MEASURING THE THERMOELECTRIC PROPERTIES OF NANOMATERIALS WITH A MICROMACHINED WORKBENCH

MATTHEW P. CHANG
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Reviewed and approved* by the following:

Srinivas Tadigadapa
Professor of Electrical Engineering
Thesis Supervisor

John D. Mitchell
Professor of Electrical Engineering
Honors Adviser

*Signatures are on file in the Schreyer Honors College.
Abstract

Thermoelectric devices, which can convert thermal energy into electrical energy or provide a method for solid state cooling, have not been used as a widespread source of renewable energy because of their unmarketably low efficiencies. Recently, however, the development of certain nanomaterials and nanostructures, and a demonstration of their enhanced thermoelectric efficiencies, have reignited the search for an efficient thermoelectric material. Investigating these enhanced thermoelectric effects has not been easy for the scientific community because studying the physics of nanomaterials is a complex and sensitive task. As such, widely accepted, conformal, or statistical data has not been gathered.

This honors thesis presents a micromachined workbench designed specifically to study the thermoelectric properties of nanomaterials in an easy and accurate way. Two generations of the workbench, consisting of different material compositions, are characterized and tested both thermally and electrically. The thermal sensitivity, thermal crosstalk, thermocouple performance, and thermal time constant are measured on all tested workbenches. On the electrical side, DC current-voltage (I-V) measurements are performed along with DC electrical crosstalk (leakage) measurements. A test system is created to perform all these measurements and is automated with LabVIEW™ code. The measurement system and associated code will be shown and described briefly.

The thermopower of 70 nm diameter gold nanowires are measured using both workbenches. The results of the gold nanowire thermopower measurements and the workbench characterization measurements are presented here. An evaluation of both workbench structures, including their benefits and flaws, are also presented along with suggested improvements for future work.
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List of Symbols

\( \Delta V \)  Thermoelectric Voltage
\( T \)  Temperature
\( S \)  Seebeck Coefficient
\( Z \)  Thermoelectric Figure of Merit
\( ZT \)  Dimensionless Thermoelectric Figure of Merit
\( \sigma \)  Electrical Conductivity
\( \kappa \)  Thermal Conductivity
\( \kappa_{ph} \)  Phonon contribution to thermal conductivity
\( \kappa_e \)  Electronic contribution to thermal conductivity
\( \eta \)  Efficiency
\( e \)  Fundamental electronic charge
\( k \)  Boltzmann Constant
\( \langle v \rangle \)  Mean phonon velocity
\( \lambda \)  Phonon mean free path
\( \rho \)  Mass Density
\( c_p \)  Specific heat
\( \nabla^2 \)  Laplacian Operator
\( Q \)  Power volume density
\( I \)  Drive current
\( I \)  Cross-sectional area

\( L \)  Length of heater

\( \Delta V_{TC} \)  Difference in voltage drops between the hot platform thermocouple and the cold platform thermocouple
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Chapter 1

Introduction

1.1 Thermoelectricity

In 1821, Thomas Seebeck discovered that a circuit composed of two dissimilar materials held under a temperature gradient produced an electrical current. Thomas Seebeck had discovered thermoelectricity: the generation of an electric field from a temperature gradient and vice versa. Since then, mankind has created and used many thermoelectric devices for practical applications. For example, NASA uses radioisotope thermoelectric generators (RTGs) in many of their missions to produce electrical energy from radioactive heating in remote regions of space where even solar cells are not sufficient [1]. Thermoelectric devices are also capable of the reverse process: they can provide solid-state cooling. Today we can find creative applications such as thermoelectrically cooled picnic baskets and heated/cooled car seats. The promise of using small, inexpensive, solid state thermoelectric devices seems like a dream come true. Thermoelectric coolers would remove the need for environmentally harmful chemicals that are currently used in refrigerators. In addition, because they would have no moving parts, thermoelectric coolers would have a reduced failure rate compared to current technology. The use of these devices to cool computer chips and laser diodes, or even better, convert the dissipated heat into reusable energy would revolutionize the industry both economically and technically. Thermoelectric devices have the potential to explode into a multi-billion dollar industry if these devices work efficiently [2].

Yet, for how fortuitously nature created such a mechanism to convert thermal
energy into electrical energy and vice versa, mankind has not taken full advantage of this gift. The reason lies in the unmarketably low efficiency of thermoelectric devices, which have stunted the growth of this technology for decades. The efficiencies of thermoelectric devices are defined relative to the Carnot efficiency of the device. To give some perspective, today’s thermoelectric devices operate at around 10% of the Carnot Efficiency (∼3-4% absolute efficiency in the room temperature regime). Current refrigerators operate at around 30% (∼8% absolute efficiency), and air conditioners at around 90% (∼24%) [2]. It is easy to see why thermoelectric devices, despite their advantages, have not become a widespread technology: it simply does not make sense economically. As a result, thermoelectric devices are typically only used in niche applications where cost and efficiency are not concerns compared to energy availability and reliability [2, 3]. The low efficiency of thermoelectric devices originates from material limitations. It is in the field of thermoelectric materials that many hope to be able to improve thermoelectric efficiencies.

There are three types of thermoelectric effects: the Seebeck Effect, the Peltier Effect, and the Thomson Effect (named after their founders, respectively). The Seebeck Effect describes the generation of an electric field due to a temperature gradient. This effect is used in temperature measurement in thermocouples, and energy generation in thermoelectric devices. The Peltier Effect describes the heat absorbed or produced when a current is passed through a junction composed of two different materials. It is the Peltier Effect that is used in reversible thermoelectric cooling/heating applications. The Thomson Coefficient describes the heat absorbed or produced when a current is passed through a homogeneous material with a temperature gradient already established. This thesis only focuses on the Seebeck Effect, although all three effects are related through the Thomson or Kelvin relations [4].
1.2 The Seebeck Effect and the Thermoelectric Figure of Merit

Every material is a thermoelectric material; in fact, thermoelectric properties are fundamental material properties akin to thermal and electrical conductivity [5]. To see this, imagine a uniform, homogeneous material. When a temperature gradient is maintained across the material, the hot charge carriers diffuse to the cold end. As a result, a charge imbalance is established in the material, creating an electric field; a state of equilibrium is reached when the diffusion current is balanced by electrostatic repulsion. Note that even in this state of equilibrium where net charge does not flow, thermal energy will continue to flow from the hot end to the cold end via mechanisms such as charge carriers and lattice vibrations (phonons). How well a material conducts heat is given by the material property of thermal conductivity.

![Diagram of temperature gradient and voltage generation](image)

**Figure 1.1.** A temperature gradient across a material creates an electric field along the temperature gradient.

A basic schematic of this concept is shown in Figure 1.1. The voltage generated across the material, called a *thermoelectric voltage*, is given by $\Delta V$. The thermoelectric voltage produced when the material is held under a differential temperature gradient is known as the Seebeck Coefficient [4]:

$$S(T) = \frac{dV}{dT}$$  \hspace{1cm} (1.2.1)
where $S$, the Seebeck Coefficient, is a function of temperature. The Seebeck Coefficient is a fundamental property of all materials. For small changes in temperature, the Seebeck Coefficient can be considered to be a constant. Thus, for a material under a small temperature gradient, we can calculate the resulting thermoelectric voltage across the material using equation (1.2.1):

$$
\Delta V = \int_{T_1}^{T_2} SdT = S(T_2 - T_1) = S\Delta T
$$

For here onwards the Seebeck Coefficient will be treated as a temperature independent value for mathematical simplicity unless stated otherwise. However, this temperature dependence is an essential property of the Seebeck Coefficient and must always be kept in mind when constructing actual applications.

It should be noted that the thermoelectric voltage is being generated along the entire length of the material (via the temperature gradient), and not just at the ends. This means that equation (1.2.2) is only valid for homogeneous materials; otherwise, the Seebeck Coefficient is also a function of position which must be taken into account. This is important to keep in mind when speaking about thermocouples, whose accuracy depends on the homogeneity and purity of the two materials which form the thermocouple junction.

The Seebeck Coefficient itself is not a sufficient measure of how well a material will perform as a thermoelectric device. An ideal thermoelectric device will have a high Seebeck Coefficient but will also have a high electrical conductivity and low thermal conductivity. Intuitively, this means that the material will conduct electricity very well while simultaneously maintaining the applied temperature gradient, which is driving the charge in a current. Together, these parameters form the Thermoelectric Figure of Merit, which is a measure of how well a material will perform as a thermoelectric device [6] and is given by

$$
Z = \frac{\sigma S^2}{\kappa}
$$

More often, the dimensionless thermoelectric figure of merit will be used. It is simply the thermoelectric figure of merit multiplied by temperature and, as the name implies, is dimensionless. It is given by [5]
\[ ZT = \frac{\sigma S^2 T}{\kappa} \]  

(1.2.3)

where \( S \) is the Seebeck Coefficient, \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity, and \( T \) is temperature. Specifically, the thermal conductivity has contributions from both the charge carriers and phonons i.e. \( \kappa = \kappa_{ph} + \kappa_e \). This difference is important to keep in mind.

The overall efficiency of any thermoelectric device can be shown to be [5]

\[ \eta = \frac{\Delta T}{T_H} \sqrt{1 + ZT} - 1 \]

\[ \frac{1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \]

(1.2.4)

**Figure 1.2.** Efficiency of thermoelectric materials as a function of ZT. Commercial \( Bi_2Te_3 \) material shown with ZT = 1. Taken from [5].

where ZT is the dimensionless thermoelectric figure of merit, \( T_H \) is the temperature at the hot end, \( T_C \) is the temperature at the cold end, \( \Delta T = T_H - T_C \), and \( \Delta T/T_H \) is the Carnot efficiency. As can be seen from the equation 1.2.4, the efficiency can never exceed the Carnot efficiency. In addition, the higher the ZT, the better the efficiency. Figure 1.2 shows a plot of efficiency against ZT. Today’s commercial \( Bi_2Te_3 \) thermoelectric devices have a ZT of about 1 with a relatively poor efficiency of around 4%, but improving ZT by even a little will have increasing gains.
1.3 Thermoelectric Materials

The goal of research into thermoelectric materials has always been to increase the ZT factor. The field of thermoelectricity met large obstacles because the three factors in the thermoelectric figure of merit, Seebeck Coefficient, electrical conductivity, and thermal conductivity are not independent parameters. Increasing the Seebeck Coefficient often led to a decrease in electrical conductivity; an increase in electrical conductivity also led to an increase in thermal conductivity [5, 7]. Very quickly, ZT approaches a limiting value in conventional materials which makes thermoelectric devices composed of these materials quite inefficient. Metals, for example, are limited by the Weidemann-Franz Law [5, 8], which states that

$$\frac{\kappa_e}{\sigma T} = \frac{\pi^2 e^2}{3k^2}$$

(1.3.1)

where $\kappa_e$ is the thermal conductivity due to charge carriers, $k$ is the Boltzmann constant, and $e$ is the fundamental electronic charge. The thermal conductivity has contributions from both charge carriers and phonons i.e. $\kappa = \kappa_{ph} + \kappa_e$. Thus for bulk metals, where electrons carry most of the heat, this fundamental limit always couples electrical and thermal conductivity in a way that limits ZT. In addition, due to the high number of mobile charge carriers in metals, most of the energy distribution in metals are occupied by electrons. By the Pauli Exclusion Principle, only the relatively few electrons at the top of the conduction band may participate in the transfer of energy with the surroundings i.e. absorb heat. As a result of these limitations, the best ZT of metals hovered around $ZT = .04$, with the best Seebeck Coefficient of about $30 \, \mu V/K$ [5].

