Thermostat for high temperature and transient characterization of thin film thermoelectric materials

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We have designed and fabricated a vacuum-insulated thermostat capable of measuring the thermoelectric properties of thin films from room temperature to 850 K. High speed Seebeck voltage transients are resolved to 200 ns with 63 dB dynamic range in order to directly measure thermoelectric device figure of merit. In-plane Seebeck coefficient probes measure voltage and temperature difference at identical locations with low parasitic contributions. In-plane electrical conductivity measurement is accomplished at high speed to avoid possible Seebeck voltage effect on van der Pauw measurements. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3072603]

I. INTRODUCTION

Thermoelectric materials have the potential to play an important role in waste heat recovery applications in a technologically advanced and resource-limited world. An important application of thermoelectric materials is in direct thermal-to-electrical energy conversion that is free of moving parts. Because a substantial amount of energy in our world is in thermal form, there are tremendous applications for thermoelectric devices. The thermal-to-electrical energy conversion efficiency of a thermoelectric material is a function of its dimensionless figure of merit that is defined as $ZT \equiv S^2\sigma T/\kappa$, where S, σ, κ, and T are the material's Seebeck coefficient, electrical conductivity, thermal conductivity, and ambient temperature, respectively.

Recent work to improve the ZT of materials designed for high temperature power generation is focused on thin films due to the variety of the growth techniques available to engineer materials at the nanoscale. Accurate high temperature characterization of thin film thermoelectrics is an important step in the development process of these materials. Previous work dedicated to equipment and techniques designed for high temperature characterization of thermoelectric materials has focused on bulk samples of relatively large dimensions.[1–3] There is little published work regarding the measurement of thin film thermoelectric properties at high temperatures. We have designed and fabricated a novel vacuum-insulated thermostat to measure thin film device and material properties from room temperature to 850 K. The unit is capable of direct device ZT measurement as well as measurement of in-plane S and σ and cross-plane κ. Direct ZT measurement is accomplished using the Harman technique[4] with Seebeck voltage transient resolution to 200 ns with 63 dB of dynamic range. In-plane S measurement utilizes a differential technique in which a temperature gradient is imposed across a sample while monitoring the generated Seebeck voltage and the temperature at the precise points of voltage measurement. In-plane σ is measured by the van der Pauw method.[5] Cross-plane κ can be measured by the 3ω technique.[6] Additional measurement capabilities can be easily implemented in the thermostat.

II. THERMOSTAT DESIGN

We utilized standard high-vacuum components to fabricate the vacuum chamber used for the thermostat. The 8 in. diameter cylindrical chamber is vacuum-welded using 304 stainless steel. The base of the chamber contains eight NW 25 ports arranged radially for electrical feedthroughs and vacuum evacuation. A circular base-plate is fabricated as a breadboard with an array of $\frac{1}{4}$-20 threaded holes to accommodate standard laboratory hardware, such as optical components. A vacuum shroud is made to mate with the chamber base using a NW 200 flange to allow quick access to the interior.

A cylindrical radiant heater of 3 in. inner diameter with integral shielding that radiates toward its axis is mounted on a hollow stainless steel standoff. This standoff is fastened to the center of the base plate. Additional radiation shielding is also installed at the ends of the heater. This shielding consists of several stainless steel shims 10 mm thick and 5 in. in diameter separated by washers 50 mm thick. This configuration permits a stage temperature of 850 K for 100 W of heater power. The lower shielding is secured to the standoff, while the upper shielding simply rests on the radiant heater. A desired measurement stage is secured at the top of the standoff. A thermocouple routed through the standoff permits stage temperature measurement via direct contact. Figure 1 below is an elevation-view diagram of the thermostat in cross section.

