Thermal Sensor Arrays for The Combinatorial Analysis of Thin Films

A dissertation presented
by
Patrick J. McCluskey
to
The School of Engineering and Applied Sciences
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Engineering Sciences

Harvard University
Cambridge, Massachusetts
September 2010
©2010 – Patrick J. McCluskey

All rights reserved.
Abstract

Membrane-based thermal sensor arrays were developed for the high-throughput analysis of the thermophysical properties of thin films. The continuous growth of integrated circuits and microelectromechanical systems, as well as the development of functional materials and the optimization of materials properties, have produced the need for instruments capable of fast materials screening and analysis at reduced length scales. Two instruments were developed based on a similar architecture, one to measure thermal transport properties and the other to perform calorimetry measurements. Both have the capability to accelerate the pace of materials development and understanding using combinatorial measurement methods.

The shared architecture of the instruments consists of a silicon-based micromachined array of thermal sensors. Each sensor consists of a SiN\textsubscript{x} membrane and a W heating element that also serves as a temperature gauge. The array design allows the simultaneous creation of a library of thin film samples by various deposition techniques while systematically varying a parameter of interest across the device. The membrane-based sensors have little thermal mass making them extremely sensitive to changes in heat.

The nano-thermal transport array has an array of sensors optimized for sensitivity to heat loss. The heat loss is determined from the temperature response of the sensor to an applied current. An analytical model is used with a linear regression analysis to fit the thermal properties of the samples to the temperature response. The assumptions of the analytical model are validated
Abstract

with a finite element model. Measured thermal properties include specific heat, thermal effusivity, thermal conductivity, and emissivity. The technique is demonstrated by measuring the thermal transport properties of sputter deposited Cu multilayers with a total film thickness from 15 to 470 nm. The experimental results compare well to a theory based on electronic thermal transport.

The parallel nano-scanning calorimeter (PnSC) has an array of sensors optimized to sense changes in enthalpy. In this case heat loss sensitivity is minimized with sensor geometry and a reference measurement scheme. The minimal heat loss and small addendum result in sensitivity on the order of 10 nJ/K at heating rates on the order of $10^4$ K/s. The sensitivity is demonstrated by measuring the characteristics of the melting transformation of a 25 nm In film. The combinatorial capabilities of the device are demonstrated by creating and analyzing a library of thin-film (290 nm) Ni-Ti-Zr samples with in-plane composition gradients. The Ni-Ti-Zr films are crystallized in-situ by local heating and the temperature dependence of the martensite transformation on Zr content is detected.

Further analysis of the Ni-Ti-Zr samples reveals that the as-deposited amorphous samples crystallize in a multi-stage process that is a function of composition. The features of the calorimetry traces are identified with the help of x-ray diffraction measurements of the crystallized samples. Crystallization at these fast heating rates results in suppression of structural relaxation, increased crystallization temperature (allowing the detection of the glass transition), and an ultra-fine nanocrystalline grain structure with non-equilibrium phases.

The characteristics of the martensite-austenite phase transformation are investigated by PnSC to determine the effects of high temperature (900°C) heat treatments and low temperature (450°C) thermal cycling. Heat treatments produce precipitates that vary with Zr content and alter the transformation temperature. Thermal cycling results in the accumulation of plastic deformation, which relaxes internal stresses and reduces the transformation temperature. This effect, known as thermal fatigue, is reduced in these samples due to the ultra-fine grain structure, which suppresses dislocation mobility.
# Table of Contents

Title Page .................................................................................................................................................. i
Abstract ................................................................................................................................................... iii
Table of Contents ....................................................................................................................................... v
List of Figures ........................................................................................................................................... viii
List of Tables ........................................................................................................................................... xii
Acknowledgements ................................................................................................................................... xiii
Dedication ................................................................................................................................................ xiv

1 Introduction

1.1 Summary ........................................................................................................................................... 1
1.2 Temperature and heat at reduced length scales ................................................................................. 1
1.3 Combinatorial analysis ....................................................................................................................... 3
1.4 Thermal transport at reduced length scales ....................................................................................... 5
   1.4.1 Nanoscale thermal transport metrology .................................................................................. 6
   1.4.2 Nanoscale thermal transport theory ...................................................................................... 7
   1.4.3 Focus of this work .................................................................................................................. 8
1.5 Calorimetry at reduced length scales ............................................................................................... 9
   1.5.1 Nanoscale calorimetry ........................................................................................................... 10
   1.5.2 Combinatorial nano-calorimetry .......................................................................................... 10
   1.5.3 Focus of this work ................................................................................................................ 12
1.6 Crystallization of Ni-Ti-Zr thin films ............................................................................................... 12
   1.6.1 Equilibrium phases of Ni-Ti-Zr ............................................................................................. 13
   1.6.2 Focus of this work ................................................................................................................ 15
1.7 The martensite transformation in Ni-Ti-Zr ...................................................................................... 16
   1.7.1 Precipitation and thermal fatigue ......................................................................................... 16
   1.7.2 Focus of this work ................................................................................................................ 18
1.8 Thesis statement and dissertation outline ......................................................................................... 18
1.9 References ........................................................................................................................................ 19

2 Nano-Thermal transport array: an instrument for combinatorial measurements of heat transfer in nanoscale films

2.1 Summary ........................................................................................................................................... 23
2.2 Introduction ...................................................................................................................................... 24
2.3 Physical description and operating principles .................................................................................. 25
Table of Contents

2.4 Thermal modeling.............................................................................................. 29
   2.4.1 Transient 2D thermal model............................................................... 29
   2.4.2 Finite element simulations................................................................. 35
2.5 Data reduction and error analysis .................................................................. 38
2.6 Experimental method.................................................................................... 46
   2.6.1 Device fabrication............................................................................. 46
   2.6.2 Measurement setup and calibration of thermistor.......................... 49
   2.6.3 Sample fabrication and measurements............................................ 51
2.7 Results and discussion................................................................................ 53
2.8 Conclusion.................................................................................................... 61
2.9 Appendix A: Coefficients of Equation (2.16)............................................. 62
2.10 Appendix B: Measurement sensitivity analysis......................................... 63
2.11 References .................................................................................................. 64

3 Combinatorial nano-calorimetry....................................................................... 67
   3.1 Summary................................................................................................. 67
   3.2 Introduction.............................................................................................. 68
   3.3 Device description and working principles........................................... 69
      3.3.1 Description of device.................................................................... 69
      3.3.2 Operating principles.................................................................... 73
   3.4 Experimental method............................................................................ 74
      3.4.1 Device fabrication........................................................................ 74
      3.4.2 Sample preparation........................................................................ 77
      3.4.3 Experimental setup and procedures............................................ 79
   3.5 Results and discussion........................................................................... 84
      3.5.1 Indium results............................................................................. 84
      3.5.2 Composition of the Ni-Ti-Zr samples......................................... 86
      3.5.3 Crystallization of the as-deposited Ni-Ti-Zr samples................. 87
      3.5.4 Martensite-austenite transformation in crystalline samples.... 89
   3.6 Conclusion............................................................................................... 94
   3.7 Appendix B: Temperature uniformity.................................................... 95
   3.8 References.............................................................................................. 97

4 Glass transition and crystallization of amorphous Ni-Ti-Zr thin films by
   combinatorial nano-calorimetry............................................................... 101
   4.1 Summary............................................................................................... 101
   4.2 Introduction............................................................................................ 101
   4.3 Experimental method........................................................................... 102
   4.4 Results and discussion........................................................................... 103
      4.4.1 Glass transition and surface crystallization................................ 103
      4.4.2 Volume crystallization.................................................................. 105
      4.4.3 Crystal phase results and comparison to calorimetry.............. 106
      4.4.4 The effects of fast heating............................................................ 109
   4.5 Conclusion............................................................................................. 110
   4.6 References............................................................................................ 110

5 Precipitation and thermal fatigue in Ni-Ti-Zr shape memory alloy thin
   films by combinatorial nano-calorimetry.................................................. 112
   5.1 Summary............................................................................................... 112
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Introduction</td>
<td>113</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental method</td>
<td>114</td>
</tr>
<tr>
<td>5.4</td>
<td>Results and discussion</td>
<td>115</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Precipitation</td>
<td>115</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Thermal fatigue</td>
<td>118</td>
</tr>
<tr>
<td>5.4.3</td>
<td>Equilibrium phases</td>
<td>121</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusion</td>
<td>122</td>
</tr>
<tr>
<td>5.6</td>
<td>References</td>
<td>122</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions and future work</td>
<td>124</td>
</tr>
<tr>
<td>6.1</td>
<td>Summary</td>
<td>124</td>
</tr>
<tr>
<td>6.2</td>
<td>Conclusions</td>
<td>124</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Nano-Thermal transport array</td>
<td>124</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Parallel nano-scanning calorimeter</td>
<td>125</td>
</tr>
<tr>
<td>6.2.3</td>
<td>Glass transition and crystallization of Ni-Ti-Zr thin films</td>
<td>126</td>
</tr>
<tr>
<td>6.2.4</td>
<td>Thermal cycling effects on the martensite transformation in Ni-Ti-Zr thin films</td>
<td>127</td>
</tr>
<tr>
<td>6.3</td>
<td>Future work</td>
<td>128</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Ongoing work at Harvard University</td>
<td>128</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Nano-Thermal transport array</td>
<td>129</td>
</tr>
<tr>
<td>6.3.3</td>
<td>Parallel nano-scanning calorimeter</td>
<td>130</td>
</tr>
<tr>
<td>6.3.4</td>
<td>Ni-Ti-Zr materials system</td>
<td>131</td>
</tr>
<tr>
<td>6.4</td>
<td>Final remarks</td>
<td>131</td>
</tr>
</tbody>
</table>
List of Figures

1.1 Transmission electron micrograph of a tungsten via showing thermal damage due to overheating during a sub-microsecond current pulse. The temperature rise is strongly dependent on the thermal transport properties of the surrounding layers (from Cahill et al. 2002). ................................................................. 2
1.2 a) Number of papers published in combinatorial materials science. b) Number of citations for combinatorial materials science papers [49]. ..................................................................................... 4
1.3 Illustration of electron scattering features in multilayer copper films deposited on a SiN X membrane .......................................................... 8
1.4 Diagrams for the analytical model (a) and finite element model (b) for describing the heat flow in the membrane of the thermal sensor. .............................................................................. 9
1.5 1.5: Illustration of a composition spread deposited on a wafer, where the hue represents the relative amount of species from the A, B and C sources, respectively .................................................. 11
1.6 Binary phase diagrams for Ni-Ti (a), Ni-Zr (b) and Ti-Zr (c) (from Gupta 1999 [50]). Partial isothermal (700°C) section of the ternary phase diagram for Ni-Ti-Zr (d) (from Hsieh and Wu 1998 [46]). The phases relevant to this study, from the ternary phase diagram, are the Ti 2 Ni base phase (η 2 ) the NiTi base phase (δ 1 ) and the Laves phase (L). .............................................................. 14
1.7 Transmission electron micrographs of a sample from this work showing the ultra-fine grain structure (a) and Ti 2 Ni precipitate (b) (Courtesy of Chunwang Zhao) ..................................................... 15
2.1 nano-Thermal transport array schematic ........................................... 26
2.2 Thermal cell schematic: (a) Plan view, and (b) Cross-section view ........................................................................................................ 27
2.3 Schematic of control volume in relation to the entire thermal cell ........................................................................................................ 30
2.4 FEM average node temperature distribution along y-direction for a bare thermal cell and cell with 50 nm Cu sample, simulated for 5 ms with respective currents of 5 and 10 mA .......................... 37
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>FEM average temperature history of control volume nodes. Data is shown as dashes and the 5th order and 7th order polynomial fits are shown for the bare cell and the cell with 50 nm Cu, respectively.</td>
</tr>
<tr>
<td>2.6</td>
<td>Radiation from CV and membrane relative to the power dissipated in the thermistor for the bare cell.</td>
</tr>
<tr>
<td>2.7</td>
<td>Results of the analysis of the FEM results (data points with error bars) compared to input values (solid line): heat capacity of the CV of a bare cell (a), effusivity of a bare-cell membrane (b), heat capacity of the CV of a cell with a 50 nm Cu coating (c), effusivity of a membrane with a 50 nm Cu coating (d).</td>
</tr>
<tr>
<td>2.8</td>
<td>Emissivity calculated from the FEM simulations along with FEM input value. The error on the calculated emissivity is large at low temperatures, but the emissivity quickly converges to the input value at elevated temperatures where radiation is a more important heat loss mechanism.</td>
</tr>
<tr>
<td>2.9</td>
<td>nTTA fabrication flow. One thermal cell is shown for clarity. Detailed step-by-step procedures can be found in the text of the chapter.</td>
</tr>
<tr>
<td>2.10</td>
<td>Schematic of the experimental setup.</td>
</tr>
<tr>
<td>2.11</td>
<td>Raw voltage data recorded from a 5 mA, 20 ms current pulse across the 100 Ω precision resistor and a narrow thermistor.</td>
</tr>
<tr>
<td>2.12</td>
<td>Thickness of the copper sample multilayers.</td>
</tr>
<tr>
<td>2.13</td>
<td>Typical temperature history for a bare cell and cell with 61 nm sample (a). Typical heating rate for bare cell and cell with 61 nm sample (b).</td>
</tr>
<tr>
<td>2.14</td>
<td>Typical fit to the power data for a bare cell and a cell with a 61 nm copper film.</td>
</tr>
<tr>
<td>2.15</td>
<td>Typical thermal parameter fit results for bare cell (a) and cell with 61 nm Cu (b) heat capacity; effusivity results for the same cases (c).</td>
</tr>
<tr>
<td>2.16</td>
<td>Heat capacity (a) and effusivity (b) results for cells with and without copper samples.</td>
</tr>
<tr>
<td>2.17</td>
<td>2.17: Calculated thermal conductivity of thin copper films from measured thermal parameters, with $k_{SiN} = 3.2$ W/m K and $(\rho c_P)_{SiN} = 2.1$ MJ/m$^3$ K [23].</td>
</tr>
<tr>
<td>2.18</td>
<td>TEM cross-section of a 3-layer Cu film showing scattering interfaces.</td>
</tr>
<tr>
<td>2.19</td>
<td>Normalized thermal conductivity measurements of thin copper multilayer films, compared to Qiu’s thermal conductivity model [27] for multilayer copper films.</td>
</tr>
<tr>
<td>2.21</td>
<td>Relative errors of measured thermal parameters as a function of the value of these thermal parameters, (a) relative error of effusivity and (b) relative error of heat capacity. Data reduction used a moving 0.3 ms time-span for the heating rate fit and a 4 ms time-span to fit a 5th order polynomial to the temperature history.</td>
</tr>
<tr>
<td>3.1</td>
<td>Photograph of the parallel nano-scanning calorimeter.</td>
</tr>
</tbody>
</table>
List of Figures

3.2 Layout of the nano-calorimeter cell: (a) cross-section schematic, and (b) plane-view schematic. Heater line-width is 0.8 mm and voltage probe line-width is 0.1 mm. ........................................................ 71

3.3 Cross section schematic of a nano-calorimeter cell during steps in the PnSC fabrication process. ........................................................ 75

3.4 Sputter deposition schematic of Ni-Ti-Zr samples. ......................... 78

3.5 Measurement setup schematic. ......................................................... 80

3.6 Typical voltage response for a PnSC cell with Ni-Ti-Zr sample to an 85 mA current pulse lasting 25 ms. ................................................ 81

3.7 Calibration fit of the temperature coefficient of resistance. ............. 83

3.8 Indium melting results. (a) Indium melting curve and reference curve. (b) Differential calorimetric signal with baseline showing the melting transformation of In nanostructures (inset). .................. 84

3.9 Typical Ni-Ti-Zr crystallization results. (a) Temperature response of as-deposited and crystallized Ni-Ti-Zr sample to an 85 mA current pulse lasting 60 ms. (b) Calorimetric signal of as-deposited and crystallized Ni-Ti-Zr sample plotted as a function of as-deposited sample temperature. (c) Differential calorimetric signal for crystallizing Ni-Ti-Zr sample. .................................................. 88

3.10 Typical Ni-Ti-Zr martensite transformation results. (a) Temperature response of the as-deposited and crystallized sample to an 85 mA current pulse lasting 22 ms, with the crystallized sample transforming martensitically. (b) Calorimetric signals of a sample in the amorphous and the crystallized phase during heating. (c) Differential calorimetric signal for the martensite-austenite transformation during heating. ................................................................. 90

3.11 Differential calorimetric signal (from -150 to 300 nJ/K) of the martensite transformation versus temperature (from 30 to 350 °C) for each sample during heating. Results are arranged as positioned on the PnSC. See Table 3.4 for composition results and Table 3.5 for quantitative transformation results. ......................................................... 91

3.12 Martensite-austenite peak transformation temperatures as a function of Zr content for two Ni poorest rows. The bulk sample results of Hsieh [25, 26] are shown for comparison. Trend lines are drawn as guides to the eye. ........................................................................................................ 92

4.1 (a) Examples of crystallization peak shapes in the calorimetric trace (offset for clarity), where exothermic is negative. The symbols represent different calorimetry trace types as described in the text. (b) Calorimetric signal showing glass transition and surface crystallization behavior in samples with a nominal Ni concentration of 51%. .......................................................................................................................... 103

4.2 (a) Enthalpy of surface crystallization, normalized by sample mass, as a function of composition. (b) Calorimetry trace type, represented by the O, □ and △ symbols (see Fig. 4.1(a)) and peak crystallization temperature as a function of composition.
Open circles (○) represent compositions of unmeasured samples.................................................................105

4.3 Examples of XRD spectra. Groups correspond to Fig. 4.4. Peaks can be indexed as: tungsten (W) from the calorimeter heating element, Ni(Ti,Zr) austenite (▼), NiTi austenite (▲), Ni(Ti,Zr) martensite (■), (Ti,Zr)₂Ni (●), and Ni₁₀(Zr,Ti)₇ (◆).........................................................107

4.4 Schematic showing the various phases in the crystallized samples as a function of composition. Solid lines separate regions with distinct phase compositions as determined by the cluster analysis of the XRD spectra. The phases between curly brackets refer to trace amounts: Region-I contains minor precipitation of (Ti,Zr)₂Ni and Ni₁₀(Ti,Zr)₇ as determined by TEM and XRD, respectively. Region-II is expected to contain (Ti,Zr)₂Ni from calorimetry as described in the text. .........................109

5.1 Evolution of the martensite-austenite transformation with high-temperature heat treatments, for the Ni₄₄.₇Ti₃₅.₇Zr₁₉.₆ sample, in the calorimetric signal (a), enthalpy (b), and transformation peak temperature (c).........................................................................................116

5.2 Evolution of the martensite-austenite transformation peak temperature with high-temperature heat treatments as a function of Zr concentration..............................................................................................117

5.3 Thermal fatigue of the martensite-austenite transformation, for the Ni₄₄.₇Ti₃₇.₁Zr₁₈.₂ sample, in the calorimetric signal (a), enthalpy (b), and temperature (c). .............................................................................................................118

5.4 Thermal fatigue of the martensite-austenite transformation before (a) and after (b) high-temperature heat treatments for 45% Ni as a function of Zr content. .........................................................119
List of Tables

2.1 Approximate dimensions of nTTA components..............................29
2.2 FEM input materials properties [18-23]...........................................36
2.3 FEM measurement simulation results..............................................44
2.4 Applied current in milli-Amperes for a given cell and measured
quantity..................................................................................................53

3.1 Dimensions of PnSC components. Note: thermal sensor center-to-center spacing is 8 mm in both the x and y-directions. .............73
3.2 Magnetron fabrication processing conditions....................................76
3.3 Current pulse amplitude and duration for calorimetric
measurements.........................................................................................83
3.4 Calorimetric cell numbering scheme with corresponding sample
chemical composition from EDS analysis (atomic %). Measurement uncertainty can be estimated as 0.6, 0.4 and 0.4
at.% for Ni, Ti and Zr, respectively.......................................................87
3.5 Martensite-austenite transformation results for compositions
demonstrating a transformation in the calorimetric signal. Chemical composition uncertainty can be estimated as 0.6, 0.4
and 0.4 at.% for Ni, Ti and Zr, respectively........................................87
3.5 Martensite-austenite transformation results for compositions
demonstrating a transformation in the calorimetric signal. Chemical composition uncertainty can be estimated as 0.6, 0.4
and 0.4 at.% for Ni, Ti and Zr, respectively........................................87
3.5 Martensite-austenite transformation results for compositions
demonstrating a transformation in the calorimetric signal. Chemical composition uncertainty can be estimated as 0.6, 0.4
and 0.4 at.% for Ni, Ti and Zr, respectively........................................87
3.B1 Thermal properties of PnSC materials [16, 35-37].---------------------96

5.1 The effect of thermal cycling on the martensite-austenite
transformation temperature. Note: bracketed values were not
used to calculate the error weighted average because 100 cycles
were not recorded, the actual number of cycles being 50† and
30††. .........................................................................................................120
Acknowledgements

Acknowledgements will be written upon the successful defense of this dissertation.
Dedicated to my father on his birthday.
September 21, 2010
Chapter 1

Introduction

1.1 Summary

The goal of this work was to develop instrumentation for the analysis of thermophysical properties of materials systems using a combinatorial approach. The capabilities of these instruments were demonstrated by performing meaningful case studies on technologically important and scientifically interesting materials systems. Chapter 1 of this dissertation motivates this thesis and provides background information that may be useful to the reader for the sections that follow. In general this overview introduces high-throughput combinatorial analysis, thermal transport at reduced length scales with a case study on thin copper multi-layers, and calorimetry at reduced length scales with a case study on a thin-film Ni-Ti-Zr combinatorial library.

1.2 Temperature and heat at reduced length scales

Over the past few decades micro- and nano-electronics have become ubiquitous in the form of integrated circuits (IC). The more recently developed
Chapter 1: Introduction

Microelectromechanical systems (MEMS) have also begun to find wider application. Such devices typically have a minimum feature size on the order of tens or hundreds of nanometers. Regardless of the type of device, all micro/nano-electronics are powered by electricity and as an unavoidable side effect generate heat through energy dissipation. As these devices become more integrated and sophisticated, thermal management to mitigate the deleterious effects of heat becomes more important and complicated. Failure to properly consider these issues is a primary cause of performance degradation and failure (Fig. 1.1).

![Image of a tungsten via showing thermal damage due to overheating during a sub-microsecond current pulse. The temperature rise is strongly dependent on the thermal transport properties of the surrounding layers (from Cahill et. al. 2002).](image)

Figure 1.1: Transmission electron micrograph of a tungsten via showing thermal damage due to overheating during a sub-microsecond current pulse. The temperature rise is strongly dependent on the thermal transport properties of the surrounding layers (from Cahill et. al. 2002).

Beyond failure analysis, heat is often necessary for the synthesis and operation of nanoscale systems. Most IC and MEMS fabrication methods simply heat the entire structure to a given temperature; however, the constant introduction of new materials, some of which are susceptible to thermal damage, may prevent this type of processing. Techniques for local heating are being developed as means to work around this issue and to selectively functionalize
structures [1]. In other cases, heat or temperature are the primary quantities of interest, either for measurement or control. A few examples include: thermal sensors, phase-change memory and thermomechanical actuators, to name a few. In such devices, precise knowledge of thermophysical properties is crucial for proper operation.

Nanoscale thermal issues extend beyond the above discussion. For instance, thermal transport and thermal stability of nanostructured bulk materials could be included; however, the practical importance of heat at the nanoscale should be apparent. Further development of nanotechnology is limited by metrology and understanding related to these phenomenon, a few examples include: 1) The time-to-breakdown for SiO$_2$ gate dielectrics becomes more temperature dependent with reduced thickness [2]. 2) Phonon waveguides along epitaxial multilayers, which could be useful to direct heat away from sensitive components, have been predicted but not realized [3]. In fact, not much data is available for thermal transport along interfaces because most thermal conductivity measurements are through-plane techniques. 3) Phase transformations, a primary mode of failure, can be monitored by many state variables. However, energetics information, the driving force behind transformations and reactions, requires calorimetry. The few nano-calorimetry studies that exist explore relatively simple materials systems and structures unlike those that exist in modern IC and MEMS. No nano-calorimetry studies have been performed as a function of composition.

