Scanning Probe Microscope to Map Thermal and Thermoelectric Properties of Combinatorial Materials

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January 2019
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Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517
ABSTRACT

The combinatorial high-throughput methodology offers potential for developing radiation-resistant sensor materials for nuclear energy applications through the synthesis and screening of large numbers of compositions and processing conditions in a single process. The combinatorial materials fabrication coupled with an automated screening process enables us to identify the optimal materials composition and processing conditions that yield both desired properties and required irradiation resistance in the most efficient and economic manner.

It has been a key challenge in combinatory materials science to map desired materials properties. The report focuses on the development of scanning probe technique to map the thermal conductivity, Seebeck coefficient, and electrical conductivity of combinatorial materials with high spatial resolution. The above three properties play important roles in many sensor materials for nuclear energy applications.
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Scanning Probe Microscope to Map Thermal and Thermoelectric Properties of Combinatorial Materials

1. INTRODUCTION

The goal of this research is to establish a high-throughput combinatorial (HTC) materials research and development process for nuclear energy application. While traditional combinatorial materials science mainly focuses on studying materials with varying compositions, we aim at exploring both composition and microstructure phase space simultaneously, so that the optimized composition and microstructure can be directly translated into the final device fabrication and its applications. The combinatorial methodology is particularly appealing for developing radiation-resistant functional/sensor materials for nuclear energy applications as it can significantly accelerate the materials research and development cycle through the synthesis and screening of large numbers of compositions and processing conditions in a single process. For example, the technique has potential to be employed in developing radiation-resistant materials for advanced nuclear reactor core (in-pile) sensors and instrumentation. The HTC materials fabrication coupled with an automated screening process enables us to identify the optimal materials composition and processing conditions that yield both desired properties and required irradiation resistance in the most efficient and economic manner.

The search for materials with improved properties for energy and other applications has traditionally been performed by combinations of various compounds being mixed, reacted, and characterized in serial experimentation. A major attraction of combinatorial approaches to materials discovery is that they are much faster and generally less costly than traditional serial experimentation. This is particularly important in cases, such as irradiation experiments, where significant time and resources are required for each specimen tested. In addition, data fidelity can be greater than with traditional methods since all of the library samples experience the same process and measurement conditions.

Combinatorial materials synthesis and screening will have a broad impact on materials research and development activities in various areas of importance to DOE including research associated with Nuclear Energy Enabling Technology (NEET), the Idaho National Laboratory (INL) Advanced Test Reactor (ATR) programs, the Transient Reactor Test (TREAT) Facility restart, Light Water Reactor (LWR) programs, and spent nuclear fuel storage.

The objective of this project is to develop scanning probe technique to map the thermal conductivity, Seebeck coefficient, and electrical conductivity of combinatory materials with gradient compositions, which has been a key challenge in combinatory materials science. The above three properties play important roles in many sensor materials for nuclear research.

2. SCANNING THERMAL MICROSCOPY TO MAP THERMAL CONDUCTIVITY AND SEEBECK COEFFICIENT

2.1 Overview of Custom-built Scanning Probe System

The custom-built scanning probe microscopy measurement system is shown in Figure 1. The setup includes a Newport RS2000 precision tuned damped research table to isolate the microscale probes from building vibrations. Measurement hardware includes a current source, nanovoltmeters, multimeters, and a waveform generator. A custom airtight box enclosing the probe station is purged with dry nitrogen before thermal measurements. Inside the nitrogen box is a 3-axis stage with inch travel distance and 100 nm resolution, and a nano-positioning stage with 200 µm travel and 1 nm resolution. Probe-sample contact force is controlled by a laser-guided photodiode system. The custom-built scanning probe system enables us to implement multiple probes to map various materials properties.
2.2 Introduction to Scanning Thermal Microscopy