This fundamental limit caused the field of thermoelectricity to go cold until the 1950’s, when Abram Ioffe discovered that doped semiconductors possessed improved thermoelectric properties [5, 7]. It was actually this discovery that led semiconductors into the world-wide stage, rather than their current use in microelectronics [9]. Semiconductors possess a lower density of carriers and as a result have a thermal conductivity that has a stronger contribution due to phonons, $\kappa_{ph}$, than charge carriers, $\kappa_e$ [8]. Because of this, semiconductors allow a possible decoupling of electrical conductivity and thermal conductivity which is not possible in metals. By creating scattering centers which preferentially scatter phonons
over charge carriers, semiconductors gave hope for improving ZT. In addition to changing the thermal conductivity, semiconductors also have an improved Seebeck Coefficient due to the semiconductor bandgap. Through the bandgap, charge carriers can absorb more heat than their metal counterparts giving semiconductor charge carriers a higher “specific heat” than metal charge carriers.

The excitement of the 1950’s and 1960’s led to the rise of a thermoelectric industry, with bismuth telluride alloys as the thermoelectric material of choice, particularly \( Bi_2Te_3 \). Commercial bismuth telluride compounds, as shown in Figure 1.2 have a peak ZT around 1. Their improved ZT comes from the compounds’ large atomic masses, which reduce mean phonon velocity. In addition, the alloying of two compounds (i.e. having two types of atoms in the lattice) creates greater scattering of phonons and a shorter mean free path while not harming electrical conductivity as much \[6\]. As the kinetic equation for thermal conductivity is

\[
\kappa_{ph} = \frac{1}{3} C <v> \lambda
\]

the phonon contribution to thermal conductivity is reduced, where \( C \) is the heat capacity, \( <v> \) is the mean phonon velocity, and \( \lambda \) is the phonon mean free path.

Despite the advances in the thermoelectric materials, scientists and researchers continued to struggle to improve ZT above 1. From the 1960’s to the 1990’s, the thermoelectric industry once more went quiet, until the arrival of nanomaterials.

1.4 Thermoelectric Nanomaterials

With the nanotechnology revolution in the 1990’s also came renewed interest in thermoelectricity. The reason was because nanomaterials possess properties different than their bulk counterparts. Particularly, researchers hoped to be able to decouple the Seebeck Coefficient, electrical conductivity, and thermal conductivity or at least reduce their coupling, so that they could improve ZT. Under the pending energy crisis and environmental concerns, the US Department of Defense began investing into thermoelectrics with hopes of reinvigorating the field, and they succeeded as research in thermoelectrics took flight once more \[3\]. The general techniques using nanomaterials to improve ZT that were explored were:
• Increasing the product of $\sigma S^2$ (also called the power factor) using quantum confinement.

• Reducing thermal conductivity without changing the power factor by increased interface scattering and specially designed nanostructures.

The ideal materials were so-called “Phonon-Glass-Electron Crystals” for their low phonon (and thus thermal) conductivity, but high electronic conductivity.

Both bulk semiconductors and low-dimensional nanomaterials experienced new approaches. For bulk semiconductors, one approach is to embed dissimilar atoms into the semiconductor crystal lattice forming what are called clathrates and skutterudites. Because the embedded atoms vibrate differently than the rest of the lattice, they disrupt the phonon transmission and reduce thermal conductivity.

Low-dimensional nanomaterials provide hope for increasing ZT for two main reasons. First, the physically small length scales of nanomaterials, whether width, length, or thickness, reduce phonon transmission. If these length scales are smaller than the phonon mean free path, then the new effective mean free path will be modified by the nano length scale \[5, 8\]. Surface interface scattering also increases phonon scattering while not increasing electronic scattering as much \[3, 6\]. Second, quantum effects, such as quantum confinement, begin to affect the system. Quantum confinement is the principle that as the size of a material decreases, so that the number of atoms become significant, the continuous energy band structure begins to show discrete bands. This changes the Density of States (DOS), and as a result the Seebeck Coefficient \[5, 3\].

![Figure 1.3. Density of States (DOS) of different quantum structures as a function of energy. Taken from [3].](image)

In particular, for quantum well, quantum wire, and quantum dot structures, sharp peaks and jumps theoretically appear in the density of states as shown in
Figure 1.3. Since the Seebeck Coefficient is related to the energy derivative of the density of states \([5]\), this results in an increase in the Seebeck Coefficient.

One method that has been met with some success is quantum well or quantum dot superlattice structures. These structures are composed of extremely thin (nanometer length scale) alternating layers of different materials. The boundaries between materials create enhanced scattering of phonons more so than charge carriers. The first demonstration of an enhanced thermoelectric effect was shown in 2D superlattices consisting of PbTe quantum wells \([10]\). Both n-type and p-type quantum well superlattice structures were successfully fabricated, which is important for practical applications. A quantum dot PbSeTe/PbTe superlattice structure was created by Harman et al. which showed a ZT of of 1.3 to 1.6 at room temperature \([11]\).

Figure 1.4. A graph of ZT versus temperature for several different materials. Bulk SiGe alloy Radioisotope Thermoelectric Generators (RTG) used by NASA are shown as the dotted line. SiGe nanocomposite alloys are measured with significant improvements. Taken from \[3\].

A similar approach that might be more suitable for mass production involves fabricating nanocomposites onto the bulk material \([12]\). These nanocomposites introduce randomly placed nanostructures and nanoparticles into a bulk material.
The idea of the nanocomposites is to reduce the thermal conductivity by increasing phonon scattering centers. Because a difference between phonon wavelengths and electronic wavelengths exist, nanostructures can be fabricated on length scales between the two, to disrupt phonon mean free path while not disrupting electronic mean free path as much. At the same time, nanocomposites also aim at increasing the power factor, \( \sigma S^2 \), by increasing S more than decreasing \( \sigma \). It has been found that these nanocomposites can increase the power factor while simultaneously decreasing the thermal conductivity [3]. SiGe alloys with nanocomposites were found with both a better power factor and a more reduced thermal conductivity, thus resulting in a higher ZT, than their bulk counterparts as shown in Figure 1.4.

Nanowires have also been studied extensively by groups for any enhanced thermoelectric effect. Bismuth nanowires were one of the first studied, due to bismuth’s success as a thermoelectric bulk material, albeit in an alloy. Bismuth alone would not be a successful thermoelectric material since the equal number of electrons and holes in the material would negate their thermoelectric effect. However, in a quantum structure, a semimetal-semiconductor transition was predicted as the conduction intersubband moved upward in the energy spectrum while the valence intersubband moved downward. This was experimentally observed by Dresselhaus et al. [6], although not by Heath et al. [13]

Quite some excitement was generated when Heath et al. and Yang et al. reported about a 100-fold increase in ZT of silicon nanowires [14, 8]. Bulk silicon is not a good thermoelectric material because of its high thermal conductivity, with a ZT of less than .01. As a result, the 100-fold increase does not provide ZT above 1; however, the 100-fold increase in conjunction with the current industry’s ability to mass produce low-cost silicon products provides hope for commercialized thermoelectric devices based off of silicon nanomaterials. Both groups reported that the enhanced ZT was a result of a significantly reduced thermal conductivity, and that the ZT was a function of (inversely related to) nanowire diameter as well as doping level (an optimal point seemed to exist). Heath et al. attributed the decrease in ZT to phonon drag.

Phonon drag is the effect of phonons “pulling” electrons down a temperature gradient. This effect is typically seen in samples held under a temperature gradient at temperatures below the Debye temperature. If the sample temperature rises
above the Debye temperature, then most phonon modes are excited and phonons
will pull electrons in both directions thus reducing the phonon drag effect. The
phonon drag induced thermoelectric enhancement is typically seen in metals at low
temperature, and has also been reported by Tadigadapa et al. in polycrystalline
gold nanowires at around 50K [7].

The search for an enhanced thermoelectric effect that can be harnessed in com-
mmercial thermoelectric generation and cooling applications continues today. Not
only are groups looking into different materials and structures, as mentioned above,
but they are also looking for different phenomena and effects to enhance the ther-
molectric effect. For example, Tadigadapa et al. have reported a significant (at
least 10-fold) thermoelectric enhancement near room temperature in junctioned
nanowires which originates from a thermotunneling effect [7]. Other groups have
also looked into using the idea of energy-filtering i.e. filtering high energy elec-
trons/phonons from low energy electrons/phonons to enhance the thermoelectric
effect. Mahan also investigated thermionic effects in the 1990’s [9]. The search,
however, has not been easy.

1.5 Measuring Thermoelectric Properties

Despite the recent push in thermoelectric research, relatively few groups have ex-
perimentally measured the thermoelectric enhancement in nanomaterials. Dressel-
haus et al. have acknowledged the difficulty in characterizing these nanomaterials
and have cautioned against jumping to conclusions with the presently reported
ZT values [6]. Even those groups that have reported ZT values appear to differ
significantly [5]. The reason is the highly sensitive nature of measuring nano-
materials, particularly their thermal characteristics, as well as the dependence of
thermoelectricity on many parameters. For example, Dresselhaus et al. found
that temperature, constituent atomic percentage, doping level, and size (such as
nanowire diameter) have a strong effect on ZT [3]. In addition, different fabrica-
tion methods with under different processing conditions yield nanomaterials with
different properties. For example, Yang et al. used an electroless etching method
to produce rough silicon nanowires. They claimed that the roughness helped to
reduce thermal conductivity and boost ZT [14].
Figure 1.5. A collection of thermoelectric workbenches fabricated by different groups. 

(a) and (b) are both the same workbench taken from [8]. This workbench was fabricated around a nanowire array (not visible in either picture) and is suspended by electrical contacts. This is why the background of image (a) is out of focus. (c) is a workbench taken from [7] and is constructed first before nanowire deposition.