1.3 Combinatorial analysis

The study of materials properties as a function of composition using high-throughput techniques, i.e. combinatorics, is an increasingly necessary and fruitful approach to materials science. It is a technique established in the biological fields [4] and adopted by materials scientists to meet the growing need to tailor and optimize materials properties. Less than 1% of materials systems, up to the quaternary level of combinations, are well characterized [5]. Despite the number of researchers involved in materials science and the significant history of
the field there remains much work to be done. The traditional one-at-a-time approach is simply too slow. In order to make an impact in this vast unknown space of approximately 4 million materials systems, combinatorial methods are required. The trend toward more combinatorial-based experimentation techniques has been growing recently (Fig. 1.2) and is yielding some impressive results, e.g., the near elimination of thermal hysteresis in Ti-Ni-Cu-Pd shape memory alloys [6]. These experimental techniques are being supported by more intelligent data mining algorithms and fast computers to analyze the vast datasets that are generated [7].

![Figure 1.2: a) Number of papers published in combinatorial materials science. b) Number of citations for combinatorial materials science papers [49].](image)

While the benefits of the combinatorial approach in terms of efficiency and economy are clear, the application of these techniques to thermophysical measurements remains limited. A couple of applied techniques include: 1) high-throughput picosecond thermo reflectance measurements of thermal transport properties [8] and 2) micro-hotplate arrays for thermal processing and as a platform for measurements as a function of temperature, although the measurement of thermophysical properties appears limited [9]. Some traditional calorimeters have been equipped with automated sample changers, but combinatorial studies may not be feasible considering measurement times are
typically 4-5 orders of magnitude longer than nano-calorimetry. Any large-scale combinatorial study would be prohibitively long on a traditional calorimetry system.

The study of thermophysical properties as a function of composition is a primary thrust of this work and its importance should be made clear. Thermophysical properties of pure substances are known to vary with composition. Mixtures and compounds of pure substances do not necessarily obey any one rule when it comes to determining the resulting properties. Thus, attempts to predict thermophysical properties a priori have not seen much success. For example, thermal transport properties are known to be a function of composition; even at dilute concentrations dopant species can act as efficient scattering sources for phonons and cause increased phonon-electron interactions [10]. Another example comes from calorimetry, which is a traditional technique for studying phase transformations. When performed as a function of composition, these studies result in phase diagrams, an indispensable reference in the materials science toolbox and a key characteristic of materials systems. Length scale is important in these cases as well. The relative stability of phases has been shown to depend on length scale [11-14]. The length scale dependence arises from interfacial energies and can cause temperature and composition shifts in phase boundaries. These examples show that there is a compelling interplay between composition and length scale, and how they can both affect thermophysical properties, an idea that will be explored further in this work.

The above discussion has outlined some of the general problems and prospects related to the measurement and understanding of thermophysical materials properties as a function of length scale and composition. What follows is a more focused discussion on how the present study relates to this field.

1.4 Thermal transport at reduced length scales

Thermal transport at reduced length scales, i.e., a length scale smaller than the mean free path of the heat carrier in the bulk material, is largely influenced by the interaction of heat carriers with interfaces. The understanding of these
interactions, from a theoretical and metrological perspective, is a significant challenge to the thermal physics community. The related chapter of this dissertation aids this endeavor through the development of a new instrument for measuring thermal transport properties of thin films in a high-throughput methodology.

1.4.1 Nanoscale thermal transport metrology

Recent advancements in thermal transport metrology have improved the understanding of thermal transport at reduced length scales. Scanning thermal microscopy (SThM) uses a sharp-tip (radius of 50-100 nm) thermocouple to measure surface temperatures with a spatial resolution less than 100 nm [15, 10]. SThM has been used to image active vertical cavity lasers and heated carbon nanotubes. Considering the scanning nature of the device it should be applicable to combinatorial measurements, although this has not been demonstrated. A limitation of SThM for quantitative measurements is the complex heat transfer mechanism involving solid-solid, air or radiation (depending on the environment), and liquid film heat transfer paths.

Picosecond reflectance thermometry and scanning optical thermometry interrogate a sample surface by heating it with a short laser pulse and then measuring the temperature response with a second probe laser or radiation signal, respectively [10]. The short measurement times associated with these technique (approximately 3 measurements per second) makes them appropriate for combinatorial measurements of thermal transport properties [8]. The probe laser or radiation measurement takes place approximately tens to hundreds of picoseconds after the pulse laser. These short times mean that the laser spot is typically much larger than the diffusion length, limiting these measurements to the through-plane geometry. Even if the time-delay were increased or the laser spot were reduced, heat still diffuses in all directions, which reduces the in-plane sensitivity of these techniques.

The most effective way to increase measurement sensitivity to in-plane thermal transport is to limit the thermal transport path to two dimensions with,
for example, a membrane or bridge type structure. A few devices with this geometry have been developed recently, facilitated by the advancements in microfabrication technology. Most of these devices, however, are not optimal for combinatorial applications due to the requirement for multiple thermal cells and/or numerous thermometers [16-18]. Some devices are steady state in nature, which imposes limits on the minimum size of the thermal cell because of temperature uniformity considerations and may require computationally expensive finite element modeling to extract materials parameters [19-23]. Both are drawbacks from a combinatorial perspective.

1.4.2 Nanoscale thermal transport theory

The experimental techniques described above have pushed the boundaries of knowledge into new regimes of nanoscale thermal transport. Along with this expansion of metrology, theory has also expanded to develop an understanding of these new results. Thermal transport theory can be complicated by phonon and electron transport because of the different wavelengths and mean free paths, as well as the interactions of these heat carriers.

Thermal conduction in electrically insulating solids is dominated by phonons. With a mean free path in the range 10-100 nm, present electronics have feature sizes well within the continuum limit [10]. As a result continuum theory, such as Fourier’s Law, no longer applies and particle based theories and simulations, such as Boltzmann’s transport equation and atomistic simulations must be used. Molecular dynamics simulations have added new insights to thermal transport at interfaces, because no a priori knowledge of heat transport is required, only Newton’s equations of motion must be considered. This approach is not a panacea. Real components are still far too large to simulate with today’s processor capabilities and it is not possible to simulate electronic thermal transport or phonon-electron interactions [3]. Much of the efforts to understand thermal transport at reduced length scales have been focused on the interaction of heat carriers and interfaces. However, current theory over predicts the range
of interface thermal conductance compared to experimentally observed values, highlighting the need for further work.

Thermal conduction in electrically conductive solids is dominated by electrons. Qiu and Tien [24] have extended the modeling of electron conductivity by Mayadas and Shatzkes [25] to describe electron dominated thermal transport in terms of bulk thermal conductivity and electron scattering features, such as free surfaces, grain boundaries, and interfaces (Fig 1.3). This model is based on the Boltzmann transport theory and uses the Weidmann-Franz law to relate electrical conductivity to thermal conductivity. The model shows good agreement with previous experimental results for effective thermal conductivities of thin-films polycrystalline metals.

![Figure 1.3: Illustration of electron scattering features in multilayer copper films deposited on a SiN\(_x\) membrane.](image)

### 1.4.3 Focus of this work

The nanoscale thermal transport chapter of this dissertation introduces the nano-thermal transport array (nTTA) and demonstrates the device with high-throughput measurements of copper multilayers. The nTTA consists of a 5\(\times\)5 array of membrane based thermal sensors micromachined on a wafer. These sensors are described with an analytical thermal model consisting of the inhomogeneous diffusion equation with time dependent boundary conditions (Fig. 1.4(a)). The model solution allows the extraction of thermal transport properties in thin films deposited on the membranes. The assumptions of the
analytical model are checked with a finite element model (FEM) of the cross section of the membrane (Fig. 1.4(b)). The FEM shows excellent agreement with the analytical model and justifies the assumptions of the analytical model, thus validating the data reduction scheme. nano-Thermal transport array measurements are used to extract the specific heat, thermal effusivity, and thermal conductivity of thin multilayers of copper ranging in thickness from of 15 to 470 nm. These results are compared to the model by Qiu and Tien using no fitting parameters. The good agreement shows that thermal transport in these films is dominated by electron transport and limited by the scattering features (Fig. 1.3) at reduced length scales. These results demonstrate the ability of the nTTA to accurately measure thermal transport properties over a wide range of thermal conductance.

1.5 Calorimetry at reduced length scales

Calorimetry is the study of enthalpy-related materials properties. Traditional calorimeters have been used by materials scientists to study various phenomenon, such as phase transformation temperatures, enthalpy of reactions,
transformation kinetics, and grain growth. The ability of a calorimeter to measure these quantities precisely depends on sensitivity, which is a function of: 1) the intrinsic sensitivity of the temperature and power measurements, and 2) the change in enthalpy of the sample compared to the change in enthalpy of the sample holder and heat lost to the environment. Improvements in sensitivity can be made by performing measurements differentially, reducing the error from the addendum and heat loss, or by physically reducing the addendum and heat loss.

1.5.1 Nanoscale calorimetry

Calorimeter addendums were reduced significantly with the advent of micromachined calorimetric cells [26-29]. Such devices have a heat capacity on the order of 100 nJ/K and a thermal conductance on the order of 1 nW m/K, resulting in sensitivities on the order 10 nJ/K. Differential measurement schemes can increase the sensitivity even further. The extreme sensitivity of these sensors makes measurements on nanoscale samples possible, such as the melting point depression of metallic nanoparticles [30-32]. Micromachined calorimeters have also been used to study the structural changes of poly(ethylene terephthalate) at fast heating rates (1000 K/s) [33] and heat capacity measurements in high magnetic fields (8 T) [34]. The small heat capacity and heat loss of these sensors also means that high heating rates are readily achieved, on the order of $10^5$ K/s. These high heating rates expand the range of kinetics studies and reduce measurement times up to 5 orders of magnitude.

1.5.2 Combinatorial nano-calorimetry

Because nano-calorimeters are fabricated with micromachining technology, they are ideal for combinatorial measurements on thin film samples. Micromachining techniques are well suited for the replication of a pattern across a substrate, which facilitates the design and fabrication of arrays of nano-calorimeters. This type of device can be combined with thin film deposition
techniques to create a library of samples with unique compositions. Figure 1.5 shows how the sputtering flux distribution from 3 distinct sources leads to a composition spread on a flat substrate. This technique has been useful for creating thin film libraries for stress analysis using arrays of cantilever beams [35-37].

The reduced measurement times typical of nano-calorimeters make such sensors ideal for high-throughput measurements. Since high-throughput measurements necessarily involve many more measurements than the typical on-at-a-time approach, it is important to make measurements fast so that such studies can be completed in a reasonable amount of time. Since nano-calorimeters can perform measurements many orders of magnitude faster than
traditional calorimeters these sensors are more appropriate for combinatorial analysis.

1.5.3 Focus of this work

The combinatorial nano-calorimetry chapter of this dissertation describes and demonstrates the parallel nano-scanning calorimeter (PnSC), which was developed as part of this work. The physical description of the device and the fundamental working principals are detailed. This discussion includes fabrication methods for the device and samples, experimental setup, and modeling the thermal characteristics of the sensor. The sensitivity of the device is demonstrated through the melting a 25 nm indium film and the combinatorial capabilities are demonstrated through the analysis of the martensite transformation in Ni-Ti-Zr thin films as a function of composition.

1.6 Crystallization of Ni-Ti-Zr thin films

The Ni(Ti,Zr) compound of the Ni-Ti-Zr materials system is a shape memory alloy (SMA). This class of alloys is known for the solid-state transformation from the low-temperature, low-symmetry, martensite phase to the high-temperature, high-symmetry, austenite phase. The various orientations of the martensite lattice, relative to the austenite lattice, are known as martensite variants. In the presence of a stress field, these variants tend to arrange in orientations that reduce the strain energy. When the material in this condition is heated to a sufficient temperature it transforms to the austenite phase and because this phase has a lower symmetry it cannot accommodate the imposed stress as well and thus it does work against the stress during the transformation back to the original shape. This phenomenon is known as the shape memory effect (SME) and has been used to actuate components for various applications in thin film and bulk form.
Since the discovery of the SME in NiTi, this alloy has been the focus of considerable research efforts. It is the most important shape memory alloy (SMA) from a practical standpoint not only because of its good mechanical properties, but also because of its good corrosion resistance and biocompatibility [38]. The characteristics of the SME in NiTi depend sensitively on processing conditions and composition. Recent efforts have considered tailoring the SME of NiTi by alloying it with other elements, for example, Cu [6] to reduce the thermal hysteresis or Zr to increase the transformation temperature [39]. Ni-Ti-Zr is seen as one of the most promising high-temperature shape memory alloys because it retains many of the positive aspects of the binary system, but with a significantly increased martensite-austenite transformation temperature.

A side effect of tertiary alloying is that it tends to stabilize the amorphous phase, which must be considered when processing these alloys in thin-film form [40]. The amorphous phase of these materials can also be useful as structural components because of their high strength, yield strain, and low damping coefficient [41]. The stability of the amorphous phase depends on the driving force to crystallize and the mobility of the atoms, which can be studied through devitrification analysis.

1.6.1 Equilibrium phases of Ni-Ti-Zr

In Ni-Ti-Zr SMA, the shape memory phase, Ni(Ti,Zr), occurs over a narrow composition range and the shape memory properties are a strong function of composition. Also, the stability of the amorphous phase depends on the possible equilibrium phases. As a result, one must consider the existing phase information when processing these alloys. The binary and ternary phase diagrams for Ni-Ti-Zr are shown in Fig. 1.6. The Ni-Ti (Fig. 1.6(a)) and Ni-Zr (Fig. 1.6(b)) phase diagrams consist of multiple intermetallic phases, while the Ti-Zr phase diagram (Fig. 1.6(a)) consists of an isomorphic system. The narrowness of the Ni(Ti,Zr) composition range and the multitude of intermetallic phases can result in precipitation for samples with non-stoichiometric or inhomogeneous compositions. Precipitates can change the shape memory behavior of the
material by altering the stress state or by changing the composition of the SMA phase. Figure 1.6(d) shows the isothermal (700°C) section of the partial ternary phase diagram and indicates that the (Ti,Zr)₂Ni (η₁) and Laves (λ) phases are the expected precipitates; however other precipitates, such as the NiZr, Ni₇(Ti,Zr)₁₂ and Ni₁₀(Zr,Ti)₇ phases have also been reported, owing to the complex nature of this materials system.

Figure 1.6: Binary phase diagrams for Ni-Ti (a), Ni-Zr (b) and Ti-Zr (c) (from Gupta 1999 [50]). Partial isothermal (700°C) section of the ternary phase diagram for Ni-Ti-Zr (d) (from Hsieh and Wu 1998 [46]). The phases relevant to this study, from the ternary phase diagram, are the Ti₂Ni base phase (η₁) the NiTi base phase (δ₁) and the Laves phase (λ).


1.6.2 Focus of this work

In the crystallization chapter of this dissertation, the amorphous and crystallization behavior of the Ni-Ti Zr system is analyzed. A combinatorial library of thin film samples is created on the PnSC by magnetron sputter deposition. The as-deposited amorphous samples are crystallized by ultra-fast heating ($15 \times 10^3$ K/s) resulting in various interesting behavior, including: suppression of structural relaxation, a temperature increase in the onset of crystallization facilitating the detection of the glass transition, and a multi-stage crystallization process resulting in an extremely fine grain structure (Fig. 1.7). X-ray diffraction analysis of the crystallized samples facilitates interpretation of the crystallization process.

Figure 1.7: Transmission electron micrographs of a sample from this work showing the ultra-fine grain structure (a) and Ti$_2$Ni precipitate (b) (Courtesy of Chunwang Zhao).
1.7 The martensite transformation in Ni-Ti-Zr

Like NiTi, Ni(Ti,Zr) austenite has the B2-cubic structure and the martensite has a final structure of B19’-monoclinic. The transformation pathway for NiTi is not always directly from B2 to B19’ but can transform through the R-phase with a rhombohedral structure or the B19-phase with an orthorhombic structure. Although for Ni(Ti,Zr) only the B2 ↔ B19’ transformation has been reported. Hsieh and Wu have reported the possibility of a change in structure for Zr ≥ 15 at.% due to a poorly matching Rietveld analysis of x-ray diffraction data and a martensitic structure model (B19’ monoclinic); however the change in structure was not described.

The significant change in symmetry associated with the B2 ↔ B19’ transformation results in 12 lattice correspondences for the Ni(Ti,Zr) martensite with 6 linearly independent deformation tensors relative to the austenite phase. Because of the small volume change (~0.3%), the shape strain can be considered a shear deformation. Using the analogy of plastic deformation and slip-systems, just 5 linearly independent variants are required to accommodate an arbitrary macroscopic strain [45]. According to this principal the material can accommodate arbitrarily imposed strains without plastically deforming.

In general Ni(Ti,Zr) shows good shape memory characteristics. Ni(Ti,Zr) has demonstrated shape recovery of 90% [46] and reversible strains of 10-12% [43]. The variation of the transformation temperature expands the active range of this alloy compared to the binary system. Some issues remain and prevent this materials system from being used in applications, including reduced ductility and increased brittleness with increasing Zr concentration and thermal cycling fatigue.

1.7.1 Precipitation and thermal fatigue

Precipitation has significant effects on the mechanical behavior of Ni-Ti-Zr SMA. Precipitates causes local changes in stress and composition in the shape
memory phase, act as obstacles to dislocation motion and may embrittle materials due to poor ductility. Different types of secondary phases have been observed in the Ni-Ti-Zr materials system depending on the composition and processing conditions. NiZr was observed in thin-film Ni_{50}Ti_{20}Zr_{30} crystallized by heating to 900°C at 10 K min⁻¹, resulting in increased critical stress for slip but reduced recovery strain [42]. The formation of NiZr was also used to explain an anomalous decrease in transformation temperature with increasing Zr content by reducing the Zr content in the SMA matrix. The formation of Ti₂Ni and Ni₇(Ti,Zr)₂ in Ti₅₀Ni₅₀₋ₓZrₓ with x ≥ 5 at.% prepared from melt solution followed by an anneal at 800°C for one hour and then quenched in water, was associated with reduced ductility and brittle fracture along grain boundaries [43]. (Ti,Zr)₂Ni precipitates were also shown to increase the hardness and thermal fatigue of thermally cycled Ni_{48.5}Ti_{41.5}Zr_{10} [44]. The Laves phase has been reported in many Ti-rich Ni-Ti-Zr alloys. This phase is known to be brittle and it is expected that the formation reduces the ductility. Ni_{10}(Zr,Ti)₇ has been observed in Ni_{50}Ti_{50₋ₓ}Zrₓ with x = 30-50 at.%; however, the affect on materials properties of the metallic composite is unclear [44]. The variety of precipitates and the effects on materials properties highlight the need to characterize this materials system as a function of composition and processing conditions. Precipitates also significantly affect the thermal fatigue behavior of the martensite transformation.

Macroscopically Ni(Ti,Zr) can accommodate any randomly imposed strain as long as the deformation does not cause the material to exceed its yield stress. Microscopically, however, the habit plane between the martensite and austenite must be invariant to avoid plastic deformation induced by internal stresses. This criterion is complicated by the presence of precipitates and grain boundaries, which can also cause interfacial stresses. NiTi and Ni(Ti,Zr) do not have an invariant habit plane and often have precipitates, resulting in complex stress fields and plastic deformation during the martensite-austenite transformation. When the material is cycled through the martensite-austenite transformation numerous times the plastic deformation accumulates in a process known as thermal fatigue, which manifests in changed transformation characteristics, such as, reduced recovery strains and transformation
temperatures. Much effort has focused on reducing thermal fatigue in SMA. Recently combinatorial techniques were used to improve the thermal fatigue behavior of NiTi by alloying with Cu and Pd to reduce lattice mismatch of the habit plane [6]. Other efforts have focused on reducing dislocation mobility through precipitation [47] or grain refinement [48].

1.7.2 Focus of this work

In the thermal cycling chapter of this dissertation the library of Ni-Ti-Zr thin-film samples are investigated by combinatorial nano-calorimetry to reveal the effects of heat treatments and thermal cycling on the martensite transformation. The effects of heat treatments are explained by precipitation that varies with Zr concentration. Thermal fatigue is reduced in these results when compared to previous results. This is explained by a reduced dislocation mobility resulting from the extremely small grain size. The short measurement times and combinatorial nature of the PnSC make these measurements possible with an efficiency and economy unachievable by previous calorimeters.

1.8 Thesis statement and dissertation outline

Membrane based thermal sensors have been shown to be useful for measuring the thermophysical properties of materials. Combinatorial methods have been shown to be useful for rapid analysis of complex materials systems. These techniques have never been integrated and applied to materials science. This dissertation will show that it is possible to integrate membrane based thermal sensors and combinatorial methods to create instruments for the high-throughput analysis of complex materials systems and that this approach accelerates materials understanding, discovery, and optimization. Furthermore, these methods are appropriate for multiple length scales and are able to reveal nanoscale effects on thermal properties. The developed techniques are
demonstrated by determining the thermophysical properties of technologically significant materials.

To support this thesis, the dissertation is organized as follows: Chapter 2 covers the measurement technique and results for thermal transport properties in thin copper multilayers. Chapter 3 describes the measurement technique and results for combinatorial nano-calorimetry applied to indium nano-particles and the crystallization and martensite transformation of Ni-Ti-Zr thin films. Chapter 4 covers the combinatorial analysis of the glass transition and crystallization of amorphous Ni-Ti-Zr samples. Chapter 5 discusses the effects of heat treatments and thermal cycling on the martensite behavior in nanocrystalline Ni-Ti-Zr. Finally, chapter 6 presents concluding remarks from this work and provides guidance for future studies.

1.9 References


Chapter 1: Introduction


Chapter 1: Introduction

Chapter 2

nano-Thermal transport array: an instrument for combinatorial measurements of heat transfer in nanoscale films

2.1 Summary

The nano-Thermal Transport Array is a silicon-based micromachined device for measuring the thermal properties of nanoscale materials in a high-throughput methodology. The device contains an array of thermal sensors, each one of which consists of a silicon nitride membrane and a tungsten heating element that also serves as a temperature gauge. The thermal behavior of the sensors is described with an analytical model. The assumptions underlying this model and its accuracy are checked using the finite element method. The analytical model is used in a data reduction scheme that relates experimental quantities to materials properties. Measured properties include thermal effusivity, thermal conductivity, and heat capacity. While the array is specifically
designed for combinatorial analysis, here we demonstrate the capabilities of the device with a high-throughput study of copper multi-layer films as a function of film thickness, ranging from 15 to 470 nm. Thermal conductivity results show good agreement with earlier models predicting the conductivity based on electron scattering at interfaces.

2.2 Introduction

The thermal transport properties of nanoscale materials can differ significantly from their bulk counterparts [1,2]. When the microstructural length scale of a material is comparable to the mean free path of the phonons and electrons responsible for thermal transport in that material, surfaces and interfaces start to influence overall thermal transport. This effect has become increasingly important, as nanotechnology has pushed device design below the applicable scales of bulk materials properties. In devices such as integrated circuits or micro-electro-mechanical systems, thermal transport can play a significant role in function and failure. Beyond technological considerations, the study of thermal properties at the nano-scale presents interesting fundamental questions into the interaction of heat transfer and microstructure at these small length scales, including thermal conductivity across and parallel to interfaces [3].

Along with length scale, thermal properties of materials also vary with composition and processing conditions [4]. Extensive studies of these considerations have been performed for bulk materials in the past, but few studies have been performed on nanoscale materials systems. A high-throughput measurement technique specifically applicable to nanoscale materials would be helpful in remedying this situation. Such a technique could be used to quickly map the thermal transport properties of very small quantities of materials as a function composition or processing conditions, thus facilitating design and optimization of nanoscale devices.

Thin-film heat transport metrology has improved significantly in recent years. Through-plane techniques such as 3-omega, time-domain...
thermoreflectance, and scanning optical thermometry can be used in a high-throughput methodology, but have limited in-plane applicability [5,6]. The most promising in-plane methods rely on membrane structures that constrain heat flow in the plane [7-9]. Until now, this class of instruments has seen no high-throughput thermal conductivity measurement application. Many of the membrane-based techniques are not compatible with high-throughput methods because they involve multiple thermal cells and/or numerous thermometers. The 3-omega method has been used to measure in-plane thermal conductivity, but the technique requires two heating elements of differing widths for each measurement, reducing the high-throughput applicability of this approach [10]. More recently the 3-omega method has been used to measure the thermal conductivity and heat capacity of silicon nitride and nickel titanium membranes. The approach used for these measurements requires multiple thermometers and up to 16 electrical connections, making it inconvenient for high-throughput application [11].

In the following chapter, we present an instrument designed to measure the in-plane thermal conductivity of nanoscale films and coatings with a high-throughput methodology. The nano-thermal transport array (nTTA) is a micromachined array of thermal sensors, so called because it uses a high-throughput approach to measuring heat transport in thin film material systems. An analytical, one-dimensional, transient heat transfer model is used to optimize the dimensions of each sensor, define the measurement range, and reduce measured data to the desired material properties. A finite element model (FEM) is used to verify the analytical model. Direct effusivity measurements of Si$_3$N$_4$ membranes and Si$_3$N$_4$/Cu multilayer-membranes as a function of film thickness, and calculated thermal conductivity measurements, demonstrate the capabilities of the nTTA.

