Parallel nano-Differential Scanning Calorimetry: A New Device for Combinatorial Analysis of Complex nano-Scale Material Systems

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Abstract

A new device is presented for the combinatorial analysis of complex nano-scale material systems. The parallel nano-differential scanning calorimeter (PnDSC) is a micro-machined array of calorimetric cells. This new approach to combinatorial calorimetry greatly expedites the analysis of nano-scale material thermal properties. A power-compensation differential scanning calorimetry measurement is described. The scanning calorimetry capability of the PnDSC is demonstrated by a specific heat measurement of an amorphous equiatomic NiTi thin film.

Introduction

Differential scanning calorimetry (DSC) is a primary technique for measuring the thermal properties of materials. A typical DSC system requires relatively large amounts of test material, making thermal measurements on nano-scale samples difficult if not impossible. Thus, while traditional DSC has proved a very useful technique, its application in nanotechnology, where sample sizes can be very small, is rather limited. Since the properties of materials on the nano-scale may differ significantly from their bulk counterparts [1], a DSC system that is sensitive enough to probe nano-scale quantities is desirable. Furthermore, traditional DSC systems are limited to taking one measurement at a time, and a new sample must be loaded between each measurement. This severely limits the use of a traditional DSC in combinatorial studies at the nano-scale. To obtain reasonable precision on thermal properties as a function of composition many samples must be measured. Anything beyond a binary material system quickly involves unreasonable amounts of time to perform a full analysis. To improve these limitations, we have developed a parallel nano-differential scanning calorimeter (PnDSC) that combines DSC and combinatorial analysis in a novel way. This system is ideal for studying complex material systems. The heart of the PnDSC measurement system is a micro-machined, 5X5 array of calorimetric cells. The PnDSC and complimentary measurement system reduce the analysis time of complex nano-scale material systems by at least an order of magnitude.

Physical description

The PnDSC is a 5x5 array of calorimetric cells supported by a square Si frame. A thin (~ 100 nm) silicon nitride film is continuous across the surface of the device. Portions of this film are freestanding, creating the membrane of the calorimetric cell. The membranes are positioned uniformly across the device. Each cell has planar dimensions of approximately 2.5 x 5 mm. A thin-film (~ 150 nm) metal strip (width ~ 400 μm), typically W, patterned on the membrane serves as a heater and resistive thermistor in a four-point measurement scheme. Probes patterned from the same metallization layer, attach close to the ends of the thermistor. The individual cells of the PnDSC are largely

based on a design by Allen and colleagues at the University of Illinois [2, 3]. Lead lines allow electrical signals to travel from each heating element and probe across the frame to electrical contacting pads at the edge of the device. A second metallization layer, typically Al, supplements the metallization layer of the heating element in the lead lines and contact pads to reduce electrical resistance and facilitate electrical contacting to the device (Fig. 1).

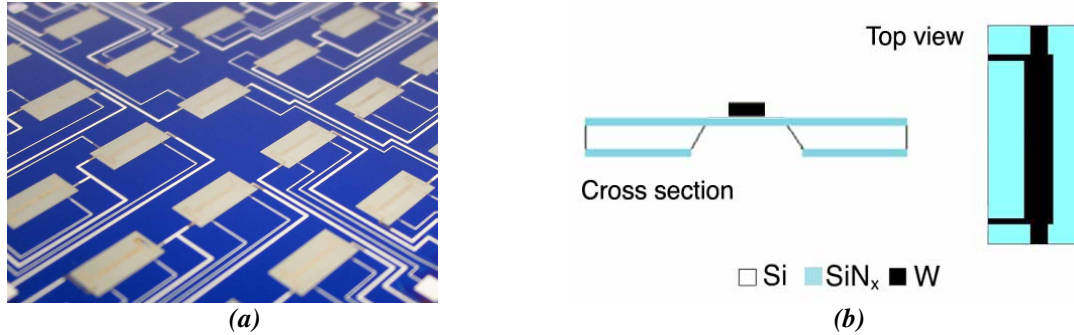| (a) | (b) |

Figure 1: (a) Photograph of the PnDSC (narrowest Al lines are 100 μm in width). Note, tungsten metallization is difficult to see because of poor contrast. (b) Diagram of a calorimetric cell (not to scale).

Fabrication

The fabrication process uses ~ 800 μm thick, 8" Si wafers polished on one side. These wafers are delivered with ~ 100 nm silicon nitride thin film on both sides. Special care is taken throughout the fabrication process to protect the silicon nitride on the polished side of the wafer. This film will eventually form the membranes of the PnDSC and even shallow scratches result in ruptured membranes.

