foil and structured by wet etching techniques$^{242}$.

Fleurial $et$ $al.$$^{243-244}$ showed the potential of TEC devices and determined that the main technological problems were the need for high thermally conductive substrates, and low ohmic contacts between the electrodes and the semiconductor material. Focusing on applications at room temperature V–VI-compounds (Bi-Te) were developed [$^{244}$]. The thermoelectric compounds were deposited using electrochemical methods. The vertical structures were defined during the electrochemical growth by 10 $\mu$m thick photolithographic masks. No device properties have been reported. Venkatasubramanian $et$ $al.$$^{245}$ reported net cooling of 32 K at room temperature for a p-type superlattice device where $ZT$ was determined to be around 2.4.

2.6.1 Microelectromechanical System (MEMS) Based $\mu$TEC

In general, two types of MEMS $\mu$TEC device configurations have been fabricated. In the first type, the cross-plane device, current and heat flow perpendicular to the film plane. In the second type of device, the in-plane device, the heat and current flow parallel to the film plane. The cross-plane devices face the challenge of establishing a large temperature difference across thin films of a few $\mu$m thickness while the in-plane devices face the issue of heat leakage through the supporting substrate. Since, the drawbacks in the in-plane technique can be easily overcome; most of the initial fabrication efforts were focused on producing in-plane microdevices $^{246}$. However, the substrate in the in-plane device acts as a thermal short which reduces the performance of the TEC and renders it unsuitable for applications which
require manipulation of the temperature of microsized subjects. For manipulation of temperatures at the microscale it is desirable to use a cross-plane device.

As a first step towards achieving such a cross-plane device Huang et al.\textsuperscript{2.47-2.48} fabricated 40 µm deep Bi\textsubscript{2}Te\textsubscript{3} microstructure via LIGA (Lithographie, Galvanoformung and Abformung) technique and formed the basis for fabrication of high-aspect ratio thermoelectric material posts. Recently, Snyder et al.\textsuperscript{2.49} deposited thick films (20 µm) of telluride compounds using electroplating for fabrication of cross-plane TECs and presented a maximum cooling effect of 2 K. However, they did not report on the material optimization and the relationship among the deposition conditions, composition, electrical performance of the films and their performance as a device. The material properties of the device were first reported by Bottner et al.\textsuperscript{2.50}. However, here the TEC was an in-plane device and the thermoelectric material was fabricated using sputtering, which makes this methodology ineffective to produce high-aspect ratio devices due to its relatively slow deposition rates. To fabricate a TEC truly capable of achieving a localized control of temperature it is essential to be able to optimize the material characteristics and deposition techniques.

\textbf{2.7 Actuating Bio-Thermal Phenomena at Cellular Level}

As mentioned earlier, the ultimate aim of this work was to achieve a localized control of temperature at the cellular level. However, to truly understand the significance and the impact that such a work may have on the current research scenario it is essential to understand few basic concepts. The following sections attempt at doing so and also highlights the impact that the fabrication of such an integrated biological and thermal system may have in the field of cryobiology.
2.7.1 Biological Effects of Ice Formation

The inherently complex nature of cells and the inability to decouple the effects of diverse insults suffered by the cell during cryopreservation, have made it exceedingly difficult to determine conclusively what exact mechanisms are responsible for cell injury during freezing and thawing. However, there is significant evidence for correlation between the cell injury and intracellular ice formation (IIF). One universal experimental observation is that IIF occurs “only” in the presence of extracellular ice and various causes like membrane failure, the pore hypothesis and plasma membrane catalization have been suggested as explanations. It is known that IIF occurs between -5 and -20 °C, although the exact intracellular ice nucleation temperature at which cell death occurs after extracellular ice formation is yet to be determined.

2.7.2 Future Research Methodology

The ATs proposed to be used will be prepared from a method adapted from Tuan et al., wherein the collagen gels are prepared from Vitrogen (Cohesion Technologies, Palo Alto, CA), at concentration of 2.0 mg/mL. Human foreskin fibroblasts (HFFs) will be suspended in the initial collagen-forming solution after which the suspension will be placed on a tissue culture plate. A more detailed description of the procedure is provided by Devireddy et al. Chemical agents called CPAs, known to improve the efficacy of cryopreservation procedure, will be equilibrated with ATs. For the purposes of this study, freezing media reported by Advanced Tissue Sciences (La Jolla, CA) will be used.

2.8 References


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2.53 S. Englich, Ch.Korber, P. Schwindke and G. Rau, “Correlation between intracellular nucleation temperatures and cell damage of human lymphocytes in the presence of various concentrations of DMSO determined by cryomicroscopy,” Cryoletters, 7, 13 (1986).


Chapter 3

Bio-Thermal System Modeling

3.1 Nomenclature

\( ZT \)  
Dimensionless figure of merit

\( \alpha(T) \)  
Temperature dependent Seebeck co-efficient (VK\(^{-1}\))

\( \kappa(T) \)  
Temperature dependent thermal conductivity (W \(\mu\)m\(^{-1}\)K\(^{-1}\))

\( \sigma(T) \)  
Temperature dependent electrical conductivity (\(\Omega^{-1}\)\(\mu\)m\(^{-1}\))

\( T \)  
Absolute temperature of the system (K)

\( Q \)  
Heat flow rate at the cold junction (W)

\( T_c \)  
Cold junction temperature (K)

\( T_h \)  
Hot junction temperature (K)

\( T_{amb} \)  
Ambient temperature (K)

\( \Delta T \)  
Temperature difference equivalent to \( T_h - T_c \) (K)

\( I \)  
Current through the thermoelements (A)

\( R \)  
Electrical resistance of the thermoelectric cooler (TEC) module (\(\Omega\))

\( V \)  
Voltage across the thermoelements (V)

\( Q_h \)  
Heat rejection of the TEC (W)

\( Q_c \)  
Cooling capacity of the TEC (W)

\( A \)  
Cross sectional area of the thermoelements (\(\mu\)m\(^2\))

\( h \)  
Height of the thermoelements (\(\mu\)m)

\( L \)  
Thickness of the thermoelements (\(\mu\)m)
Width of the thermoelements (µm)

Height of the metal interconnect (µm)

Copper thermal conductivity (bottom connections) (W µm⁻¹K⁻¹)

Gold thermal conductivity (Top interconnect) (W µm⁻¹K⁻¹)

Lower ceramic end plate (Alumina) thermal conductivity (W µm⁻¹K⁻¹)

Upper ceramic end plate (Alumina) thermal conductivity (W µm⁻¹K⁻¹)

Ice thermal conductivity (W µm⁻¹K⁻¹)

electrical contact resistance (Ω)

Spacing between the TEC posts (thermoelements) (µm)

Spacing between the micro thermoelectric coolers (µTEC) (µm)

3.2 Design Concept

To predict the performance of a single stage µTEC (Fig. 3.1) it is essential to determine the optimal operating conditions and predict the interplay among the various parameters. To do so the identification and variation of certain critical design variables are necessary. The cooling performance of the TEC materials is determined by the dimensionless figure of merit, ZT defined by the relation 3.1:

\[ ZT = \frac{\alpha(T)^2 \sigma(T)}{\kappa(T)} T \]  \hspace{1cm} (3.1)

Note that \(\alpha(T), \kappa(T), \sigma(T)\) are all temperature dependent parameters making it necessary to adapt the effective temperature dependent properties of the TEC material to the temperature range of application. Among the various TEC materials, doped semiconductors based on bismuth telluride (Bi-Te) have the best performance. Since, these Bi-Te alloys have
the best figure of merit $ZT$ (close to 1) at room temperature $^{3.1-3.2}$, their properties were utilized in the model. These temperature dependent properties of Bi-Te alloys were obtained by curve-fitting the standard curves$^{3.2}$ using MS excel and yielded the relationships in Equations 3.2-3.4:

$$\alpha(T) = -0.001 \ T^2 + 0.937 \ T + 29.684 \quad (3.2)$$

$$\kappa(T) = 0.0004 \ T^2 - 0.231 \ T + 53.21 \quad (3.3)$$

$$\sigma(T) = \frac{1}{(4.3516 \ T - 279.9)} \quad (3.4)$$

In order to set the framework for the numerical model used here it is essential to review some of the basic conventional TEC equations$^{3.1-3.2}$. The heat balance at the cold junction of the TEC leg is given by Equation 3.5:

$$Q = \alpha(T) I T_c - \frac{1}{2} I^2 R(T) - k(T) \Delta T \quad (3.5)$$

The first term in the right hand side of the equation represents the Peltier cooling effect, the second the Joule heating due to resistive losses, and the last term represents the amount of heat leaking back from the hot junction to the cold side due to finite thermal conductance of the material. The voltage across the TEC element is given by Equation 3.6:

$$V = \alpha(T) (T_h - T_c) + I \ R \quad (3.6)$$

Also, the heat rejected by the hot side of the TEC leg element, $Q_h$, can be given by Equation 3.7:

$$Q_h = Q + IV \quad (3.7)$$

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This yields Equation 3.8:

\[
T_c = \frac{T_h - (\alpha(T) I T_h + \frac{I^2 R}{2} - Q_h)}{k_{TE}}
\]  

(3.8)

The terms \(R\) and \(k\) of the TEC are dependent on the material properties \(\alpha, \kappa\) and \(\rho\) (Equation 3.8):

\[
R(T) = \frac{L}{A \sigma(T)}
\]  

(3.9)

\[
k(T) = \kappa(T) \frac{A}{h}
\]  

(3.10)

However, in this “closed form” conventional design theory the equations were derived by applying the simplifying assumption that the TEC material parameters \(\alpha, \kappa\) and \(\sigma\) are invariant with temperature. This assumption only holds for very small \(\Delta T\) differentials and various numerical methodologies have been derived to overcome these inadequacies\(^3\).\(^3\)\(-3.4\).

These derived methodologies have been very useful to define thermoelectric phenomena and provide insight into thermoelectric cooling effects. Nevertheless, these methods while useful do not provide an accurate analysis of \(\mu\)TEC performance. This is due to the neglect of both the electrical and thermal contact resistances in these models\(^3\).\(^5\)\(-3.6\). While reasonable for long TEC elements\(^3\).\(^2\) (>100 \(\mu\)m), as the height of the leg elements scale down these effects become predominant and eventually become the main determinants of the performance of the system\(^3\).\(^7\)\(-3.8\). The effect of the contact resistance on the scaling of micro coolers have been studied before\(^3\).\(^7\)\(-3.8\), but these results are not directly applicable to the biological application of \(\mu\)TEC since the object to be cooled here, an artificial tissue system, is a passive mass load with a size comparable to the proposed \(\mu\)TECs. This affects the minimum achievable temperature. To further understand the influence of the electrical contact resistances on the
proposed device, a performance analysis of the integrated cooling cell and a single stage μTEC using a lumped parameter model were performed.

The lumped parameter model guided selection of the preliminary design dimensions, but it did not reflect the exact behavior of the proposed TEC array system. To do so, it is essential to study the effects of the interference of adjacent TECs. There is a possibility that cell temperature modulation over one TEC could affect the modulation at another. An analysis of the interference effects would shed light on the individual addressing of each cell. Ideally, if the cell modulates temperature at one TEC, the adjacent cell modulations should be almost equivalent under similar design conditions due to constant interactions between the adjacent cells. In the absence of previous studies the phenomenon of the effect of the μTECs proximity on the heat transfer through the system remains unexplored. An attempt to understand this was done by the development of a thermal system model in ANSYS® (Version 9.1, ANSYS, Inc., Canonsburg, PA). It is important to note that the optimized design parameters obtained from the lumped parameter model were used as a preliminary model that analyzed further the single stage thermal system in ANSYS.

3.3 Lumped Parameter Model

The various parameters that can affect the μTEC performance are summarized below.

- Geometrical parameters: $h$, $L$, $w$, $h_{me}$
- Interfacial effects: $r_{con}$
- Device arrangement: $\delta_{posts}$, $\delta_{TEC}$

The final device arrangement was evaluated using a 3D finite element (FEA) model. The lumped parameter approach was taken for the evaluation of geometric parameters and interfacial effects, aiming for the design, fabrication and characterization of optimized μTEC
An optimal geometry was predicted using the thermoelectric properties reported given by in Equations 3.2-3.4 and the affect of the interfacial effects were described.

3.3.1 Model Development

The model development followed the approach of Yamanashi\textsuperscript{3.9-3.11}, based on a set of rate equations describing one-dimensional thermal dynamics through all of the intermediate layers, including the ceramics end plates and metal interconnects. Adiabatic boundary conditions were applied to four vertical side surfaces of the volume. Fig. 3.1 shows that there is symmetry in the single stage TEC, indicating the adequacy of considering only a single TEC element (Fig. 3.2) sandwiched between two ceramic end plates. The rest of the area between the substrates was assumed to be vacuum which allowed the representation of periodic boundary conditions\textsuperscript{3.2}.