2.3 Physical description and operating principles
Chapter 2: nano-Thermal transport array

The nTTA device consists of a substrate with a number of micromachined thermal sensors. The thermal sensors are arranged in a 5x5 array to facilitate combinatorial sample preparation (Fig. 2.1). When a thin-film sample with an in-plane composition or thickness gradient is deposited on this substrate, it is essentially discretized at each thermal sensor allowing the simultaneous measurement of 25 samples with unique composition or thickness.

The design and operation of the thermal sensors is similar to the nano-calorimetric cells developed by Allen and colleagues [12-15], but optimized for sensitivity to heat loss. Each thermal sensor consists of a thermistor on an electrically insulating ceramic membrane supported by the substrate (Fig. 2.2(a), (b)). The thermistor is fabricated from an electrically conductive film and serves both for measuring temperature and for heating the sample. Samples to be

Figure 2.1: nano-Thermal transport array schematic.
measured form a continuous film across the membrane of each sensor. Electrically insulating samples are deposited on the front-side of the membrane while conductive samples are deposited on the backside of the membrane.

Referring to the schematic in Fig. 2.2(a), the long straight line down the center of the membrane is the heating element, the metal lines connected to the heater are the voltage probes, and the portion of the heating element between the voltage probes is the thermistor. A current passed through the heating element heats the membrane along its centerline. The local temperature change is determined from the resistance of the thermistor, which is evaluated in a four-point measurement. As the thermistor heats, a temperature gradient develops in the membrane resulting in heat loss. The thermal properties of the membrane are determined from the power input and temperature history of the thermistor before a steady state is reached, i.e., they are evaluated from the transient behavior of the sensor. As will be discussed later, this approach has some benefit.
over techniques relying on the steady state in terms of improved temperature uniformity within the sensor.

Conservation of energy relates the electrical power dissipated in the thermistor to the thermal energy stored locally and the heat lost to the environment. The power dissipated is determined experimentally from the current supplied to the thermistor and the potential drop between the voltage probes. The current and the potential drop also provide the resistance of the thermistor, which is calibrated to temperature. The temperature history of the thermistor, thermal properties of the materials, and the geometry of the thermal sensor determine the energy stored and lost. The sensor array contains both sensors with narrow and wide thermistors. At moderate temperatures the heat loss from narrow thermistors is dominated by heat transfer from the thermistor to the membrane, and as a result the temperature response of the thermistor is a strong function of the thermal transport properties of the membrane. Thermal modeling is used to relate power and temperature to the specific heat and effusivity of the membrane. Wide thermistors (rightmost column of thermistors in Fig. 2.1) are paired with the neighboring narrow thermistors in a measurement scheme to decouple radiation and conduction losses and to facilitate emissivity measurements. Vacuum conditions eliminate convection losses and provide a chemically inert testing environment.

Two measurements are required to extract the thermal properties of the sample film: One reference measurement on the bare thermal cell and one on the cell with the sample film. The reference measurement characterizes the heat loss through the bare membrane, while the cell with sample film provides effective thermal properties for the ceramic/sample bilayer membrane. Combining the results of both measurements allows determination of the sample thermal properties. A wide range of samples can be deposited and measured as long as they do not fracture the membranes due to high stresses.

Materials chosen for the nTTA device are based on the functional requirements placed on each structure, cost and fabrication knowledge base. The substrate is made of silicon, chosen because of the availability of relatively low-cost and high-quality wafers. Silicon also has established anisotropic etching
procedures for forming cavities. The ceramic membrane is made of Si$_3$N$_4$, selected because of its electrically insulating properties and a demonstrated ability to form thin membranes. The thermistor is made of tungsten, because of its relatively large temperature coefficient of resistance and its small resistivity, which are beneficial to measurement sensitivity [13]. Also, tungsten has a very high melting point, so that the material has excellent thermal stability compared to conductors with lower melting temperatures. The electrical leads and contact pads on the substrate are made of copper to reduce the resistance of the lead lines and to facilitate contact to the device. The high-temperature stability of nTTA materials means that the device is compatible with high-temperature sample fabrication methods. Specific dimensions of the nTTA device can be found in Table 2.1.

<table>
<thead>
<tr>
<th>Table 2.1: Approximate dimensions of nTTA components.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (x)</td>
</tr>
<tr>
<td>Substrate (Si)</td>
</tr>
<tr>
<td>Membrane (Si$_3$N$_4$)</td>
</tr>
<tr>
<td>Narrow thermistor (W)</td>
</tr>
<tr>
<td>Wide thermistor (W)</td>
</tr>
</tbody>
</table>

2.4 Thermal modeling

2.4.1 Transient 2D thermal model

This section is focused on the derivation of the thermal model that describes the sensor. Much of the detail of the modeling consists of formulating the heat flow in the membrane. To accomplish this task we consider a control
volume CV. The CV is defined by the volume of the thermistor and the volume of the membrane (including any sample) directly below the thermistor (Fig. 2.3). The CV is bounded by the two $xz$-planes located at the edges of the heating element, the two $yz$-planes at the voltage probes, and the two $xy$-planes at the top and bottom free surfaces of the thermal cell.

![Figure 2.3: Schematic of control volume in relation to the entire thermal cell.](image)

The electrical power dissipated in the thermistor, $P$, is partly stored as internal energy in the CV $U$, and partly lost to the environment by conduction and radiation, $Q$:

$$ P = U + Q. \quad (2.1) $$

The energy storage rate is

$$ U = \iiint_{CV} \rho c_p \frac{\partial T}{\partial t} \, dV, \quad (2.2) $$

where $\rho$ is the density, $c_p$ is the specific heat, $T$ is the temperature, $t$ is time and $V$ is the volume. The total energy loss to the environment $Q$ is decomposed as,

$$ Q = Q_x + Q_y + Q_z, \quad (2.3a) $$

$$ Q_x = \iint -2 k_x \frac{\partial T}{\partial x} \, dA_x, \quad (2.3b) $$
Chapter 2: nano-Thermal transport array

\[ Q_y = \iint -2 k_y \frac{\partial T}{\partial y} \, dA_y, \quad (2.3c) \]

\[ Q_z = \iint 2 \varepsilon_{CV} \sigma (T^4 - T_0^4) \, dA_z, \quad (2.3d) \]

where \( x, y, \) and \( z \) represent the respective directions of the heat flow. Physically, \( Q_x \) represents the conduction losses at the ends of the thermistor, \( Q_y \) refers to the conduction losses into the membrane, and \( Q_z \) represents the radiation losses from the top and bottom free surface of the CV. Within the definition of these terms, \( k \) is the thermal conductivity, \( \varepsilon \) is the emissivity, \( \sigma \) is the Stefan-Boltzmann constant, \( T_0 \) is the temperature of the environment, and \( A \) is the respective cross-sectional area. The factor of two in each term arises from the symmetry of the CV. Convection losses are neglected because the measurements are performed in vacuum.

The relations expressed in Eqs. (2.2) and (2.3) can be simplified significantly. Since the physical length scale in the \( z \)-direction is much smaller than a typical diffusive length scale, the temperature is uniform in this direction. Conversely, in the \( x \)-direction the thermal diffusion length in a typical experiment is much smaller than the distance from the voltage probes to the substrate. Therefore, significant temperature gradients are constrained to the inactive portions of the heater; the temperature of the active portion of the heater (i.e. the thermistor) can be considered uniform in the \( x \)-direction. This transient temperature profile is in contrast to steady-state hot strip techniques, where temperature variation along the heater can be significant. Finally, we assume that temperature variation in the \( y \)-direction is small within the CV, and confirm this with finite element modeling later in the chapter. From these assumptions, the \( Q_x \) term vanishes while the energy storage rate and the radiation loss reduce to

\[ U = C_P \frac{df[t]}{dt} \quad \text{and} \quad Q_z = 2A_{CV} \varepsilon_{CV} \sigma ((f[t] + T_0^4 - T_0^4), \text{ respectively. Here } C_P \text{ is the total heat capacity of the CV (including sample when applicable) and } f[t] \text{ represents the average temperature change of the heater, } f[t] = T_{\text{ave}} - T_0, \text{ as a function of time. Finally, since } Q_y \text{ must be continuous across the CV-membrane boundary, this term can be rewritten as } Q_y = -2A_M k_M \frac{\partial T_M}{\partial y}, \] where the subscript \( M \) denotes membrane parameters and the membrane temperature gradient is
evaluated at the edge of the heating element. Substituting the expressions for $U$, $Q_y$, and $Q_z$ into Eq. (2.1) results in

$$P = C_p r[t] - 2A_M k_M \frac{dT_M}{dy} + 2A_\varepsilon \varepsilon_{CV} \sigma ((f[t] + T_0)^4 - T_0^4).$$

Here $r[t]$ is the heating rate of the CV, $A_M$ is the cross-sectional area of the membrane, $k_M$ is the thermal conductivity of the membrane, $A_\varepsilon$ is the emitting surface area of the CV, and $\varepsilon_{CV}$ is the effective emissivity of the CV. The emissivity $\varepsilon_{CV}$ is an effective value because the top and bottom surfaces of the CV are made of different materials with different emissivity values. Equation (2.4) is not yet explicit in terms of the relevant thermal parameters because the temperature gradient in the membrane cannot be measured directly and it depends on both $k_M$ and the volumetric heat capacity of the membrane $(\rho c_p)_M$.

To determine the temperature gradient in the membrane, we solve the one-dimensional thermal diffusion equation for the temperature profile in the membrane,

$$(\rho c_p)_M \frac{T_M}{\partial t} = k_M \frac{\partial^2 T_M}{\partial y^2} - 2 \varepsilon_M \sigma \frac{\varepsilon_{CV}}{h_M} (T_M^4 - T_0^4).$$

Here $\varepsilon_M$ and $h_M$ are the emissivity and the thickness of the membrane, respectively. The factor of two in the radiation term arises because the membrane radiates from the top and bottom surfaces. If we let $\tau = T_M - T_0$ and approximate the radiation term with a linear Taylor expansion about $\tau = 0$, then the radiation term becomes $(8 \varepsilon_M \sigma T_0^4 / h_M) \tau$. By letting $\alpha = k_M / (\rho c_p)_M$, and $\beta = 8 \varepsilon_M \sigma T_0^4 / h_M (\rho c_p)_M$, Eq. (2.5) reduces to,

$$\frac{\partial \tau}{\partial t} = \alpha \frac{\partial^2 \tau}{\partial y^2} - \beta \tau,$$

with initial and boundary conditions,

$$\tau[y, 0] = 0, \quad \tau[0, t] = f[t], \quad \tau[\infty, t] = 0.$$  

Here the temperature in the membrane is assumed to be initially uniform. The temperature at the left boundary ($y = 0$) evolves as a function of time, while the right boundary ($y = \infty$) remains fixed at the initial value. Comparing these
conditions to the physical thermal cell, the initial condition is satisfied by letting
the sensor equilibrate with its surroundings for an appropriate length of time (on
the order of seconds for these sensors). The left boundary condition is given by
the experimentally measured temperature history of the thermistor. The right
boundary condition remains valid as long as the thermal diffusion length is
smaller than the distance to the edge of the membrane. The linearization of the
radiation term in the membrane is valid as long as the temperature difference
between the membrane and its surroundings remains appropriately low.

To solve Eq. (2.6), we follow Sneddon’s example for the solution to Eq.
(2.6) without the radiation term [16]. Starting with an auxiliary problem, we first
solve the case where the left boundary condition satisfies \( \tau[0, t] = f[t'] \), where \( t' \) is
a fixed parameter, i.e., \( f[t'] \) is a constant. Let \( \tau^*[y, t] \) be the solution to the
auxiliary problem. Applying the Fourier sine transform,
\[ \Theta[y, t] = \sqrt{2\pi} \int_{0}^{\infty} \tau^*[y, t] \sin[y \psi] dy, \tag{2.7} \]
to Eq. (2.6) and taking into account the boundary conditions yields
\[ \frac{\partial \Theta}{\partial t} + (\beta + \alpha \psi^2) \Theta[y, t] = \sqrt{\frac{2}{\pi}} \alpha \psi f[t']. \tag{2.8} \]
With \( \Theta[y, 0] = 0 \) from Eq. (2.6b), Eq. (2.8) can be solved with a result
\[ \Theta[y, t] = \sqrt{\frac{2}{\pi}} \frac{\alpha \psi f[t']}{\beta + \alpha \psi^2} (1 - e^{-(\beta + \alpha \psi^2)t}). \tag{2.9} \]
Applying the inverse Fourier sine-transform yields the solution of the auxiliary
problem
\[ \tau^*[y, t] = \frac{2}{\pi} \int_{0}^{\infty} \frac{\alpha \psi f[t']}{\beta + \alpha \psi^2} (1 - e^{-(\beta + \alpha \psi^2)t}) \sin[y \psi] d\psi. \tag{2.10} \]
Equation (2.10) represents the solution to Eq. (2.6a) for the case that \( \tau^*[0, t] \) is
constant. This result can be used with Duhamel’s theorem to solve Eq. (2.6a)
when the boundary condition is a function of time. According to Duhamel’s
theorem [16], the solution for the problem with the variable boundary condition,
\( \tau[0, t] = f[t] \), is related to the solution \( \tau^*[y, t] \) for the fixed boundary condition \( \tau[0, t] = f[t'] \) by
Chapter 2: nano-Thermal transport array

\[
\tau[y, t] = \frac{\partial}{\partial t} \int_0^t \tau[y, t-t'] \, dt'.
\]  
(2.11)

Substituting Eq. (2.10) into Eq. (2.11) results in,

\[
\tau[y, t] = \frac{\partial}{\partial t} \int_0^t \frac{2}{\pi} \int_0^\infty \frac{\alpha \psi \, f[t']}{\beta + \alpha \psi^2} (1 - e^{-(\beta + \alpha \psi^2)(t-t')}) \sin[\psi \, y] \, d\psi \, dt'.
\]  
(2.12)

Taking the derivative and simplifying gives,

\[
\tau[y, t] = \frac{2}{\pi} \alpha \int_0^t f[t'] \int_0^\infty \psi \sin[\psi \, y] e^{-(\beta + \alpha \psi^2)(t-t')} \, d\psi \, dt'.
\]  
(2.13)

Using the result from reference [17],

\[
\int_0^\infty \psi \sin[\psi \, y] e^{-\alpha \psi^2(t-t')} \, d\psi = \frac{\sqrt{\pi} \, y \, e^{-y^2}}{4 \, (\alpha(t-t'))^{3/2}},
\]  
(2.14)

and substituting into Eq. (2.13), yields,

\[
\tau[y, t] = \int_0^t f[t'] \, \frac{y \, \text{Exp}\left[-\frac{y^2}{4 \alpha(t-t')} - \beta(t-t')\right]}{2 \sqrt{\pi} \alpha (t-t')^{3/2}} \, dt'.
\]  
(2.15)

Equation (2.15) represents the temperature profile in the membrane for a given temperature history of the heating element. The first factor inside the integral is the forcing function, while the second factor is the Green’s function of the problem. If the temperature history of the thermistor \( f[t'] \) is represented by an \( n^{th} \) order polynomial with coefficients \( \{a_0, a_1, a_2, ..., a_n\} \), then Eq. (2.15) can be expressed analytically, although the result becomes complicated quickly with increasing order of the polynomial. Taking the derivative of the resulting analytic function with respect to \( y \) and evaluating at \( y = 0 \), gives the temperature gradient in the membrane at the edge of the CV in terms of the polynomial coefficients \( a_i \):

\[
\left. \frac{\partial \tau}{\partial y} \right|_{y=0} = \sqrt{\frac{1}{\alpha}} \sum_{i=1}^n a_i \, b[i, \beta],
\]  
(2.16)

where the \( b[i, \beta] \) are functions of \( t \) and \( \beta \) alone. They follow from the operations described above and can be found in Appendix A for polynomials up to order
five for $\beta > 0$ and order seven for $\beta = 0$. Since $\frac{\partial\tau}{\partial y} = \frac{\partial T_m}{\partial y}$, we substitute Eq. (2.16) into Eq. (2.4) and let $g[t] = \sum a_i b_i[t, \beta]$ to get,

$$P = C_P r[t] + 2A_M \phi_M g[t] + 2A \varepsilon_{CV} \sigma(T[t] + T_0)^4 - T_0^4). \quad (2.17)$$

Here the effusivity is defined as $\phi = \sqrt{k \rho c_P}$. Equation (2.17) establishes the power balance of the CV in terms of the unknown thermal parameters $C_P$, $\phi_M$, and $\varepsilon_{CV}$. Data analysis will focus on using Eq. (2.17) to evaluate these thermal parameters.

### 2.4.2 Finite element simulations

A two-dimensional transient finite element model (FEM) has been created to simulate the heat flow in the thermal cell and to evaluate the accuracy of the analytical model. The model represents a cross-section of the sensor in the $yz$-plane (Fig. 2.2(b)), reduced by the mirror symmetry at the center of the heating element. The dimensions of the model are based on the actual thermal cell used in our experiments (Table 2.1). The left-end boundary condition, at the mirror plane, imposes zero heat flux, while the right-end boundary condition maintains the edge of the membrane at $T_0$. The top and bottom surfaces allow radiative heat loss to a blackbody at $T_0$. The initial condition is $T[0, y] = T_0$ everywhere.

In order to simulate a measurement, two finite element models are required: a model of a bare cell consisting of a silicon nitride membrane and a tungsten heater, and a model of a cell with a representative sample, in this case a 50 nm copper film. Based on experimental results presented in a subsequent section, the initial resistance of the heating element is set to $R_0 = 45 \Omega$, while the temperature coefficient of resistance is $\lambda = 1.65 \times 10^{-3} K^{-1}$. The remaining materials properties are based on literature values, shown in Table 2.2.
The finite element simulations have been performed with the commercial code ABAQUS. The heat transfer is modeled using the diffusive heat transfer element DC2D8, an 8-node biquadratic element. The $y$-spacing of the elements inside the CV is approximately 4 nm, while the spacing in the membrane is approximately 21 nm. The heater is represented by 4 elements through the film thickness; the membrane (membrane plus sample when present) is represented by 2 elements. Heat generation is accomplished via a user subroutine associated with the elements of the thermistor. A constant current $I$ (5 mA for the reference case and 10 mA for the sample case) and a resistance $R = R_0 \left(1 + \lambda (T - T_0)\right)$ determine the electrical power dissipated in the heating element. A time step of 0.05 ms is used in the simulations.

The output of the simulations is in the form of the nodal temperature history. The nodal temperatures show that the temperature variations through the thickness of the membrane and heating element are small ($\Delta T < 0.1^\circ$C). The FEM neglects interface resistances between the layers in the CV as does the analytical model. This assumption can be justified by considering the worst case conditions of a heat flux through the interface equal to the entire power dissipated in the heater (4.5 mW) and a very low thermal conductance (20 MW/m² K) [1], which produces a temperature difference across the interface of just 0.001°C. This temperature error is insignificant and can be neglected. Averaging the temperature of the nodes through the thickness of the model produces a temperature distribution along the $y$-direction. Figure 2.4 shows temperature

<table>
<thead>
<tr>
<th></th>
<th>$k$ (W/m K)</th>
<th>$\rho$ (kg/m³)</th>
<th>$c_p$ (J/kg K)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermistor (W)</td>
<td>174</td>
<td>19300</td>
<td>132</td>
<td>0.02</td>
</tr>
<tr>
<td>Membrane (Si$_3$N$_4$)</td>
<td>2.3*</td>
<td>3000</td>
<td>700</td>
<td>0.18</td>
</tr>
<tr>
<td>Sample (Cu)</td>
<td>401</td>
<td>8960</td>
<td>384</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* Value is from a SiN$_x$/SiO$_2$/SiN$_x$ film stack.
distributions in a reference cell and in a sample cell with 50 nm of copper for a representative set of experimental conditions. These temperature distributions confirm the earlier assumption that the lateral temperature variation within the CV is small ($\Delta T < 0.1^\circ C$). From these observations, we conclude that the temperature boundary condition $f[t]$ in the analytical model can be represented by the average temperature of the thermistor. This is equivalent to the actual experiments where the average temperature is measured. The temperature-time data generated by the finite element models (Fig. 2.5) are then analyzed using the method described in the next section to determine the heat capacity of the control volume $C_P$ and the effusivity of the membrane $\phi_M$. 

Figure 2.4: FEM average node temperature distribution along $y$-direction for a bare thermal cell and cell with 50 nm Cu sample, simulated for 5 ms with respective currents of 5 and 10 mA.
2.5 Data reduction and error analysis

A data reduction method based on the analytical model has been developed to analyze the FEM results and the experimental data. Analysis of the FEM data allows for verification of the data reduction method by accurate reproduction of input values; analysis of the measured data produces the desired materials properties that are the goal of this investigation. The following discussion is based on the FEM data, but the analysis of experimental data proceeds along the same line.

The data reduction begins with the temperature history of the thermistor obtained from the FEM calculations. To simulate experimental noise in the FEM
results, a normally distributed temperature error $\sigma_t[p]$ was added to the FEM temperature results at each time step in the temperature report. The width of the $\sigma_t[p]$ distribution was representative of the measurement noise observed experimentally. Equation (2.17) can be used with this data set to estimate the thermal parameters $C_p$ and $\phi_m$. For each time step $t[N]$, the function $f[t']$ and the $a_i$ in Eq. (2.16) are found from a polynomial fit to the temperature history up to that particular point $N$. The fit is obtained by minimizing the merit function,

$$\chi^2_a = \sum_{p=1}^{N} \left( \frac{T[p] - (a_0[N] + a_1[N] t[p] + \ldots + a_n[N] t^n[p])}{\sigma_T[p]} \right)^2.$$  \hspace{1cm} (2.18)

The order of the polynomial is determined by the linearity of the temperature history. For the bare cell, $n = 5$ is sufficient to represent the simulation results; for the cell with sample, $n = 7$ is required. The merit function $\chi^2_a$ is minimized by applying the normal equations in a matrix formulation. Following this approach, we define the matrices,

$$v[N] = \begin{bmatrix}
\sum_{p=1}^{N} \frac{1}{\sigma_T^2[p]} \sum_{p=1}^{N} t[p] & \sum_{p=1}^{N} t^2[p] & \ldots & \sum_{p=1}^{N} t^n[p] \\
\sum_{p=1}^{N} t[p] \sum_{p=1}^{N} \sigma_T^2[p] & \sum_{p=1}^{N} \sigma_T^2[p] & & \\
\vdots & & \ddots & \\
\sum_{p=1}^{N} t^n[p] & & & \sum_{p=1}^{N} \sigma_T^n[p]
\end{bmatrix},$$ \hspace{1cm} (2.19)

and

$$\omega[N] = \begin{bmatrix}
\sum_{p=1}^{N} T[p] \sum_{p=1}^{N} \frac{t[p]}{\sigma_T^2[p]} & \sum_{i=1}^{N} \frac{T[p] t[i]}{\sigma_T^2[p]} & \ldots & \sum_{i=1}^{N} \frac{T[p] t^n[i]}{\sigma_T^2[p]}
\end{bmatrix}. \hspace{1cm} (2.20)$$

Then the $a_i$ are given by,

$$a_i[N] = \sum_{j=0}^{a_i} v_{(i+1),j}[N] \omega_j[N]. \hspace{1cm} (2.21)$$

Equation (2.21) is used to evaluate the function $g[t]$ in Eq. (2.17). The error $\sigma_g$ on $g[t]$ is then given by
\[ \sigma_s^2 = \sum_{j=1}^{n} \sum_{i=1}^{a} \frac{\partial g}{\partial a_i} \frac{\partial g}{\partial a_j} v_{(i+1)(j+1)}^{-1}, \]  
(2.22)

The covariances of the \( a_i \) parameters are significant and must be included for an accurate estimation of \( \sigma_s \).