Two stages are designed and fabricated for the measurements presented here: a stage for measuring high speed device transients and a stage capable of inducing temperature gradients across a sample for in-plane S measurement. The high speed stage is fabricated of copper and is designed to interface high temperature coaxial cable to microstrip lines fastened to the stage in order to conduct source-measure experiments at high speeds. A schematic of the high speed stage is shown in Fig. 2. The thermoelectric device shown in the figure is the sample under study in this case. The second stage is fabricated of a copper base and two adjustable standoffs made of boron nitride. Boron nitride is chosen as the

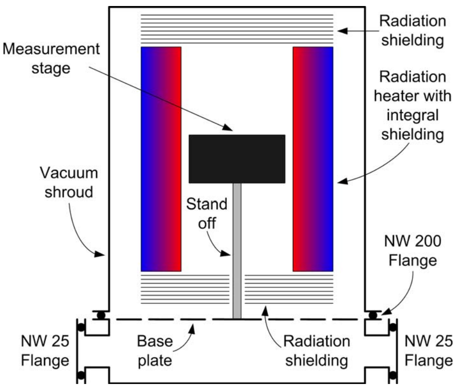

FIG. 1. (Color online) Side-view cross-sectional diagram of the vacuum-insulated thermostat (not to scale).

standoff material due to its large thermal and small electrical conductivities. One standoff contains a small 0.25 in. diameter cartridge heater capable of dissipating 75 W. A sample is intended to bridge the standoffs in order to undergo a temperature gradient generated by the cartridge heater. A schematic of the in-plane S measurement stage is shown in Fig. 3 below.

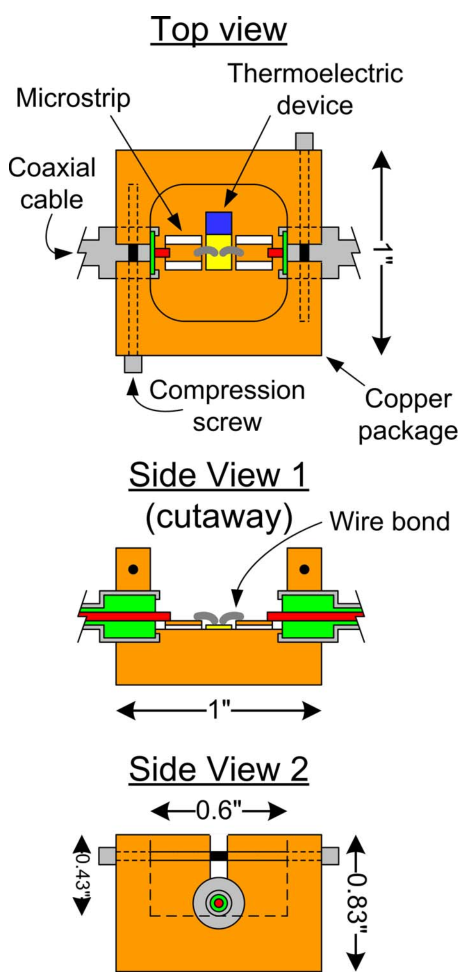

FIG. 2. (Color online) Schematic diagrams of the high-speed measurement stage and associated components capable of operation to 850 K (not to scale).

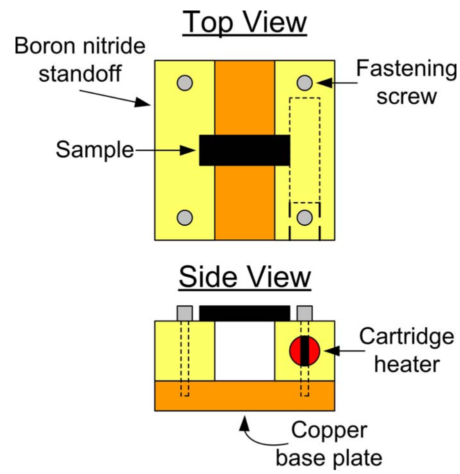

FIG. 3. (Color online) Schematic diagrams of the in-plane Seebeck coefficient measurement stage (not to scale).

III. MEASUREMENT STAGE COMPONENTS

High speed coaxial cables are fabricated of a stainless steel outer conductor and a copper center conductor separated by a silicon dioxide dielectric.[7] The cables are terminated with male SMA (SubMiniature version A) connectors also containing a silicon dioxide dielectric. The ends of the coaxial cables at the high speed stage are secured using compression fittings and the center conductors are connected to microstrip lines using an alloy of indium and gallium that melts below room temperature. This is necessary because no "sparkplug" launcher connectors capable of operation at high temperature are available. The cables are routed from the high speed stage through the radiant heater and base plate to flanges where they mate with female SMA NW 25 feedthroughs. Total cable length is 2 ft in order to reduce thermal conductance from the sample stage to the feedthroughs.