Figure 3.1: Schematic of a single TEC.
Any heat flow between the TEC and the ambient surroundings in the direction perpendicular to the line of symmetry (Fig. 3.1) was ignored and only the heat transfer along the line of symmetry which accounted for the cooling capacity in the cold end and heat rejection in the hot end was taken into consideration. Various design conditions for the proposed \( \mu \)TECs were analyzed to obtain optimum performance. Two “free” variables were arbitrarily chosen: (1) a constant temperature difference, \( \Delta T \) or a constant heat load, \( Q \) and (2) the base temperature, \( T_h \). The problem formulation also allowed accounting for the temperature dependence of thermoelectric parameters and time-temperature dependence properties of the TEC materials. Initially the model was solved by setting all the TEC material variables (i.e. \( \alpha, \kappa, \sigma \)) at 300 K (i.e. 27 °C). This newly obtained temperature distribution was then used to specify the variables \( \alpha, \kappa, \sigma \) at each level yielding a new temperature distribution. This procedure was repeated until the transient time of 10 minutes was reached.

A first law analysis of heat transfer from the cold junction to the hot junction of the TEC leads to a set of modified energy balanced equations (Equations 3.11-3.15):\[
Q + k_{ice}(T_{amb} - T_c) - k_{up\_cer}(T_c - T_1) = 0 \\
n_1 = -\kappa_{up\_cer}(T_c - T_1) + k_{Au}(T_2 - T_1) = 0 \\
\alpha I T_2 - \frac{1}{2} I^2 (R + \frac{r_{con}}{2}) - k_{Au}(T_1 - T_2) - \kappa_{TE}(T_3 - T_2) = 0 \\
\alpha I T_3 - \frac{1}{2} I^2 (R + \frac{r_{con}}{2}) - k_{TE}(T_2 - T_3) - k_{cu}(T_4 - T_3) = 0 \\
k_{cu}(T_3 - T_4) + k_{low\_cer}(T_h - T_4) = 0
\]
Figure 3.2: Temperature distribution in a TEC.

$T_1$, $T_2$, and $T_3$, $T_4$ are the junction (lump) temperatures above and below $T_c$ and $T_h$ respectively.

The cell to be subjected to temperature modulation by the µTEC was simulated as a heat generation input in its frozen state, ice, so the uppermost layer in the model represented ice with a thermal conductivity, $k_{\text{ice}}$ (Fig. 3.2). An exact treatment of the coexistence of the thermal and electrical contact resistance requires the detailed knowledge of where the heat is generated due to the electrical contact resistance and whether the heat is transferred across the interface. Equations (3.10) and (3.11) imply that the heat due to the electrical contact resistance is generated in the thermoelectric elements and is equally distributed to the cold and the hot side.

The problem formulation involved a few assumptions; chief amongst which were (1) presumption of either $Q$ or $\Delta T (T_h - T_c)$ value; (2) neglect of the Joule and the Peltier heating of the interconnect (assumed to be negligible when compared with the TEC element); (3) and
treatment of the heat sink as a node at constant temperature. Depending on the final packaging of the µTEC system there may be convective, conductive and radiative losses laterally from the elements. As a limiting case it was assumed that these losses can be made negligible. These losses were included later in the FEA model and the results obtained from that model closely matched the lumped parameter model, indicating the validity of the neglect of these losses.

3.3.2 Results and Discussion

The effect of varying the following device parameters on the performance of µTEC was studied:

- TEC leg element dimensions
- Height of the metal interconnects
- Electrical contact resistance
- Operational current limitation
- TEC leg shape

The maximum temperature gradient was experienced in the TEC element region (Fig. 3.3); making the TEC leg dimensions an important design parameter. For ease in modeling, in both the lumped and FEA models, the TEC elements were assumed to be cubic in shape with its lateral dimension, the width, equivalent to the length of the each individual TEC element. Only two TEC element parameters were varied: (a) height of the TEC element and (b) thickness of the TEC element (Fig. 3.1). To understand the influence of the TEC dimensional parameters, the nominal device dimensions which were well within the fabrication and application limitations were initially used (Table 3.1). After establishing baseline performance the required design parameters were varied and
analyzed by the parametric method. The hot junction temperature, $T_h$ was maintained at 300 K for all of the studies.

![Graphical representation of the expected temperature distribution.](image)

**Figure 3.3:** Graphical representation of the expected temperature distribution.

**Table 3.1:** Initial device dimensions for a single TEC leg element (all values are in µm’s).

<table>
<thead>
<tr>
<th>Component</th>
<th>Height</th>
<th>Width</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell (Ice)</td>
<td>3</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>Upper end plate (Alumina)</td>
<td>5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Upper Interconnect (Gold, Au)</td>
<td>To be determined</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>TEC leg element (Bi-Te)</td>
<td>To be determined</td>
<td>To be determined</td>
<td>To be determined</td>
</tr>
<tr>
<td>Lower Interconnect (Copper, Cu)</td>
<td>To be determined</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Lower end plate (Alumina)</td>
<td>10</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Fig. 3.4 gives the $\Delta T$, ($T_h - T_c$), as a function of current for zero external heat load (i.e. $Q = 0$). Due to large heat leakage through the air gap between the two ceramic end plates the increase in the height of the TEC element increases the heat load at the cold junction, leading
to a small junction temperature decrease. This implies that there is an inverse proportionality between the height of the leg element and $\Delta T$. Therefore in order to achieve better temperature drops the TEC leg element height should be as small as possible. However, the smallest achievable leg height is limited by the ability to plate the alloy of Bi-Te uniformly in a recess. Through experimentation, it was determined that the most uniform deposition occurs at the minimum height of 20 µm, so the height of the TEC leg was fixed at 20 µm. Further analysis of the TEC was done with this fixed height.

Fig. 3.4 shows that at a height of 20 µm the maximum achievable $\Delta T$ is around 4 K. This effect of a small temperature decrease due to the fixed height of 20 µm could be minimized by varying the thickness of the leg element. Increasing the thickness of the TEC element increases the conductance which causes the heat leakage load to decrease, so the junction temperature increases (Fig. 3.5). In order to achieve a larger temperature drop the TEC element length should be as large as possible. However due to the proposed end application of modulating local temperatures in cells in tissues there is a design constraint on the maximum thickness of the µTEC. The model cells will be spherical shaped NHDF (Normal Human Dermal Fibroblast) cells that are in the order 30-50 µm in diameter. This implies that the total contact cross sectional area of each individual µTEC, including the thickness of the two TEC elements and space in between the two thermoelectric legs in each µTEC, should be a maximum of 30-50 µm. The thickness of each element was restricted to a maximum of 10 µm. It was found that an optimal cooling is achieved when the ratio between the TEC element height and thickness was around 1.8. Hence, for a thickness of 10 µm, the TEC leg element height should be between 15-20 µm.
After fixing the dimensions of TEC element (height 20 µm, thickness 10 µm, width 10 µm) it was also essential to explore the effect of the metal interconnect height on the µTEC system performance. To establish its influence on the cooling rate its effect under ideal conditions, neglecting electrical and thermal contact resistances, were studied. It was observed (Fig. 3.6) that the temperature drop increased as the height of the interconnect decreased. However, the minimum height of the interconnect should be such that it allowed for a proper passage of current through the two TEC elements. To do so it should be at least 1/10 of the TEC leg element height. This is the standard dimensional trend followed by the commercial macro-TEC systems like Melcor thermal solutions and TE tech. So the height of the interconnects was selected to be at 2-3 µm.

However, the electrical contact resistance also becomes a major determinant of the achievable temperature drop at micro scale\(^ {3.7-3.8}\), less than 100 µm. To achieve the actual device configuration, the electrical contact resistance was varied and corresponding trend of temperature drop were established. A small increase in contact resistance, of the order 10\(^{-6}\),
reduced the achievable temperature drop (Fig. 3.7) and could prove to be critical for micro-
device functioning. Since the exact value of this resistance cannot be determined and depends
on the final fabrication process it is supposed that the actual temperature drop will be less than
estimated.

![Figure 3.5](image1.png)

**Figure 3.5**: Influence of the thickness of the TEC system at zero external heat load.

![Figure 3.6](image2.png)

**Figure 3.6**: Influence of the height of the metal interconnects at zero external heat load.
The parametric study investigated the influence of the geometry on the device performance and helped obtain and fix the device dimensions in accordance with the proposed application. Since the µTEC is a thermoelectric device it was essential to set a range of operational current values within which the TEC would function without electrical breakdown. As evident from the Equations 3.10-3.11 the Peltier cooling term $\alpha I T$ varies linearly with current whereas, the Joule heating term $I^2 R/2$ varies as a square of the current indicating that the existence of a particular current, $I$, at which the cooling power reaches its maximum value. At this current the Joule effect begins to dominate through $I^2 R$ power losses, a function of $L/A$, overcome the heat losses, resulting in a constant rise in temperature. This constant temperature rise in the device instead of the expected temperature decrease is called the breakdown of the µTEC and the current at which this breakdown occurs is known as Joule breakdown. The maximum operational current should be less than the Joule breakdown current. Mathematically, the Joule breakdown current can be described as the value of current at which the $\Delta T$, $(T_h - T_c)$, becomes negative. In Figs. 3.4, 3.5 and 3.6 the Joule breakdown for the proposed device dimensions occurs at approximately 0.046 A, 46 mA. So, the applied current value should be less than 46 mA.

There may be further limitations on the applicable current for microscale TECs unlike with macroscale TEC systems. The existence of such limitations on current could explain why the previously designed and fabricated µTEC systems [3.12-3.16] using Joule breakdown current as the limiting design parameter functioned less effectively than their predicted design values. This failure may result from another current value, well below the Joule breakdown current, beyond which the ceramic end plates and the metal interconnects fail to support a beneficial temperature gradient (Fig. 3.8).
A temperature gradient can be defined as beneficial when there is a monotonic decrease in temperature on moving progressively from the hot to cold junction in a TEC. This value of current at which a beneficial temperature gradient is no longer maintained was called the “Secondary breakdown current” and it could be related to the existence of phonon-scale defects. Further experimental work is necessary to verify this. When the applied current
exceeds the secondary breakdown value, the breakdown is limited only to the ceramic end plates and metal interconnect areas with the TEC leg element functioning as expected (Fig. 3.8), therefore, the system still operates and experiences a drop in temperature. However, keeping the value of the current below this breakdown current could help obtain the operational results closer to the estimated values unlike the previously designed and fabricated µTEC systems\textsuperscript{3,12-3,17}. For the proposed prototype dimensions it was observed that this secondary breakdown current was 1.2 mA (Fig. 3.9). It is proposed to vary the current over the range of 0.1-1 mA during the operation.

For ease of analysis by both lumped parameter and FEA methodology it was assumed that the TEC leg element was a cubic. However, during fabrication it was found that due to the inability to etch straight walls at the same etch rates during fabrication it was easier to fabricate cylindrical elements. The effects of different element shapes, both cubic and cylindrical, on the performance of the µTEC system were modeled. At higher values of operational current there was a marked difference in the device performance with different element shapes (Fig. 3.10). However for the operational range of 0.1-1 mA this effect was almost negligible and the cubic TEC leg element shape was assumed for the FEA analysis.

The parametric study helped improve understanding of the thermal performance as a function of the system design and obtain a range of operating conditions. However, assumptions and neglect of certain effects in the model meant that the model was not an exact prediction of the µTEC system behavior. The assumptions were (1) presumption of either $Q$ or $\Delta T$, $(T_h - T_c)$ value; (2) the neglect of Joule and the Peltier heating of the interconnect (assumed to be negligible when compared with the TEC leg element); (3) treatment of the heat sink as a node at constant temperature. In addition to these assumptions the model also
did not include the following effects: (1) thermal contact resistance; (2) the effect of leg spacing between the TEC legs; (3) radiation effects; and (4) lateral effects. Also, since the proposed instrument will eventually consist of an array of TECs adjacent to each other it was essential to study the effect of adjacent TECs on the device performance.

Figure 3.9: Secondary breakdown current values at different $\Delta T$.

Figure 3.10: Performance variation with TEC leg shape design.
3.4 3D-Finite Element Model

To model self-consistently thermal and electrical properties of a complete device structure and study the effect of the proximity of TECs on heat transfer through the system, a three-dimensional (3D) finite element model was developed and simulated in ANSYS® (Version 9.1, ANSYS, Inc., Canonsburg, PA).