The average heating rate of the control volume, \( r[t] \), is the derivative of the temperature history. In the data analysis, this derivative is calculated by performing a linear least square fit of the temperature data around the time step of interest. The fit is found by minimizing the merit function

\[ \chi^2[N] = \sum_{p=N-M}^{N+M} \left( \frac{T[p] - (c_0[N] + c_1[N] t[p])}{\sigma_T[p]} \right)^2, \]  
(2.23)

using the normal equations in a matrix formulation. The corresponding right hand side (RHS) of Eq. (2.19) is now a 2x2 matrix, and the RHS of Eq. (2.20) is a 2-component vector. In both equations, the upper and lower limits for the summations are the same as in Eq. (2.23), i.e., \( N - M \) and \( N + M \), respectively. The heating rate is then,

\[ r[N] = c_1[N] = v_{21}^{-1}[N] \omega_1[N] + v_{22}^{-1}[N] \omega_2[N], \]  
(2.24)

with associated error,

\[ \sigma^2_r[N] = v_{22}^{-1}[N]. \]  
(2.25)

Before \( C_p \) and \( \phi_M \) can be determined from Eq. (2.17), it is necessary to know \( \beta \) and \( \varepsilon_{CV} \). We will show later in this section how these parameters can be estimated from experiments. In many cases, however, the effects of \( \beta \) and \( \varepsilon_{CV} \) are small enough that they can be neglected without significant loss of accuracy. Alternately literature values can be used. Figure 2.6 shows the radiation loss from the CV and the membrane of a bare thermal cell relative to the total power input for a heating rate of 7.5 K/ms. In the analysis of the FEM data, the FEM input values were used for \( \varepsilon_{CV} \) and \( \beta \). Because radiation from the membrane in the sample cell was insignificant, \( \beta \) was taken as zero for the sample cell.
All parameters in Eq. (2.17) are now known except for $C_p$ and $\phi_M$, which are determined by a least squares fit of Eq. (2.17) to the $P$ data. The error on the electrical power, $\sigma_P$, is typically much smaller than the errors on $g[t]$ and $r[t]$. To account for the uncertainty in these two terms, an effective error is defined for the electrical power, $\sigma_{\text{eff}}$, as [18],

$$\sigma_{\text{eff}}^2 = \sigma_P^2 + \left( \frac{\partial P}{\partial r} \sigma_r \right)^2 + \left( \frac{\partial P}{\partial g} \sigma_g \right)^2,$$

(2.26)

and used in the merit function for the fit. The partial derivatives in Eq. (2.26) require some knowledge about the unknown parameters $C_p$ and $\phi_M$. For the FEM data, the input values are used; for the experimental analysis, $C_p$ and $\phi_M$ are first estimated with a least squares fit using $\sigma_p$ only and then $\sigma_{\text{eff}}$ is evaluated using
Chapter 2: nano-Thermal transport array

the estimated values. The merit function for the least squares fit of the thermal parameters is defined as,

\[ \chi^2 = \sum_{p=1}^{N} \frac{[P[p] - 2A_{\xi_cv} \sigma \left( (f[p] + T_0) - T_0' \right) - (C_p[N] r[p] + 2A_{\phi_m[N]} g[p])]^2}{\sigma_{eff}[p]} \].

(2.27)

Equation (2.27) is minimized as described above to produce the best-fit values of \( C_p \) and \( \phi_m \). These terms can be written explicitly as,

\[ C_p[N] = \frac{1}{\Gamma[N]} \left( \sum_{p=1}^{N} \frac{P_{eff}[p] r[p]}{\sigma_{eff}[p]^2} \sum_{p=1}^{N} \frac{g^2[p]}{\sigma_{eff}[p]^2} - \sum_{p=1}^{N} \frac{g[p] r[p]}{\sigma_{eff}[p]^2} \sum_{p=1}^{N} \frac{P_{eff}[p] g[p]}{\sigma_{eff}[p]^2} \right) \],

(2.28)

and

\[ \phi[N] = \frac{1}{2A_m \Gamma[N]} \left( \sum_{p=1}^{N} \frac{r^2[p]}{\sigma_{eff}[p]^2} \sum_{p=1}^{N} \frac{P_{eff}[p] g[p]}{\sigma_{eff}[p]^2} - \sum_{p=1}^{N} \frac{r[p] g[p]}{\sigma_{eff}[p]^2} \sum_{p=1}^{N} \frac{r[p] g[p]}{\sigma_{eff}[p]^2} \right) \],

(2.29)

with associated errors,

\[ \sigma^2_{C_p[N]} = \frac{1}{\Gamma[N]} \sum_{p=1}^{N} \frac{g^2[p]}{\sigma_{eff}[p]^2} \],

(2.30)

and

\[ \sigma^2_{\phi[N]} = \left( \frac{1}{2A_m} \right)^2 \frac{1}{\Gamma[N]} \sum_{p=1}^{N} \frac{r^2[p]}{\sigma_{eff}[p]^2} \].

(2.31)

In these equations,

\[ \Gamma[N] = \sum_{p=1}^{N} \frac{r^2[p]}{\sigma_{eff}[p]^2} \sum_{p=1}^{N} \frac{g^2[p]}{\sigma_{eff}[p]^2} - \left( \sum_{p=1}^{N} \frac{r[p] g[p]}{\sigma_{eff}[p]^2} \right)^2 \],

(2.32)

and \( P_{eff} = P - Q_x \). Analysis results of \( C_p \) and \( \phi_m \) are plotted along with input values for the bare cell in Figs. 2.7(a) and 2.7(b), while the values for the cell with the sample are plotted in Figs. 2.7(c) and 2.7(d), respectively. It is evident that the analysis results converge rapidly to the input values. The average analysis result is calculated with an error-weighted mean and shown in Table 2.3 along with input values and reproducibility error. A reproducibility error of approximately 3% or less provides confidence in the analytical model and the data reduction.
Figure 2.7: Results of the analysis of the FEM results (data points with error bars) compared to input values (solid line): heat capacity of the CV of a bare cell (a), effusivity of a bare-cell membrane (b), heat capacity of the CV of a cell with a 50 nm Cu coating (c), effusivity of a membrane with a 50 nm Cu coating (d).

The error analysis presented here is extended to a sensitivity analysis in Appendix B that provides relative errors for the effusivity, heat capacity, and thermal conductivity. These relative errors can be used to judge the capability of the device and to guide experimental work on other materials systems.
The FEM results have also been used to simulate measurement of the emissivity $\varepsilon_{CV}$ of the CV. This is achieved by heating narrow (400 $\mu$m) and wide (1000 $\mu$m) heating elements at approximately the same rate of 20 K/ms to a temperature of 400°C. Under these conditions the difference in conductive loss between the two sensors is small, while the difference in radiation loss is significant. By taking the difference in the power balance for each heater (Eq. 2.17) and assuming that conductive losses cancel exactly, the effective emissivity of the CV can be written as,

$$
\varepsilon_{CV} = \frac{\Delta P - \Delta \left( C_p \left( \frac{dT}{dt} \right) \right)}{l \Delta w \sigma \left( T^4 - T_0^4 \right)}.
$$

(2.33)

Using this method, the effective emissivity of a bare cell is determined to be $\varepsilon_{CV} = 0.104$, which differs from the input value by 1% (Fig. 2.8). This method of evaluation can be used when the $\varepsilon_{CV}$ term is significant and measured values are preferred over literature values. The emissivity of the tungsten film, which is used for the heating element, can be obtained from this method by depositing tungsten as a sample film. In this case the $\varepsilon_{CV}$ is the emissivity of tungsten. Once the emissivity of tungsten is known, then the emissivity of the membrane can be estimated from the effective emissivity of the bare cell CV.
Determination of $C_p$ by fitting Eq. (2.17) to the power data requires a value for $\varepsilon_{CV}$. Determination of $\varepsilon_{CV}$ from Eq. (2.33), on the other hand, requires a value for $C_p$. For the finite element model the input values can be used, but for experiments these values are not known a priori. They are, however, easily determined iteratively. More specifically, Eq. (2.17) is fitted to the experimental data using literature values for $\varepsilon_{CV}$; then the $C_p$ result from this fit is used to calculate an experimental value for $\varepsilon_{CV}$. This value of $\varepsilon_{CV}$ is then used in Eq. (2.17) to produce the final result. Because the effect of radiation is very small in the temperature and heating rate range considered, one iteration is sufficient.

Figure 2.8: Emissivity calculated from the FEM simulations along with FEM input value. The error on the calculated emissivity is large at low temperatures, but the emissivity quickly converges to the input value at elevated temperatures where radiation is a more important heat loss mechanism.
Chapter 2: nano-Thermal transport array

The accurate reproduction of FEM input values with the analytical model and data reduction scheme validates the assumptions made in the analytical model and lends credibility to the measurement approach. The same analysis method can now be applied to experimental results obtained for real devices. The following sections describe how the device is made and the measurements are performed, as well as the results of the measurements.

2.6 Experimental method

2.6.1 Device fabrication

The fabrication process starts with (100) oriented Si wafers, 200 mm in diameter and polished on one side. These wafers are delivered with a coating of approximately 80 nm of Si₃N₄ grown on both sides using low-pressure chemical vapor deposition (Fig. 2.9(a)). Special care is taken throughout the fabrication process to protect the Si₃N₄ on the polished side of the wafer. This film will eventually form the membranes of the nTTA and even shallow scratches result in ruptured membranes.
Each Si wafer is cleaved into seven 55 mm x 55 mm square substrates. The substrates are rinsed in deionized water and blown with nitrogen to remove any particles. Then 125 nm of tungsten and 1.2 μm of copper are deposited on the

Figure 2.9: nTTA fabrication flow. One thermal cell is shown for clarity. Detailed step-by-step procedures can be found in the text of the chapter.
polished side of a square substrate using direct current (DC) magnetron sputtering (Fig. 2.9(b)). Immediately prior to film deposition, the substrates are sputter-cleaned using an Ar plasma to remove any contamination and to improve adhesion of the sputtered coatings.

With the materials necessary for forming the sensors in place, material is now selectively removed to form the appropriate structures using standard photolithography and etch processes. After the wafer is baked at 150°C for 5 min, Shipley 1805 photoresist (S1805) is spin-coated and patterned on both sides of the wafer. The front side of the substrate is exposed to UV light through a mask with the metallization artwork, and the backside is exposed through a mask with the cavity window artwork. Both sides of the substrate are developed simultaneously in Microposit CD-30 for 1 minute (Fig. 2.9(c)). The Si₃N₄ on the backside of the wafer is reactively etched in CF₄ to create rectangular openings in the silicon nitride layer. Copper is etched in a solution of phosphoric, nitric, and acetic acid at 50°C. The Cu etch exposes the underlying W, which is then etched in 30% H₂O₂ at 50°C (Fig. 2.9(d)). Both etch steps take approximately three minutes. After the wet-etch processes, the remaining resist is exposed and removed. Next S1805 is re-applied to the metallization side and patterned with the rectangular cavity artwork (Fig. 2.9(e)). Copper is then etched from the membrane area, leaving only W within the area that will form the membrane. After patterning of the metallization, the freestanding membranes are created by anisotropically etching the Si in a solution of 15 g KOH in 50 ml H₂O at 85°C for approximately 9 hours. The patterned Si₃N₄ coating on the backside of the substrate serves as a hard mask for this step. During this procedure, the metallization is protected by a sample holder that exposes the backside of the device to the KOH solution, while isolating the front side from the KOH solution. For added protection, a layer of Cyclotene resist (Dow Chemical) is spin-coated on top of the metallization and cured at 130°C for 70 min. After the Si etch, the Cyclotene is removed in a bath of Primary Stripper A at 75°C for 1 hour (Fig. 2.9(f)). The device fabrication process is completed with an anneal at 450 °C for 8 hours in a vacuum furnace with a base pressure of 10⁻⁵ Pa.
2.6.2 Measurement setup and calibration of thermistor

nTTA measurements are controlled and recorded with a personal computer and a National Instruments PCI-6221 data acquisition card (DAQ) (Fig. 2.10). The DAQ is used to send a control voltage to a voltage-to-current converter, with a linear mapping of 1 V to 10 mA. The current source consists of a precision operational amplifier (OPA227), a power operational amplifier (OPA549), and a differential amplifier (INA133) arranged in a modified Howland configuration. It is powered by a Protek 3030D dual DC power supply running in series mode, providing a constant 30 V controlled power. Excluding internal losses, the current supply is limited by approximately 20 V of compliance and can supply 100 mA of current.

Figure 2.10: Schematic of the experimental setup.

The output of the current source is monitored by the DAQ via the voltage drop $V_i$ across a 100 $\Omega$ precision resistor $R_i$. The DAQ also reads the voltage drop $V$ across the thermistor. This is shown in schematic form in Fig. 2.10 and a typical result is shown in Fig. 2.11. All signals are recorded at a sampling rate of 100 kHz and with a 16-bit resolution. Voltage signals are used to determine the resistance
of the thermistor by $R = R_iV/V_i$ and the electrical power dissipated in the thermistor by $P = V_iV/R_i$. The temperature of the thermistor is then calculated from,

$$T = T_0 + \frac{\Delta R}{\lambda R_0},$$

(2.34)

where $\lambda$ is the temperature coefficient of resistance of the heating element, $R_0$ is the room temperature resistance, $\Delta R$ is the change in resistance, and $T_0$ is the ambient temperature.

Prior to depositing sample material onto the nTTA substrate, the thermal sensors need to be calibrated. To measure the temperature coefficient of resistance, the nTTA substrate is placed in an oven and stepped through a temperature range, while the temperature of the substrate is measured with a

Figure 2.11: Raw voltage data recorded from a 5 mA, 20 ms current pulse across the 100 $\Omega$ precision resistor and a narrow thermistor.
thermocouple. The resistance of the thermistor is recorded at each temperature step by applying a 1 mA monitoring current for 20 ms. This current pulse causes a small amount of Joule heating (~0.3 °C). To eliminate this effect, \( R \) is measured as a function of time and back extrapolated with a linear fit. \( R_0 \) and the ratio \( \Delta R / \Delta T \) are determined from a linear least squares fit of the resistance data as a function of temperature. The value of \( \lambda \) is then calculated using Eq. (2.34), yielding a value of \( (1.65 \pm 0.02) \times 10^{-3} \text{K}^{-1} \) for the W thermistors in the cells. The value of \( \lambda \) is typically determined for one cell on each substrate, while the value of \( R_0 \) is measured for each cell on a substrate.

All thermal transport measurements are conducted in a vacuum chamber with a vacuum level of \( 10^{-3} \text{ Pa} \) to eliminate convection losses. Bare cells with narrow heating elements are subjected to a current of 5 mA, while the wide heating elements receive an 80 mA pulse. The voltage response of the thermistor is recorded and transformed into a temperature history. This temperature history is then analyzed as described previously. Emissivity measurements are performed in a similar fashion. In this case, however, the current of the narrow thermistor is varied (11-12 mA) to match the temperature history of the neighboring wide thermistor. After bare cell measurements are completed, samples are deposited on the thermal cells and the measurements are repeated.

### 2.6.3 Sample Fabrication and Measurements

We have demonstrated the capability of the nTTA device by measuring the thermal transport properties of thin Cu films as a function of film thickness. After the sensors in an nTTA device were characterized as described in the previous section, Cu films were deposited using DC magnetron sputtering and a 50.8 mm diameter Cu target. The depositions were performed at a power of 100 W and a pressure of 0.67 Pa using Ar as a working gas. The deposition rate was calibrated at each sensor location by depositing for a known length of time and measuring the resulting thickness with a Veeco Dektak profilometer. The thickness of each sample was then determined from the sample deposition time.
The substrate was not rotated during the deposition so that the natural sputtering flux distribution would create a Cu thickness gradient along the columns of the nTTA (Fig. 2.1). A larger thickness gradient was created between the columns of the nTTA by stepping a shadow mask from left to right (Fig. 2.1). This process required a vacuum break and proceeded in such a way that the leftmost column (cells 1-5) had four discrete layers of copper, the next (cells 6-10) had three, the middle (cells 11-15) had two, and the two rightmost columns (cells 16-25) had just one layer. Cells 16-20 have narrow thermistors and cells 21-25 have wide thermistors. Neighboring thermistors in these columns form emissivity measurement pairs. Emissivity measurement pairs had the same Cu film thickness to ensure that the conductive heat losses would cancel as required for forming Eq. (2.33). The copper film thicknesses that resulted from this process are shown in Figure 2.12.

Figure 2.12: Thickness of the copper sample multilayers.
As with the bare thermal cells, the thermal transport measurements on the Cu-coated sensors were performed in vacuum. The currents that were used for the measurements were chosen to approximately match the heating rates of the bare thermal cell measurements and can be found in Table 2.4. The emissivity measurements were performed by varying the current applied to the narrow thermistor of the pair to match the heating rate of the wide thermistor.

### Table 2.4: Applied current in milli-Amperes for a given cell and measured quantity.

<table>
<thead>
<tr>
<th></th>
<th>Cells 1-5</th>
<th>Cells 6-10</th>
<th>Cells 11-15</th>
<th>Cells 16-20</th>
<th>Cells 21-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>$\phi_M C_p$ (cell)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>$\phi_M$ (sample)</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>$C_p$ (sample)</td>
<td>24</td>
<td>20</td>
<td>16</td>
<td>12</td>
<td>80-90</td>
</tr>
<tr>
<td>$\varepsilon_z$ (cell)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11-12</td>
<td>80</td>
</tr>
<tr>
<td>$\varepsilon_z$ (sample)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.5-18</td>
<td>80-90</td>
</tr>
</tbody>
</table>

### 2.7 Results and discussion

Initial resistance measurements taken at various instances throughout the experimentation demonstrate that the tungsten thermistors are stable during storage and low-temperature measurements, up to 450°C, the temperature at which the device was annealed. The error on each $R_0$ measurement is approximately $8 \times 10^{-3}$ Ω, while the standard deviation of the $R_0$ results for cells 1-20 is 2 Ω (i.e. 4%). Since the measurement error is much smaller than the standard deviation of the group, we conclude that the cell-to-cell variation in
resistance is real and most likely caused by slight variations in the thermistor dimensions as a result of the fabrication process.

With \( R_0 \) known for each cell, the temperature history of the CVs can be calculated from the voltage measurements using Eq. (2.34). Representative temperature curves for a bare cell and a cell with sample are shown in Fig. 2.13(a). Typical heating rates are shown in Fig. 2.13(b). The effective emissivity of

![Figure 2.13: Typical temperature history for a bare cell and cell with 61 nm sample (a). Typical heating rate for bare cell and cell with 61 nm sample (b).](image)

the CV was determined from the heating curves of the narrow-wide thermistor pairs 16-21, 17-22, and 20-25. Pairs 18-23 and 19-24 were not included because cell 23 was broken and the data obtained from cell 24 was corrupted. The measured emissivity values are \( \varepsilon_{CV} = 0.14 \pm 0.01 \) for the bare cells and \( \varepsilon_{CV} = 0.17 \pm 0.01 \) for the cells with Cu samples. These results compare well with literature values of 0.10-0.17 and 0.03-0.15 respectively [19-22]. The literature results vary considerably, typically explained by surface conditions. Our Cu films emit around the upper end of reported emissivity values, which is most likely due to slight oxidation of the film surface. The temperature curves of the other sensors
were analyzed to determine $C_p$ and $\phi_M$ using the appropriate emissivity values listed above.

Figure 2.14 shows representative fits of Eq. (2.17) to the power dissipated in the thermistors by minimizing the merit parameter $\chi_x$ (Eq. 2.27). Typical $C_p$ results for bare cell and cell with 61 nm Cu sample are shown in Figs. 2.15(a) and (b) respectively. Typical $\phi_M$ results for the same cell conditions are shown in Fig. 2.15(c). It is evident that after some initial variability the parameters quickly converge to specific values. It should be noted that the $C_p$ result for the cell with the Cu sample was obtained by doubling the current over the $\phi_M$ measurements (Table 2.4) and reducing the considered time scale (1 ms) because of the large amount of heat conducted away by the Cu films.
The results for all bare cells and cells with samples are compiled in Figure 2.16. The $C_p$ results of the bare cells (Fig. 2.16(a)) show a similar distribution as the $R_0$ results with a standard deviation of approximately 3.7%. This observation suggests that the distribution is again caused by variability in the fabrication process and not measurement error. The average value of the heat capacity, $126 \pm 6 \text{nJ/K}$, compares well to the value of 123 nJ/K obtained from the literature.
values of the constituents (See Table 2.2). The average measured effusivity value of the bare membrane is $2580 \pm 90$ J/m$^2$s$^{1/2}$K, which compares closely with reported silicon nitride values on the order of $2600$ J/m$^2$s$^{1/2}$K [23]. The results for the cell with the Cu samples (Fig. 2.16) show the expected trend considering the Cu film thickness. The total heat capacity $C_p$ is an extrinsic materials property and the variation shown is caused by a change in sample mass; $\phi_M$ is an intrinsic materials property and the variation is caused by a change of the membrane effusivity as the film thickness varies.

The experimental values of $C_p$ and $\phi_M$ can be used to determine the volumetric heat capacity and the thermal conductivity of the Cu films: The volumetric heat capacity ($\rho c_p$) of the films is readily found by taking the difference between the total heat capacities of the cells with and without samples and by normalizing that value with the Cu sample volume. The average experimental value thus obtained is $(3.7 \pm 0.2) \times 10^6$ J/m$^3$ K, which is larger than the reported bulk value of $2.6 \times 10^6$ J/m$^3$ K [19]. Similar increases in specific heat for nanocrystalline copper have been reported previously [24, 25]. The error in

Figure 2.16: Heat capacity (a) and effusivity (b) results for cells with and without copper samples.
the volumetric heat capacity of each Cu sample is relatively large for the thinnest samples, approximately 25 %, and reduces with film thickness to approximately 10 % for the thickest samples. Errors result from the small volume of material measured and the significant amount of heat conducted away through the Cu film – in a sense Cu is probably one of the most challenging materials for these experiments (e.g., Appendix B). Further increasing the heating rates and decreasing the measurement times reduces this error. Samples with smaller thermal conductivity evidently result in smaller \((\rho c_p)\) errors. If necessary, very accurate and precise measurements of the heat capacity can also be made with a parallel nano-scanning calorimeter [26], a device similar to the nTTA but with slightly different thermistor and sample geometry.

The thermal conductivity of the copper films is calculated as,

\[
k_{Cu} = \frac{(h_S \phi_S)^2 - h_{SiN} k_{SiN} (h \rho c_p)_{Cu} - (h_{SiN} \phi_{SiN})^2}{h_{Cu} ((h \rho c_p)_{Cu} + (h \rho c_p)_{SiN})},
\]

where the subscript \(S\) refers to a value for a \(Si_3N_4/Cu\) multilayer membrane (Fig. 2.17). Also shown in Fig. 2.17 are additional measurements for thicker multilayer Cu films (approximately 180 to 480 nm) obtained from a second nTTA device. Evidently the error introduced by any uncertainty in the copper heat capacity is quite small for the thinnest films and it increases slightly with increasing film thickness (Eq. 2.35). The thermal conductivity of the copper films increases non-monotonically from approximately 15 to 300 nm, where the values apparently plateau around 300 W/m K, well below the bulk value of 410 W/m K [19]. This behavior can be explained by the multilayer structure of the Cu films and by scattering of electrons from the surfaces and interfaces of the copper films (Fig. 2.18).
Figure 2.17: Calculated thermal conductivity of thin copper films from measured thermal parameters, with $k_{\text{SiN}} = 3.2 \text{ W/m K}$ and $(\rho c_p)_{\text{SiN}} = 2.1 \text{ MJ/m}^3 \text{ K}$ [23].

Figure 2.18: TEM cross-section of a 3-layer Cu film showing scattering interfaces.
To gain further insight into these results we consider the model by Qiu and Tien [27],

\[
\frac{k_{\text{film}}}{k_{\text{bulk}}} = \left(1 + \frac{3}{8} \frac{B}{\eta} + \frac{7}{5} \frac{G}{1 - G} \frac{B}{D} \right)^{-1}.
\] (2.36)

Equation (2.36) relates the thermal conductivity of a metal film to its bulk thermal conductivity based on the bulk electron mean free path \(B\), the film thickness \(\eta\), the grain boundary reflection coefficient \(G\), and the grain boundary diameter \(D\). This formulation of the model assumes diffuse reflections at the interfaces. We use literature values for \(B\) and \(G\) – \(B = 42\) nm [28], \(G = 0.25\) [27] – and take \(D = \eta\) based on our TEM observations. Finally we define the normalized conductivity as \(\kappa = k_{\text{film}} / k_{\text{bulk}}\), and the effective normalized thermal conductivity of a multilayer film as,

\[
\kappa_{\text{eff}} = \frac{\eta_1 \kappa_1 + \eta_2 \kappa_2 + \ldots + \eta_n \kappa_n}{\eta_1 + \eta_2 + \ldots + \eta_n},
\] (2.37)

for an \(n\)-layer stack of films, where \(\kappa_i\) and \(\eta_i\) represent the thermal conductivity and thickness of the \(i\)th layer. Our measured results and the model predictions are compared in Fig. 2.19. The good agreement indicates that the internal copper interfaces and grain boundaries indeed act as scattering surfaces for electrons. They clearly replicate the non-monotonic behavior and the relatively low plateau value of the films, indicating that both are caused by the multilayered structure of the Cu coatings.
2.8 Conclusion

Many capable in-plane thermal conductivity measurement devices exist. Some of these devices have better accuracy than the nTTA because they use multiple measurement points. Other devices that rely on a steady state have no dependence on volumetric heat capacity, simplifying data reduction. The nTTA technique, however, has the unique feature that it can be used as a combinatorial device. To accomplish this, it is necessary to trade multiple measurement locations for a single line measurement. Extraction of material parameters can be accomplished using an analytical model for the thermal behavior of the sensors. This analytical model was verified with finite element simulations and input parameters were reproduced with high accuracy. The capabilities of the nTTA
were demonstrated by measuring thermal transport properties of Cu films with thicknesses less than the mean free path of the dominant heat carriers.