Measuring the nanomaterial is a complex task. Isolating an individual nanomaterial is difficult and some groups choose to measure clumps or clusters of the nanomaterial for fabrication simplicity. However, a single nanomaterial’s properties cannot be easily extracted from this data. To measure a single nanomaterial, the nanomaterial must be fabricated and somehow isolated and deposited onto a test workbench. There are two conventional approaches to this process: fabricate a workbench first and deposit the nanomaterial on the workbench or deposit the nanomaterial first and fabricate the workbench around it. There are benefits and flaws to both of these methods. In the case of fabricating a workbench first, deposition of the nanomaterial in the exact proper position on the workbench is difficult. Most groups who take this approach use a stochastic process of drop-casting nanomaterials onto the workbench [14, 7] and hope that a nanowire falls in an active region. The test workbench must have a high enough active area so that the yield of testable samples is high enough to collect statistically relevant data. Figure 1.5c shows a workbench which is fabricated prior to nanowire depo-
sition. Single nanowires can be readily found due to the high density of the test workbenches on the chip [7]. In the case of building the workbench around the nanowire, this circumvents the task of depositing the nanomaterial in the proper spot on the workbench. However, this method exposes the nanomaterial to processing conditions of high temperatures, different pressures, and processing gases, potentially varying the nanomaterial’s properties. Figure 1.5a and b show a workbench which has been fabricated around the nanowire array [8]. In Figure 1.5a, a zoomed-in view of the workbench is shown with the nanowire array in the green area (actual nanowires cannot be resolved). The resistive coils on either side of the array are resistors to create a temperature gradient, with electrodes coming in to perform thermometry and measure the thermoelectric voltage. The workbench is suspended by the electrical contacts (which is why the background in Figure 1.5a is out of focus) and this is shown in Figure 1.5b. While this ensures electrical contact and that the nanowire will be in the correct place, it is also difficult to produce high quantities of this type of workbench-nanowire set up.

To measure the ZT of any device, one must measure electrical conductivity, thermal conductivity, and the Seebeck Coefficient. Measuring the Seebeck Coefficient itself requires that a temperature gradient be generated across the nanomaterial, and both the resulting thermoelectric voltage as well as the temperature gradient be measured. Measuring absolute or relative temperature on the nanoscale has proven to be a difficult task. One method is to use a Platinum Resistive Heater (PRT) which uses the temperature dependence of resistance to determine absolute temperature as in [15]. However, the very act of measuring temperature will then affect the local temperature, introducing uncertainties into the measurement. Other alternatives include using a thermocouple or using different types of microscopy such as SThM (Scanning Thermal Microscopy) [5] and SJEM (Scanning Joule Expansion Microscopy) [16]. When measuring something like thermoelectric voltage, contributions may also come from the other materials used in the connecting wires, the interconnects, and the contact pads. A good set up must be sure to account for all these extra effects.

Needless to say, the act of measuring thermoelectric properties of nanomaterials is no simple task. Duarte has fabricated a thermoelectric workbench that has a high density of test sites, thus preventing any unnecessary post-processing of nano-
materials while still obtaining high sample yield. It has a platform arrangement that can generate a temperature gradient and extract the resulting thermoelectric voltage [5]. In addition, the temperature can be determined by measuring the AC resistance of the nickel heater. This thesis project characterizes a second and third generation of Duarte’s workbench, and tests nanomaterials using them. Significant design changes were made to the workbench to improve sample yield and obtain accurate results on a variety of nanomaterials. The workbench and associated workbench theory will be described in Chapter 2. The results of the workbench characterizations and nanomaterial measurements will be reported in Chapter 3. An evaluation of the workbenches will be given with suggestions for future improvements in Chapter 4.
A Micromachined Thermoelectric Workbench

2.1 Description

In this thesis project, a micromachined workbench has been fabricated and used to characterize nanomaterial thermoelectric properties. The workbench was designed to achieve the following objectives:

- Set up easy, reliable, and accurate measurements of nanomaterial thermoelectric characteristics
- Generate a high yield of testable samples
- Generate a relatively large and controllable temperature gradient
- Produce a method to determine thermoelectric voltage and temperature gradient
- Interfere as little as possible with the nanomaterial’s thermal and electrical physics.

These objectives influenced the workbench design, which will be elaborated upon in this chapter. Chapter 4 will present an evaluation of the fabricated workbench structures based on these objectives. Fabrication of these workbenches was done
tirelessly and painstakingly by Dr. Prasoon Joshi; this thesis will not focus on workbench fabrication, but rather on characterization and measurements. Details of the fabrication may be found in [17].

Figure 2.1. The general thermoelectric workbench structure is composed of a grid of interlocking, but isolated, platforms. Each platform has a conductive nickel surface, and a built in resistive heater and thermocouple to generate and measure a temperature gradient, respectively. The platform on the right is transparent to show the location of the heater and thermocouple. Nanomaterials are suspended across two platforms for testing. All active components are electrically isolated with silicon nitride. Taken from [18].

The micromachined workbenches used to characterize nanomaterials in this thesis project adopt the approach of fabricating the workbenches prior to nanomaterial deposition. This design strategy avoids exposing the nanomaterials to post-processing after deposition. It also helps increase throughput and simplicity, since a new specialized fabrication mask won’t have to be designed for each nanomaterial case. The design calls for a high test site density to yield many testable samples per die: there are 48 test sites/5 mm$^2$ on each 5 mm$^2$ die. A 10 x 10 array of such dies is fabricated on 4” wafers [17]. The active portion of the workbench, where nanomaterials are actually deposited, is in the central region of every die, and is composed of an interlocking grid of isolated platforms as shown in Figure 2.1. The platform is the basic component of the workbench. Each platform has a
conducting nickel top layer. Fabricated beneath this top nickel layer are a built-in resistive heater and thermocouple to generate and measure a temperature gradient, respectively. The thermocouple reads temperature in the open-circuit condition so that the natural temperature distribution won’t be disturbed by joule-heating as is the case in platinum resistive thermometers (PRTs). In Figure 2.1, the heater is a gold (Au) resistive coil while the thermocouple is a gold-nickel (Au-Ni) thermocouple. All electrically active regions of the workbench are isolated by a silicon nitride layer to prevent electrical leakage and crosstalk. Contact pads away from the center of the die allow electrical contact to each component of the workbench (not shown in Figure 2.1).

Figure 2.2. The general measurement process is shown between two platforms with a bridging nanomaterial. $\Delta T$ and $\Delta V$ are extracted.
The general measurement idea is shown in Figure 2.2. Ideally, nanomaterials are suspended between two adjacent platforms. By heating one platform and not the other, a temperature gradient is generated; this temperature gradient can then be measured by taking the difference of the thermocouple voltages between the two platforms. Because of the conductive nickel top layer, the thermoelectric voltage between two platforms (i.e. across the nanomaterial) can be measured directly. The determination of $\Delta V$ and $\Delta T$ will lead to the Seebeck Coefficient$^1$. Each platform is thermally isolated from its neighboring platforms by a deep trench (values to be specified later) to help maintain the temperature gradient and prevent thermal crosstalk between platforms. This trench, and the suspension of the nanomaterial, is designed to help maintain a large temperature gradient across the nanomaterial and prevent any substrate interference with the nanomaterial thermal and electrical transport.

All the features mentioned above are illustrated in Figure 2.1. Two types of workbenches were studied in this work: gold-nickel workbenches and polysilicon-gold workbenches. In general the workbench platforms have identical geometrical structures but different material composition; the differences will be motivated and explained below.

### 2.1.1 Gold-Nickel (Au-Ni) Workbenches

The first generation of this project’s workbenches (the second generation of Duarte’s workbenches) is shown in Figure 2.1, and is called a gold-nickel workbench (based off the fact that the built-in thermocouples have one leg of gold and one leg of nickel). Nickel ($S \approx -15 \mu V/K$ at 20°C) and gold ($S \approx +6.5 \mu V/K$ at 20 °C) are used for fabrication simplicity and because they have Seebeck Coefficients with opposite signs. Together, $S \approx 21.5 \mu V/K$ at 20 °C [5, 17]. In these workbenches, the heater is also composed of gold. The trench between platforms for these workbenches is around 5 $\mu m$.

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$^1$The thermoelectric voltage between the two platforms is not necessarily the thermoelectric voltage across the nanomaterial due to thermoelectric contributions from other parts of the measurement circuit. Corrections can be made by first measuring the thermoelectric voltage without any nanomaterial present and then subtracting this factor out from the actual measurement. More details of this measurement process are given later.
2.1.2 Polysilicon-Gold (Poly-Au) Workbenches

The second generation workbenches in this project used a polysilicon-gold thermocouple, with polysilicon heaters. The Seebeck Coefficient of polysilicon is a function of its doping level. According to [19], polysilicon with a Boron doping of approximately $10^{19} \text{cm}^{-3}$ has a Seebeck coefficient of approximately $350 \mu \text{V/K}$ at $20^\circ \text{C}$. Together with gold, the polysilicon-gold thermocouple has a Seebeck Coefficient of $344.5 \mu \text{V/K}$ - over an order of magnitude improvement over the gold-nickel thermocouple. This was the main motivation of the polysilicon-gold workbenches: to increase temperature sensitivity. In addition, to improve the thermal isolation between platforms, the trench between platforms was extended to 30 $\mu \text{m}$.

2.1.3 Post-Processing

The micromachined thermoelectric workbench is designed so that the nanomaterial under test will not be exposed to any post-processing conditions after deposition. Ideally, the nanomaterial is deposited and is ready for testing right away - or at the very most, after a voltage sweep to break down any native oxides that have formed. Despite this effort, two independent post-processing steps were found to be helpful in increasing sample yield and improving thermal isolation.

![Figure 2.3. SEM images of a gold nanowire (a) before and (b) after clamping by EBID. The clamp are the transparent rectangular blocks in (b).](image)

The first post-processing step involves clamping the nanomaterial to the workbench. It was very quickly discovered that random Electro-Static Discharge (ESD) events led to the demise of many nanomaterials devices during preparation. Whether
wire-bonding, transporting, or testing the devices, random ESD events decreased sample yield significantly. To counter this, nanomaterials were anchored to the platform after deposition and before characterization with Electron Beam-Induced Deposition (EBID) of platinum clamps, as shown in Figure 3.2. In EBID, a gas with platinum and carbon is released into the chamber that is holding the workbench with a nanomaterial deposited on it. An electron beam induces the deposition of the platinum/carbon composite on the surface where the electron beam strikes. The process was performed by a FIB, and the SEM environment may have introduced unknown contaminants to the nanomaterial. The EbeamPtDep recipe from the Penn State Nanofabrication Facility was used to perform the EBID. A spot current of .67 nA at 5kV acceleration voltage was used to establish rectangular platinum clamps with z-depth of 2 µm. The area of the platinum clamp was based on the shape and size of the nanomaterial to be clamped.

![Figure 2.4. An SEM image of a released workbench after XeF₂ etch.](image)

The second post-processing step involves releasing the workbench platforms with an isotropic XeF₂ etch. Currently, the platforms are simply isolated from each other with the deep trench described in previous sections. The objective of the release is to turn the platform into more of a cantilever structure so that heat will be better isolated on the tip of the platform. In addition, this will increase the temperature at the tip, since there will be a smaller thermal mass to heat up. Figure 2.4 shows an SEM image of a platform that has been released by a XeF₂ etch. XeF₂ etches the silicon substrate much more preferentially than anything
else on the workbench including the nanomaterial. As long as the number of etching cycles is kept low, the XeF$_2$ etch should be an acceptable process.

