Design of a thermoelectric characterization platform for thin-film bismuth telluride

Siddharth Narayanan, Jiajun Luo, and Matthew Grayson

Department of Electrical Engineering and Computer Science, Northwestern University

(Funded by the Initiative for Sustainability and Energy at Northwestern University)

In this paper, we discuss the construction of a small apparatus - less than 3cm large - to characterize the thermoelectric properties of a small thermoelectric sample that can be easily used in cryogenic environments. The device was then used to measure the thermal conductivity of silicon and the Seebeck coefficient of thin film bismuth telluride. Thin film bismuth telluride has become of particular interest in recent years because of its possible high $zT$ thermoelectric figure of merit enhanced by the topological surface state. Measuring the Seebeck coefficient of the thin film is an important step towards determining $zT$ coming from the surface state.

INTRODUCTION

Bismuth telluride (Bi$_2$Te$_3$) has been recently recognized as a topological insulator [1]. This class of materials are known for the curious property of having metallic surface states and an insulating bulk. This behavior originates from strong spin-orbit coupling of the bulk material. On the surface, the band structure has a shape of single Dirac cone, and backscattering is suppressed, thus novel thermoelectric properties may be expected of thin layers of these materials. Because space inversion symmetry is always broken at a material surface, this metallic surface state is topologically protected.

Bismuth telluride is experimentally confirmed to be a topological insulator. [1] It has a quintuple layer sandwich structure, in which each quintuple layer is a unit of Te-Bi-Te-Bi-Te hexagonal layers. Inside each quintuple layer, the Te-Bi bonding is covalent; between quintuple layers, the Te-Te bonds are relatively weak Van der Waals bonds. Hence, thin films can be cleaved easily. In thin film samples of bismuth telluride, the surface area to volume ratio is high. As the thickness of the sample decreases, we can, in principle, thermoelectrically characterize the surface state.

The Seebeck effect is an important thermoelectric phenomenon: if two ends of a conductor or a semiconductor are held at different temperatures, there will be a voltage difference across the sample. The strength of this voltage per unit temperature difference is defined as Seebeck coefficient. Materials with high Seebeck coefficients have applications in thermocouples, and increasingly, in harvesting energy from cooling systems. A heat source (such as an engine) is connected to a heat sink through material of large Seebeck coefficient. This thermal gradient builds up an electric potential difference which can be harvested as electrical energy (for example, to charge a battery).

The figure of merit $zT$ is widely used to characterize the performance of a material in thermoelectronic applications. It is defined as the temperature $T$ times $z$:

$$z = \frac{\sigma \cdot S^2}{k}$$

where $\sigma$ = electric conductivity, $S$ = Seebeck coefficient, and $k$ = thermal conductivity. The ideal thermal electronic material has a high electric conductivity and Seebeck value, while remaining thermally insulating. This allows for conversion of heat flow into electrical power, or, conversely, electrical current flow into cooling power. The topological surface state is predicted to increase the $zT$ value of bismuth telluride. [2]

METHODS

In order to measure the Seebeck coefficient of bismuth telluride, a measurement apparatus
was built. This apparatus (Figures 1 and 2) consisted of two thermistors to measure temperature, a resistor to provide heat, and a cold sink to dissipate heat.

![FIG. 1. Schematic of thermal apparatus. Current is applied to the 8Ω heater resistor (B), which heats one end of the sample (C). The heat flows through the sample and is quickly dissipated through the copper heat sink (A). Once the sample has reached thermal equilibrium, we can measure the thermal gradient using the two thermistors above and below position (D). Heat flow $Q$ is in the direction of red arrow.](image)

This apparatus represents the "thermal" portion of thermoelectric characterization. Figure 1 shows the schematic design of the apparatus. The device applies heat to one end of the sample by a 8Ω resistor that emits heat when current is running through it. The other end of the sample is attached to a copper strip that acts as a heat sink. This creates a noticeable temperature difference between the ends. The resistances of the thermistors, placed 3mm apart, are a linear function of their temperature. By measuring their resistances, the thermal gradient can be determined. All thermal contacts were made using thermally conductive Arctic Silver epoxy. The entire device was mounted on a 16-pin header as shown in Figure 2.

In order to ensure that the thermal device was working properly, it was first used to measure the thermal conductivity of silicon. Since there is an established value, it served as a good benchmark to ensure that everything was calibrated properly and all contacts were properly made. A 5mm×8mm×500µm silicon substrate with a 300nm SiO$_2$ top layer was used. This sample was of the same material as the substrate used in later steps, so testing the device on this particular sample was key. The silicon dioxide coating acted as an electrical insulator between the silicon substrate and the bismuth telluride samples used below. Thermal conductivity was measured by recording the voltage applied to the resistor, and recording the temperature of the two thermistors. Voltages applied ranged from 2V to 6V. This corresponded to a maximum temperature of approximately 400 K. The heat emitted by the resistor was in the range of 1 to 3W, giving thermal gradients as large as 15 K/mm. Then, the thermal conductivity $k$ can be determined:

$$k = \frac{P}{A\Delta T}$$

where $P = \frac{V^2}{R}$, where $V$ is applied voltage and $R = 8Ω$. $A$ = cross-sectional area for heat flow = $200 \times 10^{-6} m^2$, and $\Delta x$ = distance between thermistors = 3 mm. This experiment was performed on two identical substrates, and the results are described in the Results section.