2.9 Appendix A: Coefficients of Equation (2.16)

Expressions for the coefficients in Eq. (2.16) for $\beta > 0$ and $n = 5$.

\[
b_1 = t^{1/2} \frac{e^{\beta t}}{\sqrt{\pi}} + \left( \frac{1}{2} \beta^{-1/2} + \beta^{1/2} \right) \text{Erf}[\sqrt{\beta t}]
\]

\[
b_2 = \left( \frac{1}{2} \beta^{-1/2} + \beta^{1/2} \right) \frac{e^{\beta t}}{\sqrt{\pi}} \left( -\frac{1}{4} \beta^{-3/2} + \beta^{1/2} t + \beta^{3/2} t^2 \right) \text{Erf}[\sqrt{\beta t}]
\]

\[
b_3 = \left( \frac{3}{4} \beta^{-3/2} + \beta^{1/2} \right) \frac{e^{\beta t}}{\sqrt{\pi}} \left( \frac{3}{8} \beta^{-3/2} - \frac{3}{4} \beta^{1/2} t + \frac{3}{2} \beta^{3/2} t^2 + \beta^{5/2} t^3 \right) \text{Erf}[\sqrt{\beta t}]
\]

\[
b_4 = \left( \frac{15}{8} \beta^{-5/2} - \frac{7}{4} \beta^{-3/2} + \frac{3}{2} \beta^{1/2} \right) \frac{e^{\beta t}}{\sqrt{\pi}} + \left( \frac{15}{16} \beta^{-7/2} + \frac{3}{2} \beta^{3/2} t - \frac{3}{2} \beta^{5/2} t^2 + 2 \beta^{7/2} t^3 + \beta^{9/2} t^4 \right) \text{Erf}[\sqrt{\beta t}]
\]

\[
b_5 = \left( -\frac{105}{16} \beta^{-9/2} + 5 \beta^{-7/2} - 3 \beta^{-5/2} + 2 \beta^{1/2} \right) \frac{e^{\beta t}}{\sqrt{\pi}} + \left( \frac{105}{32} \beta^{-11/2} - \frac{75}{16} \beta^{-7/2} t + \frac{15}{4} \beta^{3/2} t^2 - \frac{5}{2} \beta^{5/2} t^3 + \frac{5}{2} \beta^{7/2} t^4 + \beta^{9/2} t^5 \right) \text{Erf}[\sqrt{\beta t}]
\]

Expressions for the coefficients in Eq. (2.16) for $\beta = 0$ and $n = 7$.

\[
b_1 = 2 \frac{t^{1/2}}{\sqrt{\pi}}
\]

\[
b_2 = \frac{8}{3} \frac{t^{3/2}}{\sqrt{\pi}}
\]

\[
b_3 = \frac{16}{5} \frac{t^{5/2}}{\sqrt{\pi}}
\]

\[
b_4 = \frac{128}{35} \frac{t^{7/2}}{\sqrt{\pi}}
\]

\[
b_5 = \frac{256}{63} \frac{t^{9/2}}{\sqrt{\pi}}
\]

\[
b_6 = \frac{1024}{231} \frac{t^{11/2}}{\sqrt{\pi}}
\]

\[
b_7 = \frac{2048}{429} \frac{t^{13/2}}{\sqrt{\pi}}
\]
2.10 Appendix B: Measurement sensitivity analysis

Equations (2.28-2.32) from the main body of the chapter can be used to define the relative errors for the heat capacity and effusivity, i.e. \( \delta_{c_p} = \sigma_{c_p} / c_p \) and \( \delta_\phi = \sigma_\phi / \phi \), which are metrics for the sensitivity of the technique. Figure 2.B1 shows contour plots of the relative errors as a function of the thermal parameters assuming a constant heating rate of 3000 K/s for 5 ms and a temperature error \( T = 0.1 ^\circ C \). It is evident from the figure that the relative error on the effusivity increases with increasing \( c_p \) and decreasing \( A_M \times \phi_M \). Conversely, the relative error on the heat capacity decreases with increasing \( c_p \) and decreasing \( A_M \times \phi_M \). Similar plots are readily created for other experimental conditions to evaluate the effects on measurement sensitivity of experimental parameters such as the heating rate or sensor dimensions.

The relative errors on \( c_p \) and \( \phi_M \) can be used to estimate the errors on the thermal properties of the materials. Equation (2.B1) defines the error on the heat capacity of a Cu sample deposited on the nTTA,

\[
\delta_{c_p,Cu} = \frac{\sqrt{(\delta_{c_p,S} c_p,S)^2 + (\delta_{c_p,B} c_p,B)^2}}{c_p,S - c_p,B}.
\]

Here the subscripts B and S indicate a bare thermal cell and a cell with sample, respectively. Applying Eq. (2.B1) to the example of a 61 nm thick Cu sample gives, \( c_p,B = 126 \text{ nJ/K} \) and \( c_p,S = 173 \text{ nJ/K} \), with respective errors from Fig. 2.B1 \( \delta_{c_p,B} = 1.6 \% \) and \( \delta_{c_p,S} = 2.7 \% \), so that \( \delta_{c_p,Cu} = 11 \% \). The determination of \((\rho c_p)\) requires a volume measurement of the sample, which has a relative error of 10 \%. Combining these errors gives a relative error of 15 \% on \((\rho c_p)\) for the 61 nm Cu film. The relative errors on \((\rho c_p)\) for 23 nm and 120 nm Cu films are estimated at 22 \% and 12 \% respectively.

Similarly, the relative error of the thermal conductivity of thin-films deposited on the nTTA can be defined in terms of the errors on the measured
thermal properties. The relative error on the thermal conductivity of the sample film follows from the effective thermal conductivity of a multilayer film (Eq. 2.35). Using the example of the 61 nm Cu film, from Fig. 2.B1 \( \delta_{\phi,s} = 0.75\% \), \( \delta_{(\rho,c_p),Cu} = 15\% \), \( \delta_{\phi,SN} = 2.9\% \), and \( \delta_{(\rho,c_p),SN} = 1.6\% \), produces an error on the thermal conductivity of the Cu film of \( \delta_{k,Cu} = 8.6\% \), in good agreement with the experimental results. The error analysis can be used to estimate errors in thermal parameters and thermal materials properties; it serves as a guide when planning measurements on other materials systems and for optimizing the measurement technique.

![Figure 2.B1: Relative errors of measured thermal parameters as a function of the value of these thermal parameters, (a) relative error of effusivity and (b) relative error of heat capacity. Data reduction used a moving 0.3 ms time-span for the heating rate fit and a 4 ms time-span to fit a 5th order polynomial to the temperature history.](image)

**2.11 References**


Chapter 2: nano-Thermal transport array


[18] P.R. Bevington, D.K. Robinson, Data reduction and error analysis for the


Chapter 3

Combinatorial nano-calorimetry

3.1 Summary

The parallel nano-scanning calorimeter (PnSC) is a silicon-based micromachined device for calorimetric measurement of nanoscale materials in a high-throughput methodology. The device contains an array of nano-calorimeters. Each nano-calorimeter consists of a silicon nitride membrane and a tungsten heating element that also serves as a temperature gauge. The small mass of the individual nano-calorimeters enables measurements on samples as small as a few hundred nanograms at heating rates up to $10^4$ K/s. The sensitivity of the device is demonstrated through the analysis of the melting transformation of a 25 nm indium film. To demonstrate the combinatorial capabilities, the device is used to analyze a Ni-Ti-Zr sample library. The as-deposited amorphous samples are crystallized by local heating in a process that lasts just tens of milliseconds. The martensite-austenite transformation in the Ni-Ti-Zr shape memory alloy system is analyzed and the dependence of transformation temperature and specific heat on composition is revealed.
3.2 Introduction

As materials scientists strive to optimize the performance of materials, often the best performers are found in complex materials systems, i.e., materials systems with three components or more. This class of materials systems is still largely unexplored. The reason why complex materials systems remain unexplored is twofold: first, the scope of the problem is vast and second, conventional measurement methods are too slow. For example, considering ternary and quaternary combinations of elements leads to over four million materials systems of which fewer than 1% are well known [1]. Conventional measurement methods consider just one composition of one material system at a time. This approach is insufficient to explore the vast materials space in a reasonable amount of time. The dependence of materials properties on temperature, scale, and processing conditions further increases the scope of the problem. Clearly, high-throughput techniques can improve the efficiency of materials discovery and property optimization.

This chapter introduces an instrument, the parallel nano-scanning calorimeter (PnSC), which combines techniques from combinatorics and nano-calorimetry to create a useful tool for materials research and discovery [2]. More specifically, the PnSC allows high-throughput measurement of enthalpy-related materials properties in thin-film samples. The design of the PnSC allows for fast synthesis of sample libraries by conventional thin-film growth techniques. Samples can range from nanometer to micrometer thickness and libraries can vary by composition, thickness, temperature history, etc. Once created, the entire sample library is measured sequentially with millisecond measurement times, allowing fast sample analysis over a wide range of temperatures.

Combinatorial materials science is a rapidly growing field of materials research that pairs traditional measurement techniques with high-throughput methods to accelerate materials discovery [3-6]. The combinatorial approach has been applied to such diverse applications as catalysis of transition-metal-containing compounds [7], polymer thin-film dewetting [8], and more recently to the optimization of shape memory alloy (SMA) transformation behavior [9, 10].
This is a very limited sample of the growing field of combinatorial material science; nevertheless these examples demonstrate the broadly applicable nature, the efficiency, and the economy of the combinatorial approach.

Calorimetry is an essential tool in the study of materials that is used to measure transformation temperatures, enthalpies, and heat capacities. It is also used to investigate the kinetics of phase transformations and reactions. Nano-calorimetry makes use of thin-film and micromachining technologies to significantly reduce the addendum of the calorimeter, enabling ultra-sensitive calorimetric measurements [11-14]. Allen and colleagues in particular have demonstrated sensitivities on the order of 10 pJ/K using a differential measurement scheme [15]. Nano-calorimetry is a proven method for measuring the thermal energies of nanoscale quantities of materials. Nano-calorimetry, in general, possesses characteristics that make it suitable for combinatorial material science: sample fabrication methods are generally compatible with combinatorial sample library fabrication techniques and short measurement times facilitate high-throughput measurements.

By combining nano-calorimetry with combinatorial methods, the PnSC accelerates materials synthesis and analysis. The sensitivity of the PnSC is first demonstrated by measuring the heat of fusion and melting temperature for a 25 nm indium thin film. The combinatorial capabilities of the device are then demonstrated by synthesizing a sample library of the high-temperature shape memory alloy Ni-Ti-Zr with a two-dimensional composition gradient to reveal the dependence of the martensite transformation temperature on the Zr concentration.

### 3.3 Device description and working principles

#### 3.3.1 Description of device

The PnSC device consists of a substrate with a number of micromachined thermal sensors. The thermal sensors are arranged in a 5x5 array to facilitate
combinatorial sample preparation (Fig. 3.1). When a thin-film sample with an in-plane composition gradient is deposited on this substrate, the film is essentially discretized at each thermal sensor, allowing the simultaneous creation of 25 samples with unique composition. One can also envision systematic variations of other parameters, such as sample thickness, processing conditions, etc.

The design and operation of the thermal sensors is similar to the nano-calorimetric cells developed by Allen and colleagues [13, 15], with different materials, fabrication method and geometries. Each nano-calorimetric sensor consists of a thin-film thermistor sandwiched between two electrically insulating ceramic layers that form a membrane supported by the substrate (Fig. 3.2(a)). The thermistor is fabricated from an electrically conductive film and serves to both measure temperature and heat the sample. Samples to be measured are limited to the thermistor area of each sensor, and may be deposited on either side of the membrane. The membrane design of the sensor insulates the sample from the
surroundings and ensures that the thermal mass of the sensor, i.e., the addendum, is very small.

Figure 3.2: Layout of the nano-calorimeter cell: (a) cross-section schematic, and (b) plane-view schematic. Heater line-width is 0.8 mm and voltage probe line-width is 0.1 mm.

Referring to the schematic in Fig. 3.2(b), the wide straight line down the center of the membrane is the heating element; the metal lines connected to the heater are the voltage probes, and the portion of the heating element between the
voltage probes is the thermistor. A current passed through the heating element heats the sample and the calorimetric cell. The power dissipated in the thermistor is determined experimentally from the current supplied to the thermistor and the potential drop between the voltage probes. The local temperature change is determined from a four-point thermistor resistance measurement that has been calibrated to temperature.

Not all power dissipated in the thermistor is used to heat the sample and addendum; some power is lost to the environment. At moderate temperatures, heat transfer from the thermistor to the membrane dominates this heat loss. As the temperature increases, radiation from the thermistor and the membrane becomes important and eventually dominates the heat loss. Measurements are performed in vacuum to eliminate convection losses and to provide a chemically inert testing environment. Conduction and radiation heat losses can be accounted for by modeling or through use of a reference measurement scheme. In this chapter, results are generally analyzed using a reference measurement scheme; a thermal model for the sensor is given in Chapter 2.

The substrate of the PnSC device is made of silicon, which is readily micro-machined. The ceramic membrane consists of silicon nitride, selected because it is a good electrical insulator and because it is made easily into thin membranes. Silicon nitride also has a low thermal effusivity, which reduces the heat loss into the membrane. The thermistor is made of tungsten, because of its large temperature coefficient of resistance and its small resistivity, both of which are beneficial to measurement sensitivity [13]. The very high melting temperature of tungsten also results in excellent thermal stability of the thermistor. The electrical leads and contact pads on the substrate are made of copper to reduce the resistance of the signal lines on the substrate and to facilitate contact to the PnSC device. Specific dimensions of the components of the PnSC device can be found in Table 3.1.
Chapter 3: Combinatorial nano-calorimetry

3.3.2 Operating principles

The power dissipated in the thermistor can be parsed into stored power and power lost to the surroundings. At constant pressure, the stored power results in a change of the enthalpy of the sample and calorimeter addendum. If we define a control volume CV that comprises the sample and the calorimeter addendum, then

\[ P = \dot{H} + Q \]  \hspace{1cm} (3.1)

where \( P \) is the total power dissipated in the thermistor, \( \dot{H} \) is the time rate of change of the enthalpy within the CV, and \( Q \) is the heat loss through the boundaries of the CV. The rate of change of the enthalpy can be written as

\[ \dot{H} = \frac{dH}{dT} \frac{dT}{dt}, \]  \hspace{1cm} (3.2)

where \( T \) is the temperature of the thermistor. Substituting Eq. (3.2) into Eq. (3.1) and rearranging results in,

\[ \frac{P}{\dot{T}} = \frac{dH}{dT} + \frac{Q}{\dot{T}}, \]  \hspace{1cm} (3.3)

where \( \dot{T} \) is the heating rate of the thermistor. The left hand side of Eq. (3.3) can be directly calculated from measured quantities and is defined as the calorimetric signal from the sensor. If \( Q \) is known or if its contribution to Eq. (3.3) is negligible (e.g., in the case of very large heating rates), the change in enthalpy with temperature, \( dH/dT \), can be determined directly from the calorimetric signal. If

<table>
<thead>
<tr>
<th></th>
<th>Length (x)</th>
<th>Width (y)</th>
<th>Thickness (z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate (Si)</td>
<td>55 mm</td>
<td>55 mm</td>
<td>0.7 mm</td>
</tr>
<tr>
<td>Membrane (Si₃N₄/SiNx)</td>
<td>5 mm</td>
<td>2.9 mm</td>
<td>80 nm/100 nm</td>
</tr>
<tr>
<td>Thermistor (W)</td>
<td>3 mm</td>
<td>800 μm</td>
<td>125 nm</td>
</tr>
</tbody>
</table>

Table 3.1: Dimensions of PnSC components. Note: thermal sensor center-to-center spacing is 8 mm in both the x and y-directions.
no phase transformations or reactions take place, \( dH/dT \) is equal to the heat capacity \( C_P \) of the control volume; during a phase transformation this term also includes the latent heat of transformation \( H_L \).

To reduce the effect of the calorimeter addendum and/or heat loss on the measurement, it is often convenient to perform a reference measurement. Equation (3.3) can then be rewritten to define the differential calorimetric signal as,

\[
\frac{\Delta P}{T} = \Delta \frac{dH}{dT} + \Delta \frac{Q}{T}
\]

where \( \Delta \) represents the difference between a sensor with a sample and a sensor that is either empty or contains a reference sample. Comparing measurements in this manner eliminates the contribution of the addendum and reduces heat loss contributions to the signal (see Chapter 2). If the heating rate of both sensors is identical, then the heat conducted into the membrane is the same for both sensors and the heat loss term in Eq. (3.4) vanishes. The differential calorimetric signal is the quantity that is analyzed to determine transformation temperatures and latent heats throughout this study. In addition to performing differential measurements, the effect of heat losses can also be reduced by increasing the heating rate of the calorimeter.

In deriving Eq. (3.3) temperature uniformity in the CV is implicitly assumed. Any non-uniformity of the temperature results in a broadening of features in the calorimetric signal curve. At short times this effect is small and it increases with time. An approximate analysis of the temperature non-uniformity of the CV is presented in Appendix B.

### 3.4 Experimental method

#### 3.4.1 Device fabrication

The fabrication process starts with (100) oriented Si wafers, 200 mm in diameter and polished on one side. These wafers are delivered with a coating of
approximately 80 nm of Si$_3$N$_4$ grown on both sides using a low-pressure chemical vapor deposition process (Fig. 3.3(a)). Special care is taken throughout the fabrication process to protect the Si$_3$N$_4$ on the polished side of the wafer. This film will eventually form the base membrane layer of the PnSC; even shallow scratches may result in ruptured membranes.

Figure 3.3: Cross section schematic of a nano-calorimeter cell during steps in the PnSC fabrication process.
Each Si wafer is cleaved into seven 55 mm x 55 mm square substrates. The substrates are rinsed in DI water and blown with nitrogen to remove any particles. Next, 125 nm of tungsten and then 1.2 \( \mu \text{m} \) of copper are deposited on the polished side of a square substrate using DC magnetron sputtering. Substrate rotation produces uniform film thickness (Fig. 3.3(b)). Immediately prior to film deposition, the substrates are sputter-cleaned using an Ar plasma to remove any contamination and to improve adhesion of the sputtered coatings. The sputter chamber used for the fabrication of the PnSC device has a base pressure of approximately \( 8 \times 10^{-8} \text{ Torr} \); other processing conditions are shown in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>Pressure (mTorr)</th>
<th>Power (W)</th>
<th>Time (min)</th>
<th>Thickness (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter clean</td>
<td>20</td>
<td>25</td>
<td>5</td>
<td>NA</td>
</tr>
<tr>
<td>Tungsten</td>
<td>6</td>
<td>151</td>
<td>15</td>
<td>0.125</td>
</tr>
<tr>
<td>Copper</td>
<td>5</td>
<td>200</td>
<td>60</td>
<td>1.2</td>
</tr>
</tbody>
</table>

After deposition of the metal coatings, the wafer is baked at 150\(^\circ\)C for 5 min. Then, Shipley 1805 photoresist (S1805) is spin-coated and patterned on both sides of the wafer. The front side of the substrate is exposed to UV light through a mask with the metallization artwork, and the backside is exposed through a mask with the cavity window artwork. Both sides of the substrate are developed simultaneously in Microposit CD-30 for 1 minute (Fig. 3.3(c)). The Si\(_3\)N\(_4\) on the backside of the wafer is reactively etched in CF\(_4\) to create rectangular openings in the silicon nitride layer. Copper is etched in an aqueous solution of phosphoric, nitric, and acetic acid at 50\(^\circ\)C. The Cu etch exposes the underlying tungsten, which is then etched in 30\% H\(_2\)O\(_2\) at 50\(^\circ\)C (Fig. 3.3(d)). Both etch steps take approximately three minutes. After the wet-etch processes, the remaining resist is exposed and removed. Next, S1805 photoresist is re-applied to the metallization side and patterned with the rectangular cavity artwork (Fig. 3.3(e)). Copper is then etched from the membrane area, leaving only tungsten within the area that will form the membrane. After patterning the metallization layers, the device is coated with approximately 100 nm plasma-enhanced chemical vapor
deposition (PECVD) silicon nitride (SiNₓ) (Fig. 3.3(f)) using a Nexx Systems Cirrus 150 with 265 W microwave power, 40 sccm 3% SiH₄ in Ar, 5.8 sccm N₂, 20 sccm Ar gas flow rates, and a working pressure of 100 mTorr. Using the previously described lithography and etch procedure, the SiNₓ is removed from the Cu contact pad area. At this point, the device is annealed at 450°C for 8 hours in a vacuum furnace with a base pressure of 10⁻⁷ Torr to stabilize the SiNₓ and tungsten thermistor.

In a last step, freestanding membranes are created by an anisotropic etch of the Si in a solution of 15 g KOH in 50 ml H₂O at 85°C for approximately 9 hours (Fig. 3.3(g)). The patterned Si₃N₄ coating on the backside of the substrate serves as a hard mask for this step. During this procedure, the metallization is protected by a sample holder that exposes the backside of the device to the KOH solution, while isolating the front side from the KOH solution. If a membrane happens to break as this etch step is completing, the PECVD silicon nitride layer protects the metallization.

3.4.2 Sample preparation

It is possible to deposit samples on the PnSC using several different techniques. In this study, indium samples were deposited by thermal evaporation and Ni-Ti-Zr samples were deposited by magnetron sputtering (Fig. 3.4). In each case, samples were deposited through a shadow mask micromachined from a silicon wafer coated with LPCVD Si₃N₄. The deposition shadow mask is formed so that extrusions in the shadow mask fit into the recesses of the PnSC and align an opening in the shadow mask with each thermistor on the PnSC. Each opening of the shadow mask has nominally the same area, although small variations in the dimensions caused by the shadow mask fabrication process require direct measurements of the opening areas for accurate sample volume determination. The areas of the openings in the shadow mask were measured by optical transmission microscopy using a Nikon Eclipse ME600L microscope equipped with a CCD camera. Digital images were then processed to determine the opening areas with a pixel counting scheme.
volumes of the samples are determined by depositing reference samples on a dummy substrate immediately prior to depositing the calorimetry samples and by measuring the reference sample thickness with a Veeco Detek 6M profilometer to determine the deposition rates. The deposition rate at each sensor location and the area of the corresponding shadow mask opening determine the flux of sputtered material; therefore, controlling the deposition time controls the volume of material deposited.

Indium samples were deposited to a thickness of 25 ± 1 nm in a thermal evaporator with a base pressure in the $10^{-7}$ Torr range. Ni-Ti-Zr samples were sputter deposited in a chamber with a base pressure in the $10^{-8}$ Torr range to a thickness of about 290 nm at a deposition rate of approximately 11 nm/min. The

Figure 3.4: Sputter deposition schematic of Ni-Ti-Zr samples.
Ni-Ti-Zr samples were deposited from confocal sputtering guns using three elemental targets, each with a 25.4 mm diameter (Fig. 3.4). The sputtering guns were tilted toward the concentric point so that the chimneys were close to touching. This positioned the guns, directly under the device and reduced the possibility of any secondary shadowing from the opening of the shadow mask. By this same reasoning, the working distance was set to the maximum for the sputtering system, i.e. approximately 120 mm. The DC power to each gun was determined from an iterative calibration process to obtain the desired composition range, resulting in 72 W, 150 W, and 60 W to the Ni, Ti, and Zr guns respectively. Sample film compositions were measured by energy dispersive x-ray spectroscopy (EDS) using an EDAX system installed on a Zeiss Ultra55 field emission scanning electron microscope (SEM). The compositions were also measured by wavelength dispersive x-ray spectroscopy (WDS) using a JEOL JXA-8200 Superprobe. Both instruments were calibrated using pure element standards for the Ni-K and Ti-K lines at 15 kV accelerating voltage. For Zr, the L-line was used for EDS and the M-line was used for WDS. Ni-Ti-Zr deposition reference samples were relatively thick, approximately 1 μm, for accurate quantitative composition analysis. The reference samples were deposited through a shadow mask with openings defined by the same dimensions as the PnSC membranes (Table 3.1). Composition measurements were made at the center of each reference sample. The composition variation within the samples was determined by measuring the composition along the centerlines of a reference sample. Measurements were performed at five locations in each direction, spaced 0.83 mm along the length and 0.48 mm across the width of the sample.