Scanning Thermal Microscopy (SThM) is a powerful tool to measure thermal and thermoelectric properties on a micro- or nanoscale. For instance, SThM can be used to simultaneously measure thermal conductivity and Seebeck coefficient of thin films which are challenging to measure using other techniques. SThM can also map microscale thermal conductivity variations due to radiation damage or other structural defects, and identify the optimal composition and phase of desired properties on combinatorial films. SThM probes have been developed to resolve temperature distribution and/or thermal conductivity with spatial resolution ranging from several tens of nanometers to a few microns. The SThM technique is especially advantageous to map thermal properties on inhomogeneous samples, and probe thermal properties on micro/nanoscale samples with minimal sample preparation and without known sample density or specific heat. The value of SThM is further amplified when multiple properties can be obtained simultaneously at the same location. In particular, thermoelectric materials have figure of merit defined by both thermal and electrical properties. However, it is very challenging to perform simultaneous microscale thermal and electrical property mapping using SThM, which has only been demonstrated on a very limited number of materials. The majority of the SThM methods reported to date suffer from relatively low sensitivity and accuracy due to inadequate thermal and electrical contact conductance between the probe and sample, especially when a native oxide layer is present on the sample surface. The necessity of very fine probe tip to realize high spatial resolution often limits the amount of contact force and the resulting thermal and electrical contact conductance. Furthermore, there exist large uncertainties in the reported thermal contact resistances and contact radius primarily determined using theoretical modeling combined with calibrations, which inevitably compromise the accuracy of the thermal conductivity measurement.

Described herein is the development of a novel SThM probe capable of applying magnitudes higher probe-sample contact force than the conventional version to realize simultaneous microscale measurement of thermal conductivity and Seebeck measurement with unprecedented accuracy and sensitivity. This significantly increased contact force considerably reduces the thermal contact resistance between the probe and sample, greatly increasing thermal measurement sensitivity over an increased range of sample thermal conductivity. Additionally, the increased contact force yields consistent and
reliable electrical contact on samples with native oxide layers, which is critical to Seebeck coefficient measurement. Also introduced herein is a method to experimentally measure the probe-sample thermal contact geometry and area. The probe is demonstrated with simultaneous thermal conductivity and Seebeck coefficient mapping on a combinatorial Ti-Ni-Sn thermoelectric film and an irradiated nanostructured thermoelectric half-Heusler Hf$_{0.25}$Zr$_{0.75}$NiSn$_{0.99}$Sb$_{0.01}$ with relatively thick native oxide layer.

2.3 Experimental

The conventional Wollaston SThM probe consists of a highly conductive silver wire of 75 µm diameter with a resistive Pt-Rh wire core of about 5 µm in diameter. The wire is bent into a V-shape, and the silver is etched away at the bend to expose the active Pt-Rh core near the tip region, as shown in Figure 2(a).

Figure 2. Microscope images of the in-house fabricated thermal microprobe (a) without support structure and (b) with transparent support structure behind the probe tip.

In order to enhance probe strength and, thus, contact force without sacrificing the spatial resolution, we developed a process to add a microscale support structure made of rigid and transparent cyanoacrylate of low thermal conductivity behind the probe tip while keeping the probe front tip apex intact as shown in Figure 2(b). The support structure effectively transfers the contact force from the Pt-Rh core to the significantly larger silver wire. During measurement, an electrical current is passed through the probe, which generates a microscale heated region on the sample due to Joule heating in the resistive probe tip. The probe tip transfers heat through three primary heat transfer mechanisms: (i) heat transfer from the probe tip to the sample, (ii) conduction from the resistive tip to the conductive silver clads, (iii) combined loss of convection to air and conduction to the support structure along the probe length. Thermal measurement sensitivity can be increased when the heat transfer to the sample increases relative to all other heat losses by enhancing the tip-sample contact force and, thus, thermal contact conductance.

Since the measured thermal contact area is much larger than the phonon mean free path in the probe tip and sample materials, diffusive heat transfer is considered. The steady-state heat transfer between the probe tip and sample consists of the probe-sample thermal contact resistance $R_c$ and the effective sample resistance $R_s$ related to the sample thermal conductivity $k_s$. The average temperature rise along the probe wire is determined by the probe electrical resistance measurement and the known temperature coefficient of resistivity $\lambda$. The thermal conductivity of the sample can then be determined by the measured probe effective thermal resistance using a heat transfer model with calibrated thermal contact parameters. The sample Seebeck coefficient is extracted from the sample temperature rise at the contact region and Seebeck voltage between the probe-sample contact and the unheated region of the sample.
A one-dimensional heat conduction model along the probe tip length is considered due to the small Biot number of the Pt-Rh wire. Based on the probe symmetry, only half of the probe length is modeled. Let \( x = 0 \) denote the junction of the resistive probe tip and the silver clad and let \( x = L_p/2 \) represent the center of the probe-sample contact area, located halfway along the probe length. If \( \theta = T(x) - T_\infty \), where \( T_\infty \) is the ambient temperature, and radiation losses are neglected, the energy balance of a differential element in the probe tip yields