3.4.1 Model Development

The 3D thermal system model constructed within ANSYS assumes a symmetrical system with 7 TEC pairs, a simple ramped current pulse in addition to transient-state bias of heat conduction, Joule heating and thermoelectric cooling were included alongside non-ideal effects due to contact resistances, and heat generation in the interconnects. The finite thermal resistance between the object to be cooled, ice, and the TEC was also included in the model. The model validation was done using data from commercially available macro TEC systems. The available performance data were matched consistently with the estimates obtained from the ANSYS FEA model. The optimized µTEC element dimensions obtained from the lumped parameter model were used. To make the model as close to the final configuration as possible, the whole µTEC system was assumed to be embedded within a block of poly methyl-methacrylate (PMMA). It was assumed that leaving the PMMA used during initial fabrication steps would not only provide structural stability to the system but also allow accurate modeling of the conduction between the two TE leg elements. The results from the ANSYS model were used to identify the final parameters in our device, including the distance between µTEC leg element in each individual µTEC and the distance between the µTECs in the proposed array.

Fig. 3.11a shows the complete meshed model for a particular TEC geometry and Fig. 3.11b shows the meshing of each individual µTEC. The meshing was done using tetrahedral
elements and different mesh sizes were used for the different volumes in the model. The PMMA block was meshed using uniform mesh size of 0.1 mm, the mesh refinement was performed on the μTEC and the cell with a mesh size of 2 μm. The model assumed a steady-state temperature equilibrium at the start, then the current pulse was linearly ramped up at 0.1 mA/s until a desired time was reached after which the current pulse was reduced back to zero. The automatic time stepping was enabled with time of 300 seconds at the end of each load step. The hot face temperature was fixed at $T_h = 27^\circ C$. An electrical current of 0.25 mA, which was within the current range 0.1-1 mA as determined from the lumped parameter model, was used.

Figure 3.11: (a) The 3D thermal model scheme with symmetrical distribution of 7 μTECs mesh size of 0.1 mm (b) Meshing of individual μTECs in the array with mesh size of 2 μm.

3.4.2 Results and Discussions

The effects of the following parameters on the TEC performance were studied:

- TEC element spacing
- Effect of interference of adjacent TECs
- Duration of pulsing for the applied current

The spacing between the two leg elements in each individual μTEC was a very important design parameter which was not determined using the lumped parameter model.
Figure 3.12: Influence of the TEC leg spacing on the $\Delta T$.

The FEA model analysis evaluated the influence of the space on the device performance. The initial 3-D ANSYS analysis indicated that a further increase in the $\Delta T$ values were achieved by placing the leg elements as close as possible to each other (Fig. 3.12). However the placement of the leg elements was limited by fabrication constraints, which limited the closest achievable distance between the two µTEC legs to 10 µm. It was observed that having the posts closer than 10 µm resulted in placement problems at the wiring level. The final optimized device geometry of the individual µTECs in the array were defined and are given in Table 3.2. All of the fabrication limitations used with both models are explained in further detail in the chapter on fabrication.

After fixing the individual device dimensions it was essential to understand the influence of the spacing between µTECs on the device performance. The proposed TEC system consists of an array of individual µTECs with the singular aim of cooling all the cells in the given tissue system in a uniform manner. It was essential for the array of TECs to be placed in a manner which allows for the cells which are not in direct contact with a TEC to
experience a temperature drop almost equivalent to that experienced by those in direct contact. To do so it was important to study the effect of different configurations, varied distances of placement between individual TECs in array, on the total heat transfer through the system.

Table 3.2: The dimensions of the proposed µTEC device (all values are in µm’s).

<table>
<thead>
<tr>
<th></th>
<th>Height</th>
<th>Width</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological Cell (Ice)</td>
<td>3</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td>Upper end plate (Alumina)</td>
<td>5</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>Upper Interconnect (Gold, Au)</td>
<td>3*</td>
<td>11</td>
<td>32</td>
</tr>
<tr>
<td>TEC leg element (Bi-Te)</td>
<td>20*</td>
<td>10*</td>
<td>10*</td>
</tr>
<tr>
<td>Lower Interconnect (Copper, Cu)</td>
<td>3*</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Lower end plate (Alumina)</td>
<td>10</td>
<td>12</td>
<td>36</td>
</tr>
<tr>
<td>Distance between the TEC legs</td>
<td></td>
<td></td>
<td>10**</td>
</tr>
</tbody>
</table>

*based on the lumped parameter model
**based on the ANSYS FEA model

To study this interference, a spacing of 72 µm from center to center of the µTEC was chosen (Fig. 3.13a). As the assumed cell diameter was 35 µm, this distance of 72 µm allowed for individual addressing of alternate cells in the tissue system. After this many alternative configurations were analyzed, amongst which four are as illustrated in Figs. 3.13-3.14. To cool all of the cells in a given tissue system in a uniform manner, the heat transfer throughout the TEC system array should be similar under similar operational parameters. As expected under similar operating conditions, decreasing the distance between µTECs decreased the variation in the temperature field. To achieve a uniform temperature throughout the device the µTECs should be spaced as closely as possible.
Figure 3.13: (a) The thermal heat distribution in µTECs arrays with 72 µm center to center spacing between adjacent µTECs @ I= 0.75 mA (b) The thermal heat distribution in µTECs arrays with 48 µm center to center spacing between adjacent µTECs @ I= 0.75 mA.

Figure 3.14: (a) The thermal heat distribution in µTECs arrays with 40 µm center to center spacing between adjacent µTECs @ I= 0.75 mA (b) The thermal heat distribution in µTECs arrays with 30 µm center to center spacing between adjacent µTECs @ I= 0.75 mA.

It is also proposed to use this device to establish discrete and distinct temperatures between adjacent cells embedded in an extracellular matrix. So, it was essential to identify the minimum possible spacing between two adjacent µTECs that will establish discrete temperatures within each µTEC with minimal interference between the respective temperature fields. To do so, a system with two µTECs separated from each other at various distances from 10 to 100 µm (Fig. 13.15) was considered. The vertical walls were subjected to periodic boundary conditions by treating them as insulation. The minimal distance for establishing distinct temperature profiles within each µTEC was defined as the minimum distance required to maintain the temperature at the midpoint between the µTECs at 60 % (or lower) of $\Delta T_i$; $\Delta T_i$
= \text{T}_h - \text{T}_c \text{ of each individually addressable \( \mu \text{TEC}. \) ANSYS simulations were performed by maintaining \( \mu \text{TEC}_1 \) at a constant \( \Delta T_1 \) and subjecting \( \mu \text{TEC}_2 \) to varying current within the desired operating range of 0.1-1mA (Fig. 13.16).

Figure 3.15: Discrete temperature profile can be established when the temperature at the midpoint between the \( \mu \text{TECs} \) is at 60% of \( \Delta T_1 \) (Midpoint show by the cross in the Figs. a and b). Constant \( \Delta T_1 \) (1.099K) is maintained at \( \mu \text{TEC}_1 \). (a) Discrete and distinct temperatures established as defined at a distance of separation equal to 50 \( \mu \text{m} \) (b) Non discrete temperature profile established at a distance of separation equal to 30 \( \mu \text{m} \).

Figure 3.16: The temperature at the midpoint between the two \( \mu \text{TECs} \) was maintained below 60% of \( \Delta T_2 \) only when they were at least 50 \( \mu \text{m} \) away from each other.
Under varying currents, the minimum required distance of separation between individual µTECs in the array was found to be 50 µm (Fig. 13.15). For adjacent µTECs to operate with minimal interference it was required to place them at least 50 µm apart. There may be additional limitations on the separation distance depending on the fabrication and packaging which will be discussed later on in the fabrication chapter.

A thermoelectric system will have a certain time beyond which the operation would result in its electrical breakdown. For proper function of the TEC system the operational conditions in addition to the geometrical dimensions and the physical placement of the each individual TEC in the array also have to be determined. Though the lumped parameter model was used to set an operating current range between 0.1-1 mA, it did not determine the pulse width. The final temperature drop depends on the current pulse shape as well as its duration\textsuperscript{3.17-3.21}. The reason for this is that the Peltier effect is a fast electronic effect and depends only on the electrical time, while the backflow of Joule heating and thermal leakage are dependent on the thermal time constant. It has been assumed that this will hold good for
the µTEC as well and there will be a certain time beyond which the operation of the µTEC would result in its breakdown\(^3\). This breakdown time was estimated to be around 60 seconds for the selected device dimensions indicating that the device would perform as expected if pulsed at either less than or equal to 60 seconds. In the experiments conducted later on, initially steady state current is applied for duration of less than 60 seconds without pulsing to get a temperature drop across the junction and incorporation of pulsing current into the system could be one of the future areas to concentrate on.

### 3.5 Conclusions

A lumped parameter model was developed and numerical simulations were carried out to investigate the influence of critical parameters related to integrated biological cell and the single stage µTECs system under steady state conditions. The effects of electrical contact resistance and element shape were included. Results showed that the smaller the height and larger the length of the TEC element the better the cooling. For optimal cooling, the ratio between the TEC element height and thickness was predicted to be around 1.8. Because the thickness of the leg element is constrained by the size of biological cell to be cooled to 10 µm, the height should ideally range between 15-20 µm.

It was also shown that a smaller interconnect height is beneficial for achieving a better temperature drop across a µTEC device. A new limitation, the secondary breakdown current, was observed for µTECs due to a thermal breakdown in the ceramic end plates and metallic interconnects. This secondary breakdown current is much lower than the primary breakdown due to Joule heating and was found to be < 1 mA for the µTEC. Hence, the effective operational value of the current was shown to be around 0.1-1 mA range. Further
investigations are necessary to verify the reason behind the existence of the secondary breakdown current.

Using the geometrical analysis from the lumped parameter model, a complete model including the ideal and non-ideal effects using the 3D finite element method was developed. The FEA model was used to determine the effect of the leg spacing within an individual µTEC and the interaction between µTECs in the array. The total temperature drop across the junctions was found to be inversely proportional to the TEC element space, making it desirable to have the thermoelectric branches placed as close as possible in each TEC system. It was determined that for adjacent µTECs to operate with minimal interference between their respective temperature fields and have discrete and distinct temperature profiles, it was required to interperse them at least 50 µm apart. Current and future studies include fabrication and characterization of individually addressable µTECs located at discrete intervals in an array. It was determined that the current should be pulsed at 60 seconds.

3.6 References


Chapter 4
Electrodeposition of Bismuth-Telluride Alloys

4.1 Introduction

The relative efficiency of a TEC material is measured in terms of its dimensionless figure of merit, $ZT$. At present, the TEC material with the highest $ZT$, capable of achieving the best thermoelectric cooling at room temperature is considered to be bismuth telluride (Bi$_2$Te$_3$) and its doped alloys$^{4.1-4.2}$, which possess highly desirable qualities like moderate electrical resistivity, low thermal conductivity, and a high Seebeck coefficient. The Bi$_2$Te$_3$ was used to fabricate both p- and n-type junctions of the proposed µTECs.

Previously, studies of bulk samples of Bi$_2$Te$_3$ have been carried out$^{4.3-4.6}$ and thin film depositions have been performed$^{4.7-4.17}$. The fabrication of the proposed µTECs require thin film deposition of Bi$_2$Te$_3$ and classically have been synthesized by sputtering$^{4.7-4.8}$, metal-organic chemical vapor deposition$^{4.5-4.6}$, molecular-beam epitaxy$^{4.9-4.10}$ and evaporation$^{4.11}$. These classical processes, however, often resulted in disassociation of the Bi$_2$Te$_3$ and a consequential lack of stoichiometry; and also, are not suitable for depositing in holes or onto irregular shaped substrates. This can be alleviated by using deposition. Electrodeposition offers advantages of low synthesis temperature, low cost, large area deposition with minimum weight and thickness, and high growth rates. Moreover, the synthesis experiments can be made in the laboratory, as opposed to growth physical techniques. Electrodeposition has been successfully applied earlier to the production of Bi$_2$Te$_3$ and its corresponding alloys$^{4.12-4.17}$. This work focuses on producing Bi$_2$Te$_3$ alloys suitable for thermoelectric applications by exploring a new potentiostatic process. The potentiostatic method used for electrodeposition
here makes the introduction of doping agents unnecessary by allowing Bi$_2$Te$_3$ to be doped into n-type or p-type by simply increasing or decreasing, respectively, the tellurium concentration about the stoichiometric ratio, through the choice of applied potential.

The overall reaction response for the deposition of Bi-Te alloys from aqueous acidic solutions, excluding the side reactions due to hydrogen evolution$^{4,14}$ has been described by Equation 4.1:

$$3HTeO_2^+ + 2Bi^{3+} + 18e^- + 9H^+ \rightarrow Bi_2Te_3(s) + 6H_2O$$  \hspace{1cm} (4.1)

Although this is a general reaction, the processes involved in the deposition are more complicated. In order to control the electrodeposition of the microstructures, it is essential to understand these processes fully. To gain insight into the electrodeposition of Bi$_2$Te$_3$ necessary for the proposed µTECs fabrication a brief review of the basic concepts involved, a description of the methodologies used and the current experimental results are presented in the following sections in sequence..