3.4.3 Experimental setup and procedures

PnSC measurements are controlled and recorded with a personal computer and a National Instruments PCI-6221 data acquisition card (DAQ) (Fig. 3.5). The DAQ is used to send a control voltage to a voltage-to-current converter, with a linear mapping of 1 V to 10 mA. The current source consists of a precision
operational amplifier (OPA227, Texas Instruments), a power operational amplifier (OPA549, Texas Instruments), and a differential amplifier (INA133, Texas Instruments) arranged in a modified Howland configuration. It is powered by a Protek 3030D dual DC power supply running in series mode, providing a constant 30 V controlled power. Excluding internal losses, the current supply is limited by approximately 20 V of compliance and can supply a maximum current of 100 mA.

![Figure 3.5: Measurement setup schematic.](image)

The output of the current source, $I$, is monitored with the DAQ by measuring the voltage drop $V_i$ across a 100 $\Omega$ precision resistor $R_i$. The DAQ also reads the voltage drop $V$ across the thermistor. This is shown in schematic form in Fig. 3.5 and a typical result is shown in Fig. 3.6. All signals are recorded at a sampling rate of 100 kHz and with a resolution of 16 bits. In this setup, the voltage range of the DAQ is adjusted based on the maximum expected value for each measurement to maximize the precision of the 16-bit analog to digital conversion.
With reference to Fig. 3.5, the voltage signals are used to determine the resistance of the thermistor by \( R = R_0 \frac{V_0}{V_0} \) and the electrical power dissipated in the thermistor by \( P = V_0 \frac{V_0}{R_0} \). The temperature of the thermistor is then calculated from,

\[
T = T_0 + \frac{R - R_0}{\lambda R_0},
\]

(3.5)

where \( \lambda \) is the temperature coefficient of resistance of the heating element, \( T_0 \) is the ambient temperature, and \( R_0 \) is the resistance at \( T_0 \). The heating rate is calculated from,

\[
\dot{T} = \frac{R}{\lambda R_0} \left( \frac{V}{V} - \frac{V_l}{V_l} \right),
\]

(3.6)

where \( \dot{V} \) and \( \dot{V}_l \) are the voltage rates calculated from a linear least squares fit to the respective data histories. With the power input and heating rate known, the
calorimetric signal can be expressed explicitly in terms of measurable quantities as,

\[ \frac{P}{T} = \lambda R_0 I^2 \left( \frac{\dot{V}}{V} - \frac{\dot{V}_f}{V_f} \right)^{-1}. \] (3.7)

This calorimetric signal still contains the contributions from heat loss to the environment and from the calorimeter addendum. These contributions were eliminated through use of reference measurements: for the indium measurements, two cells were used – a cell with an indium sample and a bare neighboring cell for a reference measurement. To reduce random noise, 100 temperature cycles were averaged for the sample measurement and 10 cycles were averaged for the reference measurement. In the case of the Ni-Ti-Zr samples, both the sample measurements and the reference measurements were made using the same cell in a scheme where calorimetric measurements on non-transforming phases were used as reference measurements for transforming phases: The as-deposited amorphous films were fully crystallized in one cycle. Subsequent cycles showed no indication of further crystallization; ten of these cycles served as the reference measurement for the crystallization process. The as-deposited amorphous samples cycled 100 times in a low temperature range served as the reference for the martensite-austenite measurements on the crystalline samples. An advantage of using a cell plus sample as its own reference, as opposed to a bare reference cell, is that its mass is exactly the same. Consequently, any deviation between calorimetric signals must be related to a change in the enthalpy of the sample.

All calorimetric measurements were conducted in a vacuum chamber with a vacuum level of \(10^{-5}\) Torr to eliminate convection losses and side reactions. Applied current amplitudes and durations for each measurement can be found in Table 3.3. Prior to performing calorimetric measurements, the thermistors need to be calibrated. The temperature coefficient of resistance was measured by
placing the PnSC substrate in an oven and stepping the oven through a
temperature range. During this calibration process the temperature of the
substrate was measured with a thermocouple. The resistance of a thermistor was
recorded at each temperature step by applying a 1 mA monitoring current for a
period of 20 ms. Since this measurement was performed under atmospheric
conditions, the 1 mA current pulse caused a negligible amount of Joule heating.
The initial resistance $R_0$ and the temperature coefficient of resistance $\lambda$ were
determined from a linear least squares fit of the resistance data as a function of
temperature (Fig. 3.7). The value of $\lambda$ was calculated using Eq. (3.5), yielding a

\[ y = 6.721 + 0.010407x \quad R = 0.9999 \]
\[ \lambda = (1.50 \pm 0.04) \times 10^{-3} \text{K}^{-1} \]

**Table 3.3: Current pulse amplitude and duration for calorimetric measurements.**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Amplitude (mA)</th>
<th>Duration (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>28</td>
<td>20</td>
</tr>
<tr>
<td>Ni-Ti-Zr Crystallization</td>
<td>85-90</td>
<td>60</td>
</tr>
<tr>
<td>Ni-Ti-Zr Martensite</td>
<td>85-90</td>
<td>22-25</td>
</tr>
</tbody>
</table>

**Figure 3.7: Calibration fit of the temperature coefficient of resistance.**
value of \((1.50 \pm 0.04) \times 10^3 \text{ K}^{-1}\) for the tungsten thermistors on the device with the Ni-Ti-Zr samples, and a similar value for the device with the indium sample. The value of \(\lambda\) was determined for one cell on each substrate, while the value of \(R_{\text{eq}}\) was measured for each cell on a substrate.

### 3.5 Results and discussion

#### 3.5.1 Indium Results

The calorimetric signals from a PnSC cell with an indium sample and a cell without indium sample are shown in Fig. 3.8(a). The small offset between the two signals is caused by the presence of the indium sample; the slope is primarily the result of heat loss to the ambient. Because these cells were heated at the same rate (approximately \(14 \times 10^3 \text{ K} / \text{s}\)), the heat loss is the same for both cells and the difference in calorimetric signals (Fig. 3.8(b)) represents the calorimetric trace for the indium sample.

![Figure 3.8: Indium melting results. (a) Indium melting curve and reference curve. (b) Differential calorimetric signal with baseline showing the melting transformation of In nanostructures (inset).](image)
A linear baseline is used to determine the melting temperature $T_{M}$, the heat of fusion $H_f$, and the heat capacity $C_p$ of the indium sample. The melting temperature is taken as the temperature at which the calorimetric signal peaks, and is found to be $157^\circ$C, in excellent agreement with the reported literature value of $156.6^\circ$C [16]. Unlike traditional calorimetry, the peak of the melting signal is the most appropriate point to define the melting temperature, because the very small thermal resistance between the sensor and sample produces a negligible temperature difference between them (see Appendix B). The shape of the melting peak is determined mainly by the temperature distribution within the heating element. Thus, the peak temperature represents the average heater temperature at which most of the sample melts. This temperature is a better approximation for the melting temperature than the onset of the peak used traditionally. This approach is confirmed with heating rate experiments, which do not show an increase in the peak temperature with increased heating rates as with traditional calorimeters.

The specific heat of fusion is obtained by numerically integrating the peak area between the differential calorimetric signal $\Delta P/\dot{T}$ and the baseline, and normalizing this result by the mass of the sample. The mass of the sample is calculated using the measured sample volume, $V_{In} = (27.5 \pm 3) \times 10^3 \ \mu m^3$, and the handbook value for the density, $\rho_{In} = 7.31 \ \text{g/cm}^3$ [16], and is equal to $(201 \pm 20) \ \text{ng}$. This procedure results in $h_f = (23 \pm 2) \ \text{J/g}$, which is less than the literature value of $28.7 \ \text{J/g}$ for bulk indium [16]. Similar reductions in $h_f$ have been demonstrated for nanostructures by Allen and colleagues [17, 18, 19].

The fact that the specific heat of fusion is reduced, while the melting temperature remains unchanged compared to bulk indium, is explained by the observation that the indium film breaks up into droplets when it is first melted. When the film cools, these droplets solidify into particles with a broad range of sizes as illustrated in the SEM micrograph in Fig. 3.8(b). The smallest particles have a reduced $h_f$ and $T_{M}$; the largest particles with diameters in excess of $100 \ \text{nm}$ have values that are the same as for bulk indium [18, 19]. From the position of the low-temperature shoulder, the small indium particles begin to melt at
approximately 125 °C. According to Ref. [19] this corresponds to a particle size on the order of 7 nm, which is consistent with SEM observations. Because the mass of the small particles represents only a small fraction of the total sample mass, the small particles give rise to a low-temperature shoulder on the melting peak in Fig. 3.8(b), leaving the peak temperature unaltered from its bulk value. The specific heat of fusion, by contrast, is determined by integrating over the entire peak, including the low-temperature shoulder, and is reduced as a result.

The room-temperature specific heat of the indium sample is found by evaluating the baseline at $T_0$ and normalizing that value by the sample mass. This procedure results in $c_p = (260 \pm 60) \text{ J/kgK}$, which is comparable to the literature value of 230 J/kgK [16]. Most of the error in the specific heat measurement is associated with taking the difference between the sample and reference measurements, which were performed on two different cells with slightly different addendum. As the sample makes up only 8% of the total heat capacity of the sample cell, a small difference in addendum between the two cells can result in a much larger error in the heat capacity of the sample. The accuracy of the $c_p$ measurement could be improved considerably by performing the reference measurement on the same cell as the sample measurement before the sample is deposited.

### 3.5.2 Composition of the Ni-Ti-Zr samples

The compositions of the Ni-Ti-Zr samples are listed in Table 3.4, arranged by sample location on the device. The concentration of a particular element is greatest closest to the respective target. The sample library covers an atomic composition range of 44.6-52.7 at.% Ni, 27.7-38.5 at.% Ti, and 15.1-22.6 at.% Zr. Chemical composition results measured by EDS are within 0.5 at.% of the composition results obtained by WDS, good agreement considering an uncertainty in the measurements of approximately 0.5 and 0.7 at.% for EDS and WDS, respectively. Composition variations within individual samples are readily estimated from the dimensions of the cells and the composition spread across the substrate. The maximum variation in Ni content within a sample is 0.7%, which
is approximately the same as the uncertainty in the Ni measurements. The concentration variations for Ti and Zr are significantly smaller than for Ni. These observations are borne out by the experimental measurements of the within-sample composition variation, which do not show any trends and are all within experimental error.

Table 3.4: Calorimetric cell numbering scheme with corresponding sample chemical composition from EDS analysis (atomic %). Measurement uncertainty can be estimated as 0.6, 0.4 and 0.4 at.% for Ni, Ti and Zr, respectively.

<table>
<thead>
<tr>
<th>Cell # 1</th>
<th>Cell # 2</th>
<th>Cell # 3</th>
<th>Cell # 4</th>
<th>Cell # 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.6 % Ni</td>
<td>52.7 % Ni</td>
<td>52.7 % Ni</td>
<td>Broken cell</td>
<td>52.7 % Ni</td>
</tr>
<tr>
<td>32.3 % Ti</td>
<td>31.3 % Ti</td>
<td>30.3 % Ti</td>
<td>17.0 % Zr</td>
<td>27.7 % Ti</td>
</tr>
<tr>
<td>15.1 % Zr</td>
<td>16.0 % Zr</td>
<td>17.0 % Zr</td>
<td>17.0 % Zr</td>
<td>19.6 % Zr</td>
</tr>
<tr>
<td>Cell # 6</td>
<td>Cell # 7</td>
<td>Cell # 8</td>
<td>Cell # 9</td>
<td>Cell # 10</td>
</tr>
<tr>
<td>50.4 % Ni</td>
<td>50.6 % Ni</td>
<td>50.8 % Ni</td>
<td>50.6 % Ni</td>
<td>50.5 % Ni</td>
</tr>
<tr>
<td>34.0 % Ti</td>
<td>32.8 % Ti</td>
<td>31.5 % Ti</td>
<td>17.7 % Zr</td>
<td>30.3 % Ti</td>
</tr>
<tr>
<td>15.6 % Zr</td>
<td>16.6 % Zr</td>
<td>31.5 % Ti</td>
<td>17.7 % Zr</td>
<td>19.1 % Zr</td>
</tr>
<tr>
<td>Cell #11</td>
<td>Cell #12</td>
<td>Cell #13</td>
<td>Cell #14</td>
<td>Cell #15</td>
</tr>
<tr>
<td>48.2 % Ni</td>
<td>48.6 % Ni</td>
<td>48.9 % Ni</td>
<td>48.6 % Ni</td>
<td>48.3 % Ni</td>
</tr>
<tr>
<td>35.8 % Ti</td>
<td>34.3 % Ti</td>
<td>32.8 % Ti</td>
<td>31.6 % Ti</td>
<td>30.5 % Ti</td>
</tr>
<tr>
<td>16.0 % Zr</td>
<td>17.1 % Zr</td>
<td>18.3 % Zr</td>
<td>19.8 % Zr</td>
<td>21.2 % Zr</td>
</tr>
<tr>
<td>Cell #16</td>
<td>Cell #17</td>
<td>Cell #18</td>
<td>Cell #19</td>
<td>Cell #20</td>
</tr>
<tr>
<td>46.4 % Ni</td>
<td>46.6 % Ni</td>
<td>46.8 % Ni</td>
<td>46.6 % Ni</td>
<td>46.4 % Ni</td>
</tr>
<tr>
<td>37.1 % Ti</td>
<td>35.7 % Ti</td>
<td>34.3 % Ti</td>
<td>33.0 % Ti</td>
<td>31.7 % Ti</td>
</tr>
<tr>
<td>16.5 % Zr</td>
<td>17.7 % Zr</td>
<td>18.9 % Zr</td>
<td>20.4 % Zr</td>
<td>21.9 % Zr</td>
</tr>
<tr>
<td>Cell #21</td>
<td>Cell #22</td>
<td>Cell #23</td>
<td>Cell #24</td>
<td>Cell #25</td>
</tr>
<tr>
<td>44.6 % Ni</td>
<td>44.7 % Ni</td>
<td>44.7 % Ni</td>
<td>44.7 % Ni</td>
<td>44.6 % Ni</td>
</tr>
<tr>
<td>38.5 % Ti</td>
<td>37.1 % Ti</td>
<td>35.7 % Ti</td>
<td>34.3 % Ti</td>
<td>32.8 % Ti</td>
</tr>
<tr>
<td>16.9 % Zr</td>
<td>18.2 % Zr</td>
<td>19.6 % Zr</td>
<td>21.0 % Zr</td>
<td>22.6 % Zr</td>
</tr>
</tbody>
</table>

3.5.3 Crystallization of the as-deposited Ni-Ti-Zr samples

X-ray diffraction showed that the as-deposited Ni-Ti-Zr samples were amorphous. An 85-90 mA current pulse lasting 60 ms was used to crystallize the samples. Figure 3.9(a) shows typical temperature responses of a calorimetric cell with a sample in the as-deposited amorphous state and of the same cell with the
sample in the crystalline state. The exothermic crystallization of the amorphous sample creates a step in the temperature history of the as-deposited sample.

The crystallization peak for the as-deposited sample is evident in the calorimetric signal (Fig. 3.9(b)); the lack of transformation is apparent in the crystallized sample. The nonzero slope in the calorimetric signal at low temperatures is caused primarily by the temperature dependence of the specific heat and to a lesser extent by the conductive heat loss into the membrane. The steep rise in the signal at elevated temperatures is the result of radiative heat loss to the environment.

Figure 3.9: Typical Ni-Ti-Zr crystallization results. (a) Temperature response of as-deposited and crystallized Ni-Ti-Zr sample to an 85 mA current pulse lasting 60 ms. (b) Calorimetric signal of as-deposited and crystallized Ni-Ti-Zr sample plotted as a function of as-deposited sample temperature. (c) Differential calorimetric signal for crystallizing Ni-Ti-Zr sample.

The differential calorimetric signal is plotted as a function of temperature in Fig. 3.9(c). Plotting the differential signal further amplifies the crystallization peak and reveals the onset of the glass transformation (475 ± 2°C) immediately prior to crystallization. The crystallization peak temperature (733 ± 3°C) is significantly higher than previously reported values (~500°C) for thin films of similar composition [20]. This difference is due to the kinetics of the crystallization process and the difference in heating rates between the studies. In this study the heating rate is nominally 2.0 × 10^4 K/s while Miyazaki and colleagues [20] reported using a heating rate of approximately 0.17 K/s. All Ni-Ti-Zr samples were crystallized in a similar fashion. The width of the
crystallization peak in this study can be attributed to the kinetics of the crystallization process, the formation of multiple phases, and the temperature non-uniformity in the thermistor (Appendix B). A detailed analysis of the crystallization process as a function of film composition and the resulting microstructure is the subject of a future publication.

3.5.4 Martensite-austenite transformation in crystalline samples

Typical low-temperature responses of a cell with a sample in the amorphous state and of the same cell with the sample in the crystalline state are shown in Fig. 3.10(a). The martensitic transformation in the crystalline sample is not immediately obvious from the temperature histories because the martensite-austenite latent heat is significantly smaller than the crystallization latent heat, but the transformation shows up clearly in the calorimetric signal (Fig. 3.10(b)). The differential calorimetric signal is shown in Fig. 3.10(c). The peak transformation temperature $T_{M-A}$ and the enthalpy of transformation $H_{M-A}$ are readily obtained from the curve: $H_{M-A}$ is given by the area between the transformation peak and a linear baseline fit to the calorimetric signal outside the transforming region; $T_{M-A}$ is defined as the temperature where the calorimetric signal during the transformation is furthest from the baseline. For this particular sample $T_{M-A} = (183 \pm 2) ^\circ C$ and $H_{M-A} = (32.0 \pm 0.5) \mu J$. Also apparent from Fig. 3.10(c) is the negative slope of the differential calorimetric signal at temperatures above $T_{M-A}$. This negative slope is observed for all samples, independent of composition, and is a clear indication that the specific heat capacity of the amorphous samples increases faster with temperature than that of the crystalline samples.
Repeating the above analysis on the remaining samples reveals that only the rows with the two lowest Ni content demonstrate a measurable transformation signal (Fig. 3.11). The analysis results are summarized for the transforming samples in Table 3.5, where \( H_{M-A} \) has been normalized by the sample mass to produce the specific latent heat of transformation \( h_{M-A} \). The mass \( m_s \) of each sample was determined from the measured sample volume \( V_S \), the measured sample composition, the volume of the martensite unit cell \( V_{UC} \) for Ni\(_{49.5}\)Ti\(_{50.5-x}\)Zr\(_x\) with \( x = \{5, 10, 15, 20\} \) [21], the molar mass \( M_i \), and the fact that Ni-Ti-Zr martensite has 4 atoms per unit cell [22, 23],

\[
m_s = 4 V_S \left( \frac{f_{Ni} M_{Ni} + f_{Ti} M_{Ti} + f_{Zr} M_{Zr}}{N_A V_{UC}} \right),
\]

where \( f \) represents atomic fraction and \( N_A \) is Avogadro’s number. The sample volume measurements were obtained from as-deposited amorphous samples and the unit cell volume is for the crystalline martensite phase. This discrepancy does not cause a significant error, as Inoue has reported previously that the density change on crystallization is small (< 1%) [24].

Figure 3.10: Typical Ni-Ti-Zr martensite transformation results. (a) Temperature response of the as-deposited and crystallized sample to an 85 mA current pulse lasting 22 ms, with the crystallized sample transforming martensitically. (b) Calorimetric signals of a sample in the amorphous and the crystallized phase during heating. (c) Differential calorimetric signal for the martensite-austenite transformation during heating.
Figure 3.11: Differential calorimetric signal (from -150 to 300 nJ/K) of the martensite transformation versus temperature (from 30 to 350 °C) for each sample during heating. Results are arranged as positioned on the PnSC. See Table 3.4 for composition results and Table 3.5 for quantitative transformation results.

Table 3.5: Martensite-austenite transformation results for compositions demonstrating a transformation in the calorimetric signal. Chemical composition uncertainty can be estimated as 0.6, 0.4 and 0.4 at.% for Ni, Ti and Zr, respectively.

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Composition (Atomic %)</th>
<th>T_{M-A} (°C)</th>
<th>h_{M-A} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Ni_{46.4}Ti_{37.1}Zr_{16.5}</td>
<td>136 ± 2</td>
<td>8.4 ± 0.2</td>
</tr>
<tr>
<td>17</td>
<td>Ni_{46.6}Ti_{35.7}Zr_{17.7}</td>
<td>149 ± 3</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>18</td>
<td>Ni_{46.8}Ti_{34.3}Zr_{18.9}</td>
<td>180 ± 3</td>
<td>0.80 ± 0.03</td>
</tr>
<tr>
<td>19</td>
<td>Ni_{46.6}Ti_{33.0}Zr_{20.4}</td>
<td>229 ± 3</td>
<td>1.14 ± 0.03</td>
</tr>
<tr>
<td>20</td>
<td>Ni_{46.4}Ti_{31.7}Zr_{21.9}</td>
<td>250 ± 1</td>
<td>10.3 ± 0.2</td>
</tr>
<tr>
<td>21</td>
<td>Ni_{44.6}Ti_{38.5}Zr_{16.9}</td>
<td>150 ± 3</td>
<td>9.0 ± 0.2</td>
</tr>
<tr>
<td>22</td>
<td>Ni_{44.7}Ti_{37.1}Zr_{18.2}</td>
<td>183 ± 2</td>
<td>9.8 ± 0.2</td>
</tr>
<tr>
<td>23</td>
<td>Ni_{44.7}Ti_{35.7}Zr_{19.6}</td>
<td>209 ± 1</td>
<td>10.4 ± 0.2</td>
</tr>
<tr>
<td>24</td>
<td>Ni_{44.7}Ti_{34.3}Zr_{21.0}</td>
<td>252 ± 3</td>
<td>11.2 ± 0.2</td>
</tr>
<tr>
<td>25</td>
<td>Ni_{44.6}Ti_{32.6}Zr_{22.6}</td>
<td>277 ± 1</td>
<td>10.6 ± 0.3</td>
</tr>
</tbody>
</table>
The visual representation of the martensite-austenite transformation temperature results can be found in Fig. 3.12, along with results compiled from Hsieh [25, 26]. The transformation temperature varies linearly with Zr content in the range of 16-23%. This result confirms the trend previously reported by Hsieh. The Ni content, by contrast, does not seem to affect the transformation temperature, at least for the samples in which transformations were observed. This behavior is also observed for binary Ni,Ti_{50-x} alloys with x < 50% [27]. If x > 50%, however, the transformation temperature can decrease by as much as 200°C for a 1% increase in Ni concentration. This behavior, which also occurs in Ni-Ti-Zr [28], may provide an explanation as to why no transformations are observed in the Ni-rich samples – the transformations take place at temperatures well below the measured range. The temperature dependence of the heat capacity provides indirect evidence that the “non-transforming” samples are in the high-temperature phase: The slope of the calorimetric signal of the “non-
transforming” samples is the same as the slope for the austenitic phase in the transforming samples. The slope of the martensitic phase, by contrast, is closer to that of the amorphous samples. It is interesting to note that the transition between transforming samples and “non-transforming” samples takes place at a Ni concentration between 46.8 and 48.2 atomic %, which is smaller than for the bulk NiTi system.

It is apparent from Fig. 3.12 that the thin-film samples show a marked depression in $T_{M-A}$ compared to the results for bulk Ni-Ti-Zr. This depression of the transformation temperature is caused by the fine microstructure of the samples. SEM observations show that the films in this study have a nanoscale grain structure (10-50 nm diameter) as a result of the fast heating and cooling rates. A similar depression of the transformation temperature has been demonstrated for NiTi samples with a nanoscale microstructure [29, 30] and is attributed to a decrease in the stability of the martensite, related to the energy-cost of forming twin-boundary interfaces.

The dependence of $h_{M-A}$ on chemical composition (Table 3.5) is somewhat more complicated than the transformation temperature. The majority of samples (cells 16, 20, 21-25) transform with a similar specific enthalpy, averaging $\overline{h}_{M-A} = 10 \pm 1$ J/g, which is less than the reported bulk value of 21.4 J/g, but comparable to the value of 9.8 J/g reported for melt-spun ribbons with micron scale thickness [28]. A few samples (cells 17-19) transform with a reduced enthalpy, which may be an indication that the R-phase is formed instead of the B19′ martensitic phase. In the binary NiTi system, a reduced enthalpy of transformation is indeed associated with the R-phase [31]. The R-phase has a reduced lattice distortion relative to the austenite phase, which decreases the entropy of transformation and therefore the specific latent heat [32]. In NiTi, the R-phase has been shown to stabilize at reduced length scales [33] and with increasing Ni concentration [34]. It is reasonable to expect that the reduced specific latent heats in cells 17-19 are the result of an R-phase transformation. However, a competing hypothesis could be that the martensite volume fractions in these samples are simply reduced [33], which would also reduce the effective
specific latent heats of transformation. Structural analysis is required to draw an unambiguous conclusion.