\[
\frac{\partial^2 \theta}{\partial x^2} - \left( \frac{2h}{k_p r_p} - \frac{l^2 \rho_o \lambda}{k_p \pi^2 r_p^4} \right) \theta = -\frac{l^2 \rho_o}{k_p \pi^2 r_p^4} \theta \tag{1}
\]

where \( h \) is an effective heat transfer coefficient that includes heat losses due to convection to the air and conduction to the support structure, \( I \) is the electrical current, and \( k_p, r_p, \) and \( \rho_o \), are the probe tip thermal conductivity, radius, and nominal electrical resistivity, respectively. The temperature profile of the probe tip is

\[
\theta(x) = C_1 \exp(\sqrt{\beta} x) + C_2 \exp(-\sqrt{\beta} x) + \frac{l^2 \rho_o}{2h \pi^2 r_p^3 - \lambda l^2 \rho_o} \tag{2}
\]

where \( \beta = \frac{2h}{k_p r_p} - \frac{l^2 \rho_o \lambda}{k_p \pi^2 r_p^4} \). To solve for the constants of integration \( C_1 \) and \( C_2 \), it is noted that the silver clads act as ideal heat sinks and, thus, \( \theta(0) = 0 \). The other boundary condition at \( x = L_p/2 \) reflects the heat flow into the sample and includes the thermal contact resistance \( R_c \) and the sample resistance containing the sample thermal conductivity \( k \). When the geometric quantities \( r_p, L_p \) and the probe material properties \( k_p, \rho_o, \lambda \) are well known, the only unknowns in the coefficients \( C_1 \) and \( C_2 \) are the sample thermal conductivity \( k_s \), the effective heat transfer coefficient \( h \), the probe-sample thermal contact resistance \( R_c \), and the thermal contact radius \( r_c \). To reduce the number of unknowns and increase the fidelity of the model, \( r_c \) is determined experimentally by measuring the probe thermal resistance when the probe tip moves from the center to the edge of the sample. A significant increase of the probe thermal resistance was observed when the tip and sample edge distance reduced to a value smaller than \( r_c \). Due to the biplanar symmetry of the probe, the thermal contact area is roughly elliptical with 1.4 µm minor axis and 3.2 µm major axis. The radius of a circle with equivalent area is 2.1 µm. In order to ensure repeatable thermal contact conditions, all measurements were performed on well-polished samples in a dry nitrogen environment with the same probe and identical contact force.

### 2.4 Results and Discussion

Five samples of known thermal conductivity were measured, and the method of least squares was implemented to determine the combination of \( R_c \) and \( h \) that provides the best fit of the model to the experimental data (Figure 3). The effective convection coefficient is 1,800 W/m²K in contact mode. The effective probe-sample thermal contact resistance \( R_c \) is 13 K/mW for this probe, while the minimum \( R_c \) that can be realized using the conventional probe is about 60 K/mW. Figure 3 shows measurements on samples of thermal conductivity ranging from 0.52 to 22 W/mK using the supported probe and the conventional probe. Also shown are the modeling results which were fit to the data by simultaneously varying the effective heat transfer coefficient \( h \) and the probe-sample thermal contact resistance \( R_c \).
Figure 3. Probe thermal resistance vs. sample thermal conductivity of five calibration samples using the conventional probe and the supported probe. The dashed curves are the results of the model fit to the measurement data.

The measured thermal resistance using the supported probe continues to drop with increasing sample thermal conductivity up to at least 22 W/m·K. On the other hand, the thermal resistance of the conventional probe becomes insensitive to sample thermal conductivity above 6.7 W/m·K. Defining the probe sensitivity as the gradient of probe thermal resistance with respect to sample thermal conductivity, the supported probe shows 340, 890, 1,810, and 2,530% percent improvement in measurement sensitivity between the thermal conductivity ranges of 0.5 – 1.4, 1.4 – 3.3, 3.3 – 6.7, and 6.7 – 22 W/m·K, respectively, owing to the significantly reduced tip-sample thermal contact resistance.