### 4.2 Basic Concepts

Electrodeposition of metals or alloys involves the reduction of metal ions from aqueous, organic, or fused salt electrolytes. It is performed in a liquid solution called an electrolyte, otherwise referred to as the "plating bath". The bath is a specially designed chemical solution that contains the desired metal, $M$, dissolved in an ionic form from an appropriate salt, $M^{n+}$. The object that is to be plated is submerged into the electrolyte, where it acts as a negatively charged cathode, referred to as working electrode (WE). The positively charged anode(s) completes the electric circuit; those may be at opposite edges of the plating tank, causing the film to deposit on both sides of the cathode. A power source in the form of a battery or rectifier, which converts ac electricity to regulated low voltage dc current provides
the necessary current/potential. In the case of potential control, the deposition at the cathode is controlled with respect to a standard potential, the reference electrode (RE). This type of circuit arrangement directs electrons, negative charge carriers, into a path from the power supply to the cathode, the object to be plated. In the bath the electric current is carried largely by the positively charged ions from the anode(s) toward the negatively charged cathode. This movement makes the ions in the bath migrate toward the extra electrons that are located at or near the surface of the cathode. In case of a supporting electrolyte, containing an excess of non-reating ions, these ions primarily carry charge. Thus, migration of the metal ions is typically negligible. By electrolysis the metal ions are removed from the solution by reduction and are deposited on the surface of the object as a thin layer.

In its simplest form the reaction in an aqueous medium at the cathode follows the Equation 4.2:

\[ \text{Equation 4.2: } M^{n+} + ne^- \rightarrow M(s) \]

with a corresponding anodic reaction. The deposition reaction presented is a reaction of charged particles at the interface between a solid (metal) electrode and a liquid solution. Also, from Equation 4.2 it is evident that there are three issues with the deposition reaction:

- Electron transfer at the metal-solution interface (electrode kinetics).
- Thermodynamics of the deposition process.
- Mass transport of the deposition

The following sections give a brief overview of these issues and their influence in the electrodeposition.
4.2.1 Electrode Kinetics

4.2.1.1 Electrochemical Double Layer

The electrochemical reactions occur at the electrolyte-electrode surface. In order for the electron transfer to happen a double layer forms, which is on the order of 1nm thick. The potential difference across the thin double layer establishes a strong electric field. The field orients the dipole molecules of water in the electrolyte and the excess charge on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the electrolyte. The amount of charge is a function of the electrode potential so that the double layer is similar to a simple parallel plate capacitor. It is this structure of the double layer, which is dependent on the total ionic concentration in electrolyte that is responsible for the electron transfer at the electrode surface and accounts for the number (n) of electrons, e⁻ in the governing Equation 4.1.

![Diagram of Standard polarization curve.](image)

Figure 4.1: Standard polarization curve.
4.2.1.2 Butler-Volmer Equation

Experience demonstrates that the potential of an electrode strongly affects the rate of the reactions occurring on its surface when the reaction is kinetically controlled. When the potential of an electrode is forced away from its value at open circuit it is referred to as polarizing the electrode. When an electrode is polarized, it can cause current to flow via electrochemical reactions that occur at the electrode surface. This gives rise to kinetics that are described by the Butler-Volmer equation (Equation 4.3):

\[ i = i_0 \left\{ \exp\left( \frac{\beta nF}{RT} \eta \right) - \exp\left( - (1 - \beta) \frac{nF}{RT} \eta \right) \right\} \]  

(4.3)

where \( F \) is the Faraday’s constant, \( R \) the universal gas constant, \( T \) the absolute temperature, \( i \) is the anodic or cathodic current, \( \beta \) is the charge transfer barrier or symmetry coefficient for the anodic or cathodic reaction typically close to 0.5 and overpotential, \( \eta = E - E^0 \) is the difference between the actual (measurable) reversible potential of an electrode, \( E \), and the standard reversible potential of the electrode couple, \( E^0 \). The overpotential gives the measure of the extent of polarization, wherein polarization defines the departure of the electrode potential from equilibrium value upon passage of current. Under steady-state conditions, this can be depicted in a current-potential curve known as polarization curve (Fig. 4.1).

4.2.2 Thermodynamics of the Deposition Process

The thermodynamics of the deposition process determines the limit of applied potential needed to initiate a reaction. It is dependent upon the Gibb’s free energy of the reaction which is a function of concentration; given by Equation 4.4:

\[ \Delta G = -nF\Delta E \]  

(4.4)

where \( F \) is the Faraday's constant equivalent to 96485 C, \( \Delta E \) is the electromotive force, (EMF) and \( n \) is the number of electrons.
4.2.2.1 Nernst Equation

The Nernst equation correlates the $\Delta G$ and the EMF of a deposition system and is used to optimize the pH of the electrolyte. For the standard electrode reaction (Equation 4.2), it is known that the Nernst equation is given by the Equation 4.5:

$$E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_{\text{red}}}{a_{\text{oxd}}} \right)$$

(4.5)

The notation $a_{\text{red}}$ represents the chemical activities of all of the species which appear on the reduced side of the electrode reaction, i.e. $M$ in Equation 4.1, and the notation $a_{\text{oxd}}$ represents the chemical activities of all of the species which appear on the oxidized side of the electrode reaction, i.e. $M^{n+}$ in Equation 4.2. The value of $E^0$ for Bi and Te were taken to be 0.286 V and -0.739 V. These data are in good agreement with those observed by Magri et al.

4.3.3 Mass Transport

The Butler-Volmer equation (Equation 4.2) indicates that with increasing potential, the current will increase without limit. However, this is not correct as the reaction is limited by the rate at which the reactant arrives at the electrode. This leads to a situation when further changes in the electrode potential do not increase the current density. At this point, the deposition created a concentration gradient near the electrode surface, referred to as the diffusion layer. This phenomenon is known as mass transport and is characterized by a limiting or maximum current density (Fig. 4.1). This limiting current establishes the maximum rate of reaction and is given by Equation 4.6:

$$i_L = \frac{-nFD(C_{\text{bulk}} - C_s)}{\delta}$$

(4.6)

where, $D$ is the diffusion coefficient of the deposited metal, $C_{\text{bulk}}$ is the bulk concentration of the metal ions in the solution, $C_s$ is the surface concentration of the metal ions and $\delta$ is the
diffusion layer thickness. Ultimately, at the limiting current, $C_s = 0$, the current distribution over the cathode is entirely governed by mass transport and becomes independent of the potential distribution in the bulk electrolyte.

### 4.3 Experimental Details

The deposition conditions, experimental set-up, and various data analyses are discussed in the following sections.

#### 4.3.1 Electrolyte Composition

The electrolyte used for electrodeposition in this work was a slight variation from the one pioneered by Miyazaki and Kajitani$^{4,16}$. Initially, 10 mM Bi$_2$O$_3$, 10 mM TeO$_2$ are dissolved in pure HNO$_3$ (assay) with a concentration of 69.7% with constant stirring at 25°C. It was found that at least 36 hours was needed to obtain a clear transparent solution as the dissolution of tellurium took longer than bismuth, which dissolved immediately. DI water (200 cc) was subsequently added while stirring. After 15 minutes another 200 cc of DI water were added. This process was continued until the desired amount of solution was obtained. The progressive addition of DI water over time was used to insure complete dissolution of the Bi-Te ions in the solution.

It was reported that Bi$_2$Te$_3$ can be formed directly by the reduction of its cations and is stable over an entire range of pH as a bulk material, at potentials more negative than 0.5 V vs. NHE$^{4,20}$. Based on this study it was assumed that the choice of pH was determined solely by the solubility of Te and Bi ions. In order to control the electrodeposition of microstructures it was also necessary to find the range of pH over which it was possible to dissolve both Bi and Te ions, such that they can be reduced to form Bi$_2$Te$_3$. For this purpose, Nernst equations showing the relationship between the concentrations and either $E^0$ or pH$^{4,19}$ were used to
calculate which species were most favorable for a particular pH and potential. With this information, a Pourbaix diagram (pH vs. potential) under the planned conditions for Bi₂Te₃ was calculated. From Equation 4.10, the stable species of Bi and Te are Bi³⁺ and HTeO₂⁺. This stability was achieved for Bi at pH< 2. At higher pH, Bi precipitates as Bi₂O₃. It was also observed that Te is stable as HTeO₂⁻ at pH< 0.5, so the working pH had to be as close to zero as possible in order to dissolve enough cationic species of both metal. For the planned experiment, a pH of 0.25 was maintained at a concentration of ~70 % assay.

4.3.2 Experimental Set-up

The doped alloys of Bi-Te were electrodeposited with the intention of forming the branches of the proposed µTECs. Ultimately these metals will be electrodeposited into recesses to form the needed geometry and it was essential to determine the process parameters of the deposition system. Since achieving the proper composition of the deposit for Bi-Te was a function of both solution composition and current, or potential, used in the deposition process, a rotating Hull cell (Autolab HT Rota-Hull®, Eco-Chemie B.V., Utrecht, Netherlands) was used to facilitate the process of solution optimization (Fig. 4.2). The working electrode (WE) for this modified Hull cell device was a rotating cylinder electrode (RCE). This cylindrical WE allowed the cell to perform under well-defined hydrodynamic conditions and produce non-uniform current distributions. It was possible to determine the influence of mass transport, and different bath components at low concentrations. The counter electrode (CE) for the Rota-Hull® was shielded in part from the WE by an insulating cylindrical separator. The current flow was facilitated by the presence of holes at the bottom of the shield. The current density was subsequently higher at the bottom of the WE than the top (Fig. 4.3). This led to the presence of a calibrated ratio of current density along the length of the WE. Fig 4.4 shows the calibration curve for the current density along the length of the
WE. The average current density, $i_{\text{avg}}$ of the Hull cell occurred when the ratio of the actual current to the average current equaled unity. The $i/i_{\text{avg}}$ ratio at all the points on the WE were calculated. The distances were measured from the top, along the length of the cylinder. It was assumed that the kinetics and mass transfer were negligible and field effects were controlling.

A cylindrical brass rod of diameter 0.6 cm and height 12 cm was used as the WE. The active length was 8 cm with 0.15 cm$^2$ active surface area. To ensure a clean surface for each run prior to deposition the brass WE’s were polished and cleaned. The CE was a cylindrical platinum (Pt) mesh which was placed at a distance of 1.5 cm from the bottom of the glass electrolyte container. The upper sleeve protruded by 0.8 cm from the WE and formed an 90° angle with it. The deposition was carried out galvanostatically at room temperature. This apparatus was used to investigate the optimization of the deposition parameters including the current density, electrode rotation rate, electrolyte temperature, and species concentration which were all shown to influence the Bi-Te alloy composition.

Figure 4.2: A schematic of a commercial Rota-Hull® cell$^{4,21}$. 
Figure 4.3: Rota-Hull® cell current calibrator.

Figure 4.4: Current density as a function of distance where zero represents lower end of the WE.
4.3.3. Data Evaluation Process

Data evaluation for the Rota-Hull® cell required two stages. Initially, deposits were produced galvanostatically in the cell where composition and thickness were determined as a function of position using Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer (Kevex Omicron). The second stage involved producing a polarization curve using a RCE which was used to determine the potential as a function of position. Finally, the results from EDXRF Rota-Hull® cell, and RCE polarization cell were combined to give a complete set of current density versus potential curves.

4.3.3.1 EDXRF Analysis

In EDXRF the species specificity is obtained by measuring the energy spectrum of the induced X-rays. Initially, to enable identification of Bi and Te, the EDXRF was calibrated with 99.99 % pure, bulk samples of Bi and Te. The electrodeposited sample was then placed on an orthogonal stage and was allowed to moved along the x-axis. This minimized X-ray scattering and allowed measurement of elemental concentrations as small as 0.5 % of Bi and Te. The analysis was carried out at equidistant points along the length of the sample and a raw data file containing the elemental percentage compositions and thickness of the deposit with the corresponding distances along the electrode was obtained. Using the standard calibration curve in Fig. 4.3, under specific applied current conditions the relationship between the total current densities and the corresponding distances of the electrode/electrolyte system were calculated. The partial current density was obtained as a function of position using Faraday’s law where the subscript $i$ refers to the corresponding species, either Bi or Te (Equation 4.7):

$$I_i = \frac{m_i n_i F}{s_i M_i t}$$  \hspace{1cm} (4.7)
where \( m \) is the mass of the deposited species \( i \), \( I \) the current passed in mA, \( M \) the molecular weight of the metal deposited on the WE, \( s \) the stoichiometric constant and \( t \) the elapsed time in seconds. The volume percentage, \( V_i \) of Bi and Te in the data was calculated using Equation 4.8:

\[
V_i = \frac{C_i}{\rho_i} \left( \frac{C_i + C_k}{\rho_i + \rho_k} \right)
\]

where \( C_i, C_k \) are the percentage compositions and \( \rho_i, \rho_k \) the corresponding densities of species \( i \) and \( k \) respectively (in this case these species are either Bi or Te). The mass, \( m \) of the deposited species \( i \) can be determined using the percentage volume, \( V_i \) calculated earlier (Equation 4.8) using Equation 4.9:

\[
m_i = \frac{V_i A \rho_i}{10000} T
\]

where \( A \) is the circumference of the WE and \( T \) the thickness of the deposited material. Finally the percentage efficiency, \( \varepsilon \) of the electrode/electrolyte system is determined by Equation 4.10:

\[
\varepsilon = \frac{I_{Bi} + I_{Te}}{I_{total}}
\]

where \( I_{total} \) is the total current density of the system

**4.3.3.2 Polarization Curve Analysis**

In an independent experiment, a polarization curve was used to establish the relationship between the potential and the current density obtained from the compositional analysis. This was done by using a RCE (Fig. 4.5). The rotator system was mounted on a vertical post and the vertical position of the WE was adjusted by sliding the entire motor
assembly up or down the post. One end of the WE was fixed to the mounting arbor on the rotator. A single banana jack connector was used to make electrical connection to the electrode brush holder. Contact to the electrode was made via a silver carbon brush, providing a consistent, reliable connection. The WE was rotated using a controller (Pine Instrument Company, MSRX Speed Control), the rotation rate was the same as that used by the EDXRF Rota-Hull® data analysis. The other end of the WE was immersed in the Bi-Te electrolyte solution. Only a very small area was exposed to the electrolyte while the rest of the WE was covered with the insulating tape. A platinum mesh formed the CE and was placed such that it surrounded the WE. The potential curve was measured and expressed by reference to the aqueous KCl saturated calomel electrode (SCE). In order to order to minimize ohmic drop the reference electrode (RE) was placed at the shortest distance possible from the WE.