The apparatus was now ready to characterize Bi$_2$Te$_3$. The samples were produced by Scotch tape exfoliation. A large and thick flake was peeled off from a p-type doped single crystal Bi$_2$Te$_3$ bulk material. This flake is repeatedly peeled by Scotch tape to make it thinner, and
then transferred onto the silicon substrate with 300nm SiO$_2$ top layer. The size of this sample is measured by atomic force microscopy to be about 130nm thick and 10$\mu$m $\times$ 30$\mu$m large. Previous studies [3] on the electrical properties of this material show a bulk hole density of $6.4 \times 10^{18}$ cm$^{-3}$ and surface electron density of $1.3 \times 10^{13}$ cm$^{-2}$ from each surface at 3.5K.

FIG. 3. Optical microscope picture of the bismuth telluride flake placed on silicon substrate, with gold contacts attached. Large wires (A) were defined by photolithography. Thin wires (B) placed were defined by electron-beam lithography. The thin wires are all parallel where they touch the flake and are 3 -- $4\mu$m apart. The thermal gradient is applied perpendicular to the strips, so each strip is considered an equipotential.

Then, the voltage contacts were deposited by E-beam evaporation. First, large strips of 5nm of titanium and 45nm of gold(Figure 3A) were define by photolithography. Titanium served as a sticking layer between gold and the substrate; and gold is chosen for its high electrical conductivity and stability. Those large strips would be used as contact pads for connecting gold wires as well as alignment marks for later steps. Then E-beam lithography is used to define the narrow leads directly in contact with the sample (Figure 3B). Since the sample thickness is around 130nm, 5nm of titanium and 195nm of gold was deposited for those leads.

Then, the Seebeck coefficient of bismuth telluride was measured by measuring the voltage difference between two leads at different positions along the thermal gradient. Once the sample was attached to the thermal contacts in the device, the voltage contacts were attached to the base, and then attached to a voltmeter.

Again, we varied the applied heater voltage between 2V and 6V ($P = 0.5W$ to 4.5W), allowing $\Delta T$ to vary between 0K and 30K. Using the voltage contacts, we measured the potential difference across the sample for each applied heat. Specifically, the two contacts used were $d = 4\mu$m apart. From here, the Seebeck coefficient can be determined:

$$S = -\frac{(V_{\text{hot}} - V_{\text{cold}}) \cdot \Delta x}{\Delta T \cdot d}$$

RESULTS

First, the thermal conductivity of silicon was measured. Figure 4 shows how temperature difference measure by the two thermistors varies with the power applied. In general, we see that data points at low applied powers tend to be less reliable. This is because the temperature difference is relatively low, giving us a small signal subject to noise. For this reason, only powers greater than 2W were considered in our calculations. The thermal conductivity of silicon can be calculated from the slope of the fitted line. We achieved an average result of $129 \frac{W}{K \cdot m}$ on the first sample and $145 \frac{W}{K \cdot m}$ on the second (Figure 4). This was reasonably close to the expected value of $149 \frac{W}{K \cdot m}$.

Finally, the Seebeck coefficient of bismuth telluride was measured. Figure 5 shows how the voltage measured across the sample changed with the temperature difference of those two contacts, estimated from that measured by the thermistors. By calculating the slope in this plot, the measured Seebeck value was derived as $-1.23 mV/K$. When making this measurement, the thermal conductivity was also measured, with a value of $254 \frac{W}{K \cdot m}$, about 40% larger than expected.
FIG. 4. Temperature difference plotted versus the applied power in both silicon samples. The slopes of the lines of best fit (fitted to high-power data only) are roughly equal, implying that the two samples have the same thermal conductivity.

FIG. 5. Observed voltage across bismuth telluride flake as a function of temperature gradient. The slope of the line of best fit is $-S$.

DISCUSSION AND FURTHER STUDY

As our results have demonstrated, our apparatus can, with reasonable accuracy, measure the thermal conductivity and Seebeck coefficient of a material. The device has been constructed so that it is simple to put in and remove a sample.

To ensure accuracy of the Seebeck coefficient, it will be necessary to perform the experiment on multiple samples. Because we can determine the value of $k_{\text{substrate}}$ (which should be approximately equal to $k_{\text{Si}}$) when measuring $S_{\text{Bi}_2\text{Te}_3}$, we can check whether the device is working properly. In our measurement of the sample with $\text{Bi}_2\text{Te}_3$ thin film, the measured thermal conductivity was significantly higher than expected. Therefore, it is necessary to try the experiment again on several samples to ensure reproducibility of our results.

Once we can be sure that the method accurately measures the Seebeck coefficient, the resistor and thermistors can be replaced with their on-chip equivalents. This approach allows for more precise measurements. It ensures that all of the heat from the resistor is transferred to the sample.

Topological insulators are a class of materials that show promise in thermoelectric applications. In order to understand how they behave, we must characterize their surface states. This study represents a step towards that ultimate goal.