While previous works have reported a near saturated probe thermal response with very limited contact force, there is a significant reduction in probe thermal resistance with increasing contact force due to the unprecedented probe-sample contact force attained with this robust supported probe (shown in Figure 4).
In congruence with prior research, there is a relatively constant thermal response between the 1st and 2nd contact points corresponding to 0x and 10x of the conventional probe typical contact force. Beyond 10x normalized contact force, the thermal contact resistance quickly drops. The large drop in thermal contact resistance is attributed to a decrease in the solid-solid thermal contact resistance which has been shown to be the dominant thermal resistance compared to ballistic air conduction around the periphery of the probe contact. The significantly decreased contact resistance due to increased contact force increases the probe thermal sensitivity and accuracy, especially for samples of relatively high thermal conductivity above 5 W/m K.

The newly-developed supported probe is demonstrated on multiple materials with local property variations. The conventional SThM probe failed to make adequate electrical contact with these samples due to nonconductive native oxide layers present on the sample surfaces. The supported probe can make electrical contact with 100% reliability due to the dramatically increased probe-sample contact force.

Ti-Ni-Sn half-Heuslers are promising thermoelectric materials due to their high performance, abundance of constituent elements, and ease of synthesis. In order to identify the optimal composition with highest thermoelectric efficiency, a combinatorial film with gradient composition of all three elements was fabricated. The Seebeck coefficient and thermal conductivity were mapped in a 5 x 4 mm region of interest with 100 µm grid spacing (Figure 5).
Figure 5. (a) Optical image of the region of interest on the Ti-Ni-Sn combinatorial film, (b) Seebeck coefficient, and (c) thermal conductivity from SThM using the supported probe.

Figure 5 (a) is an optical microscope image of the combinatorial Ti-Ni-Sn film. The cross and numbers associated with 0 µV/K Seebeck coefficient and 1.4 W/m K thermal conductivity in Figure 5(b) and Figure 5(c) are laser etched lithographic markings. The optical image also shows the upper right portion of the film is of visibly lighter color and with a greater density of white precipitates compared to the bounding region below and to the left. The boundary of these two optically distinct regions corresponds to a sharp transition in both Seebeck coefficient and thermal conductivity. The drastic change in properties over such a small distance is attributed to diffusion and phase segregation during sintering. The relatively small size of the region with maximum Seebeck coefficient highlights the importance of high resolution SThM. Conventional approaches consisting of measurements several millimeters apart might overlook the tiny region of optimal properties. This location consists of approximately 33.1 at.% Ti, 32.1 at.% Ni, and 34.8 at.% Sn, resulting in a multiphase region consisting of TiNiSn, Ti2Sn3, and Sn. The region of highest thermal conductivity and lowest Seebeck coefficient is Sn rich and Ti deficient with respect to stoichiometric TiNiSn.

Next, the supported probe is demonstrated on an irradiated sample. Nanostructured bulk Hf0.25Zr0.75NiSn0.99Sb0.01 was irradiated with 2.5 MeV protons to a fluence of $2 \times 10^{16}$ cm$^{-2}$, resulting in a damage depth of approximately 40 µm. Thermal conductivity and Seebeck coefficient are mapped as a function of depth from the irradiated surface. The results are compared to the irradiation-induced vacancy concentration calculated with Transport of Ions in Matter (TRIM) simulation.
Figure 6. (a) Thermal conductivity and (b) Seebeck coefficient as a function of depth from the irradiated surface of the Hf0.25Zr0.75NiSn0.99Sb0.01 sample obtained using SThM on the cross section of the irradiated bar. The solid red curve represents the concentration of irradiation-induced vacancies calculated using TRIM simulation.

Figure 6 shows a clear reduction in thermal conductivity up to 40 µm deep with maximum damage occurring at 34 µm – an excellent agreement with the damage profile calculated using TRIM. The profile of property change is a characteristic shape with two distinct regions: a relatively uniform reduction in thermal conductivity up to 30 µm from the surface followed by a sudden decrease in thermal conductivity from 31 to 35 µm – the depth where a significant portion of irradiation-induced defects accumulated. Beyond 35 µm, the thermal conductivity quickly recovers to the non-irradiated value as the irradiation damage decays to naught. Thermal conductivity decreased from 5.4 W/m·K in the non-irradiated region to 4.1 W/m·K in the irradiated region up to 30 µm deep. There is no statistically significant change in Seebeck coefficient, which was validated with a separate bulk film measurement. The reduction in thermal conductivity is attributed to irradiation-induced point defects that act as scattering sources for phonons.