Two probes capable of measuring temperature and voltage simultaneously at identical points are made of matched type R bare wire thermocouple leads that are inserted through four-bore alumina rods that provide electrical isolation as well as the mechanical rigidity necessary for positioning.[1] An additional two probes for in-plane σ measurements are made of a single platinum wire. Platinum is chosen as the reference leads for most voltage measurements due to its relatively small Seebeck coefficient (from +4 to +10 $\mu V\ K^{-1}$) throughout the temperature range. These (six) leads exit the thermostat through a custom NW 25 feedthrough. Therefore, all connections to thermocouple and reference wires are made outside the thermostat at room temperature on an isothermal block.

IV. EXPERIMENTAL CONFIGURATIONS

To directly measure the ZT of thin film devices of resistance on the order of 0.1 Ω, a pulsed voltage source with a 50 Ω output impedance is connected to the thermoelectric device in series with a 50 Ω coaxial matching resistor mounted at the exterior side of a SMA feedthrough, which is an acceptable location considering a wavelength of over 4 ft in the high temperature coaxial cables at 100 MHz. The re-

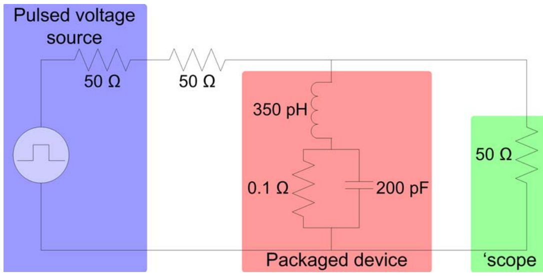

FIG. 4. (Color online) Circuit diagram of the high-speed transient measurement system with packaged device circuit (package values measured using TDR at 300 K).

sistor serves to match the small device impedance to the transmission lines to avoid reflections, convert the voltage source to a current source (thereby minimizing source output variations in response to generated Seebeck voltages in the thermoelectric device), and prevent shorting of the device when the source pulse has terminated. The device anode is wire-bonded to both source and measure microstrips, while the backside cathode is bonded with electrically and thermally conductive paste to the high speed stage that serves as electrical and thermal ground. The measurement side of the circuit is connected directly across the device and to an oscilloscope with a 500 MHz bandwidth and a 50 Ω input impedance. Upon investigation of the entire source-measure circuit shown in Fig. 4, it can be seen that the thermoelectric device is in parallel with an equivalent resistance of roughly 33 Ω when the voltage source is in the off state and the Seebeck voltage is being measured. This resistance will not load the thermoelectric device due to the device's relatively small output impedance. The measurement is essentially an open-circuit measurement. This is confirmed by changing the input impedance of the oscilloscope to 1 MΩ (which increases the equivalent resistance in parallel with the device to about 100 Ω) and observing no change in measured Seebeck voltage at 1 μs (the time at which the parasitic signal oscillations due to the mismatch of the 1 MΩ input impedance dampen) and beyond.

Measurement of in-plane S is accomplished by bridging a sample across the two boron nitride standoffs and generating a temperature difference across the sample by sending a desired power to the heater embedded into one standoff. This configuration is shown in Fig. 3. Two thermocouples placed on the edges of the sample are used to measure temperature and the voltage difference generated across the sample. The weights of the thermocouple probes maintain intimate physical contact between the thermocouple junctions and the sample's surface during the experiment. The measurement circuit schematic is shown in Fig. 5. Four HP 34420A nanovolt meters are used to monitor both temperature readings independently as well as the Seebeck voltage generated in the sample with respect to various leads of the type R thermocouples. These four values are measured simultaneously in real-time. T_1 and T_2 are measured absolutely rather than relatively so that actual sample temperatures, which may be substantially different than the stage temperature reading, can be determined. The relative S of the sample is measured either referenced to platinum, which is the industry standard, or with respect to type R thermocouple leads. Since the S of type R thermocouple is well known over a wide temperature range, the absolute S of the sample can be extracted provided that the temperature difference $T_1 - T_2$ is sufficiently small. Both lead types are in direct contact with the sample and the thin junction between the two leads is assumed to be isothermal. Random measurement noise in the system is ±200 nV in Seebeck voltage and ±30 mK in temperature difference.