![Figure 4.5: A schematic of a rotating cylinder electrode (RCE) apparatus for polarization curves and EIS analysis.](image-url)
Before recording the polarization curve it was essential to obtain the value of the ohmic drop which was generated in the system by the current flowing between the RE and WE. The potential seen by the WE was reduced by $RI$, where $R$ is the resistance in the electrolyte between the reference electrode and the working electrode and $I$ the current flowing through the system. To correct for the ohmic drop, electrochemical impedance spectroscopy (EIS) was performed at open circuit, which yielded the ohmic resistance. This was used to correct the measured over-potentials in the polarization dataset. For obtaining the polarization curve, a current range between -1 A to 1 A was applied with a slew rate of 1 mV/s for linear sweep voltammetry. The frequency for ohmic drop correction was maintained at 15 KHz with a voltage of 20 mV. The data obtained were digitized and served as a boundary condition, giving the potential as a function of position.

4.4 Results and Discussion

To determine the electrodeposition characteristics of Bi-Te, current densities ranging from 0.2 to 13.88 mA/cm² were studied. Depositions were carried out using a Rota-Hull® on a brass WE for 30 minutes each at the room temperature onto which the deposit appeared after a few minutes. In all of the cases, for a large range of current values, a nearly perfect stoichiometry was found. This can be explained by the parallel partial current densities.

The composition of the deposits along the length of the WE were analyzed using an EDXRF. A raw data file containing the thickness of the deposit and elemental percentage compositions with corresponding distances was obtained (Figs. 4.6 and 4.7). It was found that the thickness of the deposit increased along the length of the WE.
Figure 4.6: The growth rate (thickness) of the deposit increases along the length of the WE, rotation rate of 450 rpm, and average current density of 2.9 mA/cm².

Figure 4.7: Elemental percentage compositions and the corresponding distances along the WE, rotation rate of 450 rpm, and average current density of 2.9 mA/cm².
Using the standard calibration curve (Fig. 4.3), the composition measured at each point was then associated with a current density. The appearance of the deposits varied with the current density. It was observed that at the lower values of applied current densities the growth rate of the deposit was slow, whereas at the higher values in spite of having a good growth rate the surface was black and porous and did not adhere to the electrode (Fig. 4.6). The deposited films displayed desirable characteristics of metallic, regular pearl-gray deposition for current densities in the range of 0.3 to 7.5 mA/cm² with corresponding growth rates of 0.34 to 3.9 µm per half hour.

Also, from the obtained EDXRF data, the volume percentage was determined (Equation 4.11). With the volume percentage and thickness at each point the partial current densities of for both Bi and Te were determined (Equation 4.6), wherein the number of electrons for Bi and Te were $n_{Bi} = 3$ and $n_{Te} = 4$ respectively. These values of $n$ were assigned due to the reduction of $Bi^{3+}$ to Bi and $HTeO_2^+$ to Te according to the following reactions\(^{4,19}\) (Equations 4.11-4.12),

\[
Bi^{3+} + 3e^- \rightarrow Bi \quad (4.11)
\]

\[
HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O \quad (4.12)
\]

The polarization curve, which gives the relationship between potential and current under identical deposition conditions, was obtained using completely independent RCE experiment (Fig. 4.8). The data from this polarization curve were combined with that obtained earlier from the EDXRF analysis to determine the deposited concentrations of Bi at a particular voltage from the values of the partial currents (Fig. 4.9).
Figure 4.8: Polarization curve of Bi-Te electrodeposition on a brass RCE.

The specific range of potential values for fabricating p-type or n-type can be determined from the Fig. 4.7. It was already known that Bi-Te with the stoichiometric composition ratio Bi₂Te₃ (Bi% - 52.2%, Te% - 47.8%) was electronically neutral⁴¹⁴. This optimal Bi:Te stoichiometry of 2:3 was achieved for depositions performed at 0.23 – 24 V Vs SCE. However, upon decreasing the potential further, with the values of E<0.23 V, a stoichiometric ratio as large as 4:3 was observed (Table 4.1). This indicated that p-type material would be obtained for values of E< 0.23 V and n-type for values of E>0.23 V.

Table 4.1: Stoichiometry dependence on applied potential (Vs SCE).

<table>
<thead>
<tr>
<th>E applied potential (V)</th>
<th>Te (%)</th>
<th>BiₓTeₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.12</td>
<td>40-42</td>
<td>Bi₁.₇Te₂.₆</td>
</tr>
<tr>
<td>0.12-0.19</td>
<td>42.19-45</td>
<td>Bi₁.₇₅Te₂.₆₃</td>
</tr>
<tr>
<td>0.19-0.23</td>
<td>45-47.8</td>
<td>Bi₁.₉Te₂.₈₆</td>
</tr>
<tr>
<td>0.23-0.25</td>
<td>47.9-56</td>
<td>Bi₂.₃Te₃.₆</td>
</tr>
<tr>
<td>0.25-0.27</td>
<td>56-88</td>
<td>Bi₃.₆Te₅.₄</td>
</tr>
</tbody>
</table>
Figure 4.9: Percentage weight of Bi and the corresponding deposition current efficiency.

Fig. 4.10 shows the final deposition characteristics observed from the analysis of the Rota-Hull® and polarization data. The side reactions in the experiments increased as the current increased and initially the side reaction partial current was much higher than those of Bi and Te. The current efficiency, which describes how much current is lost in deposition to side reactions, was low (Fig. 4.9). This indicates that potentiostatic control for p-type deposition (i.e. at lower potential range) and galvanostatic control for n-type material deposition may provide a better control on the finally intended recess-deposition processes.

The data from the Rota-Hull® are for a particular rotation rate. The rotation rate was related to the same limiting current conditions as those found in a corresponding recess depth, through the well-established Eisenburg Equation (Equation 4.20), assuming that the boundary layer thickness, $\delta$, was approximately equal to recess depth$^{4,24}$,

$$\delta = 99.62d^{0.4}v^{0.344}D^{0.356}S^{0.7}$$  \hspace{1cm} (4.20)
Figure 4.10: Partial currents for the Bi-Te deposition along with side reactions, rotation rate of 450 rpm, and average current density of 2.9 mA/cm$^2$.

where, \(d\) is the diameter of the WE (brass rod), \(\nu\) the viscosity coefficient, \(D\) the diffusion coefficient and \(S\) the stirring speed. From the polarization data (Fig. 4.6) it was evident that the Bi-Te system was kinetically controlled; it did not reach a point of limiting current. This indicates that deposition was independent of recess depth and not dependent on the stirring speed. Therefore, the deposition characteristics were the same at all speeds and all the depositions were carried out at a standardized stirring rate of 450 rpm. Therefore the deposition characteristics of Bi-Te were determined from both the Rota-Hull® calibration curve and polarization curve (Figs. 4.3 and 4.6).

The existence of such large side reactions indicated the presence of hydrogen evolution. Such large amounts of hydrogen could block the electrode surface, result in surface pH changes and reduce the cathodic efficiency, the ratio of the weight of metal actually deposited to the weight that would have resulted if all the current had been used for depositing, leading to non-uniform deposition during the recess plating. To overcome these
drawbacks during recess plating, a pulse scheme with long relaxation times of 40 seconds was adopted. The relaxation time enabled reacting species to be replenished within the recess and allows the products of side reactions to diffuse out of the recess. Both the p-type (Bi rich) and n-type (Te-rich) branches of the TEC could be created by pulsing the potential.

4.5 Conclusions

The n-type and p-type leg element deposition can be achieved by varying the cathodic potential while maintaining the same bath composition. It was determined that the deposition reaction was kinetically controlled and hence independent of the rotating speed. It was also found that due to the existence of large side reaction, it is desirable to pulse plate while depositing into a recess. Both the p-type (Bi rich) and n-type (Te-rich) branches of the TEC were created by pulsing the potential independent of the electrode rotating speed.

4.6 References


Chapter 5

Device Fabrication and Characterization

5.1 Introduction

The fabrication of the prototype µTEC used a modified multistep LIGA (Lithographie, Galvaniformung and Abformung) technique in combination with the electrodeposition of Bi-Te alloys. This method gives high flexibility of adjusting geometry, material composition or batch scalability while allowing for the production of high density wiring required for the device. The following sections outline briefly the background, the fabrication constraints, preparation of p- and n-type thermoelectric posts, their structural and thermoelectric properties, details about the device fabrication, and preliminary results.

5.2 Background

Over the past decade only a few approaches to understanding, manipulating and manufacturing µTECs have been made. Synder et al. fabricated µTECs at approximately 20 µm in structure height and with a device area close to 1700 µm x 1700 µm, presenting a maximum cooling effect of 2 K\(^{5.1-5.3}\). The development of these µTECs was based on V-VI compounds and were grown using electrochemical methods. However, no device properties were reported and no material optimization was performed. The relationship among the deposition conditions, composition, electrical performance of the films and their performance as a device were not established. The first µTEC material properties were characterized and reported by Bottner et al.\(^{5.4}\). They developed column-type micro cooler using a “two-wafer” concept where n- and p-type materials were first deposited on separate wafers by sputtering, patterned, and soldered together. This allowed for an optimal post-processing of the n- and p-
type wafers. The relatively slow deposition rates in sputtering made this methodology ineffective for fabricating μTECs with the proposed dimensions. It is important to note that in addition to the above mentioned previous work, other groups such as Rabin et al.5,5, Li et al.5,6, Bae et al.5,7, Abramson et al.5,8 and Lim et al.5,9 have investigated and demonstrated various approaches of patterning nanoposts of TEC material. However, due to the fabrication constraints at CAMD, LSU and time limitations involved, the fabrication of TEC material at the nano-scale have not yet been explored as a part of this study.

5.3 Fabrication

The goal of the present work was to build on the previously reported studies and fabricate μTECs of the smallest possible dimensions. The design and fabrication of the arrays of μTECs was based on electrodeposition and photoresist patterning of the n- and p-type Bi-Te films. The proposed μTECs were fabricated using a bottom-up approach. The column-type structure of the μTECs (Fig. 5.1) could be divided into four layers: hot (bottom) connectors (wiring layer), p-type posts and n-type posts (TEC elements), and cold (top) interconnects. The major challenges encountered in fabrication were the alignment of the various layers, patterning of high performance thermoelectric films, realization of TEC columns with the optimal distance between the TEC legs, and the fabrication cold (top) connectors.

![Figure 5.1: A schematic of the column type structure of μTEC.](image)
5.3.1 UV Mask Patterning

The initial step towards the fabrication of the 4-layered µTEC involved the design of four ultraviolet (UV) masks with each mask accounting for one layer. A dark field mask was used to pattern each layer. In such a mask, the dark field regions are chrome covered and block the UV light whereas the clear field regions allow the UV light to pass through and modify the photoresist (PR) (Fig. 5.2).