### 2.1.4 Platform organization and nomenclature

![Diagram of the thermoelectric workbench with mask layouts showing the central region and contact pads.](image)

**Figure 2.5.** Mask layouts of the thermoelectric workbench. (a) shows the mask of the entire die with quadrants of the central region labelled. Transmission lines connect the platforms to the contact pads on the outside. (b) shows a zoomed-in view of the central region with each platform labelled in each quadrant.

So far, only the central active region of the thermoelectric workbench has been discussed. The rest of the workbench serves to connect the central region to the contact pads near the edges of the die, where wirebonds can connect the contact pads to an external package. Figure 2.5 shows mask layouts of the workbench. Figure 2.5a shows the layout of the entire die, with quadrants of the die labelled in the familiar Cartesian coordinate system. The central region is not resolved in this image. Transmission lines connect the electrical components of the central region platforms with contact pads on the outside. There are five contact pads per platform, with the following organization scheme:

- The outer two contact pads correspond to the thermocouples. The contact pad closest to the central transmission lines is the positive terminal (i.e. the

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$^{2}$There may be some risk of fluorinating graphene via the XeF$_2$ etch.
leg of the thermocouple with higher Seebeck Coefficient).

- The next two inner contact pads correspond to the heater. There is no polarity.

- The central contact pad corresponds to the top nickel layer of each platform. It is shown as a clear contact pad in Figure 2.5a.

- In the case of the set of contact pads farthest from the central region, the only rule that must be changed is that of the positive thermocouple terminal. Here, the positive thermocouple terminal is given by the outer pad on the left, if one is looking from the central region toward the contact pads.

Figure 2.5b shows a close up version of the central region. Each platform can now be resolved, and the idea of interlocking platforms and adjacent platforms should now be a little clearer. The platforms are labelled based on the location of their associated contact pads in a Cartesian coordinate system. For example, the platform labelled 3 in the Q1X quadrant corresponds to the contact pads located in quadrant 1 that are three contact pad sets down along the horizontal transmission lines (as if the horizontal transmission lines were the x-axis). More information about the workbench nomenclature is given in Appendix A. The important thing to note is that all the electrical components are connected to contact pads via the central transmission lines. Although the transmission lines are all electrically isolated, they do run down the center of the workbench creating parasitic reactances. Different transmission lines are different lengths, depending on the location of the contact pads vs. the platform.

### 2.2 Workbench Theory

With the workbench fully described, we may turn our attention to characterization. The workbench structures are characterized both thermally and electrically. Thermally, the following characteristics are measured:

- Thermal Time Constant

- Thermoelectric Voltage vs. Heater Power (Thermal Sensitivity)
• Thermal Crosstalk (between platforms)

Electrically, the following characteristics are measured:

• DC Current-Voltage (I-V) characteristics

• Electrical Crosstalk (leakage)

Each characteristic will be described further below.

2.2.1 Thermal Characteristics

In order to make sure that heat is flowing or staying localized as expected, the workbench must be fully understood thermally. Some work has been done to do this via finite-element simulations. This thesis will describe the experimental efforts.

The thermal characteristics of the workbench can be understood by solving the heat equation for the workbench. Because the unheated platform is considered to be clamped at ambient temperature, all one needs to do is solve the heat equation for the heated platform:

\[ \rho c_p \frac{\delta}{\delta t} T(x,t) - \kappa \nabla^2 T(x,t) = \frac{Q}{A} = \left( \frac{I}{A} \right)^2 \left( \frac{1}{\sigma} \right) \]  

(2.2.1)

where

\[ I = I_0 \sin(\omega t) \]  

(2.2.2)

Equation 2.2.1 is the one-dimensional heat equation where \( \rho \) is the mass density, \( c_p \) is the specific heat, \( T(x,t) \) is the temperature at time \( t \) and position \( x \) along the heater, \( \kappa \) is the thermal conductivity, \( Q \) is the power density applied to the heater, \( I \) is the driving current applied to the heater, \( A \) is the heater cross-sectional area, and \( \sigma \) is the heater electrical conductivity. It should be noted that equation 2.2.1 does not account for the temperature dependence of the heater resistance; for mathematical simplicity, it is purposefully left out. In addition, it is assumed that the end of the nanomaterial touching the heated platform is at the same temperature as the platform heater (for which equation 2.2.1 applies).
2.2.2 is the equation for the driving current, which will be sinusoidal for reasons shown below.

The solution of the heat equation can be found in Duarte [5], and gives the temperature of the heated platform:

\[ T(x, t) - T_o = \Delta_o \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{2n^3} \sin \left( \frac{n\pi x}{L} \right) \left[ 1 - \frac{\sin(2\omega t + \phi_n)}{\sqrt{1 + \cot^2 \phi_n}} \right] \]  

(2.2.3)

where

\[ \cot \phi_n = \frac{2\omega L^2 \rho c_p}{\pi^2 \kappa n^2} \]

\[ \Delta_o = \frac{2I_o^2 RL}{\pi \kappa A} \]

where R is the heater resistance.

Our interest lies in the temperature difference \( T(L^2, t) - T_o \) where \( T_o \) is the ambient temperature and \( L \) length of the entire heater (and therefore \( L^2 \) is where the tip of the platform is). Among the mathematical cacophony of the solution, several important qualitative characteristics can be found. First, the temperature difference is a function of the second harmonic of the drive current, or \( 2\omega \). This will be of utmost importance, since now a lock-in amplifier may be used to lock onto the second harmonic of the resulting temperature signal, improving accuracy and noise. This is one reason why an AC signal was chosen for the drive current.

The solution also shows that as the frequency of the drive signal increases, the maximum amplitude of the resulting temperature signal will converge to a minimum value. This lowpass behavior of the temperature signal can also be measured, either on a nanomaterial or a thermocouple, and is a characteristic property of every workbench structure. The 3-dB cutoff frequency of the temperature signal’s frequency response is associated with the thermal time constant i.e. \( 1/f_{3\text{-}dB} = \tau \). The thermal time constant is a useful metric to make sure that all workbench

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3The temperature gradient is really what should matter. However, since we are assuming both the platform thermocouple and nanomaterial are homogeneous materials, this simply reduces to the temperature difference
structures are functioning as expected in terms of heat flow. It is a function of both material composition as well as the geometric structure, but should always demonstrate a lowpass behavior. The thermal time constant can be determined by sweeping the drive signal frequency and measuring the resulting thermoelectric voltage at $2\omega$, and finding the 3-dB frequency.

The thermoelectric voltage of the nanomaterials can be measured by joule heating the heater, and recording the thermoelectric voltages from both the nanomaterial as well as the thermocouples. Both thermoelectric voltages should be found at $2\omega$ since they are directly related to the temperature signal. All thermocouples are assumed to have the “cold junction” at identical ambient temperature. Because the thermocouples are made of well-known materials with established Seebeck Coefficients, the resulting temperature difference can be calculated from the voltage difference between the thermocouples. It should be noted from Equation 2.2.3 that the AC temperature signal rides on top of a DC component. Because both the nanomaterial and the thermocouples will be measured at $2\omega$ they will not include this DC component. However, the DC component can be determined from the $2\omega$ signal and the workbench material and geometrical properties, if needed.

While using thermocouples sound like an ideal case to determining the temperature gradient, we will see in Chapter 3 that this is not quite so ideal. The thermoelectric power (i.e. Seebeck Coefficient) of the nanomaterials will be measured as a function of heater power, frequency (thermal time constant measurement), and ambient temperature.

Thermal crosstalk describes the process of heat spreading from one platform to the neighboring platform and reducing the temperature gradient. Thermal crosstalk can take place through the nanomaterial (there may be nanomaterials bridging the platforms elsewhere as well as an artifact of the stochastic deposition), or through the workbench substrate itself. The deep trench between platforms and the XeF$_2$ release are designed to reduce thermal crosstalk. However, it is important to measure thermal crosstalk in evaluating workbench performance. This can be done by taking two platforms prior to nanomaterial deposition, heating one platform, and measuring the thermocouple voltages on both platforms. The $2\omega$ signal on the “cold” platform is a measure of thermal crosstalk. If the platforms are perfectly isolated, there will be no $2\omega$ signal on the “cold” platform.
2.2.2 Electrical Characteristics

Basic DC current-voltage (I-V) measurements can be used to determine connectivity of heaters and thermocouples. Because both heater and thermocouples are composed of well-known materials, their resistances can be calculated based off of material resistivity, cross-sectional area, and length. Heaters and thermocouples from different platforms should exhibit different but predictable resistances based off of transmission line length. DC I-V measurements can also be used to confirm the presence of a nanomaterial between two platforms. Care should be taken in this process, however, since the act of testing DC I-V may destroy the nanomaterial via ESD.

Electrical leakage is important to characterize, since electrical leakage can corrupt the thermoelectric voltage signals and show up as a false signal. Although any electrical leakage should be at $\omega$ while the thermoelectric voltage signals should be at $2\omega$, electrical leakage can still corrupt the thermal signal via nonlinearities in the workbench as well as an insufficient lock-in notch/lowpass filters. Electrical leakage can be characterized by driving the heater and measuring the thermocouple or top nickel at $\omega$. Electrical leakage will manifest itself as a significant $\omega$ signal. Alternatively, one may also apply a voltage signal between the heater and thermocouple, or heater and top nickel, and measure the current that flows between the two terminals. Again, electrical leakage will manifest itself as a significant leakage current. All permutations of heaters, thermocouples, and top nickel should be measured (i.e. driving either the heater or thermocouple and measuring the other two) for electrical leakage.

2.3 Implementation

A schematic of the circuit used to perform the characterizations, with the exception of electrical leakage, is shown in Figure 2.6. Conceptually, the instrumentation required is actually quite simple. One only needs a power source and a lock-in amplifier to generate a temperature gradient and extract the thermoelectric voltage at $2\omega$, respectively. To joule-heat the heater, an HP8165A signal generator is used. The signal generator can change both frequency and amplitude of the
Figure 2.6. A schematic showing the instrumentation and circuit used to characterize the thermoelectric workbench and nanomaterials.

AC drive signal. In addition, the HP8165A provides a reference signal (simply a square wave), which is sent to the lock-in amplifier to select the lock-in frequency. Although the signal generator is not a power generator, it is still quite sufficient to provide enough power at the micro level. Even at watt of power is sufficient to create a significant temperature gradient on the thermoelectric workbench. However, because the HP8165A is not a power generator, large loads have been shown to limit the power output of the HP8165A and cause voltage clipping issues. Clipping ruins the shape of the sinusoidal signal and introduces higher harmonics into the temperature signal. Therefore, An Agilent 54624A Oscilloscope is used to monitor the voltage output of the HP8165A to make sure that clipping does not occur.