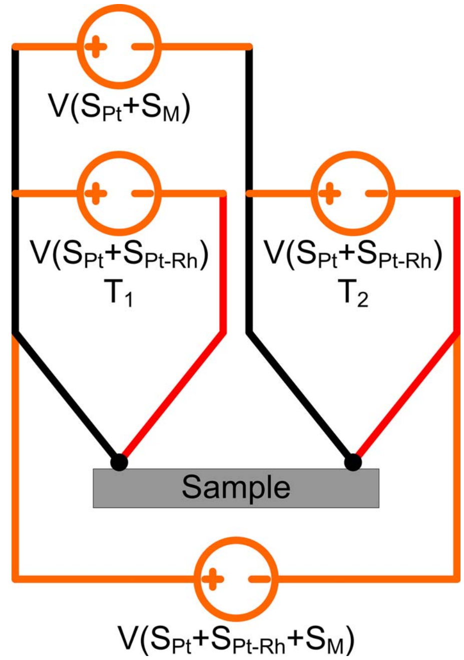

FIG. 5. (Color online) Circuit diagram of in-plane Seebeck voltage measurement showing four quantities measured from type R thermocouples in real time.

Measurement of in-plane σ is made using the van der Pauw technique. The two thermocouple probes used for in-plane S measurements are used in conjunction with the two probes made of single platinum leads to source current and measure voltage in various sample configurations with respect to platinum, which has the lower Seebeck coefficient of the two lead types. Pulsed current of low duty cycle is used in the measurements to minimize the affect of sample Seebeck voltage on the measured Ohmic voltage. The voltage response is measured with the oscilloscope, which allows the observation of potential Seebeck voltage transients affecting the measurement. Using the platinum leads, a voltage measurement resolution of 2 μs after the rising edge of the current pulse is achieved.

V. HIGH-FREQUENCY RESULTS

The temperature-dependent frequency response of the high speed measurement circuit is validated using an Agilent 8510C vector network analyzer (VNA). A 50 Ω microstrip line of alumina dielectric is used in place of a sample to connect the source and measure lines in the high speed stage. The VNA is calibrated for full two-port measurement. The calibration standards are connected to low temperature coaxial cables at the point that the cables are connected to the SMA feedthroughs mounted on the thermostat. Therefore,

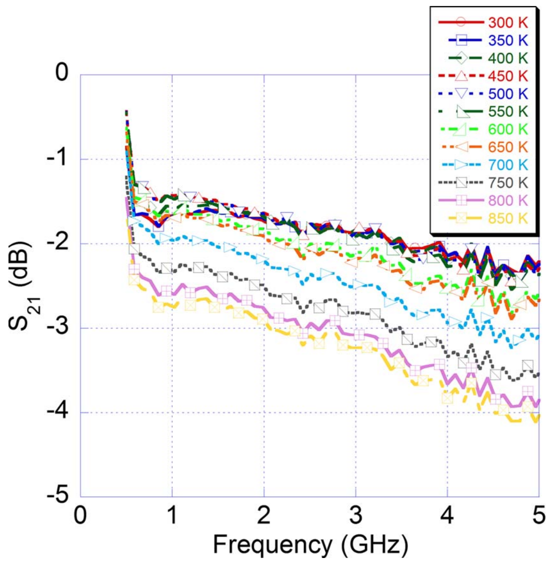

FIG. 6. (Color online) Measured temperature-dependent transmission loss of high-speed circuit of thermostat with 50 Ω microstrip line installed in stage.