To pattern the multiple layers it was essential to have accurate alignment between all of the required dark field masks. This was achieved by having alignment marks on every layer so that the masks could be properly registered with each other. Maximum alignment accuracy was achieved by aligning each mask with respect to the first one. This ensured that no masks were more than two alignment errors off from each other. Identical sets of alignment marks were positioned horizontally opposite each other (Fig. 5.3). This allowed accurate positioning of all patterns up to ± 2 µm. Two alignment marks, placed on the horizontal axis near each edge of the Si wafer, were used at each subsequent level to align the mask and wafer. By placing these marks both the xy, and theta (rotational), errors were reduced. The locations of the objective lenses of the microscope on the Quintel UL7000-OBS Aligner and DUV Exposure Station (Quintel Corp., Morgan Hill, CA) at CAMD that were used for mask alignment and exposure varied approximately between 1.5 and 4.5 cms in xy direction from the center of the wafer. The alignment marks on the masks were positioned within this range. To account for edge bead removal, the alignment marks were located 3 mm more than the edge of the wafer. For coarse adjustment, each mask had clear areas through which the edge of wafer beneath the mask could be easily located (Fig. 5.3).
Due to the absence of previous pattern on the Si wafer, the first photolithography level was simply aligned to the wafer flat. The first mask, Mask #1, transferred a set of target alignment marks to the Si wafer which were used as references while positioning subsequent patterns with respect to the first. Each subsequent layer to be aligned had a pattern on the masks, with the patterns on Masks #2-4 progressively larger than the previous one. This ensured that the pattern on the Si wafer from Mask #1 could be seen (Fig. 5.4) through structures from the other masks. In order to ensure that the subsequent processing did not completely remove alignment marks, the alignment marks in one layer were masked during the processing of other layers. The Quintel at CAMD has an error of $\pm 1 \ \mu m$. 

Figure 5.2: Transfer of pattern to a PR material using dark field mask $^{5,10}$.

Figure 5.3: Schematic of the placement of clear areas and alignment marks in the dark field UV masks.
Figure 5.4: The type of alignment marks on the UV mask. Mask #1 had the smallest alignment marks while Masks #2-4 had larger alignment mark by 7 µm.

To ensure accurate alignment of all the layers, the alignment marks on Masks #2-4 were bigger from the alignment marks on Mask #1 by 7 µm (Appendix A). The 7 µm distance was chosen by simple tolerance analysis. Such small dimensional difference allowed for the fine optical alignment.

It was necessary to design masks that would allow for uniform current conditions during deposition. This was achieved by laying the design at the center of the wafer and having a pattern with gradually increasing size. For the wiring layer, Mask #1, a radial pattern was designed (Fig. 5.5). The minimum feature size on the mask was 3 µm. The p-type and n-type contacts were distinguished by a square and a semi-circular contact pads, respectively. The subsequent masks had patterns at the center of the wafer. A detailed layout of the masks used for fabrication of the device is available in the Appendix A. The UV lithography mask patterns of µTECs were laid out using AutoCAD 2000 (AutoDesk, San Rafael, CA). The AutoCAD drawing was converted to the .dxf file format and sent out for bids. Four dark field masks of sizes 5” x 5” x 0.06” were purchased from Advance Reproductions (North Andover, MA). The dimensions of the masks were well within the tolerance limit of ±0.4 µm specified by the mask manufacturer.
5.3.2 Fabrication Methodology

The modified LIGA method used for device fabrication involved a multistep procedure of (1) photoresist (PR) spinning, (2) PR patterning by exposure and development, (3) deposition of the material and (4) etching of the PR. The selection of the type of PR was an important step during fabrication. Due to the need for multiple exposures in same layer, for making p- and n-type posts, a positive PR was used. The reasons for using a positive PR were twofold. First, with negative PR, if there is not enough energy to drive the cross-linking reaction at the base, the PR will remain unexposed and subsequent development will lift the entire structure from the substrate. Second, aligning a mask to an underlying feature can be challenging with negative PR. During alignment, the mask is brought into close proximity with the substrate, allowing features on both the mask and substrate to be co-focal. If the PR is negative, it may not be possible to focus on the mask and substrate simultaneously.\textsuperscript{5.11-5.12}
Due to fabrication limitations and feature sizes as small as 3 \( \mu m \), it was necessary to optimize the exposure dose PR resist developing time and the vacuum contact strength experimentally. Too long an exposure or developing time produced larger structures than desired and too short did not allow the PR to develop fully, which prevented further electrodeposition. It was also observed, that low vacuum strength while exposure resulted in larger structures, so high vacuum conditions were maintained during exposure. Based on the model development results, the \( \mu \)TECs were designed with the distance between the TEC legs, \( d_{te} \), varying between 5 and 15 \( \mu m \), including the optimum geometry, with \( d_{te} \) of 10 \( \mu m \). The column thickness of the TEC elements was limited to 10 \( \mu m \), to allow for uniform stoichiometry of the Bi-Te compounds.

5.3.2.1 Wiring Layer

The fabrication steps for the hot connectors and pads are shown in Fig. 5.6. To provide electrical insulation for the device, an 850 nm thick silicon dioxide (\( SiO_2 \)) layer was grown on the Si wafer (Fig. 5.6a). Since the minimum required thickness of \( \sim 2 \mu m \) could be achieved by either electron beam (ebeam) or sputtering technique, electrodeposition was used to fabricate the copper (Cu) wiring layer. To facilitate this the oxidized silicon wafer (SOI) was ebeam evaporated with a titanium (Ti) adhesion layer (30 nm) and a Cu plating base (100 nm) (Fig. 5.6b). The Ti, had an electrical resistivity about 32 times larger and a thermal conductivity about 23 times smaller than Cu, and was used for its good adhesion properties. The presence of Ti as adhesion layer could prevent the diffusion of Cu into the thermoelectric elements. Initially, the ebeamed Si wafer was dehydrated by pre-baking at 90 \( ^\circ C \) for 1.5 minutes. To get the wiring thickness of \( \sim 2 \mu m \), around \( \sim 10-12 \) mL of the PR S1813 was spun cast at 2000 rpm for 1 minute (Fig. 5.6c). Then the wafer was soft-baked at 90 \( ^\circ C \) for 1
minute. This made the resist photosensitive. A lift-off pattern for the hot connectors and electrical connectors (pads) was then defined using Mask #1 (Fig. 5.1d). This was done by exposing the spin coated wafer to UV light through the Mask #1. The wafer was exposed with vacuum contact at an intensity of 150 mJ/cm² at 365 nm wavelength. A high vacuum condition of 22.3 was maintained to insure good contact between the mask and the spun wafer. The PR was developed with MF-321 developer for 2 minutes (Fig. 5.6d), rinsed with DI water, dried with nitrogen gas and the resulting structures were electrodeposited (Fig. 5.6e).

Figure 5.6: Fabrication processes of wiring layer.
5.3.2.2 TEC Posts

Each column of a TEC pair was patterned consecutively as shown in Figs. 5.7 and 5.8. The n-type and p-type thermoelectric elements were electrodeposited using the electrolyte solution described in Section 4.3. Prior modeling results (Chapter 3) indicated the need for TEC posts of \( \sim 20 \mu m \) height. The thin film PR S1813 used for the wiring layer cannot be spin coated to achieve the required height of \( \sim 20 \mu m \). To pattern 20 \( \mu m \) tall TEC posts a thick film PR AZ P4620 was used \(^5,13\). It was observed that spinning AZ P4620 over the underlying S1813 resist in the wiring layer introduced undesirable reactions like bubble formation. This smudged the alignment marks making future alignments difficult. To ameliorate this, alignment marks were initially covered with aluminium foil. Then the S1813 resist was flat exposed at an intensity of 400 mJ/cm² at wavelength of 365 nm and developed using MF-321 developer for 2 minutes (Fig. 5.7a). After developing, a polyester tape (Harman Corporation, Rochester, MI) was used to cover the alignment marks. Approximately \( \sim 10-12 \) mL of PR AZ P4620 was spun at 2000 rpm for 5 seconds \(^5,13\) (Fig. 5.7b). Prior to baking, the edge bead was removed by using a glass slide and the polystyrene tape was removed. The processed wafer was baked in an M326 Mechanical Oven at CAMD at 85 °C for 5 minutes and soft-baked on a hot plate at 115 °C for 1 minute. The wafer was allowed to cool for 20 minutes before the exposure. The wafer was aligned and exposed at an intensity of 650 mJ/cm² at wavelength of 365 nm and a high vacuum condition of 22.3 was maintained. The PR was developed with AZ 400 K developer for 4.5 minutes (Fig. 5.7c), rinsed with DI water, dried with nitrogen gas. The first set of TEC posts, p-type, were electrodeposited into the developed patterns using the electrolyte solution described in Section 4.3 (Fig. 5.7d).
Figure 5.7: Fabrication processes for p-type TEC posts.

Figure 5.8: Fabrication processes for n-type TEC posts.
To electrodeposit n-type TEC posts, the alignment marks were covered again with polyester tape and PR S1813 was spun at 2000 rpm for 1 minute (Fig. 5.8a). The thin layer of S1813 at 2 µm acted as a shield for the p-type elements. Next, the tape was removed and the wafer was soft-baked at 95 °C for 1.5 minutes. After this, the processing steps were identical to the ones used to fabricate the p-type TE posts (Fig. 5.8b). This opened a second set of holes in the resist. The n-type TEC elements were then grown by electrodeposition (Fig. 5.8c).

5.3.2.3 Top Interconnects

The final steps of the fabrication process are presented in Fig. 5.9. To ensure a clean electrical contact opening, the PR on top of the TEC posts was overexposed with an intensity of 100 mJ/cm² at wavelength of 365 nm. The PR was overexposed to account for the variations in the PR thickness, caused by differences in the height of the TEC elements. Differences as large as 0.8 µm between the n-type and p-type TEC elements heights were observed using a surface profilometer. The PR was developed using MF-321 developer for 2 minutes. The height of the PR above the TEC posts, ranged from 1 to 2 µm. Due to this surface non-uniformity, two interconnect deposition techniques were used. The first technique involved electrodepositing Cu into the developed recesses. For the second technique a Ti (30 nm) and Cu (100 nm) seed layer were ebeam evaporated over the surface of the sample. The sample was then subjected to a lift off process, leaving behind the seed layer on previously exposed areas. Next, around ~10-12 mL PR AZ P4620 was spun at 2000 rpm for 6 seconds and the junction layer mask was used to re-expose the Cu-Ti seeded junctions. An intensity of 100 mJ/cm² at wavelength of 365 nm was used. Finally, Cu was electrodeposited onto this seeded Cu-Ti junction layer allowing for good step coverage.
5.3.2.4 Plating Base Etching

The final step towards the fabrication of the 4-layered µTEC array involved isolating the electrical connection between all of the individual µTECs in the array. This was achieved by removing the Ti adhesion layer and the Cu plating base from the SOI wafer (Fig. 5.8c and 5.8d). Initially all of the resist was removed using acetone, rinsed in IPA and then rinsed with DI water and dried. The wafer was placed in a Cu etching solution (Transene Company, Inc, Danvers, MA) for 10 seconds and then placed in DI water. Next, the wafer was etched in 1% HF acid solution for 10 seconds and rinsed with DI water. This etched away the Ti/Cu plating base leaving behind the fabricated array of µTECs.
5.3.3 Electrodeposition

At each layer, prior to deposition, the patterned wafer was placed in a vacuum chamber and 5 mL of DI water was placed over the patterns. A vacuum pump was used to depressurize and remove any air bubbles over the patterned areas leaving the wafer ready for deposition. Electrodeposition was carried out in a conventional three-electrode cell with 5 liters capacity at room temperature. Fig. 5.10 shows the schematic setup for such an arrangement. A square Pt mesh acted as CE while a SCE acted as a RE. A mechanical stirrer was used to agitate the electrolyte. A custom designed electroplating jig (Appendix B) was used to hold the WE. The jig with the WE was placed in placed in the electrolyte bath and the Cu-wire end of the jig was connected to a Model 273A differential electrometer (Ametek Princeton Applied Research, Inc, Oakridge, TN).

5.3.3.1 TEC Posts

The n- and p-type TEC posts were electrodeposited into the developed recesses using the electrolyte solution described in Section 4.3. Initially, the range of cathodic potentials within which the p- and n-type leg element can be deposited were determined using a rotating Hull cell device (Autolab HT Rota-Hull®, Eco-Chemie B.V., Utrecht, Netherlands). However,
the WE for this modified Hull cell device was a brass RCE (Section 4.3). Since the patterned wafer has a Cu plating base, it was essential to determine the plating range with respect to Cu. This was done by combining the Cu WE polarization data with the EDXRF Rota-Hull® cell data of the brass RCE WE.