For the gold-nickel workbenches (Ni-Au), an amplitude of 10 V (20 V_{pp}) was used in thermal time constant measurements, while the frequency was swept from 1 Hz to \approx 256 Hz in logarithmic steps. A frequency of roughly 8.6 Hz was determined to produce the maximum temperature response (measurement to be shown in Chapter 3). When measuring thermoelectric voltages from both nanomaterial and thermocouple as a function of heater power, the signal was held at 8.6 Hz while the amplitude was swept from 0 V to 10 V in equal steps. The HP8165A was set to 1 k\Omega output impedance to maximize the power output. For the polysilicon-gold (Poly-Au) workbenches, the identical procedure was used except the HP8165A was set to 50 \Omega output impedance to avoid voltage clipping. In addition, thermoelectric measurements were performed at 6 Hz because this was determined to be the optimal frequency based on time constant measurements.

Theoretically, knowing the amount of power applied to the heater is unnece-
sary for determining the Seebeck Coefficient \( \frac{\Delta V}{\Delta T} \) of the nanomaterial. However, it does provide another measure of the amount of thermal energy being applied to the nanomaterial system. In order to measure the amount of power being applied to the heater, the current flowing through the heater must be determined. A Keithley 2001 Multimeter is used as an ammeter and put in series with the heater for this purpose. At low frequencies \(<4\) Hz, the Keithley 2001 has some averaging issues, but at high frequencies it is reliable.

An SR830 Lock-in Amplifier is used to lock onto the \(2\omega\) thermoelectric signal from the nanomaterial and thermocouples, and cut out signals and noise from all other frequencies. A 24 dB/octave slope was used for the lowpass filter, with a 10 second time constant under normal dynamic reserve. The lock-in frequency comes from the HP8165A signal generator and is input to the SR830 through the Reference In terminal.

During measurement, the entire workbench is enclosed within a Cryodyne Closed-Cycle Refrigerator (CCR) to allow control of pressure and temperature, and reduce the electromagnetic noise. The temperature of the CCR is controlled with a Lakeshore 321 temperature controller which controls a heater directly in the CCR. The Lakeshore 321 uses a PID controller to control temperature; the measurements in this thesis were done with the PID on manual setting with \(P = 50, I = 30,\) and \(D = 100,\) although this can probably be optimized further. Autotuning tends to cause too much overshoot in temperature. Because of the risk of oil contaminants condensing in the chamber at low temperature, the temperature was not reduced below 100 K. To go under 100 K, the chamber must be properly cleaned. In addition, because the heater is not strong enough to completely overcome the CCR cooling above 200 K, the temperature becomes more unstable at \(T \geq 200\) K. Therefore, the temperature resolution in this range must be reduced.

Pressure inside the CCR was controlled with a roughing pump and several valves. The pump allows a minimum pressure of around 140 mT. The CCR is equipped with a secondary pump which can reduce the pressure even further, but this capability requires liquid nitrogen cooling and was not used in this thesis. Electrical contact to the workbench while inside the CCR was established by mounting the workbench on a 24-pin chip holder. The contact pads on the workbench were wirebonded to the chip holder’s pins, and the package was inserted into a match-
Figure 2.7. The experimental set up showing the instrumentation and associated equipment used to characterize the workbench and nanomaterials. The actual workbench is stored in a pressure and temperature controlled environment of the closed-cycle refrigerator’s cold head and sample holder.

The actual experimental set up is shown in Figure 2.7, with the cold head and sample holder on the left.

All thermal characterizations and measurements were performed with the aforementioned set up with the exception of electrical leakage measurements. These measurements were done prior to any other measurement to ensure the integrity
of the workbench. Electrical leakage measurements are performed with a Keithley 4200 Semiconductor Characterization System. Using one of the 4200’s source meters, one could apply a voltage between two terminals and measure the resulting leakage current. Typical voltage sweeps of up to 10 V provided sufficient measurement of leakage between components, or a short circuit. DC I-V measurements were performed in the aforementioned set up except with a Keithley 2400 source meter, which can apply a voltage and simultaneously measure current. Simple I-V sweeps indicated connectivity and linearity of heaters, thermocouples, and nanomaterials.

2.4 LabVIEW™ Automation

With the exception of electrical leakage, all measurements were automated with LabVIEW™. GPIB or RS-232 interfaces existed in all the instruments used in the experimental set up with the exception of the roughing pump. Programming commands were found in all the respective programming manuals. The following programs allowed control of most instrument settings relevant to the measurement, and also allowed control of voltage, frequency, and temperature sweeps. Four primary LabVIEW™ programs were used to perform characterizations and measurements:

- **TimeConstant_Controller.vi** - *Thermoelectric Time Constant Measurement Program* - This program held the HP8165A voltage amplitude constant while sweeping through a user-defined frequency sweep. Both linear and logarithmic sweeps could be selected. The front panel of this program is shown in Figure 2.8.

- **HeaterPowerVsTC.vi** - *Heater vs. Thermocouple Measurement Program* - This program held the HP8165A frequency constant while sweeping through a user-defined voltage sweep. Both linear and logarithmic sweeps could be selected. The front panel of this program is shown in Figure 2.9. This program could be used to measure both thermocouple as well as nanomaterial thermoelectric voltage.
Figure 2.8. LabVIEW™ front panel of the TimeConstant_Controller.vi measurement program

- **TempvsThermopower.vi** - Temperature vs. Thermopower Measurement Program - This program held the HP8165A frequency and amplitude constant while sweeping through a user-defined temperature sweep. Both linear and logarithmic sweeps could be selected. The front panel of this program is shown in Figure 2.10.

- **IVSweep.vi** - IV Sweep Program - This program was used to perform DC I-V measurements. It allows a user-defined voltage sweep while simultaneously measuring current. If desired, a Keithley 2001 can also be used to measure the DC thermocouple response from a thermocouple. Most of the time, however, this program was used to perform resistance measurements. It is not suggested to use this program to perform measurements on the nanomaterial due to the risk of ESD (instrument configuration causes voltage spikes). Instead, DC I-V characterization of nanomaterials should be performed manually by first configuring all instruments while the grounding box switches are grounded. Once instruments are fully configured and,
Figure 2.9. LabVIEW™ front panel of the HeaterPowervsTC.vi measurement program then the proper electrical connections can be made. The front panel of this program is shown in Figure 2.11.

Full documentation of each LabVIEW™ program may be found in the MEMS and Nanoscale Devices Laboratory group server.
Temperature vs. Thermopower Measurement Program

Instruments: SR830 Lock-in Amplifier, HP8165A Signal Generator; Keithley 2001 Multimeter; LakeShore 321 Temperature Controller

Dependencies: 2001_Read.vi, Create_log.vi, WaitTimeConstant.vi, Config Instruments.vi, WaitEquilibrationTime.vi

Figure 2.10. LabVIEW™ front panel of the TempvsThermopower.vi measurement program
Figure 2.11. LabVIEW\textsuperscript{TM} front panel of the IVSweep.vi measurement program
Chapter 3

Results

The results of both gold-nickel and polysilicon-gold workbench characterizations are presented in this chapter. Thermoelectric measurements of gold nanowires using both workbenches will be presented as well. Unless stated otherwise, all measurements were performed in the CCR. While a large number of measurements were performed on a wide variety of samples, only two such samples (one from each type of workbench) will be presented for conciseness. They are shown in Figure 3.1. These two samples represent typical observations that were made about the workbenches and the gold nanowires, as well as some of the reoccurring problems. Full datasets may be found on the MEMS and Nanoscale Devices Laboratory group server.

3.1 Nanowire Deposition

70nm diameter gold nanowires were deposited onto the workbench by suspending the nanowires in solution, and spinning the solution onto the workbench to create a uniform distribution of nanowires. The solution was allowed to evaporate in room temperature, leaving the nanowires behind. Typically, a good number (roughly 10) of testable nanowires can be found after this step. The difficulty is in isolating an individual nanowire rather than several nanowires or a clump of nanowires, as shown in Figure 3.1a. Typically, nanowires that bridge parallel platforms (i.e. Q3Y3 and Q3Y4) are not used due to a larger amount of thermal crosstalk between platforms. Perpendicularly adjacent platforms (i.e. Q3Y3 and
Figure 3.1. Nanowire test samples. (a) is a nanoclump sample spanning across perpendicularly adjacent platforms on a Ni-Au workbench. (b) is a single nanowire spanning across perpendicularly adjacent platforms on a Poly-Au workbench.

Examples of two test sites are shown in Figure 3.1. Figure 3.1a shows a nanowire clump (called the nanoclump) deposited onto a Au-Ni workbench. As can be seen from the labels, the nanoclump bridges two perpendicularly adjacent platforms. There is also an individual nanowire bridging between Q1Y4 and Q1X3. This nanowire, unfortunately, was lost to ESD before any successful measurements could be made. Figure 3.1b shows a nanowire bridging between two adjacent platforms (Q3Y3 and Q3X3, not labelled in figure) on a Poly-Au workbench. The nanowire appears to have a kink in the middle, or alternatively, might be composed of two nanowires “junctioned” in the middle.

Both samples in Figure 3.1 were clamped to the workbench via EBID. Figure 3.2 shows the nanowire from Figure 3.1b before and after EBID clamping. The nanowire was clamped with a .67 nA spot current under 5 kV acceleration voltage. The rectangular platinum clamp has a z-depth of 2.00 μm (from the procedure settings - not experimentally verified). The clamp area is 1.26 μm x 1.77 μm. Sample contact was verified with DC I-V measurements.
3.2 Electrical Leakage Measurements

Table 3.1. 15V electrical leakage measurements between the heaters and thermocouples of a radial distribution of platforms on an empty workbench. 15 V was applied to the heaters, while leakage currents and voltages were measured in the thermocouple. $P_{HTR}$ is the power applied to each heater under 15V.