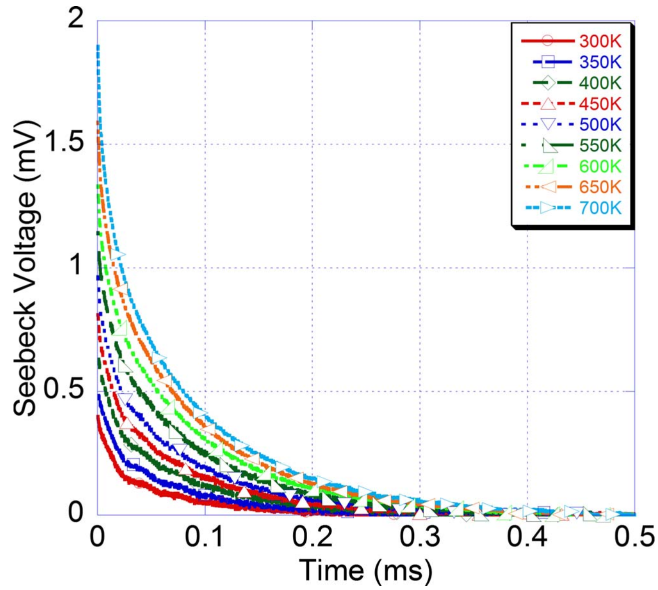

FIG. 8. (Color online) Seebeck voltage transients across a thin film thermoelectric device.

the measured frequency response represents the response of the entire component system in the thermostat. The temperature dependence of the system's transmission loss (S_{21}) from 500 MHz to 5 GHz is shown in Fig. 6. Although measurement hysteresis is observed beginning at 600 K due to degradation of the 50 Ω microstrip line, these results compare favorably with reported values[8] achieved using off-the-shelf rf components calibrated directly before coplanar probe tips. After replacement of the microstrip line, measurement hysteresis is not observed below 600 K. Transmission losses in the *ZT* measurement become negligible due to the fact that the extracted *ZT* value is a ratio of two components in the signal. Figure 7 is a plot of the transient response of the source-measure system of the thermostat at 300 K across a 400 mΩ surface-mount resistor installed in the high speed stage. The response is due to a voltage pulse across the

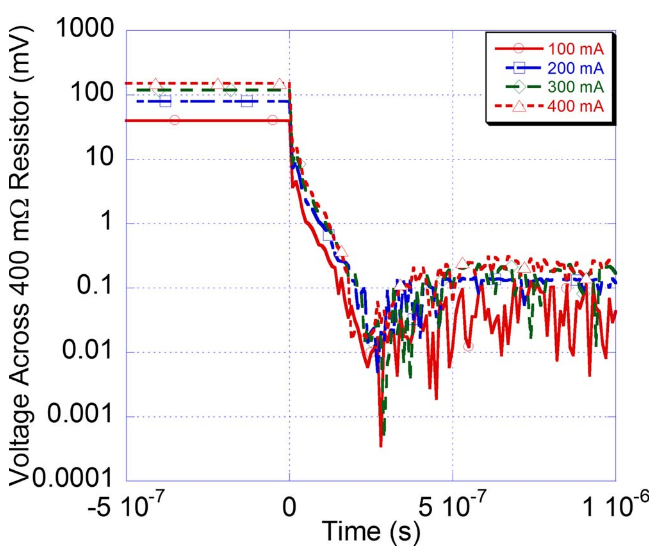

FIG. 7. (Color online) Transient response of the thermostat's high speed source-measure system to a current pulse terminating at $t=0$ s across a 400 mΩ resistor.

400 mΩ resistor in series with a 50 Ω matching resistor. The transient voltage resolution is approximately 200 ns with an average dynamic range of 63 dB. The measurement resolution and sensitivity are limited by the pulsed voltage source characteristics. Figure 8 contains the measured Seebeck voltage transients across a 20 μm thick thermoelectric device[9] of 100×100 μm^2 mesa area from 300 to 700 K for a current of 100 mA. The film is composed of an InGaAlAs matrix with embedded ErAs nanoparticles. The maximum measurement temperature is limited by device Ohmic contact failure that occurs below 750 K. Extrapolation of biexponential curve fits is used to determine the value of the Seebeck voltage at $t=0$ s. The isotropic material's experimental transient Seebeck voltage of 420 ± 13 μV at 300 K agrees well with a measured in-plane Seebeck coefficient of -224 ± 19.6 $\mu V\ K^{-1}$ and a Peltier cooling of 1.74 ± 0.01 K measured using a microthermocouple of 13 μm diameter leads placed on top of the device mesa. The high speed Seebeck voltage measurements in Fig. 8 for both positive and negative polarities are used along with the Ohmic voltage drop to extract device *ZT* directly. Application of this transient Harman method to thin films needs specific device geometries that minimize parasitic heat losses. Details of device optimization and the associated coupled electro-thermal transport will be discussed in an upcoming publication.[10]