The fabrication process starts by cleaving each wafer into 7, 5.5 cm square partitions. First tungsten then aluminum is deposited on the polished side of the square wafer using a magnetron sputtering system. Shipley 1805 photoresist (S1805) is spun and patterned on both sides of the wafer. The silicon nitride on the backside of the wafer is reactively etched with CF_4 to create rectangular windows. Al is etched using a commercial Al wet etch. This exposes the underlying W, which is then etched with H_2O_2. Remaining resist is developed and removed. S1805 is re-spun on the metallization side and patterned with the rectangular window artwork. Al is then etched from the membrane area. After the metallization patterning, the membranes are created by anisotropically etching the Si. The metallization is protected during this etch procedure by a specially designed sample holder. This fabrication process differs from that used by Allen et. al. [2, 3] in that the Si etch is performed near the end of the fabrication rather than near the beginning. This protects the delicate membranes from being exposed until the very end of the fabrication and allows more complicated processing on the polished side of the wafer.

Design principles

Design of the calorimetric cell and cell array

The calorimetric cell has been modeled by a one-dimensional transient thermal model. This model considers effects from thermal mass, conduction, radiation and Joule

heating to give the time-dependent temperature profile of the heating element. Using this temperature profile conclusions can be made about the performance of the calorimetric cell, such as; heat loss rates, temperature uniformity, and signal noise levels. Figures of merit as functions of design parameters (e.g. device dimensions/ materials) were developed to explore these important characteristics of the design.

The array design allows the PnDSC to perform combinatorial studies with great efficiency. Current fabrication techniques produce 25 calorimetric cells on each PnDSC device. This allows for 25 samples of unique composition to be prepared simultaneously. This is accomplished conveniently by using a multi-gun sputtering system, although other techniques can be used as well. When material is deposited through a shadow mask on the surface of the PnDSC, an array of samples is created with 25 unique compositions. These samples can then be measured sequentially without the need to reload between measurements. The measurement sequence can be selected manually or computer controlled for full automation.

Measurement techniques

Power input and temperature are the essential values for a calorimetric thermal measurement. Equation 1 shows heat capacity (Cp) as a function of power supplied to a cell (P) and the heating rate (dT/dt):

$$C_p = \frac{P}{dT/dt} \quad \text{(Equation 1)}$$

The sensitivity of the thermal measurement depends on how these values are obtained. The sensors in the PnDSC can be operated in 3 modes: scanning calorimetry (SC), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). SC and DTA measurement modes were developed by Allen et. al. [2, 3], while the DSC mode is a new measurement technique for this type of device. The type of measurement technique used depends on the sample to be measured.

SC is the least sensitive measurement type, but it offers the greatest compositional precision and is the simplest measurement to take. Two separate measurements must be performed to obtain the heat capacity of the sample, one with and one without the sample. The heat capacity of the sample is then equal to the difference of the two. SC is sufficient to measure a sample with large thermal mass or a large enthalpy of reaction. A current (I_S) through the heating element provides Joule heating to the calorimetric cell. The current is measured (V_{IS}) across an external precision resistor (R_{IS}). The voltage across the heating element (V_S) is measured via two sense probes (Fig. 2). In this way, the resistance of the heating element (R_S) and power supplied can be easily calculated. The temperature of the cell is then determined from the thermal coefficient of resistivity (α). Thus, power and temperature are determined and heat capacity can be calculated, see equations 2 & 3.
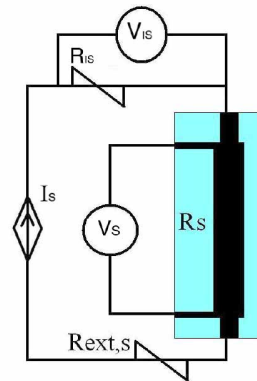

Figure 2: Scanning calorimetry measurement schematic.