<table>
<thead>
<tr>
<th>Platform</th>
<th>$P_{HTR}$ (mW)</th>
<th>$&lt;I_{LEAK}&gt;$</th>
<th>$I_{LEAK}\sigma$</th>
<th>$&lt;V_{LEAK}&gt;$</th>
<th>$V_{LEAK}\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1Y1</td>
<td>443</td>
<td>-60.53 nA</td>
<td>1.00 pA</td>
<td>18.90 mV</td>
<td>12.06 mV</td>
</tr>
<tr>
<td>Q1Y7</td>
<td>237</td>
<td>10-100 nA</td>
<td>N/A</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Q2Y6</td>
<td>226</td>
<td>-63.71 pA</td>
<td>34.08 pA</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Q2Y2</td>
<td>518</td>
<td>0.35 $\mu$A</td>
<td>17.37 nA</td>
<td>Heater Broke</td>
<td>N/A</td>
</tr>
<tr>
<td>Q3Y3</td>
<td>324</td>
<td>-31.59 nA</td>
<td>6.03 nA</td>
<td>10.65 mV</td>
<td>3.55 mV</td>
</tr>
<tr>
<td>Q3Y5</td>
<td>254</td>
<td>0.97 $\mu$A</td>
<td>238.89 nA</td>
<td>1.79 V</td>
<td>144.00 mV</td>
</tr>
<tr>
<td>Q4Y4</td>
<td>261</td>
<td>-110.94 nA</td>
<td>74.50 nA</td>
<td>$&gt;10.00$ V</td>
<td>Breakdown</td>
</tr>
<tr>
<td>Q4Y7</td>
<td>229</td>
<td>-104.80 pA</td>
<td>45.82 pA</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Electrical crosstalk, or leakage, of the silicon nitride was measured on all test sample platforms prior to measurement. All heater, thermocouple, and top nickel pairs of the platforms under test were examined for leakage. Although electrical leakage tests were used more as a binary fail/pass test to confirm the integrity of
workbenches, a study was also done to see at what point the silicon nitride between active electrical components would break down. Two tests were performed: a 10V test and a 15V test, in which 10V and 15V, respectively, were applied to the heater and the leakage current from the same platform’s thermocouple was measured. If the nitride had broken down, an appreciable current (voltage) would be measured in (across) the thermocouple. The tests were performed on completely empty workbenches by a Keithley 4200 Semiconductor Characterization System. In each test, a radial distribution of platforms were randomly selected for testing. No significant leakage was found in the 10V case. The results of the 15V case are shown in Table 3.1, and as can be seen severe leakage was systematically seen when 15V was applied to the heater. As such, all subsequent measurements were kept at or under 10V to prevent breakdown.

3.3 Gold-Nickel (Au-Ni) Workbenches

Gold-Nickel workbenches were the first generation of workbenches tested in this thesis project. All the characterizations described in Chapter 2 were performed on the workbench with the HP8165A on 1 kΩ output impedance. The nanoclump sample was also characterized using this workbench both before and after workbench release. The results are reported in this section.

The typical resistance of heaters were around 500 Ω to 1000 Ω depending on heater length. Thermocouples were typically double that. Both heaters and thermocouples demonstrated linear I-V curves.

3.3.1 Thermal Time Constant

The results of the thermal time constant on this unreleased Ni-Au workbench are shown in Figure 3.3. The nanomaterial bridged across platforms Q1Y4 and Q1X4. Platform Q1Y4 (as indicated on Figure 3.3) was heated, and the thermal time constants were measured on the thermocouples of three separate platforms: Q1Y4, Q1X3, Q1X4. Because only one lock-in amplifier was used, there had to be three iterations of the same measurements with the SR830 measuring a different thermocouple every time. Frequency was swept from 1 Hz to 256 Hz in base two
Figure 3.3. Thermal time constant measurement of three thermocouples in the nanoclump sample. Q1Y4 was the heated platform, and the nanomaterial bridged across Q1Y4 and Q1X4. Gains were normalized from 2ω signals of 3.16, 3.20, and 3.34 V for platforms Q1Y4, Q1X3, and Q1X4, respectively. Time constants were roughly 50 seconds. The high gain at high frequencies is predicted to be a result of noise and other device effects. Inset shows the lowpass portion of the curves.

These are typical characteristics of a time constant measurement: lowpass behavior at low frequency before diverging at high frequencies. In order to maximize the output as a function of frequency, it was decided that 8.6 Hz is the optimal frequency to do all future constant-frequency measurements on the Ni-Au workbenches. Thermal time constants on this sample were also measured as a function of temperature, and the results are shown in Table 3.2. The time constant is not a strong function of temperature, although there should be a relationship due...
Table 3.2. Thermal time constant measurements on a single gold-nickel workbench from 125 K to 273 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>3-dB Frequency (Hz)</th>
<th>Time Constant (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>21.0</td>
<td>47.62</td>
</tr>
<tr>
<td>150</td>
<td>21.0</td>
<td>47.62</td>
</tr>
<tr>
<td>175</td>
<td>19.0</td>
<td>52.63</td>
</tr>
<tr>
<td>200</td>
<td>20.0</td>
<td>50.00</td>
</tr>
<tr>
<td>225</td>
<td>19.0</td>
<td>52.63</td>
</tr>
<tr>
<td>250</td>
<td>18.0</td>
<td>55.56</td>
</tr>
<tr>
<td>293</td>
<td>19.0</td>
<td>52.63</td>
</tr>
<tr>
<td>Average</td>
<td>19.57</td>
<td>51.24</td>
</tr>
<tr>
<td>Std. Deviation</td>
<td>1.13</td>
<td>2.95</td>
</tr>
</tbody>
</table>

To the time constant’s dependence on material properties which are temperature dependent.

Time constant measurements on a large number of Ni-Au workbenches showed a reliable and repeatable time constant of around 50 ms. The time constant measurement can be used as a diagnostic tool in future measurements to ensure that the workbench structure is not compromised. The astute observer will notice that although Q1Y4 was the heated platform, and the nanomaterial bridged across Q1Y4 and Q1X4, the thermal $2\omega$ signal was equally strong on all three thermocouples. This is a sign of severe thermal crosstalk between platforms to the point that even though only one platform was heated, its neighboring platforms were at roughly the same temperature (to within noise and thermocouple process variations).

### 3.3.2 Nanoclump Thermoelectric Measurements

The nanoclump shown in Figure 3.1a is characterized in the CCR. Characterizations include DC I-V measurements, as well as thermoelectric voltage measurements.

Nanoclump and nanowire DC I-V curves are shown in Figure 3.4. These measurements were performed by a Keithley 2400 in the CCR at room temperature under vacuum (about 140 mT air). Sometimes, it was necessary to breakdown the native oxide that had formed by applying up to 3V across the nanomaterial. It
Figure 3.4. Nanoclump and nanowire DC I-V curves. The nanowire was later lost to ESD. Nanowire resistance was about 1.6 kΩ, while nanoclump resistance was about 2 kΩ.

should be noted that the DC I-V curves presented here include all contact resistances. Therefore, even though we call them “nanowire resistance”, it should be interpreted as nanowire resistance plus contact resistance.

Initially, the nanowire’s resistance was about 1.6 kΩ while the nanoclump’s resistance was about 500 Ω. Later, the nanowire was lost to ESD, and the nanoclump’s resistance increased as well presumably due to oxide growth or some shift of the nanoclump during measurement. In Figure 3.4, the nanoclump has a resistance of 2 kΩ and the nanowire has a resistance of 1.6 kΩ. After subjecting the workbench to several cycles of XeF$_2$ etch, the nanoclump’s resistance increased again to 4 kΩ (after 2 cycles of XeF$_2$) and 15 kΩ (after 5 cycles of XeF$_2$) as shown in Figure 3.5. It would appear that the XeF$_2$ certainly does not come without consequences.

Thermoelectric voltage measurements were performed in the CCR at room temperature. Thermopower measurements are only performed on the nanoclump, since at this point the nanowire had been destroyed. The HP8165A was set at 1 kΩ output impedance to maximize output power. The first set of measure-
Figure 3.5. Nanoclump DC I-V curves after several cycles of XeF$_2$ etch.

ments are reported on an unreleased workbench. The same measurements are repeated after multiple cycles of XeF$_2$ and a difference can be seen. Releasing of the workbenches were done with multiple 60 second, 2 Torr XeF$_2$ etches. In these measurements, platform Q1Y4 was heated, and is designated as the “hot” platform. Recall that the nanoclump bridges between platforms Q1Y4 and Q1X4 (see Figure 3.1a); therefore, the difference in thermocouple readings between these two platforms ($\Delta V_{TC} = \Delta V_{TC,HOT} - \Delta V_{TC,COLD}$) produces a measure of temperature difference. Absolute temperature is unknown without calibration of the thermocouples, which is out of the scope of this thesis. Three sets of data are presented here in three different environments:

- vacuum (meaning about 140 mT air) - workbench unreleased
- vacuum - workbench released by 3 cycles of XeF$_2$
- vacuum - workbench released by 5 cycles of XeF$_2$

Preliminary measurements of nanoclump thermoelectric voltage were performed on an unreleased workbench. In addition to measuring the nanoclump’s thermo-
Figure 3.6. Nanoclump thermoelectric voltage and thermocouple voltage $2\omega$ signals plotted against $P_{HTR}$ on an unreleased workbench in 140 mT air. Nanomaterial thermoelectric voltage is labelled as “thermopower”. Q1Y4 is the heated platform.

The same data is plotted in Figure 3.7 except now $\Delta V_{TC}$ is plotted with nanoclump thermoelectric voltage as a function of heater power. The paradox stated above now manifests itself in the form of opposite slopes of $\Delta V_{TC}$ and nanoclump thermoelectric voltage (again labelled thermopower in the figure). In Figure 3.8, nanoclump thermoelectric voltage is plotted directly against $\Delta V_{TC}$. If everything is correct, then the negative slope implies that the gold nanoclump has a negative Seebeck Coefficient. Bulk gold has a positive Seebeck Coefficient, and we would
Figure 3.7. Nanoclump thermoelectric voltage and $\Delta V_{\text{TC}}$ plotted against heater power.

...expect the nanoclump to exhibit the same behavior since it is of too large a size to demonstrate the low-dimensional effects mentioned in Chapter 1.
Figure 3.8. Nanoclump thermoelectric voltage and $\Delta V_{TC}$ plotted against heater power.

Figure 3.9. Nanoclump and thermocouple thermoelectric voltages plotted against heater power after three cycles of XeF$_2$ release.

In order to reduce the level of thermal crosstalk, three cycles of XeF$_2$ etching were performed to release the platforms. Identical measurements were performed after the release, and the results are shown in Figures 3.9 to 3.11. Figure 3.9
Figure 3.10. Nanoclump and $\Delta V_{TC}$ plotted against heater power after three cycles of XeF$_2$ release.

Figure 3.11. Nanoclump thermoelectric voltage plotted against $\Delta V_{TC}$ after three cycles of XeF$_2$ release.

shows that the thermocouple voltage from platform Q1X4 increased significantly after the etch. While we expect the magnitude of thermocouple voltage to increase
due to the better thermal isolation, it was the “cold” platform that got hotter, not the “hot” platform. Meanwhile, the “hot” platform remained at the same thermocouple voltage. The nanoclump thermoelectric voltage also increased slightly, hopefully as a result of the increased temperature difference. Similar data is shown in Figure 3.10 and 3.11. The slope in Figure 3.11 has decreased because $\Delta V_{TC}$ increased more than the nanoclump thermoelectric voltage.

![Thermopower and Thermocouple Response after 5 cycles of XeF$_2$ Etch](image)

**Figure 3.12.** Nanoclump and thermocouple thermoelectric voltages plotted against heater power after a total of five cycles of XeF$_2$ release.