VI. IN-PLANE MEASUREMENT RESULTS

The measurement of *S* is accomplished by sending increasing power to the differential heater in steps, waiting for the sample to achieve a steady-state temperature gradient for each step, and then measuring the Seebeck voltage and temperature difference. The amount of time required to achieve a steady-state temperature gradient after each differential heater power step depends upon the characteristics of the sample being measured. Data are taken for both increasing and decreasing temperature differences in order to examine

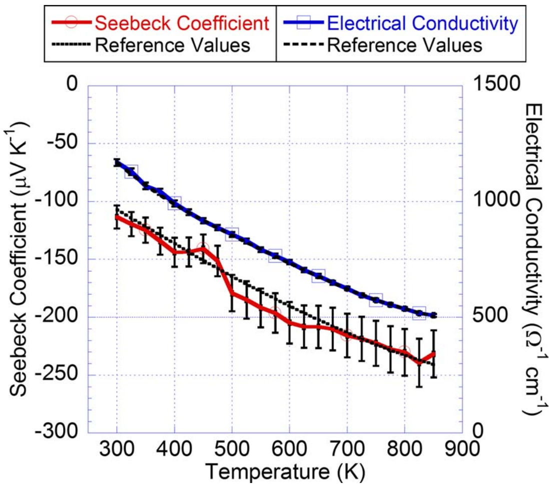

FIG. 9. (Color online) Measured S and σ of SiGe vs temperature. X-axis and y-axis error bars are due to both random and systematic measurement errors.

measurement hysteresis. Figure 9 contains the measured absolute S and σ from 300 to 850 K of a SiGe bar-shaped sample. The error percentage in S and σ from measurement of the SiGe sample is 8.75% and 1.27%, respectively. The error in S measurement is mainly systematic and is due to the finite thermal resistance between the sample surface and the thermocouple probes. The effect of these thermal resistances on the measurement can be reduced by waiting longer after a differential heater power step to achieve a steady-state temperature gradient across the sample before recording a data point. The wait time for the S data in Fig. 9 is 1 min. Waiting longer for steady-state conditions reduces the heat flux between the probes and the sample surface to minimize the temperature difference between them for finite thermal resistances. The error in σ measurement is dominated by random instrument (current output, voltage detection) noise.

VII. CONCLUSIONS AND FUTURE WORK

We have designed and fabricated a vacuum-insulated thermostat for complete thin film thermoelectric characterization from 300 to 850 K. The thermostat is fabricated using readily available vacuum components and utilizes a radiant heater to achieve a uniform stage temperature with fast response time. Accessory stages are fabricated to measure Seebeck voltage transients as well as in-plane Seebeck coefficient and electrical conductivity. Measurement of the transmission loss of the entire high speed system of the thermostat at 500 MHz resulted in −0.43 and −0.45 dB for stage temperatures of 300 and 550 K, respectively. Transient Seebeck voltage resolution of 200 ns is achieved with 63 dB of dynamic range throughout the temperature range. Cross-plane transient Seebeck voltage measurements of isotropic 20 μm thick films agree well with independent in-plane S measurement results along with thermocouple measurements of Peltier effect induced temperature change. Results of measured thin film in-plane Seebeck coefficient contain errors of less than 10% for a measurement delay of 1 min after a step power increase to the sample differential heater.

Future work will be dedicated to improving the design and fabrication of thin film devices dedicated to extracting the intrinsic ZT of novel nanostructured thermoelectric materials over a wide temperature range. This will include the minimization of the device parasitics such as series of electrical resistances and thermal shunts as well as the design of reliable electrical contacts for high temperature operation.

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