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$$P = I_S V_S \quad \text{(Equation 2)}$$

$$\frac{dT}{dt} = \frac{1}{\alpha V_S}\frac{dV_S}{dt} - \frac{1}{\alpha V_{IS}}\frac{dV_{IS}}{dt} \quad \text{(Equation 3)}$$

Samples on the order of nanograms require greater sensitivity than a single cell measurement can provide. For this case a differential measurement is required (Fig. 3). In DTA mode, decoupled current sources apply equivalent currents to a reference cell and a cell with sample. The current supplied and the voltage drop across the sensing portion of the heaters is measured similarly to the non-differential mode. A

Figure 3: Differential measurement schematic.

fifth differential voltage is measured on the high voltage side of the heating element. This differential voltage allows a more sensitive heat capacity measurement because the temperature difference is measured directly, rather than independently, and subtracted after the fact.
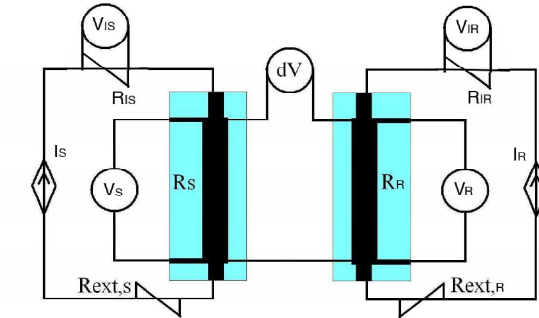
A sample with a thermal mass comparable to the addendum but a small enthalpy of reaction requires a DSC measurement. The DSC measurement is similar to DTA, however the current to the cell with sample is actively controlled. This technique compensates for the additional heat capacity of the sample and the enthalpy of reaction by actively controlling the power required to maintain equivalent heating rates between the sample and reference cells.

Maintaining the cells at the same temperature has a dramatic effect on error in differential measurements. Figure 4 shows the fractional error in heat capacity as a function of normalized sample size. Idealized error estimates in measured quantities were assumed equal to the resolution of an 18 bit analog to digital converter. SC and DTA error estimates are from Efremov et. al. [3], DSC error estimates were calculated using an error propagation analysis of the describing equations. An additional error term was added to the DTA measurement to account for the disparity in heating rate between the sample and reference cell. DSC outperforms both measurement techniques for all but the smallest samples, where DTA has the lowest error.

Supporting systems

The desired signals in a nano-calorimetric measurement require specialized electronics. The calori-metric cell has a thermal diffusion time constant on the order of milliseconds. In order to assume adiabatic conditions heating rates must be at least an order of magnitude greater than cooling rates. This requires heating rates greater than 10 K/ms. To obtain a reasonable resolution of the
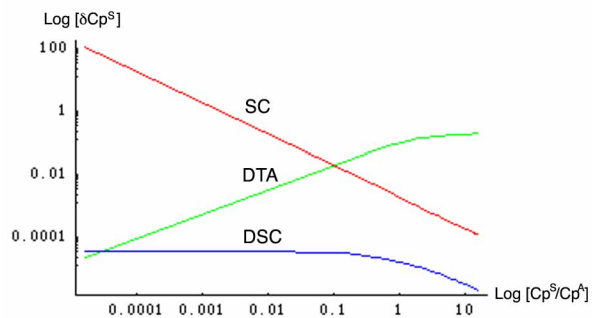

Figure 4: Logarithmic plot of the fractional error in heat capacity of the sample versus normalized sample size (i.e. heat capacity of the sample / heat capacity of addendum).

temperature requires a fast data acquisition board (DAQ). Also measuring the desired quantities in nano-samples requires a resolution of ~ 10 μV in a ~ 1V signal. This requires careful signal conditioning and isolation.

Attached to the vacuum chamber containing the PnDSC is a sensor interface subsystem. This unit serves to shield the weak device signals from the noisy laboratory environment. Housed in this compartment are voltage amplifiers and MOSFET switches for each sensor. Attached to the sensor interface subsystem is a current control unit. Figure 5 depicts the current source used in SC mode; the control voltage (V_{Cont}) is from the analog output on the DAQ board. Differential measurements require decoupled current sources to avoid introducing spurious signals in the differential voltage measurement. In DSC mode one of the low-noise decoupled current supplies will be supplemented by a low power version of the actively controlled current source to regulate the heating rate.