To improve thermal isolation even more, an additional two cycles of XeF$_2$ were performed, for a total of five cycles of XeF$_2$ release. Figures 3.12 to 3.14 show the results. Figure 3.12 shows a remarkable increase in the nanoclump thermoelectric voltage (2x) despite only a slight, if at all, increase in $\Delta V_{TC}$. Consistent with the former measurements, 5 cycles of etching appeared to do nothing to the thermocouple responses of Q1Y4 (hot platform) and Q1X3 (neutral platform) besides perhaps a slight separation between the usually identical readings, while the thermocouple response of platform Q1X4 (cold platform) increased slightly.

The large increase in thermoelectric voltage may have something to do with the increased resistance of the nanoclump after the etching cycles. Gold is known to be etched by XeF$_2$, so although the nanoclump was not entirely etched by only five
cycles of XeF$_2$, the etch may have caused some physical change in the nanoclump which resulted in an increased thermoelectric voltage. On a separate note, these results may indicate that the thermocouple readings are not representative of the workbench surface temperature since nanoclump thermoelectric voltage appeared to double while thermocouple voltage did not change much. Further studies need to be done to confirm these speculations. A summary of the results are shown in Table 3.3

**Table 3.3.** A summary of the measurements on the gold nanoclump on the Ni-Au workbench.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Slopes ($\mu V/W$)</th>
<th>Unreleased</th>
<th>3 cycles of release</th>
<th>5 cycles of release</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1Y4 Thermocouple (Hot)</td>
<td>30.0</td>
<td>28.5</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td>Q1X3 Thermocouple</td>
<td>30.2</td>
<td>28.9</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>Q1X4 Thermocouple (Cold)</td>
<td>32.1</td>
<td>37.9</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td>Nanoclump Thermovoltage</td>
<td>16.5</td>
<td>17.6</td>
<td>40.0</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.13.** Nanoclump and $\Delta V_{TC}$ plotted against heater power after a total of five cycles of XeF$_2$ Etch.
3.4 Polysilicon-Gold (Poly-Au) Workbenches

Polysilicon-gold workbenches were fabricated after the Ni-Au workbenches to increase the temperature sensitivity of the thermocouples and decrease thermal crosstalk. As shown in the previous section, there was severe thermal crosstalk between neighboring platforms. To decrease thermal crosstalk, the trench between platforms was deepened from 5 $\mu m$ to 30 $\mu m$. Polysilicon-gold thermocouples also possess a much larger Seebeck Coefficient ($S \approx 340 \mu V/K$ at $10^{19} cm^{-3}$ Boron doping and near room temperature) than Gold-Nickel thermocouples ($S \approx 20 \mu V/K$ at 20°C). For fabrication simplicity, the heater was also fabricated out of polysilicon instead of gold.

The sample shown in Figure 3.15 is a single nanowire found spanning between platforms Q3Y3 and Q3X3 of a polysilicon-gold nanowire. It appears to have a kink in the middle, or be composed of several “junctioned” nanowires, although this is unconfirmed. The nanowire was anchored to the platform with EBID (Figure 3.2) and measurements similar to those on the gold-nickel workbench were performed, with some additions:
3.4.1 DC I-V Characteristics

To begin characterizing the workbench, DC I-V curves were measured for all heaters and thermocouples. It was quickly found that the doped polysilicon was not doped enough, as the resistances were several orders of magnitude higher than gold heaters and gold-nickel thermocouples of the previous workbench.

In addition, a non-ohmic contact was formed in many thermocouples, presumably due to some sort of barrier forming between the polysilicon and gold as shown in Figure 3.16. Sometimes thermocouples were perfectly linear, other times they
Figure 3.16. A selection of thermocouple DC I-V curves showing the variation between nonlinear and linear DC I-V curves.

were nonlinear. Because the DC I-V’s are an odd function, it is not a rectifying junction ruling out a Schottkey barrier.

Table 3.4. Measured heater and thermocouple resistances.

<table>
<thead>
<tr>
<th>Component</th>
<th>Resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1X4 Heater</td>
<td>100</td>
</tr>
<tr>
<td>Q1X4 Thermocouple</td>
<td>Nonlinear</td>
</tr>
<tr>
<td>Q1Y4 Heater</td>
<td>163</td>
</tr>
<tr>
<td>Q1Y4 Thermocouple</td>
<td>80</td>
</tr>
</tbody>
</table>

The actual heater and thermocouple resistances of the platforms that the nanowire under test was touching were measured and the results are shown in Table 3.4. The increased polysilicon heater resistance (by several orders by magnitude) means that applying the same voltage as the gold-nickel workbenches will result in a lower amount of power being dissipated in the heater, since \( P = V^2/R \). This lower power defeats the purpose of using a polysilicon-gold thermocouple in
the first place, since it cancels out the increase in sensitivity that the polysilicon-gold thermocouple provides. In addition, because Johnson noise is related to $\sqrt{R}$, the thermal noise is increased in the measurement as well. Because of the larger load, the HP8165A must also run in the 50 Ω output impedance mode to prevent clipping.

![Figure 3.17. Initial nanowire DC I-V curve. Resistance is around 300 Ω.](image)

The nanowire DC I-V was also measured prior to any measurements. These measurements confirmed the presence of the nanowire; initially the DC I-V showed a resistance of about 300 Ω as shown in Figure 3.17. Again, this resistance includes all the contact resistances, so it should not be taken as the nanowire resistance. A four-point probe measurement must be done to determine actual nanowire resistance. Midway through the measurement, the nanowire I-V suddenly increased resistance by several orders of magnitude as shown in Figure 3.18. This “change of state” of the nanowire was also accompanied by a drastic change in many other properties of the nanowire including thermoelectric properties and thermal time constant. This section will also report on the before and after comparison of the nanowire.

Despite the successful nanowire IV, it was also discovered that there was heavy leakage between the heater, thermocouple, and top nickel network of each platform.
Figure 3.18. Nanowire DC I-V curve after the “state change”. Resistance is around 1.76 MΩ.

(but no cross-platform leakage). The leakage was so severe that the resistance between components had dropped to around 50 kΩ. Despite this, the measurement process continued since the leakage would theoretically be at ω while all thermoelectric signals of interest would be at 2ω. Of course, this leakage must be kept in mind when analyzing any results.

3.4.2 Thermal Time Constant

The thermal time constant of the polysilicon-gold workbench was measured in an identical fashion to the gold-nickel workbench. For these measurements, Q3X3 was the “hot” platform, and Q3Y3 was the “cold” platform (see Figure 3.15). All thermal time constant measurements were performed in the CCR at room temperature. The results of the measurement performed on the thermocouple of Q3Y3 (“cold” platform) before and after the nanowire state change is shown in Figure 3.19. In its initial state, the workbench behaved as expected, exhibiting a beautiful lowpass behavior. The 3-dB cutoff frequency is roughly 6 Hz, with a time constant of roughly 160 ms. The strong signal (an order of magnitude stronger than the Gold-Nickel workbench) on the “cold” platform implies either that the
Figure 3.19. The thermal time constant of the polysilicon-gold workbench before and after the nanowire “state change”. Measurements were performed on the Q3Y3 thermocouple while heating Q3X3. Lowpass behavior in the temperature signal is clearly seen in the initial state.

thermal crosstalk is still very strong or the nanowire is conducting lots of heat.

After the nanowire changed state, however, the lowpass structure completely vanished. In fact, the magnitude of the thermocouple response also degraded by two orders of magnitude. Assuming nothing else in the workbench changed, the degradation in signal seems to imply that the nanowire’s state change lowered its thermal conductivity significantly. This is good news in the sense that it implies that thermal crosstalk was not the method by which heat was spreading from the hot platform to the cold platform.

3.4.3 Nanowire Thermoelectric Measurements

The thermoelectric voltage of the nanowire was measured as a function of both heater power as well as ambient temperature. All measurements were performed
in the CCR at a frequency of 6 Hz. Measurements were performed both before and after the nanowire state change.

![Thermopower vs. Heater Power](image)

**Figure 3.20.** Nanowire thermoelectric voltage before the nanowire state change. Platform Q3X3 was heater. Thermoelectric voltage had a slope of about 5.2 mV/W.

Figure 3.20 shows nanowire thermoelectric voltage against heater power *before* the nanowire state changed. It is linearly related to heater power with a slope that ranged between from 4.3 mV/W to 5.2 mV/W. In comparison, after the state changed, thermoelectric voltage vs. heater power slope grew to 84 mV/W as shown in Figure 3.21. The measurement from Figure 3.21 appears to imply that the high impedance of the nanowire DC I-V measurement means only a poor electrical connection and not that the nanowire has been lost. Not only is there a linear thermoelectric voltage vs. heater power relationship, it seems significantly cleaner and more linear than the previous measurements. In the measurement after the nanowire state change, the maximum heater power has dropped by almost an order of magnitude because the Q3Y3 platform was heated, rather Q3X3. Switching the hot platform from Q3X3 to Q3Y3 while not switching the polarity of the measuring terminals also induced a phase change of 180° in the lock-in measurement result as expected (not shown).

For comparison, the nanowire thermoelectric voltages before and after the state
Figure 3.21. Nanowire thermoelectric voltage after the nanowire state change. Platform Q3Y3 was heater. Thermoelectric voltage had a slope of about 84 mV/W.

Figure 3.22. Nanowire thermoelectric voltage plotted against heater power before and after the state change for comparison.

change are plotted in Figure 3.22. The thermoelectric voltage/heater power slope increased by an order of magnitude after the nanowire state change. This, com-
combined with the time constant measurement, certainly indicates that the nanowire changed state somehow. However, recall that the time constant measurement was performed on the thermocouple of Q3Y3, not on the nanowire as in these measurements. For comparison, a before and after plot of the Q3Y3 thermocouple voltage vs. heater power is shown in Figure 3.23. Here, the thermocouple voltages have basically remained unchanged unlike the nanowire thermoelectric voltage. This implies that the nanowire state change did not affect the nanowire thermal conductivity like the thermal time constant measurement implied. More studies need to be done to truly understand what is happening in the nanowire system and these state changes.

Nanowire thermoelectric voltage was also studied as a function of ambient temperature before and after the state change. This study is important to understand the Seebeck Coefficient as a function of temperature. Figure 3.24 shows the nanowire thermoelectric voltage plotted against ambient temperature before the state change. Thermoelectric voltage peaks around 130 K. This peak could be the phonon drag peak mentioned in [5, 7]. After the state change, however, the magnitude of the thermoelectric voltage rises by about two orders of magnitude,
Figure 3.24. Nanowire thermoelectric voltage as function of temperature before the nanowire state change.

Figure 3.25. Nanowire thermoelectric voltage as function of temperature before and after the state change. Both before and after measurements exhibit a peak at around 100 K.
consistent with the results of the thermoelectric voltage measurements as a function of heater power. The low temperature peak also shifts from 130 K to 100 K. Figure 3.25 shows the temperature profile both before and after the state change for comparison, from 100 K up to room temperature.
Evaluation of the Thermoelectric Workbench

After measuring numerous samples on both the gold-nickel and polysilicon-gold thermoelectric workbenches, several consistent successes and flaws stood out. This chapter summarizes these observations, evaluates the workbench based on the goals it was originally designed for, and makes suggestions for future work.