### 3.6 Conclusion

A device has been developed, the parallel nano-scanning calorimeter, which combines nano-calorimetry and combinatorial methods to create a powerful instrument for materials screening and analysis. The device consists of a substrate with an array of micromachined nano-calorimeter sensors, each one of which is individually addressable. The nano-calorimeter sensors are very sensitive with a resolution of approximately 10 nJ/K, allowing thermal analysis of very small quantities of material. The small mass of the sensors makes it possible to achieve heating rates as fast as $10^4$ K/s, thus making the device a useful tool for exploring the kinetics of phase transformations and reactions. Measurements can be performed over a temperature range from room temperature to approximately 900°C. By depositing samples with a composition gradient onto the PnSC, combinatorial studies can be performed much faster than by conventional techniques. In short, the PnSC enables the thermal study of complex materials systems at the nano- and the micro-scale. The capability of the PnSC is demonstrated by applying it to a 25 nm coating of indium and to a library of thin-film Ni-Ti-Zr samples. The PnSC readily detects the melting point of the indium coating. After the first heating cycle, the indium breaks up into islands with a wide size distribution. The peak melting temperature, which corresponds to the melting of the larger islands, is in good agreement with the bulk value. The average specific heat of fusion, however, is depressed below the bulk value because of the size dispersion of the indium islands. The characterization of the Ni-Ti-Zr sample library illustrates the use of the PnSC device in combinatorial studies. As-deposited Ni-Ti-Zr samples are amorphous and are crystallized during the first temperature scan. The PnSC readily reveals the crystallization reaction, as well as the glass transition temperature of the samples in their amorphous state. After crystallization, the martensite
transformation is detected in a subset of the samples depending on chemical composition.

### 3.8 Appendix B: Temperature uniformity

The assumption of temperature uniformity of the control volume CV can be addressed by considering the temperature gradients in the $x$, $y$, and $z$-directions (Fig. 3.2). Starting with the $z$-direction, we can take the temperature in this direction to be uniform because at the time scale of the measurements the thermal diffusion length is generally much longer than the sensor thickness. The relationship between the diffusion length and the length scale relevant to a problem is commonly represented by the Fourier number, $F_o = \frac{\alpha t}{h^2}$, where $\alpha$ is the thermal diffusivity, $t$ is the relevant timescale for the problem, and $h$ is the length scale. Even the worst-case scenario of a 1 $\mu$m sample of silicon nitride and an experimental sampling rate of 100 kHz yields a Fourier number in excess of ten. For comparison, a simple one-dimensional model shows that the temperature deviation in the sample is less than 1% of the measured temperature if the Fourier number is greater than two. This example uses the shortest relevant timescale for the measurements and a relatively thick and poorly conducting sample, yet the Fourier number is still approximately five times the value that would produce a 1% temperature deviation. This analysis demonstrates that the temperature through the thickness can be considered uniform, i.e., the temperature measured at the thermistor is also the temperature of the sample. Similar findings have been demonstrated using finite elements (Ch. 2).

The temperature distribution in the $y$-direction can be estimated by assuming the shape of the steady-state solution (a worst-case assumption) to the one-dimensional diffusion problem with uniform heat generation, i.e., a parabolic temperature distribution. The temperature distribution is defined by considering the symmetry of the heating element, which causes the temperature gradient at the center of the heater to be zero, $\left.\frac{dT}{dy}\right|_{\text{center}} = 0$, and the fact that the temperature and heat flow must be continuous across the CV-membrane
transition, \( k_{CV} A_{CV} \frac{dT}{dy} = k_M A_M \frac{dT}{dy} \), where the subscripts \( CV \) and \( M \) denote control volume and membrane values, respectively. By assuming a constant heating rate of the thermistor and neglecting radiation from the membrane, the temperature gradient in the membrane at the edge of the thermistor can be defined as, \( \left( \frac{dT}{dy} \right)_M = -2 \sqrt{\pi / (\pi \alpha)} T \). The temperature profile can then be written as,

\[
T = T_0 + T \left( t - \frac{2}{\sqrt{\pi}} \frac{A_M k_M}{A_{CV} k_{CV}} \alpha_M^{-1/2} \left( \frac{y^2}{w} - \frac{w}{12} \right) \sqrt{t} \right),
\] (3.B1)

with the origin of \( y \) at the center of the heater. Equation (3.B1) can be used to calculate the standard deviation of the temperature \( s_T \), which is a measure of the temperature non-uniformity in the heater. For example, using literature materials properties (Table 3.B1) and a typical heating rate \( (\dot{T} = 15 \times 10^3 \text{ K/s}) \) yields \( s_T = 0.4 \% \) for an empty sensor at 400°C. For a sensor at 900°C and the same heating rate, we find \( s_T = 0.3 \% \). The addition of a sample increases the difference in conductance between the membrane and the CV, reducing the gradient at the edge of the thermistor and improving the temperature uniformity.

**Table 3.B1: Thermal properties of PnSC materials [16, 35-37].**

<table>
<thead>
<tr>
<th>Material</th>
<th>( k ) (W/m K)</th>
<th>( \rho ) (kg/m³)</th>
<th>( c_p ) (J/kg K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermistor (W)</td>
<td>174</td>
<td>19300</td>
<td>132</td>
</tr>
<tr>
<td>Membrane (SiNx)</td>
<td>3.2</td>
<td>3000</td>
<td>700</td>
</tr>
<tr>
<td>Sample (NiTi)</td>
<td>5.5</td>
<td>6500</td>
<td>500</td>
</tr>
</tbody>
</table>

The temperature non-uniformity in the \( x \)-direction can be estimated by solving for the approximate one-dimensional temperature distribution along the length of the heater, governed by,

\[
V_h (\rho c_p) \frac{\partial T}{\partial t} = V_h k_h \frac{\partial^2 T}{\partial x^2} - \frac{2}{\sqrt{\pi}} A_M \Phi_M \sqrt{t} \frac{\partial T}{\partial t} - 2A_M \varepsilon_m \sigma (T^4 - T_0^4) + P_h
\] (3.B2a)

with boundary and initial conditions all equal to the initial temperature \( T_0 \),

\[
T[x,0] = T[0,t] = T[l,0] = T_0 \quad t \geq 0.
\] (3.B2b)
In Eqn. (3.B2a), $V_H$ is the volume of the heater including the silicon nitride in direct contact with the heater and any sample. As the sample is discontinuous along the length of the heater, the volume and thermal properties along the heater are discontinuous as well. With this in mind, $(\rho c_P)_H$ is the effective volumetric heat capacity and $k_H$ is the effective thermal conductivity along the heater. The second term on the right hand side represents the heat loss into the membrane for a constant heating rate, with $A_M$ as the cross-section area of the membrane perpendicular to the heater, and $\phi_M$ is the thermal effusivity of the membrane where $\phi_M = (k_M (\rho c_P)_M)^{1/2}$. The third term represents the radiative heat loss from the heater, and $P_H$ is the power dissipated in the heater. Equation (3.B2) was solved for a cell with a sample by the finite difference method using literature values for materials properties (Table 3.B1) and typical experimental parameters (see Experimental section). For the region inside the voltage probes, the standard deviation of the temperature is better than 1% at moderately elevated temperatures ($T < 450 ^\circ C$) and better than 6% at elevated temperatures ($T < 950 ^\circ C$). This result shows that for typical experiments the temperature distribution in the CV is quite uniform. Consequently, the assumption, $Q_x = 0$, in the thermal analysis is valid (Ch. 2), and peak broadening is minimal for short measurement times.

### 3.9 References


Chapter 3: Combinatorial nano-calorimetry

Chapter 3: Combinatorial nano-calorimetry


Chapter 4

Glass transition and crystallization of amorphous Ni-Ti-Zr thin films by combinatorial nano-calorimetry

4.1 Summary

The glass transition and devitrification of Ni-Ti-Zr thin films were analyzed as a function of composition using a high-throughput array of nano-calorimeters. The 290 nm thin-film samples were heated to 900°C at a rate of approximately $15 \times 10^3$ K/s, resulting in nanocrystalline grains and non-equilibrium phases. The calorimetry scans reveal the glass transition, as well as a multi-stage crystallization process. Features of the calorimetry traces correlate one-to-one with the resulting crystal phases, as determined by x-ray diffraction.

4.2 Introduction

Ni-Ti-Zr is a promising alloy for micro-electro-mechanical systems (MEMS) because of its known glass forming ability [1] and shape memory properties [2]. The high strength, and yield strain, along with low damping make
metallic glasses (MG) prime candidates for structural elements in MEMS [3]. The advantages of shape memory alloys (SMA) used as high-power-density actuators are also well known [4]. One can envision using the positive aspects of each phase by crystallization through local heating, making possible elastic hinges (MG) and actuators (SMA) from a single film [5]. The materials properties of MGs and SMAs depend sensitively on composition and synthesis [2, 6-8], an important consideration for optimizing MEMS device performance, and a motivating factor for combinatorial methods [6, 9].

Recently combinatorial methods have been extended to include techniques for determining thermal properties of thin-film materials through the use of membrane-based thermal sensor arrays [10, 11]. The parallel nano-scanning calorimeter (PnSC) is such a device; the technique is characterized by fast heating rates (1-100 K/ms) and high sensitivity (10 nJ/K), enabling precise calorimetry measurements on sample masses as small as a few hundred nanograms. The PnSC consists of a Si substrate with a 5×5 array of membrane calorimeters, described in detail elsewhere [11]; here it was used to study the crystallization behavior of amorphous Ni-Ti-Zr samples as a function of composition.

### 4.3 Experimental method

Ni-Ti-Zr samples were deposited onto a PnSC substrate using a magnetron sputter system (AJA Int., Inc., Scituate, MA) with three elemental targets to a thickness of approximately 290 nm and mass of approximately 3.6 μg. The inclination of the sputter guns was set to generate a combined uniform deposition flux, while generating a composition gradient across the substrate. Sample composition was measured by energy and wavelength dispersive x-ray spectroscopy [11]. The as-deposited Ni-Ti-Zr samples were confirmed as amorphous by x-ray diffraction (XRD) and crystallized at a heating rate of approximately 15×10^3 K/s to a temperature of approximately 900°C. Two additional cycles were performed under the same conditions to stabilize the microstructure. The crystallized samples were then re-measured ten times under
the same conditions to create the reference measurements. XRD measurements were performed on the crystallized samples using a Brucker D8 system with a Cu Kα x-ray radiation source and a Vantec2000 2D area detector. XRD results were analyzed with the commercially available HighScore Plus software by PANalytical.

4.4 Results and discussion

4.4.1 Glass transition and surface crystallization

Figure 4.1(a) shows representative calorimetry traces over the entire temperature range; Fig. 4.1(b) shows the temperature range right below crystallization. The calorimetry traces lack the exothermic feature, associated with structural relaxation, typically observed before the glass transition. This process is suppressed due to the fast heating. For all samples, the glass transition

Figure 4.1: (a) Examples of crystallization peak shapes in the calorimetric trace (offset for clarity), where exothermic is negative. The symbols represent different calorimetry trace types as described in the text. (b) Calorimetric signal showing glass transition and surface crystallization behavior in samples with a nominal Ni concentration of 51%.
Chapter 4: Glass transition and crystallization of Ni-Ti-Zr

temperature $T_G$ is determined by the first significant endothermic deviation of the calorimetry trace from a linear-baseline fit to the low-temperature data. $T_G$ was detected in all samples except for two: Ni$_{53}$Ti$_{32}$Zr$_{15}$ and Ni$_{50}$Ti$_{34}$Zr$_{16}$. Here, the glass transition is obscured by a strong surface crystallization feature. In general, by shifting the crystallization process to higher temperatures, the high heating rates in these experiments make the glass transition more visible than in traditional calorimetry [2, 12, 13]. The $T_G$ results do not show any correlation with composition and can be described by a mean value and standard deviation of $T_G = 467 \pm 26^\circ$C. The high effective cooling rate of the sputter deposition process causes the material to become glassy at a high effective $T_G$ with large amounts of free volume. The high heating rates of the calorimetry scan prevent the material from relaxing structurally, so that the initial isoconfigurational state is maintained on heating, implying that the detected $T_G$ is the same as the fictive temperature of the as-deposited material.

At temperatures above $T_G$, the material has sufficient mobility to crystallize. This process starts from the surface in some samples as evidenced by the small exothermic peak preceding the larger exothermic peak (Fig. 4.1(b)) [14]. The relative amount of surface crystallization can be determined by comparing the corresponding change in enthalpy. This is accomplished by integrating the areas between the various calorimetry traces and the trace showing the least surface crystallization. The results of this analysis are shown as a function of composition in Fig. 4.2(a). It is apparent from the figure that surface crystallization, on average, decreases with increasing Ti content. Surface crystallization arises from a reduction in the energy barrier to form a nucleus at an interface. As such, the process is sensitive to composition, as previously demonstrated for the NiTi system [15].
4.4.2 Volume crystallization

As the temperature increases the samples begin to crystallize in the volume of the sample. The crystallization process manifests in various multi-peak calorimetry traces. Each crystallization curve can be grouped into one of three calorimetry trace types (Fig. 4.1(a)): a singular primary crystallization peak (O), a primary crystallization peak with a secondary peak/shoulder on the high-temperature side (□), and a primary crystallization peak with a secondary peak/shoulder on the high-temperature side plus an additional high-temperature peak (△). The three △-type curves in Fig. 4.1(a) demonstrate how the secondary shoulder/peak grows with increasing Ni content.

Figure 4.2(b) clearly shows that the calorimetry trace types group together as a function of composition. Figure 4.2(b) also shows the temperature of peak crystallization, $T_C$, which occurs between 660 and 735°C, with a minimum around 49% Ni. The lowest temperature recorded for the onset of crystallization
(\sim 580^\circ C) is well above crystallization temperatures recorded by conventional calorimetry (\sim 480^\circ C) [2] because of the fast heating rates in this study.

The enthalpy of formation $h_f$ is calculated from the calorimetry trace, starting with the onset of surface crystallization and including the primary peak and secondary peak/shoulder (when present), using a split-baseline construction [16]. The enthalpy is independent of composition, with an average value of 74 \pm 11 \text{J/g}. It is interesting to note that $h_f$ does not increase with the growth of the secondary peak or depend on the amount of surface crystallization. The measured values of $h_f$ are larger than reported values for Ni-Ti thin films measured by traditional scanning calorimetry, 36 \text{J/g} [17]. A similar disparity in $h_f$ has been observed for Ni-Ti-Hf coatings grown under the same conditions and measured by PnSC and traditional calorimetry [18]. This difference is attributed to the suppression of structural relaxation on heating [19] and the combination of primary and secondary crystallization features.

## 4.4.3 Crystal phase results and comparison to calorimetry

Figure 4.3 shows typical XRD spectra obtained for crystallized Ni-Ti-Zr samples. The crystallization process results in different phase compositions depending on the chemical composition of the samples. The two rows of samples with the lowest Ni content contain both Ni(Ti,Zr) austenite and martensite [20, 21] with some additional weak peaks. As the Ni content increases, the Ni$_{10}$(Zr,Ti)$_7$ phase with a Ni$_{10}$Zr$_7$ base structure [13] forms and the intensity of the corresponding peaks increases continuously with increasing Ni content. While no martensite peaks are detected above 47\% Ni, the austenite peaks persists, albeit with reducing intensity as Ni increases. The trends in peak intensity with Ni content hold true in general except for the two samples with the lowest Zr content: Ni$_{53}$Ti$_{32}$Zr$_{15}$ and Ni$_{50}$Ti$_{34}$Zr$_{16}$. For these samples, the strongest peaks can be indexed as NiTi austenite [22] and (Ti,Zr)$_2$Ni with a Ti$_2$Ni base structure [23, 24]. The XRD spectra were clustered into like-groups using the cluster analysis feature of HighScore Plus, which is an agglomerative clustering scheme that determines the similarity of XRD spectra based on the sum of the squared
differences in intensity as a function of scattering angle. Since the diffraction peaks are associated with particular phases, this process necessarily clusters the phases in the samples, as illustrated in Fig. 4.4.

With the calorimetry and XRD results presented, it is now possible to elucidate the relationship between both. There exists a one-to-one correspondence between the calorimetry trace groupings, as shown in Fig. 4.2(b),
and the phase regions in Fig. 4.4. This correspondence suggests the following explanation: 1) the primary crystallization peak corresponds to the formation of the Ni(Ti,Zr) austenite phase, 2) the secondary peak/shoulder is a phase-separation reaction that forms (Ti,Zr)$_2$Ni, and 3) the high-temperature peak is related to the formation of Ni$_{10}$(Zr,Ti)$_7$, at the expense of Ni(Ti,Zr). For Ni < 50% the (Ti,Zr)$_2$Ni phase is expected based on the equilibrium ternary phase diagram [24, 25], the Ni$_{10}$(Zr,Ti)$_7$ phase is not; instead, a Laves phase is predicted in this composition range. Also, the (Ti,Zr)$_2$Ni phase persists for Ni > 50%, which shows that Zr increases the solubility of Ni for this phase as compared to the binary Ni-Ti system. Additionally, some subtler observations can be made by comparing the combinatorial data sets. Trace amounts of Ni$_{10}$(Zr,Ti)$_7$ can be detected from the XRD spectra in samples from region I that show a high-temperature peak in the calorimetry trace (see the 47% Ni curves in Figs. 4.1(a) and 4.3). The intensities of the peaks in this region were too weak to be significant in the cluster analysis algorithm. Combination of the calorimetry data and the XRD spectra, and the trends in the XRD data enabled identification of these very weak peaks. Finally, (Ti,Zr)$_2$Ni is expected in region-II due to the existence of the secondary peak/shoulder in the calorimetry trace for samples in this region; however the corresponding XRD peaks cannot be confirmed because of overlapping Ni$_{10}$(Zr,Ti)$_7$ peaks.
4.4.4 The effects of fast heating

The fast heating rates are the essential difference between this study and the formation of samples in earlier studies [2, 24, 25]. The fast heating rates suppress the Laves phase, presumably because of relatively slow formation kinetics. The fast heating rates also result in a very fine (5–20 nm) grain structure and some remaining amorphous material at the grain boundaries, as observed by TEM (not shown). Samples from region III (Fig. 4.4) show more amorphous material remaining than samples from region I, indicating that the kinetics are slower in this composition region. Further confirmation of the above crystallization process would require analyzing the structure of the samples at

Figure 4.4: Schematic showing the various phases in the crystallized samples as a function of composition. Solid lines separate regions with distinct phase compositions as determined by the cluster analysis of the XRD spectra. The phases between curly brackets refer to trace amounts: Region-I contains minor precipitation of \((\text{Ti,Zr})_2\text{Ni}\) and \(\text{Ni}_{10}(\text{Ti,Zr})_7\) as determined by TEM and XRD, respectively. Region-II is expected to contain \((\text{Ti,Zr})_2\text{Ni}\) from calorimetry as described in the text.
various points during the heating procedure, followed by a long-term anneal to equilibrate the structure, a natural extension of the present study.

4.5 Conclusion

In summary, the PnSC has been used to analyze a combinatorial library of amorphous Ni-Ti-Zr thin-film samples to determine their glass transition and crystallization characteristics. The results of the experimental techniques provide the following conclusions: 1) The crystallization proceeds as a multi-stage process, starting with surface crystallization followed by volume crystallization of Ni(Ti,Zr). Next, precipitates of (Ti,Zr)\textsubscript{2}Ni form, especially at high Ni content, and finally Ni\textsubscript{10}(Zr,Ti)\textsubscript{7} forms at high temperature in some samples. The groupings of the calorimetry traces with similar features compare one-to-one with the resulting phases determined by XRD, and the variation of both data sets with composition allows identification of the features in the calorimetry traces. 2) \( T_c \) was shown to be independent of composition, which along with the lack of structural relaxation provides evidence that this \( T_c \) is for the as-deposited structure. 3) The fast heating and cooling rates lead to fine nanocrystalline grains and suppression of the Laves phase. 4) The amount of surface crystallization was shown to decrease with increasing Ti content. This type of study is not limited to Ni-Ti-Zr, but applicable to a wide range of materials systems and could help to accelerate materials analysis and discovery.

4.6 References

Chapter 4: Glass transition and crystallization of Ni-Ti-Zr

Chapter 5

Precipitation and thermal fatigue in Ni-Ti-Zr shape memory alloy thin films by combinatorial nano-calorimetry

5.1 Summary

Thin-film (290 nm) samples of Ni-Ti-Zr shape memory alloy were studied to determine the effects of ultra-fast (15 K/ms), high-temperature (900°C) heat treatments and low-temperature (450°C) thermal cycling on the characteristics of the martensite transformation by combinatorial nano-calorimetry. Samples showed a compositionally dependent response to heat treatments controlled by precipitation. Thermal fatigue behavior induced by thermal cycling was improved, compared to previous results, with a minimum transformation temperature reduction of just 11°C over 100 cycles. Improvement can be explained by the Hall-Petch relation and reduced plastic deformation.
5.2 Introduction

Shape memory alloys (SMA) have the ability to do work as a result of the martensite to austenite (M-A) phase transformation, which entails a shape change in the crystal lattice from lesser to greater symmetry. SMA demonstrate enhanced power density compared to other functional materials when used as an actuator, thus SMA are useful as thin-film actuators in microelectromechanical systems (MEMS) [1]. Modern MEMS fabrication techniques increasingly include novel and exotic materials to obtain specific functionality; some of these materials could be damaged by exposure to high temperatures. Since many SMA are deposited as amorphous coatings they require heat to crystallize. Fabrication may be simplified by crystallizing the films with local heating [2, 3], obviating the need to heat the entire device. SMA materials properties are sensitive to synthesis methods, however relatively few studies exist on SMA properties synthesized by local heating, which can involve ultra-fast heating and cooling rates, resulting in ultra-fine (5-20 nm) grain structures (Fig. 1.7).

SMA components are typically expected to perform multiple cycles over the lifetime of a device, thus an important metric for acceptable material performance is repeatable actuation. While Ni-Ti-Zr benefits from a controllable actuation temperature, by varying Zr concentration [4, 5], it tends to suffer from instabilities associated with thermal cycling, i.e. thermal fatigue [5-7]. These instabilities have been associated with geometric incompatibilities between the austenite and martensite phase, resulting in stresses and plastic deformation. Recent work has shown that this driving force for thermal fatigue can be reduced by tailoring the interface through combinatorics [8]. While this approach demonstrates the ability to nearly eliminate thermal fatigue, a potential drawback is the loss of control over the transformation temperature. Other work has shown that increasing the barrier to dislocation motion by precipitation hardening [9] or grain refinement [10] can stabilize the transformation behavior. An advantage of reducing the grain size to limit thermal fatigue is that it is composition independent and therefore control over the transformation temperature is maintained. However, geometric compatibility and precipitation
do vary with composition, therefore a study of precipitation and thermal fatigue as a function of composition in nano-grained SMA is necessary to characterize material performance.

The parallel nano-scanning calorimeter (PnSC) is the ideal instrument for studying the M-A transformation as a function of composition, heat treatments and thermal cycling in SMA films. The PnSC consists of an array of ultra-sensitive (~ 10 nJ/K) membrane calorimeters, which are capable of extreme heating rates (~ 10^5 K/s). The array design facilitates the creation of combinatorial libraries of samples, while the extreme heating rates enable novel heat treatment conditions and fast thermal cycling measurements. These characteristics are used to reveal the effect of heat treatments and thermal cycling on the M-A transformation in Ni-Ti-Zr thin films as a function of composition.

5.3 Experimental method

Samples were prepared by co-sputtering from 3 elemental targets through a shadow mask using a magnetron sputtering system (AJA Int., Scituate, MA) to create a 5x5 combinatorial library of amorphous Ni-Ti-Zr samples on the PnSC. The sputtering conditions were arranged such that the compositions of the samples varied (45-53 at.% Ni, 28-39 at.% Ti, 15-23 at.% Zr) while the thicknesses remained approximately uniform (290 ± 10 nm). The samples were crystallized by a 15x10^3 K/s temperature ramp to 900°C, followed by 2 microstructure stabilization cycles under similar conditions. At this point the samples were subjected to 100 cycles of a 20x10^3 K/s temperature ramp to 450°C. Then the high-temperature (HT, i.e., 900°C) cycles were performed 10 more times and then the low-temperature (LT, i.e., 450°C) cycles were performed an additional 100 times. Finally, an anneal at 450°C for 8 hours was performed on the entire PnSC device in an ultra-high vacuum (10^-8 Torr) furnace, after which a final 100 low-temperature cycles were performed. All told, this type of study consists of over 10,000 calorimetric measurements with a corresponding total measurement time of approximately 5 minutes. As a comparison, a similar study using traditional
calorimeters [5-7] would take approximately 180 days of continuous measurement time to perform the same measurements. X-ray diffraction (XRD) was performed with a Brucker D8 system with a Cu Kα x-ray radiation source and a Vantec2000 2D area detector, and results were analyzed with the commercially available HighScore Plus software by PANalytical.