We anticipate using a custom data acquisition system with five 18 bit analog inputs and two outputs at 333 kHz per channel. After the signal has been digitized it will be sent over a custom fiber link to a custom fiber net board. This assures galvanic isolation from PC noise. The DAQ will also include a number of digital outputs for timing and analog switch control.
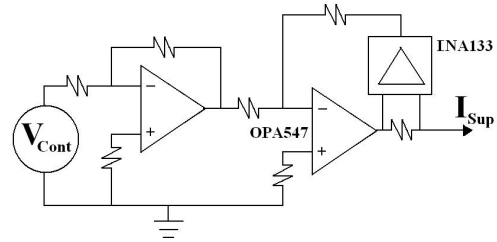

Figure 5: Actively controlled current source

Experiment

While the entire measurement system is not yet fully operational, enough has been completed to perform SC type measurements (Fig. 2). SC is used to measure the specific heat of amorphous equiatomic NiTi thin film. The current source used is shown in Figure 5. Voltage signals are unconditioned; they are measured and controlled by a National Instruments PCI-6221 board. Measurements were performed in a vacuum chamber at ~$1*10^{-5}$ Torr.

Before a thermal measurement can be performed, the thermal coefficient of resistivity, α, must be determined. Prior to operation, the device was annealed at 450 ^{o}C for 1 hour in a vacuum of ~ $1*10^{-6}$ Torr to stabilize electrical behavior. The calibration setup is identical to the experimental setup with the additional condition that the device is in an oven and an independent thermocouple is used to measure the temperature. A small monitoring current (1 mA) is applied to the device while the temperature of the oven is slowly stepped through a temperature range. This current and the resulting voltage drop across the heating element are used to calculate resistance. Resistance is then calibrated to the temperature reading of the thermocouple. This resulted in a thermal coefficient of resistivity, α = $8.5*10^{-4}$ K^{-1}. This is approximately 20% of the bulk value of W. This is caused by the extremely fine grain structure of the W film, which increases its resistivity and reduces the thermal coefficient of resistivity.

Measuring the specific heat of NiTi requires establishing a heat capacity baseline. To acquire this baseline, a 10 mA current pulse lasting 10 ms was applied to the reference cell. A 280 nm NiTi coating was then deposited at 1.5 mTorr on the backside of the PnDSC through a micro-machined shadow mask. A current pulse of 14 mA was applied

to the sample cell. The increased current partially compensates for the additional thermal mass of the sample, and reduces the heating disparity. The current monitoring voltage and voltage response of each cell, averaged over 100 cycles, was recorded at 100 kHz and is shown in figure 6(a) & (b) respectively.
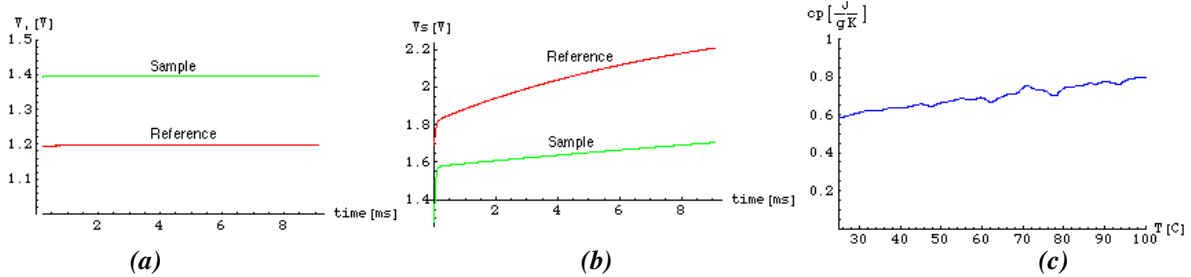

Figure 6: (a) Current monitoring voltage across 100 Ω precision resistor. (b) Voltage response of heating element. (c) Specific heat measurement of NiTi

Discussion

Using equations 1-3 and a sample mass of 2.4 μg, the specific heat of NiTi is calculated as shown in figure 6(c). For comparison, the specific heat NiTi has been reported as $c_p = 0.32\text{-}0.84$ J/g ^{o}C [4, 5]. The rising drift of the heat capacity curve is most likely caused by heat loss to the environment: In the present implementation of the device, currents larger than 14 mA fracture the membranes. This limits heating rates in the sample cell to ~ 8 K/ms. To neglect heat loss, the heating rate must be greater than 10 K/ms. Since the heating rate of the sample is slower than the heating rate of the reference, for a given temperature, the sample cell loses more heat to the environment than the reference cell. This heat loss difference appears as an increase in heat capacity of the sample. In the case of a sample this size, a lower-stress silicon nitride membrane should improve device performance by allowing faster heating rates.

Conclusion

The PnDSC is a new measurement device for studying complex nano-scale material systems. The device promises to revolutionize the development of such material systems, providing the raw material data for nano-technology innovation and design. The PnDSC will accomplish this by employing a 5x5 array of micro-machined calorimetric cells.

Acknowledgements

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