4.1 Ups and Downs

Two generations of the micromachined thermoelectric workbench were fabricated for this thesis project: a gold-nickel workbench and a polysilicon-gold workbench. The first workbench, the gold-nickel workbench, was fabricated with the intention of providing a high yield of testable samples for easy, accurate, and reliable measurements. Gold-nickel thermocouples were fabricated on the workbench to provide a non-disruptive way of measuring a temperature difference. The workbench had a test-site density of 48 sites/5 mm² on each 5 mm² die.

The following characterization tests and observations were made on the workbench:

- DC I-V
- Electrical Leakage
• Thermal Time Constant

• Thermal Crosstalk

• Thermoelectric Measurements

The workbench was used to measure the thermoelectric response of 70nm gold nanowires.

DC I-V measurements were easy, and allowed verification of workbench functionality and nanomaterial presence. Electrical leakage was measured between different electrical components of the workbench (heater, thermocouple, and top nickel). Electrical leakage tests are performed to ensure that no input signals are corrupting the thermoelectric signals. Leakage studies were performed to find out at what voltage the silicon nitride between layers would break down. It was deemed that 10V was a safe maximum voltage to apply.

![Figure 4.1. Thermal time constant measurement of three thermocouples in the nanoclump sample. Time constants were roughly 50 seconds.](image)

Each workbench had a characteristic thermal time constant, defined by the 3-dB cutoff frequency of the temperature signal’s lowpass behavior. For gold-nickel workbenches, this was consistently around 50 ms. The nanoclump sample measurement is shown in Figure 4.1. Because of the reliability and reproducibility of
time constant measurement, it can be used as a diagnostic tool to verify workbench functionality, and that heat is flowing as expected within the workbench.

Thermal crosstalk was found to be a serious problem in the Ni-Au workbench. In all thermoelectric measurements (i.e. thermal time constant and thermoelectric voltage vs. heater power) thermal crosstalk was seen in many of the neighboring platforms despite the 5 $\mu$m trench. This reduces the temperature gradient across the nanomaterial. In addition, it should be noted that the heater in all these workbenches are distributed heaters. In other words, it is simply a uniform resistor that runs from the outside contact pads to the central region. Because of this, the power being applied to the heater is being evenly distributed wherever the heater line runs, not just at the platform tip. This could be a large source of thermal crosstalk that not only lowers temperature gradients but can affect thermocouple measurements. The output voltage from a thermocouple depends on the temperature difference at the hot junction and the cold junction (assuming a homogeneous thermocouple) i.e. $\Delta V = S \Delta T$. If heat from the distributed heater spreads to the cold junction of a thermocouple it will reduce the temperature difference and therefore the output voltage. This will be interpreted as a lower temperature at the platform tip. This should be addressed by changing the workbench geometrical design.

Thermoelectric measurements on gold nanowire samples were successfully performed. A linear thermoelectric voltage vs. heater power relationship was found for a nanoclump of gold nanowires. After five cycles of XeF$_2$ etching to release the platforms the thermoelectric voltage/heater power slope increased to 40 $\mu$V/W. A relationship between the thermoelectric voltage and $\Delta V_{TC}$ was found - this is related to the Seebeck Coefficient. To find the actual Seebeck Coefficient, one will also have to be able to convert the thermocouple voltages back into a temperature. Because thin-film thermocouples have different Seebeck Coefficients than their bulk counterparts, the standard gold-nickel thermocouple Seebeck Coefficient cannot be used. As such, the thin-film thermocouples must be calibrated separately, for example, using some sort of microscopy or thermal imaging.

The thermocouples themselves are a point of concern. In the nanoclump measurements, it was seen that the gold nanoclump had a negative Seebeck Coefficient as shown in Figure 4.2. This cannot be true. The thermocouples may be the culprit.
in this case: thermocouple sensitivity might vary from thermocouple to thermocouple due to process variations causing the hot platform’s thermocouple to be less sensitive than the cold platform’s thermocouple. If this is the case, some method must be found to make thermocouples repeatable. Another possibility is that the thermocouple’s are not reliably representing the surface temperature (i.e. the nanoclump temperature). Thermal imaging can again be used to verify this. Simulations may also provide insight into the problem.

In general, however, thermoelectric measurements were successfully performed. The problem comes in verifying that they are accurate, and interpreting them correctly.

To improve thermal crosstalk and thermocouple sensitivity, a polysilicon-gold workbench was fabricated with the identical geometrical design, except a deeper, 30 µm trench. However, because the resistance of the polysilicon heaters were so high, the gain in thermocouple sensitivity was cancelled out by the inability to pump more power into the heater. In addition, the polysilicon-gold thermocouples lost their linear I-V characteristics, probably due to some barrier forming between the polysilicon and gold. This, in theory, should not affect thermometry measurements - only electrical measurements.

**Figure 4.2.** Nanoclump thermoelectric voltage and \( \Delta V_{TC} \) plotted against heater power.
Identical measurements were performed with the polysilicon-gold workbench. Thermal time constants, in general, seemed to be much harder to reproduce. Some showed the characteristic lowpass behavior while others appeared to have no pattern. In the case of the nanowire presented in this thesis, the thermal time constant began with a lowpass behavior but then lost that characteristic after the nanowire changed state. This may be due to the nonlinearities of the thermocouple, but that is unverified. Until this issue is resolved, the thermal time constant will not be as reliable for the polysilicon-gold workbenches.

Thermoelectric measurements were performed on a single gold nanowire. The magnitude of the thermoelectric voltages were much higher - most likely due to the increased sensitivity of the thermocouples. The nanowire appeared to be unstable and changed states multiple times throughout the measurement, at one point producing an order of magnitude increase in the thermoelectric voltage up to 84 mV/W. Whether this is due to different junction effects mentioned by Tadigadpaa et al. in [7] or due to another effect is unknown at this point and requires more study. The thermopower vs. temperature measurements showed a peak at around 100 K. This may be the phonon drag peak.

4.2 Future Work

Several improvements will be made to the next generation of the thermoelectric workbench that address the limitations seen in this study. First, the problem of the distributed heater will be resolved by turning it into a lumped heater: increasing the heater resistance at the tip of the platform compared to the rest of the line. This can be done by either decreasing the cross-sectional area at the tip, or changing it into a material with a much higher resistivity - or both. Changing the geometrical design will require a new mask design as well. In addition, the heater material will be returned to gold or another conductive material to avoid the problems that a polysilicon heater produced. This lumped heater will both reduce thermal crosstalk as well as allow more power to be pumped into the system. This way, both an increased thermocouple sensitivity and a high heater power density can be employed.

Scanning Thermal Microscopy (SThM) is being used to calibrate the thermo-
couples. Once an independent method can be used to calibrate the platform tip temperature, the thermocouple voltage can finally be converted into a temperature and an actual Seebeck Coefficient may be determined for the nanomaterial. This study will also enable another study on thermocouple reproducibility to see if these thin-film thermocouples are reliable, or are limited by process variations. If they are not reproducible, then using thin-film thermocouples may be an issue in the current workbench design.

Finally, a broader span of nanomaterials will be studied using the thermoelectric workbench. Graphene has been successfully deposited on the workbench and is being shaped using laser ablation in preparation for characterization.

### 4.3 Concluding Remarks

The quest to find an efficient thermoelectric material continues. The studies performed in this thesis project confirm that studying the thermoelectric properties of nanomaterials is no trivial task and requires great diligence and care. Once optimized, perhaps one day the workbench structures described and characterized in this thesis project will serve as a powerful tool for studying thermoelectric nanomaterials, and bring us one step closer towards harnessing the power of thermoelectricity.
Appendix A

Nomenclature

The location of each platform on the thermoelectric workbench is specified by a naming convention, which is used throughout this thesis. To understand the naming convention, one should superimpose a Cartesian coordinate system onto the mask layout as shown in Figure A.1. Make sure that the alignment markers are in the upper left hand corner as shown in the figure. In this orientation, the quadrants are labelled as in a standard Cartesian 2-D plane. Here, the transmission lines extend outward from the central region either horizontally or vertically, like the x-axis and y-axis, respectively. If a transmission line extends horizontally, it means the platform in the central region will also be coming in horizontally - in other words, the transmission lines don’t bend or turn anywhere in the central region. It is the same story for vertical transmission lines.

A platform is specified by its associated contact pads. Each platform has five contact pads: two for the thermocouple, two for the heater, and one for top nickel. The five contact pads are grouped together either above or below, or on the left or right of an axis. A contact pad set’s “distance” from the central region is labelled one through seven as shown in Figure A.1. The closest set of contact pads are labelled 1 going all the way to 7 at the farthest edges of the die.
Figure A.1. Mask layout with a Cartesian coordinate system superimposed.

We are now equipped to specify contact pads uniquely. Each platform is specified by a naming convention:

\[ Q\#(X/Y)\# \]

where

Q\# specifies the quadrant number (between 1-4)
X/Y specifies which axis the platform’s contact pads are branching off of (either x or y)

the last # specifies the distance of the contact pad from the central region, using the convention shown in Figure A.1

For example, the platform labelled Q3X4 corresponds to the platform with its contact pads in quadrant 3 that is the fourth set of contact pads branching off of the x-axis. This platform is highlighted in red in Figure A.2.

The only ambiguous platforms are those labelled “7”, in the sense that their quadrants are ambiguous. These platforms can be specified by any of the quadrants it touches. For example, Q1Y7 and Q2Y7 are identical. So are Q2X7 and Q3X7; Q3Y7 and Q4Y7; and Q4X7 and Q1X7.

All of these connections can be visually tracked on an optical microscope.
Bibliography


Vita
MATTHEW P. CHANG

Matthew P. Chang
731 Teaberry Lane
State College, PA, 16803
mpchang17@gmail.com

Education

Bachelor of Science Degree in Electrical Engineering, Penn State University, Spring 2010
Minor in Physics
Honors in Electrical Engineering
Thesis Title: Measuring the Thermoelectric Properties of Nanomaterials with a Micromachined Workbench
Thesis Supervisor: Srinivas Tadigadapa

Related Experience

Summer Undergraduate Research Fellowship (SURF) at the National Institute of Standards and Technology (NIST), Summer 2008
Research Experience for Undergraduates (REU) at the Center Of Integrated Nanomechanical Systems (COINS), Summer 2009
Research Experience for Undergraduates (REU) with the Electrical Engineering Department at the Penn State University, Summer 2010

Awards

College of Engineering Honors Scholarship
Larry C. and Barbara A. Burton Scholarship
Lockheed Martin Corporation Scholarship
Academic Excellence Scholarship/Schreyer Honors Scholar
Paul Morrow Endowed Scholarship
Evan Pugh Senior Award