To do so, Cu was evenly electroplated along the analyzable length of the brass RCE. For maximum efficiency, the brass WE was plated at 7 mA/cm² for 10 minutes at room temperature. The Cu-plated brass rod was then used as the WE in the Rota-hull cell and a polarization curve was obtained by linear sweep voltammetry over a current range of -1 A to 1 A at a slew rate of 1 mV/s. Ohmic drop correction was determined by varying the frequency and interpolating the real part of the impedance when frequency went to infinity and the imaginary impedance goes to zero. The amplitude of the potential during the impedance measurement was 20 mV. The polarization curve established that for a Cu WE, the amplitude of the current increased and more cathodic with potential until it reached a plateau and then rises again (Fig. 5.11). The data from the polarization curve was combined with that obtained earlier from the EDXRF analysis of the brass RCE to determine the final deposition characteristics on the Cu WE (Fig. 5.12). Fig. 5.12a are the partial current densities that explain the total polarization behavior with a Cu WE. The plateau corresponds to the case when the both the Te and Bi reach a limiting value. The rise in current at a potential of -80 mV occurs due to the large increase in a side reaction. Fig. 5.12a shows that on a Cu plating base the n-type element of the TEC could be deposited for E greater than -0.06 V while the p-type leg element can be deposited for E less than -0.06 V. Fig 5.12b that on a brass plating base the n-type leg element of TEC could be deposited for E> 220 mV and the p-type leg element could be deposited for E< 220 mV. The potential scales for brass and Cu plating
bases were different demonstrating that it was essential to determine the plating conditions as a function of the WE.

Figure 5.11: Polarization curve of Bi-Te electrodeposition on a Cu-plated brass RCE.

Figure 5.12: Partial currents for the Bi-Te deposition along with side reactions, rotation rate of 450 rpm, and average current density of 2.9 mA/cm² for (a) Cu plating base (b) Brass plating base.
5.5 Characterization of TEC Leg Elements

5.5.1 Composition

The compositional analysis was done for Bi-Te thin films. The thin film samples were prepared by electrodepositing Bi-Te on a Cu-Ti seeded SOI wafer. The relative concentrations of the Bi-Te were measured using EDXRF, and averaged over five distinct locations for each sample. A data file containing information regarding the thickness of the deposit and elemental percentage compositions was obtained. The surface morphology of the films was examined using a scanning electron microscope (SEM).

5.5.2 Seebeck Effect Measurements

The Seebeck coefficient, \( \alpha(T) \), was measured at room temperature under vacuum. Two cases were considered for measurement. The first case involved the \( \alpha(T) \) measurement of Bi-Te micro-posts, while the second involved the \( \alpha(T) \) measurement of Bi-Te thin films. In each case, the sample was prepared on a Cu-Ti seeded SOI wafer. The Bi-Te thin film samples were obtained by electrodeposition.

The preparation of micro-post samples involved the patterning and deposition of the Cu wiring layer and TEC posts using methods described earlier in Section 5.3 (Fig. 5.14a). Initially, the patterned wafer was covered with a stenciled aluminum (Al) foil (Fig. 5.14b) and flat exposed without any mask. However, the developed wafer (Fig. 5.13c) did not have the uniform surface required for the \( \alpha(T) \) measurements. To achieve this uniformity the wafer was again covered with a stenciled Al foil (Fig. 5.13d) and Au (2 \( \mu \)m) was sputtered onto the exposed wafer (Fig. 5.13e). Finally, the Al foil was removed and the wafer was flat exposed and developed. This sample was then used for \( \alpha(T) \) measurements.
Figure 5.13: Sample preparation process for $\alpha(T)$ measurements of the Bi-Te micro-posts.

In each case the data were collected by using an experimental set-up shown in Fig. 5.14. One end of the sample was thermally connected to a heat sink and the other end to a heater. The temperatures of the hot and cold sides of the sample ($T_h$ and $T_c$, respectively) were measured with fine Cu-constantan, type-T, thermocouples. The Cu leads of the thermocouples were also used to measure the potential difference, $\Delta E$, across the sample. The $\alpha(T)$ was measured using Equation 5.1:

$$\alpha(T) = \frac{\Delta E}{T_h - T_c}$$

(5.1)

The results were corrected for the thermopower of the Cu leads. The error analysis for the $\alpha(T)$ measurement involved the calculation of uncertainty factor $\Delta \alpha$. Using Equation 5.2:
\[
\Delta \alpha = \left[ \sum_{i=1}^{n} \left( \frac{\partial \alpha}{\partial x_i} \Delta x_i \right)^2 \right]^{1/2}
\]  

(5.2)

where \( x \) is either \( \Delta E \) or \( T_h \) or \( T_c \).

Figure 5.14: Schematic of \( \alpha(T) \) measuring apparatus.

Six \( \alpha(T) \) measurements were made at steady state conditions for each sample. Using an average value of \( \alpha(T) \), an uncertainty factor of \( \pm 20 \% \) was obtained. This was in accordance with the large variations observed during repetition of the \( \alpha(T) \) measurements for the same sample. These problems in repetition could be due to the presence of the Cu base. Cu has a natural tendency of intercalating and leaching into and out of Bi-Te. However, due to the presence of the Ti adhesion layer, it was assumed, that this reaction of Cu with the Bi-Te might be neglected. For future measurements, Ni or Ni-Cu or Au should be used as the plating base as opposed to Cu.

5.5 Results and Discussion

5.5.1 Fabrication

The deposition of the wiring layer formed the first step towards the fabrication of \( \mu \)TEC array. The sample was prepared by vacuum depressurizing the patterned areas on the wafer. Cu was electroplated into the patterned areas galvanostatically from an electrolyte
containing 1 M of CuSO₄, 100 mL/L H₂SO₄ diluted in DI water. The total active plating area was 1.5 cm², therefore for maximum efficiency the sample was plated for 18 minutes at 10.5 mA/cm² at room temperature. The plated Cu was fine-grained and bright and faithfully reproduced the shape of the photoresist pattern (Fig. 5.15). The uniformity was governed by the layout of the elements to be plated, and the film thickness was measured by a KLA/Tencor profilometer. It was found that the features at the center of wafer were 2.45 µm thick while the surrounding features were found to be 2.3 µm thick. This indicated desirable low variations in the across-wafer uniformity and the sample was rinsed with DI water and dried.

Next, the p-type post layer was exposed and developed (Fig. 5.8). Like the wiring layer, the sample for p-type TEC posts deposition was prepared by vacuum depressurizing of the patterned areas on the wafer. During electrodeposition, large side reactions (Fig. 5.11a) led to adoption of a pulse scheme. The ratio of the on-time:off-time of the electrode cell was maintained at 1:4. The large relaxation time enabled reacting species to be replenished within the recess and allowed the products of side reactions to diffuse out of the recess. Deposition was potentiostatically controlled and the SCE was placed as close as possible to the electroplating jig.

Uniform deposition of the TEC posts was essential for the proper function of the µTEC array. Initially while depositing the p-type posts non-uniform deposition was observed. The use of an encapsulated thief electrode made it possible to ameliorate the non-uniformity. The thief electrode was a ring-shaped auxiliary cathode placed in the electroplating jig such that it surrounded the plating areas in the WE (Fig. 5.16). Such integration with the WE allowed the thief electrode to reduce "current crowding" at the center of the WE and improve deposit thickness uniformity across the WE.
Figure 5.15: Wiring layer fabrication (a) Radial wiring layer layout with uniform Cu plating (b) The contact pad features at the center of the wafer.

Figure 5.16: (a) The electroplating jig (b) The ring-shaped thief electrode surrounding the plating area in WE. It is attached to the jig by conducting Cu tape (c), (d) The plating jig set-up with the WE and thief.
Due to the existence of very small amounts of Bi-Te ions in the electrolyte only a small thief electrode could be used. Different sizes of thief electrodes were initially tested. A 1.3 mm sized thief electrode was found to be sufficient for the plating needs. At this size the plating was observed to be uniform along the whole wafer. After positioning the thief electrode and the WE in the electroplating jig, the p-type TEC posts were potentiostatically electrodeposited into the developed recesses. After deposition, the sample was rinsed with DI water and dried (Fig. 5.17). The sample was further processed for n-type post deposition (Fig. 5.8). The patterned areas were vacuum depressurized. A plating set-up similar to that used for p-type post deposition was used. Due to the spinning of additional PR S1813, the recess for n-type deposition was deeper than that developed for p-type deposition, and the n-type posts were slightly taller than the p-type posts. After deposition, the sample was again rinsed with DI water and dried. The μTECs with leg distances > 10 μm were successfully fabricated while those < 10 μm had n-type and p-type posts overlapping and faced fabrication issues during exposure and deposition of the second TEC posts.

Figure 5.17: The p-type post fabrication (a) Layout of the contact pads onto which p-type posts were fabricated (b) A close up of a single p-type post (c) A p-type post of 10 μm diameter and 18 μm height.
The height of both the posts were limited by the recess depth between 18-19 µm. Both over-plating or under-plating the posts could have adverse effects while fabricating the final junction layer. The post plating parameters were optimized to achieve 18-19 µm tall posts (Table 5.1).

The junction layer was exposed and developed (Fig 5.18). The sample preparation involved twin steps of vacuuming and depressurization. Two methods were adopted for junction layer fabrication. The first method involved electrodepositing Cu into the developed recesses using the same Cu plating bath used for wiring layer deposition. Plating was done at 6 mA/cm² for 47 minutes. It was observed that the plating was not uniform and the junctions were not well connected. To ameliorate this non uniformity and have a good junction layer, a second technique which involved ebeam Cu-Ti seed layer into the recesses, lift-off, re-spinning and exposure of PR was adopted. Cu was electrodeposited into the resulting Cu-Ti seeded junction layer at 6 mA/cm² for 47 minutes. The sample was soaked in acetone to remove all the resist, washed with IPA and water and dried. The junction layer so fabricated was found be well connected and had a very good step coverage.

![Figure 5.17: The junction layer (a) An array of TECs (b) A close-up of the developed junction area, the posts are of different sizes due to exposure problems in the Quintel.](image)
Table 5.1: Optimized plating parameters @ 600 rpm.

<table>
<thead>
<tr>
<th>Plating potential (mV)</th>
<th>Plating time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-200</td>
<td>13</td>
</tr>
<tr>
<td>-180</td>
<td>13.5</td>
</tr>
<tr>
<td>-140</td>
<td>14</td>
</tr>
<tr>
<td>-120</td>
<td>15.5</td>
</tr>
<tr>
<td>-100</td>
<td>16</td>
</tr>
<tr>
<td>-80</td>
<td>18</td>
</tr>
<tr>
<td>-60</td>
<td>18.5</td>
</tr>
<tr>
<td>-40</td>
<td>19</td>
</tr>
<tr>
<td>-20</td>
<td>20</td>
</tr>
<tr>
<td>-5</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
</tr>
</tbody>
</table>

The final step involved the removal of the initial Cu-Ti seed layer from the SOI wafer. For removal of Cu base, the sample was placed in a commercial Cu etching solution (Transene Company, Inc, Danvers, MA) for 10 seconds, cleaned in DI water and dried. For Ti removal, the sample was placed in hydrofluoric (HF) acid for 10 seconds, cleaned in DI water and dried. It was found that Bi-Te reacted with HF acid, thereby damaging the whole structure. For future work, Cr could be used instead of Ti for adhesion in seed layer.

5.5.2 Characterization

Around 5 µm thick Bi-Te films were electroplated on a Cu-Ti plated SOI layer at different potentials. The film composition was determined by EDXRF analysis. The film composition was measured at five distinct locations on the sample.
Figure 5.19: EDXRF data from thin film analysis. The films were deposited potentiostatically on Cu-Ti seeded SOI wafer @ 450 rpm.

Table 5.2: Optimal $\alpha(T)$ values.

<table>
<thead>
<tr>
<th>Type</th>
<th>Potential range (mV)</th>
<th>Highest obtained $\alpha(T)$ values (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>&gt;-140</td>
<td>-100</td>
</tr>
<tr>
<td>neutral</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>p-type</td>
<td>&lt;140</td>
<td>80</td>
</tr>
</tbody>
</table>

Uniform plating was observed throughout the film surface. Bi-Te with the stoichiometric composition ratio Bi$_2$Te$_3$ (Bi% - 52.2%, Te% - 47.8%) is electronically neutral. From Fig. 5.19 it can be seen that this optimal Bi:Ti stoichiometry was achieved for depositions performed at -150 to -155 mV. This indicates that the p-type material was obtained for $E< -155$ mV while n-type material was obtained for $E> -155$ mV. The potential scales so obtained were different from that predicted by Rota-Hull data (Fig. 5.12a) by -80 mV. This could be due to the differences in the Cu plating base. These EDXRF results were further verified by the $\alpha(T)$ measurements.
In Table 5.2, $\alpha(T)$ values are presented for the Bi-Te posts. The optimal Bi:Te stoichiometry of 2:3 was achieved at -140 mV. This indicates that the p-type material was obtained for $E< -0.140$ mV while n-type material was obtained for $E> -0.140$ mV. The maximum of $\alpha(T)$ appeared near the stoichiometric composition. The negative values of $\alpha(T)$ indicate n-type Bi-Te while the positive values indicate p-type Bi-Te. The maximum value of n-type $\alpha(T)$, $-100 \pm 20 \% \mu$V/K, was observed at -80 mV. This was about half of that reported for the n-Bi$_2$Te$_3$ polycrystal$^{5,15}$. The $\alpha(T)$ values decreased at more negative potentials than -80 mV and showed a constant value of $-50 \pm 20 \% \mu$V/K in the potential range from -100 to -130 mV. The maximum value for $\alpha(T)$, $80 \pm 20 \% \mu$V/K, for p-type was observed at -150 mV. Thus, there is some agreement between the EDXRF results and the Seebeck $\alpha(T)$ measurements. However, the uncertainty and variability in the Seebeck measurements does suggest that further experiments are clearly needed. Surface SEM micrographs of the films are shown in Fig. 5.20. Voids were observed in all of the cases and the surface morphology changed on transition from n-type to p-type. For potentials near – 80
mV (Vs SCE) the deposit appeared to be gray and very smooth by eye. The smoothness of
the film and its uniformity can be attributed to slow growth. At more negative potentials, the
feature sizes increased and the films were much rougher. This smaller grain size and rougher
morphology could be attributed to faster growth rates.