5.4 Results and discussion

5.4.1 Precipitation

A typical result (for Zr > 18%) of the HT heat treatment effect on the M-A transformation can be found in Fig. 5.1. The HT heat treatments cause a step-wise evolution of the M-A transformation peak in the calorimetric signal (Fig. 5.1(a)). The specific enthalpy of the M-A transformation $h_{\text{M-A}}$ remains stable for the first few HT cycles and then decreases with additional cycles (Fig. 5.1(b)). At the same time, the peak transformation temperature $T_{\text{M-A}}$ rises at first, goes through a maximum and then falls (Fig. 5.1(c)). Figure 5.2 shows the evolution of $T_{\text{M-A}}$ with HT heat treatments as a function of Zr content. At approximately 18 at.% Zr there is little change in $T_{\text{M-A}}$ while below this composition $T_{\text{M-A}}$ tends to increase and above 18 at.% Zr it tends to decrease.

The trends in the M-A transformation results (Fig. 5.1) with HT heat treatments can be explained by the precipitation of secondary phases from the SMA phase. Initially the precipitates will be a small volume fraction of the material and the formation will cause little change in the composition of the surrounding matrix. The precipitates do cause internal stresses that can be relaxed by the self-accommodating twin variants of the martensite phase. The stress relaxation reduces the overall strain energy and stabilizes the martensite phase over the austenite phase, which increases $T_{\text{M-A}}$ during the initial stages of HT evolution (Fig. 5.1(c)). With additional HT heat treatments the precipitates continue to nucleate and grow and begin to change the composition of the SMA matrix more significantly. Eventually the change in strain energy becomes less
important than the change in enthalpic and entropic energies between the martensite and austenite phases, resulting from the composition shift. For the Ni$_{44.7}$Ti$_{35.7}$Zr$_{19.6}$ sample this causes $T_{M-A}$ to decrease.

The phase of the precipitate depends on the chemical composition of the sample, which explains the trends in $T_{M-A}$ with HT heat treatments (Fig. 5.2). For samples with a Zr concentration below 18 at.%, the primary precipitate is expected to be the Ti$_2$Ni base phase [4, 11], which increases the Zr content in the SMA phase and thus increases the transformation temperature. While for
samples with a Zr concentration above 18 at.%, the primary precipitation is expected to be Ni$_{10}$Zr$_7$ [4], which reduces the Zr content in the SMA phase, thus decreases the transformation temperature. Finally, the trends of $h_{M-A}$ with HT heat treatments (Fig. 5.1(b)) agree with the precipitation explanation. The fact that $h_{M-A}$ initially remains stable rather than increasing with HT heat treatments excludes grain growth by crystallization of remaining amorphous material as a mechanism for the initial increase in $T_{M-A}$. Also, the reduction of $h_{M-A}$ during the later stages of heat treatments agrees with the reduction of the SMA phase due to precipitation of secondary phases. This is not a temperature related effect since $h_{M-A}$ reduces regardless of the trend in temperature.

Fig. 5.2: Evolution of the martensite-austenite transformation peak temperature with high-temperature heat treatments as a function of Zr concentration.
5.4.2 Thermal fatigue

The effect of LT thermal cycling on the M-A transformation is demonstrated in Fig. 5.3. The evolution of the M-A transformation peak with LT thermal cycling in the calorimetric signal is shown in Fig. 5.3(a). The specific enthalpy of the transformation reduces with thermal cycling (Fig. 5.3(b)) along with the transformation-peak temperature (Fig. 5.3(c)). Figure 5.3(b) and (c) also show a temperature shift with each cycle.

Fig. 5.3: Thermal fatigue of the martensite-austenite transformation, for the Ni$_{44.7}$Ti$_{37.1}$Zr$_{18.2}$ sample, in the calorimetric signal (a), enthalpy (b), and temperature (c).
show that after 10 additional HT heat treatments the thermal fatigue mechanism is reset so that the enthalpy and temperature of the M-A transformation again reduce with thermal cycling.

Figure 5.4 shows the effect of the fatigue mechanism on the M-A transformation-peak temperature for 45 at.% Ni and multiple Zr concentrations. When comparing a sample’s thermal fatigue behavior, at a high number of cycles, before (Fig. 5.4(a)) and after (Fig. 5.4(b)) the additional HT heat treatments, no significant change can be detected. However, the initial drop in temperature between cycle 1 and 2 $\Delta_{1\rightarrow2}T_{M-A}$ is larger after the heat treatments. The difference in $\Delta_{1\rightarrow2}T_{M-A}$ is most obvious when comparing the average for all samples (Table 5.1). Table 5.1 also demonstrates that the average temperature drop between cycles 2 and 100 $\Delta_{2\rightarrow100}T_{M-A}$ and the average rate of change of temperature per cycle at the end of cycling $dT_{M-A}/dC_{100}$ are relatively independent of the number of heat treatments. After 100 cycles, the fatigue rate is small but not entirely exhausted, which contrasts previous claims [5,7].

When comparing samples across composition, significant differences are observed in both short and long-term fatigue behavior. A compositional dependence is observed in $dT_{M-A}/dC_{100}$ as it goes through a minimum around 18
at.\% Zr after 13 HT heat treatments. This dependence is in agreement with the sample showing the least thermal fatigue, Ni_{44.6}Ti_{32.8}Zr_{22.6} (-11 K for 100 cycles). The average thermal fatigue for samples in this study is less than that observed from previous studies that have temperature reductions in the 43-60 K range for 100 cycles [5,6]. The Ni_{44.6}Ti_{32.8}Zr_{22.6} sample is particularly stable and appears to be a new level of stability for this materials system [5-7].

The trends of the M-A transformation with LT thermal cycling can be explained by the accumulation of plastic deformation [12]. The fact that the magnitude of $\Delta T_{M-A}$ increases after the additional HT heat treatments demonstrates that the heat treatments anneal the dislocations and that the nucleation and growth of precipitates causes a greater constraint on the initial transformation. The results also show that once enough dislocations are formed (within the first few cycles) then the thermal fatigue behavior is similar before and after heat treatments, which is expected because the same deformation mechanism is active. The thermal fatigue is likely reduced in this study compared to previous results for Ni-Ti-Zr because of the small grain size and the well-known Hall-Petch relation, which relates the reduction in grain size to an increase in the critical stress for plastic deformation [13]. In fact, these materials

<table>
<thead>
<tr>
<th>Sample Composition (at.%)</th>
<th>After 3 HT Heat Treatments</th>
<th>After 13 HT Heat Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta T_{M-A}$ (K)</td>
<td>$\Delta T_{100/M-A}$ (K)</td>
</tr>
<tr>
<td>Ni_{46.4}Ti_{37.1}Zr_{16.5}</td>
<td>-0.4±0.7</td>
<td>-21.8±0.3</td>
</tr>
<tr>
<td>Ni_{44.6}Ti_{38.5}Zr_{16.9}</td>
<td>-3.7±1.0</td>
<td>-8.1±0.5</td>
</tr>
<tr>
<td>Ni_{46.6}Ti_{35.7}Zr_{17.7}</td>
<td>-3.7±0.5</td>
<td>-30.4±0.2</td>
</tr>
<tr>
<td>Ni_{44.7}Ti_{37.1}Zr_{18.2}</td>
<td>-2.8±0.6</td>
<td>-29.3±0.3</td>
</tr>
<tr>
<td>Ni_{46.8}Ti_{34.3}Zr_{18.9}</td>
<td>0.8±13.8</td>
<td>-26.7±6.2</td>
</tr>
<tr>
<td>Ni_{44.7}Ti_{35.2}Zr_{19.6}</td>
<td>-0.1±0.6</td>
<td>-28.1±0.3</td>
</tr>
<tr>
<td>Ni_{46.6}Ti_{33.0}Zr_{20.4}</td>
<td>-5.8±15.5</td>
<td>-16.7±7.0</td>
</tr>
<tr>
<td>Ni_{44.7}Ti_{34.2}Zr_{21.0}</td>
<td>-0.8±1.0</td>
<td>-28.5±0.5</td>
</tr>
<tr>
<td>Ni_{44.6}Ti_{31.7}Zr_{21.9}</td>
<td>1.9±3.8</td>
<td>[-20.9±1.7]               [-0.33±0.06]</td>
</tr>
<tr>
<td>Ni_{44.4}Ti_{32.3}Zr_{22.6}</td>
<td>-1.1±2.3</td>
<td>[-10.7±1.0]               [-0.18±0.03]</td>
</tr>
<tr>
<td>Weighted Mean</td>
<td>-2.2±0.3</td>
<td>-26.9±0.1</td>
</tr>
</tbody>
</table>

Table 5.1: The effect of thermal cycling on the martensite-austenite transformation temperature. Note: bracketed values were not used to calculate the error weighted average because 100 cycles were not recorded, the actual number of cycles being 50* and 30††.
are around the optimal size for increased strength [14], with grain size diameters determined from transmission electron microscopy (1.7) in the 5-20 nm range. Since the grain size is relatively constant, this mechanism cannot explain the minimum of thermal fatigue observed in the Ni\textsubscript{44.6}Ti\textsubscript{32.8}Zr\textsubscript{22.6} sample. This minimum may be explained by variations in precipitation or an improved geometrical compatibility between the austenite and martensite phases. The Ni\textsubscript{44.6}Ti\textsubscript{32.8}Zr\textsubscript{22.6} composition provides a good starting point for such studies. However in its present form, the Ni\textsubscript{44.6}Ti\textsubscript{32.8}Zr\textsubscript{22.6} material may already be stable enough for some applications, as it already shows improved thermal fatigue behavior over some NiTi binary results [8], a materials system which has seen wide application.

### 5.4.3 Equilibrium phases

The short HT heat treatments cause the material to incrementally step toward equilibrium, limited by kinetics. The evidence of this process is provided by the evolution in M-A transformation characteristics caused by precipitation. A long-term anneal equilibrates the samples and grows the grains, potentially increasing $T_{M-A}$ and causing non-transforming samples to transform. However $T_{M-A}$ was not increased and the instability of the austenite phase at 450°C and non-stoichiometry of the samples caused a decomposition to other phases. This result was determined from PnSC measurements, which did not exhibit a M-A transformation peak and XRD measurements, which did not indicate the presence the martensite phase. The phase analysis revealed that the primary phase detected in all samples was the NiTi hexagonal phase [15], accompanied by various other intermetallic phases. The next most significant phases were distributed primarily as a function of Ni Content: most Ni rich samples had the Ni\textsubscript{11}Zr\textsubscript{9} tetragonal phase [16], equiatomic samples demonstrated NiTi austenite [17], and the Ni poor samples had the Ti\textsubscript{62}Zr\textsubscript{38} hexagonal phase [18]. These results suggest that a higher annealing temperature should be used, i.e. above 630°C where the NiTi austenite phase is stable, and where more grain growth could be produced.
5.5 Conclusion

In summary, a combinatorial study of the martensite-austenite transformation in Ni-Ti-Zr shape memory alloys was performed as a function of high-temperature heat treatments and low temperature thermal cycling. Ultra-fast heating rates facilitate this type of study by reducing measurement times 4 orders of magnitude over previous studies. Changes in the enthalpy and temperature of the M-A transformation with HT heat treatments were explained by the precipitation of secondary phases, which alter the strain energy of the material and enthalpic and entropic energies of the SMA phases. The change in $T_{M-A}$ was shown to depend on the Zr concentration in the sample, and explained by the precipitation of different phases as a function of Zr content. Changes in the M-A transformation characteristics with LT thermal cycling were explained by the accumulation of plastic deformation and the associated reduction in internal stresses. The sample demonstrating the minimum thermal fatigue appears to be a new level of stability in the Ni-Ti-Zr materials system.

5.6 References

Chapter 5: Precipitation and thermal fatigue in Ni-Ti-Zr


6.1 Summary

Thermal sensor arrays were successfully designed, developed and tested. These instruments have proven useful in the analysis of complex nanoscale materials systems. The nano-thermal transport array (nTTA) was used to analyze the thermal transport properties of thin copper multilayers as a function of film thickness. The parallel nano-scanning calorimeter (PnSC) was used to analyze a library of thin film Ni-Ti-Zr samples as a function of composition. This chapter provides some concluding remarks and direction for future work. Here, the major findings of this work are reviewed. The ongoing work in the Vlassak Group at Harvard University is outlined. The sections on future work provides some guidance and interesting directions that may be pursued.

6.2 Conclusions

6.2.1 nano-Thermal transport array
The nTTA is a device for the rapid analysis of thermal transport properties of thin films using a high-throughput methodology. Sample libraries can be deposited using conventional deposition techniques and samples can be parameterized by thickness, composition, etc. The sensor interface is simple, requiring just 4 contacts per sensor, which is less than many other comparable sensor designs, while still providing a power and temperature measurement. The data analysis is also fast because it is based on an analytical model rather than a finite element model, which is used by some comparable devices. The analytical model can be used without loss of accuracy, as it was shown to agree with the finite element model to within 3%.

The nTTA is applicable over a wide range of materials systems and film thicknesses. Thermal conductivity measurements were demonstrated for copper films ranging from 15 to 480 nm, where 15 nm << the bulk mean free path of electrons in copper << 480 nm. In other words, this measurement range spans nanoscale and bulk thermal transport properties, allowing a direct comparison using one device. The thermal conductance of the sample films ranged from approximately 1 to 1000 nW m/K, demonstrating the wide range of thermal properties measurable by nTTA and hence materials systems at various thicknesses. A sensitivity analysis provides a direct means to determine the applicability of the nTTA to other film thicknesses and materials systems. The experimental results for the thermal conductivity of thin copper multilayers showed good agreement to the predictions of the thermal conductivity model by Qiu and Tien. This model relates the reduced thermal conductivity in nanoscale structures to the bulk thermal conductivity and the scattering of electrons from interfaces. The good agreement of experimental results to this model shows that the electron scattering mechanism causes the reduction in measured thermal conductivities.

6.2.2 Parallel nano-scanning calorimeter

The PnSC integrates combinatorial methods and nano-calorimeters to create a powerful tool for the rapid analysis and discovery of complex nanoscale
Chapter 6: Conclusions and future work

materials systems. Combinatorial sample libraries can be created on the PnSC using conventional sputtering techniques and vary in terms of composition, thickness, heat treatments, etc. Sample libraries can be measured very quickly because of the ultra-fast heating rate capability of the PnSC, reducing measurement times up to 5 orders of magnitude compared to traditional calorimeters. This capability makes the PnSC ideal for scanning combinatorial libraries and for performing in-situ heat treatments and thermal cycling studies. The extremely small addendum (approximately 100 nJ/K) and thermal conductance (approximately 1 nW m/K) of nano-calorimeters significantly improves sensitivity (approximately 10 nJ/K) compared to traditional calorimeters.

The sensitivity of the PnSC was demonstrated through the melting transformation of a 25 nm indium thin film. The peak melting temperature compared almost exactly with the bulk value, confirming the calibration of the sensors. The specific heat of fusion was shown to be slightly reduced compared to the bulk value, which was expected based on previous results. The combinatorial capabilities of the PnSC were demonstrated by analyzing a combinatorial library of thin-film (approximately 290 nm) Ni-Ti-Zr samples. These samples were amorphous as-deposited and crystallized in-situ. The resulting calorimetry trace revealed the glass transition and crystallization of the samples. Subsequent PnSC measurements revealed that the presence of the shape memory transformation depended on nickel concentration. Samples around 49 at.% Ni and greater did not show the shape memory transformation while samples with less than 49 at.% Ni did show the transformation. The transformation temperature was shown to be depressed compared to bulk values, although the functional dependence of the transformation temperature on Zr content was similar to the bulk behavior. The depression in transformation temperature can be explained by the destabilization of the martensite phase because of the energy cost to form interfaces at reduced length scales.

6.2.3 Glass transition and crystallization of Ni-Ti-Zr thin films
The crystallization of Ni-Ti-Zr thin films is practically important because these films could be useful as micro hinges in the glassy state or micro actuators in the shape memory phase. Since the mechanical properties of both states are known to be functions of composition, a combinatorial study is applicable. Here, a thin film library of amorphous Ni-Ti-Zr samples was studied by PnSC to determine the characteristics of the glass transition and crystallization processes. The films were crystallized in a single temperature scan to approximately 900°C in 60 ms, resulting in an average heating rate of about 15 K/ms. This extreme heating rate produced some interesting results. It suppressed structural relaxation of the as deposited samples, meaning that the measured glass transition temperature was equal to the fictive temperature for the as deposited material. The detection of the glass transition was also influenced by the heating rate because the onset temperature of crystallization was increased due to formation kinetics, revealing the glass transition. The crystallization manifested in multiple peaks in the calorimetry signal, indicating a multi-stage process. The calorimetry peaks were related to the formation of specific phases by comparison to x-ray diffraction results. The calorimetry and x-ray diffraction results showed a one-to-one correlation across all compositions. The extreme heating rates also resulted in ultra-fine grained crystalline structures and non-equilibrium phase fractions. This results in the suppression of Laves phase formation, which is expected from the equilibrium phase diagram, and the extension of the Ni16Zr7 composition range.

6.2.4 Thermal cycling effects on the martensite transformation in Ni-Ti-Zr thin films

The characteristics of the shape memory effect depend on stress and composition. Stress changes the elastic energy component of the free energy and composition changes the enthalpy and entropy contribution. Precipitation affects both of these quantities; the formation of precipitates creates internal stresses and changes the composition of the shape memory phase. The mechanism of precipitation growth explains the changes observed in the martensite-austenite
transformation resulting from high temperature heat treatments. During the first few heat treatments the transformation temperature increases as a result of precipitate nucleation and growth, which increases the internal stress and stabilizes the martensite phase. As the precipitates continue to grow they change the composition of the shape memory phase more significantly. For samples with a Zr content below 18 at.% the temperature increases because the Ti$_2$Ni base phase is precipitating, which increases the Zr concentration. For samples with a Zr concentration above 18 at.% the Ni$_{10}$Zr$_7$ base phase precipitates causing a decrease in Zr concentration and transformation temperature.

The thermal fatigue behavior of these samples was investigated after 3 and 13 high-temperature heat treatments. The thermal fatigue mechanism was reset by the recrystallization of the samples, which annealed the dislocations. The samples in this study showed less thermal fatigue than Ni-Ti-Zr samples from previous studies. This can be attributed to the suppression of dislocation mobility due to the ultra-fine (5-20 nm) grain structure and the well-known Hall-Petch relation. One sample, Ni$_{44.6}$Ti$_{32.8}$Zr$_{22.6}$, showed significantly less thermal fatigue (-11 K for 100 cycles) than previous results (-43 to -60 K for 100 cycles), and sets a new level of stability for this materials system.

6.3 Future work

6.3.1 Ongoing work at Harvard University

The work presented in this dissertation represents the inception of membrane-based thermal sensor arrays for combinatorial materials science. It is good to see that this line of work will continue beyond what has been presented here. In fact a similar study on the analysis of Ni-Ti-Hf by combinatorial nanocalorimetry has already been performed, and the dissemination of these results is in progress. Work on developing a high-temperature (1500°C) version of the PnSC is ongoing. New measurement electronics capable of differential thermal analysis and power compensation calorimetry are close to completion.
Application of the PnSC to bulk metallic glass systems such as Au-Cu-Si and high temperature shape memory alloys such as (Ti, Zr, Hf)-(Au, Cu, Ag) has begun. Work on ultra high-temperature ceramics such as the metal diborides has been proposed.

### 6.3.2 nano-Thermal transport array

The nTTA has the potential for improvement in measurement electronics and can be applied to other technologically and scientifically interesting materials systems. With the current measurement setup and data reduction scheme, the heat capacity and effusivity are determined from the same curve fit, which causes trade-offs concerning the measurement sensitivity (see section 2.10). It should be possible to decouple the heat capacity signal and the effusivity signal with an alternating current (AC) imposed on top of the steady current (DC) presently used. The heat capacity signal is sensitive to instantaneous changes in the heating rate and the effusivity signal is sensitive to the entire temperature history, so the heat capacity can be determined from the temperature response to the AC and the effusivity can be determined from the temperature response to the DC. This measurement setup would be more complicated, requiring a lock-in amplifier among other components, but it would decouple the signals and provide a more sensitive measurement.

Either with the present setup or with the improvements described above, the nTTA technique has the potential to quickly analyze the thermal transport properties of a wide array of materials systems. Multilayers of different materials seem like the obvious next application for the nTTA. It is practically easy to create multilayers on the nTTA with a sputter deposition system and vary parameters, e.g., relative interlayer thickness, because of the array design. This approach would allow studies of various interfaces. High quality epitaxial interfaces would be especially interesting because of the phonon waveguide potential. Another interesting materials system to investigate could be bulk metallic glasses. An important parameter for these materials is the glass forming ability (GFA), which is a measure of the largest feature size that can be created.
and still maintain the glassy phase. The GFA is a function of crystallization kinetics and cooling rate. So far the GFA has been studied primarily from the crystallization kinetics perspective. It may be possible through a combinatorial study to increase the GFA from a thermal transport approach by reducing the heat capacity and increasing the conductivity. The nTTA is ideal for this type of combinatorial optimization.

6.3.3 Parallel nano-scanning calorimeter

The parallel nano-scanning calorimeter also has room for improvement in terms of sensor design and operation. The most obvious improvement would be to increase the number of sensors to provide greater combinatorial precision. Also, creating a membrane-free sensor would have some distinct advantages. First, it would reduce heat loss by eliminating the conduction path into the membrane and improve the sensitivity of the measurement. Second, it would obviate the need for a sputter deposition shadow mask, which would allow steeper sputtering angles and thus greater composition gradients. It would also improve temperature uniformity by eliminating the step in the thickness profile along the heater at the extents of the sample.

The PnSC can be applied to a wide array of materials. Even within the materials sets of SMA and BMG, many systems exist that could be optimized and others are likely to exist that have not been discovered yet. Other interesting applications could include reactions at interfaces in IC and MEMS materials. Another technologically important class of materials, which depends on a phase transformation to operate, are phase-change memory materials. These materials store binary information depending on the phase of the material, which is crystalline or amorphous. The stability of a given phase depends on temperature, the amount of energy required to switch depends on the enthalpy of the sample, and the writing speed is limited by kinetics. The addendums of traditional calorimeters are too large to study the behavior of this material at a length scale typical of the application. The ultra-fast heating and cooling rates of the PnSC
may make kinetics studies possible. The reduced length scale and heating/cooling requirements make the PnSC ideal for this type of study.

### 6.3.4 Ni-Ti-Zr materials system

The crystallization of shape memory alloys by local heating presents some opportunities to improve the functional behavior of these materials. The new levels of thermal fatigue resistance as measured by PnSC may translate to mechanical properties. Films processed in this way should show improved strain recovery when subjected to cyclical shape memory cycles. The suppression of the Laves phase due to ultra-fast heating rates may also have some mechanical advantages. The Laves phase is known to be brittle and the precipitation of this phase causes brittle failure in Ni-Ti-Zr. So the suppression of the Laves phase may improve the ductility and the practical applicability of this materials system. Some mechanical testing of Ni-Ti-Zr prepared under similar conditions should be pursued.

The new benchmark of thermal fatigue resistance also begs the question of how far can thermal fatigue be reduced for this system. A study similar to that of Zarnetta et. al. could be conducted on the Ni-Ti-Zr system to improve the compatibility of the habit plane. A good place to start would be with the Ni\textsubscript{44.6}Ti\textsubscript{32.8}Zr\textsubscript{22.6} composition. This is especially important for high-temperature SMA because dislocations are thermally activated.

### 6.4 Final remarks

The nTTA and PnSC have been used to successfully analyze the thermophysical properties of complex nanoscale materials systems. These instruments are broadly applicable to the high-throughput analysis of thermophysical properties of thin films and they have the potential to significantly accelerate the pace of analysis and discovery. The presented work demonstrates the capabilities of these devices and the proposed work provides a
small sampling of potential improvements to the measurement system and expanded application of membrane-based thermal sensor arrays. It is rewarding to know that these devices are continuing to improve and the enhanced measurement capabilities will be applied to investigate other materials systems.