As a third and final demonstration, a combinatorial ZnSnN$_2$ film was scanned to map thermal conductivity and Seebeck coefficient as a function of Zn concentration.

Figure 7. Thermal conductivity and Seebeck coefficient of combinatorial ZnSnN$_2$ as a function of Zn concentration, as measured by the supported SThM probe.
Figure 7 shows a trade-off between rapidly increasing Seebeck coefficient and thermal conductivity around 0.7 \( \frac{Zn}{(Zn + Sn)} \).

The successful demonstration of the supported probe developed in this work on samples of microscale compositional/structural variations despite the presence of surface oxidation confirms the significantly enhanced thermal and electrical contact conductance and the improved sensitivity of the SThM technique applicable to a broad range of materials.

3. SCANNING ELECTRICAL MICROSCOPY TO MAP ELECTRICAL CONDUCTIVITY

Electrical conductivity plays an important role in a range of sensor materials, such as thermoelectrical materials and resistivity based sensors. Thermoelectric materials have figure of merit \( ZT \) defined by thermal conductivity \( k \), Seebeck coefficient \( \alpha \), and electrical conductivity \( \sigma \):

\[
ZT = \frac{\alpha^2 \sigma T}{k}.
\]

While the newly-developed supported probe captures two of these properties with ~2 \( \mu \)m spatial resolution, a different type of probe is needed to acquire microscale electrical conductivity. One of the most trusted options applicable to a wide range of materials is the Microscale Four Point Probe (M4PP). Such an M4PP with 10 \( \mu \)m pitch between probes is shown in Figure 8.

![Figure 8. Microscope images of the microscale four point probe manufactured by Capres.](image)

A commercial M4PP was acquired and implemented in our custom scanning probe platform that was used to operate the above supported thermal probe. As a first step, a custom apparatus was developed to hold the M4PP in our scanning probe system (shown in Figure 9).
Figure 9. Photograph of the Capres M4PP in a custom fabricated measurement apparatus. The M4PP is approaching a gold film calibration standard.

The M4PP is capable of measuring sheet resistance of films with thickness \( \ll 3 \, \mu m \) or bulk electrical conductivity of samples with thickness \( \gg 50 \, \mu m \). The bulk electrical resistivity \( \rho_b \) is extracted from measurement as

\[
\rho_b = \frac{2\pi s}{V} \left( \frac{V}{I} \right),
\]

where \( s \) is the M4PP probe pitch and \( V \) is the voltage measured for a given current \( I \). Typically, the quotient \( V/I \) in equation (4) is replaced with the slope of the best fit line of voltage vs current for several different currents. In the case of thin film measurement, sheet resistance \( \rho_s \) is given by

\[
\rho_s = \frac{\pi}{\ln(2)} \left( \frac{V}{I} \right).
\]

In both cases, the equation is simply a solution to the Laplace equation with respective limits and boundary conditions.

The M4PP is validated with measurement on a 50 nm-thick gold film with \( \sim 4.5 \, \text{nm-thick Chromium} \) adhesion layer. The measured sheet resistance using the M4PP is 0.60 \( \Omega/sq \). A separate gold film from the same batch was measured independently with the van der Pauw method, yielding a sheet resistance of 0.620 \( \Omega/sq \). The measurements agree within 4\%, where some uncertainty is introduced in possible slight thickness variations between the films.

4. CONCLUSION

We have developed a scanning probe system that can map thermal and thermoelectric properties of combinatorial films. We designed and fabricated a novel thermal probe to perform simultaneously measurements of thermal conductivity and Seebeck coefficient with unprecedented sensitivity. The thermal probe has been successfully validated and demonstrated on mapping thermoelectric properties of thin films with gradient composition. In addition, a microscale four-point probe is implemented in our custom-built scanning probe system, and its performance is validated by measuring a standard gold thin film sample. The scanning probe system developed in this project enables high-throughput discovery of combinatorial materials with highly desired properties for a broad range of nuclear energy applications.
5. REFERENCES