5.6 Conclusions

It was shown that successful production of µTECs is feasible by means of
electrodeposition techniques in combination with LIGA technology. The TE films were
optimized by performing characterizations using various film compositions. The maximum
$a(T)$ values of $80 \pm 20 \% \mu V/K$ and $-100 \pm 20 \% \mu V/K$ were measured for p-type and n-type
Bi-Te respectively. These results corresponded with that obtained from the EDXRF analysis.
However, further studies are needed to account for the variability and uncertainty in $a(T)$
measurements.

5.7 References

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Chapter 6
Conclusions and Future Work

6.1 Conclusions

As a first step towards modulating temperature changes at the cellular level, microfabricated arrays of individually addressable µTECs were thermally modeled, fabricated and characterized. The prototype device was an array of 4 x 4 µTECs that were formed by electrodeposition of bismuth, (Bi) and telluride, (Te) alloys. Within the array, the coolers were interspersed to enable each one to be individually addressable and with each individual TEC having an n-type and p-type elements.

6.1.1 Modeling

To determine the optimal operating conditions and predict the interplay among the various system parameters a design methodology involving lumped parameter and FEA was adopted. The lumped parameter model was based on a set of differential equations describing one-dimensional thermal dynamics through all of the intermediate layers and guided the choice of the preliminary dimensions. The problem formulation accounted for the temperature dependence of TE parameters and time-temperature dependence of the properties of the thermoelectric materials. The effects of electrical contact resistance and element shape were included. For maximum \( \Delta T \) value, the ratio between the TEC element height and thickness was predicted to be around 1.8. Due to the proposed end application of modulating local temperatures in biological cells there was a design constraint on the maximum thickness of the µTEC. The thickness and the width of the TEC were restricted to be 10 µm. The height of TEC leg element was constrained to lie between 15-20 µm ideally. It was also shown that a
smaller interconnect height was beneficial for achieving a larger temperature drop across a μTEC.

Unlike macro scale thermoelectric systems, a new secondary breakdown current limitation was observed for μTECs. It occurred due to a thermal breakdown in the ceramic end plates and metallic interconnects and was found to be much lower than the primary breakdown due to Joule heating. To obtain operational results closer to the estimated values, the current was varied within 0.1-1 mA range. Further investigations are necessary to verify the reason behind the existence of the secondary breakdown current.

To further understand the interactions between the μTECs within the array a thermal system model in ANSYS® (Version 9.1, ANSYS, Inc., Canonsburg, PA) was developed. The ANSYS model was used to understand the effect of TEC element spacing on the individual μTEC and the combined heat transfer through the device under various operating conditions. The combined results from the lumped parameter model and the ANSYS model were used to determine the final device dimensions and are listed in Table 3.2. Additional results from the ANSYS model showed that minimal thermal interference between adjacent μTECs was achieved when devices were 50 μm apart.

6.1.2 Characterization and Fabrication

For the fabrication of the device it was essential to electrodeposit the p-type and n-type branches of the μTECs. To achieve this, doped alloys of Bi-Te were electrodeposited with the stoichiometric composition ratio of 52.2 % Bi and 47.8 % Te being electrically neutral. The electrodeposition characteristics of Bi-Te were determined using a Rota-Hull® cell with the current densities ranging from 0.2 to 13.88 mA/cm². It was found that n-type and p-type element deposition could be achieved by varying the cathodic potential while maintaining the same bath composition. The Rota-Hull® experiments indicated that the p-
type material would be obtained for values of $E < -60$ mV and the n-type for values of $E > -60$ mV. It was determined that the deposition reaction was kinetically controlled and independent of the rotation rate. It was also found that due to a large side reaction, it was desirable to pulse plate with a cycle of 4:1, off-time:on-time, while depositing into a recess.

The compositional analysis of Bi-Te thin films further supplemented these earlier Rota-Hull® cell results. Thin film samples were prepared by electrodepositing Bi-Te on a Cu-Ti seeded SOI wafer. The relative concentrations of the Bi-Te were measured using an EDXRF Spectrometer (Kevex Omicron) and averaged over five distinct locations for each sample. Uniform plating was observed throughout the film surface. The p-type material was obtained for $E < -155$ mV while n-type material was obtained for $E > -155$ mV. The potential scales so obtained were different from those predicted by the Rota-hull® data by $-80$ mV and the discrepancy was probably related to the compositional differences in the Cu plating base between the experiments.

The EDXRF results were further verified by Seebeck coefficient, $\alpha(T)$ measurements. Using an average value of $\alpha(T)$ an uncertainty factor of $\pm 20$ % was obtained. This was in accordance with the large variations observed during repetition of the $\alpha(T)$ measurements for same sample. The maximum value of n-type $\sigma(T)$, $-100 \pm 20$ % $\mu$V/K, was observed at $-80$ mV. The $\sigma(T)$ values decreased at potentials more negative than $-80$ mV and showed a constant value of $-50 \pm 20$ % $\mu$V/K in the potential range from $-100$ to $-130$ mV. The maximum value for $\sigma(T)$, $80 \pm 20$ % $\mu$V/K, for p-type was observed at $-150$ mV. There was some agreement between the EDXRF results and the Seebeck $\sigma(T)$ measurements. However, the uncertainty and variability in the Seebeck measurements does suggest that further experiments are clearly needed.
The microfabrication process for the µTECs was divided into four layers: wiring layer (bottom connectors), p-type TEC elements, n-type TEC elements and the junction layer (top connectors). The proposed 4-layered µTEC was fabricated using a modified UV-LIGA process on a Cu-Ti seeded SOI wafer. Due to the multiple exposures of each layer, positive photoresists were used. For the thick post layers of around 19 µm, a high thickness method of spin coating was used. A three electrode set-up was used to electrodeposit each layer. Utilizing the modeling results, the µTECs were fabricated with the distance between the TEC elements varying between 5 and 15 µm, including one with an optimum value of 10 µm. The column width of the elements was limited to 10 µm, to ensure the uniform stoichiometry of the Bi-Te compounds. The µTECs with TE leg distances > 10 µm were successfully fabricated while those < 10 µm faced fabrication issues during exposure and deposition of the second TEC posts. The junction layer was successfully fabricated by ebeam evaporating a Cu-Ti seed layer, lift-off, re-spinning and exposure of PR and finally electrodeposition of Cu into the resulting Cu-Ti seeded junction layer. The final step involved the etching away of Cu-Ti seed layer to insure the electrical insulation between the individual µTECs.

The specifications obtained from modeling were achieved and future measurements are needed to characterize the working of the µTEC. A maximum $\Delta T$ of 2 K is expected for the proposed current conditions between 0.1 and 1.2 mA.

6.2 Future Work

Future work includes additional compositional analysis of the electrodeposited n- and p-type posts using wavelength dispersive x-ray microanalysis (WDS) system. The sample preparation for WDS analysis involved molding and curing the sample into an Epothin low viscosity resin [Buehler®, Lake Bluff, IL] mixed with Epothin hardener pint [Buehler],
cutting and polishing using diamond slurry, DP Spray [Struers® Cleveland, OH] (Fig. 6.1). The setting temperature was at room temperature. The WDS analysis is currently underway to help determine the local phase compositions along the height of the TEC elements.

Figure 6.1: Samples for WDS analysis (a) Sample prepared at – 80 mV (n-type post) (b) Sample prepared at -150 mV (p-type), the post did not adhere well to surface and is titled off the base.

Also, Cu has a natural tendency of intercalating and leaching into and out of Bi-Te. However, due to the presence of the Ti adhesion layer, it was assumed that this reaction of Cu with Bi-Te might be neglected. For future measurements, Ni or Ni-Cu should be used as the plating base as opposed to Cu. Cr could replace Ti as the adhesion layer thereby solving the final etching problems and insuring electrical insulation between the individual µTECs.

From the modeling results it was determined that the current for the µTEC should be pulsed at 60 seconds. The pulsing of current could be achieved by using a simple TE/thermal switch configuration. The final device should include one or more thermal switches in addition to the thermoelectric elements. The TEC couple should be subjected to a current pulse, allowing the cooling action to take place when the switch is closed. However, before the backflow of Joule heat can flow, the switch should be opened, allowing the current to return to the optimum steady state value. This could be incorporated in future attempts of
fabricating the device. The final aim of the project is to achieve localized control of temperature for biological cells. To do so it is essential to insulate the cell matrix and the device. This can be achieved by embedding the device in polymethylmethacrylate (PMMA) layer that will act as an interface between the cell matrix and the device and insulate the same.

6.2.1 Thermal Characterization and Testing
The modeling results need to be validated by thermal characterization and testing of the fabricated array of individually addressable µTECs. As a first step, the µTECs on a SOI wafer should be mounted on a temperature-controlled heat sink. The µTECs are arranged in a circular pattern on the wafer with two copper traces ending in pads radiating out from each cell. To interface the electronics to the SOI wafer, a printed circuit board (PCB) with spring loaded gold pins arranged in the same pattern has been designed and built by Don Patterson of the Center for Biomodular Multiscale Systems (CBM²). The board should then be lowered down on the wafer until the gold contacts seated on the copper pads providing the electrical connections (Appendix C). Monitoring the voltage drop across each device may be of diagnostic value. This could help establish the breakdown regions of the individual µTECs.

An infrared (IR) thermal microscope and camera can be used to obtain the thermal image of the fabricated µTECs operating between 0.1 – 1 mA. In such a case, any fabrication defects or electrical short-circuit between the wiring layer and junction layer could be detected by the presence of isolated areas with large temperature gradients. The presence of non uniform temperatures at the junction layer (top connectors) could indicate TEC element surface roughness or oxidation. Finally the device should be tested with actual biological cells. This could indicate whether the fabricated µTECs are suitable for achieving localized control of temperature in cells.
Figure A1: Layer 1, wiring layer photomask. All the masks are made on a 5” chrome glass plate.
Figure A2: Detailed view of the center of Layer 1, wiring layer photomask.
Figure A3: Layer 2, p-type posts photomask layout.

Figure A4: Detailed view of the center of Layer 2, p-type photomask.
Figure A5: Layer 3, n-type posts photomask layout.

Figure A6: Detailed view of the center of Layer 3, n-type photomask.
Figure A7: Layer 4, junction layer photomask layout.

Figure A8: Detailed view of the center of Layer 4, junction layer photomask.
Appendix B

Electroplating Jig Design
Appendix C

Testing Plans and Hardware Design

The control circuits in the PCB were designed to provide constant power to, and voltage monitoring from, four µTECs (Fig. C1). Power is programmed for each µTEC through a National Instruments NI 6229 DAQ card. The µTEC are best powered from constant current rather than constant potential sources. It was established that the fabricated µTECs require very small currents. To meet this requirement, very stable transconductance amplifiers were designed with a gain of 0.1 mA/V. These are labeled G1 thru G4 on the Fig. 6.2. Thus, a 0 to +10 V potential from the DAQ card could produce a 0 to 1 mA current through each µTEC. With the 12 bits available, this would allow a current resolution of .244 μA / LSB.

![Figure C1: Block diagram of the control circuits in the PCB](image-url)
The voltage drop can be sensed by amplifiers (labeled A1a to A4a) with a voltage gain of 100. These amplifiers were selected for their ability to operate up to the positive supply rail. The output was then buffered by differential amplifiers (A1b to A4b) and transmitted by twisted pair cables to the 12 bit A/D converters on the DAQ card. The differential signaling through the twisted pair improves signal integrity by minimizing common mode noise pickup.
Vita

Aparna Prabhakar was born on 16th July, 1981, in Bangalore, India. Being born to an army household, Aparna’s schooling was done all over India and she received her undergraduate degree in electronics and communication engineering from Visveswaraiah Technological University in July 2003. To further widen her horizons, she came to United States of America to pursue the mechanical engineering graduate program in Louisiana State University in Fall 2003. She is a candidate for the degree of Master of Science in Mechanical Engineering to be awarded at the commencement of Summer 2006. In the process of obtaining the degree, Aparna not only increased her knowledge base but also met some fantastic people. She enjoyed her area of research and worked with some of the best people. She will be moving to New York with her husband and will be actively pursuing various employment opportunities.