Micro Thermoelectric Cooler Fabrication: Growth and Characterization of Patterned Sb$_2$Te$_3$ and Bi$_2$Te$_3$ Films

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Abstract
A column-type micro thermoelectric cooler is being fabricated using $p$-type Sb$_2$Te$_3$ and $n$-type Bi$_2$Te$_3$ films (approximately 4 µm thick). The films are grown by thermal co-evaporation and patterned on Cr/Au/Ti/Pt (hot) connectors, which are deposited onto a silicon dioxide coated wafer. The column height is limited by control of the Te deposition rate. Although a high substrate temperature during thermoelectric film deposition is desired, it has been limited by the degradation of the photoresist used for patterning. The measured Seebeck coefficient and electrical resistivity of the thermoelectric films are reported, and preliminary results show that excess tellurium increases the Seebeck coefficient.

Introduction
Telluride compounds are the thermoelectric materials used in the fabrication of the micro thermoelectric cooler, since they currently have the highest cooling performance at room temperature. The techniques used for fabrication of these compounds are dependent, among other factors, on the desired film thickness.

Zou et al. [1] deposited thin films (700 nm) of $n$-type Bi$_2$Te$_3$ and $p$-type Sb$_2$Te$_3$ by vapor deposition, which had a room temperature dimensionless figure of merit approximately equal to 0.3. The Seebeck coefficient and electrical resistivity were -200 µV/K and 1.29x10$^{-5}$ Ω-m for the $n$-type, and 171 µV/K and 3.12x10$^{-5}$ Ω-m for the $p$-type material. Min and Rowe [2] have proposed a micro thermoelectric cooler where the thermoelectric thin films are grown on a very thin, low thermal conductivity SiC membrane (PECVD) to minimize the heat leakage effect. The electrical current and heat flow parallel to the film plane.

Lim et al. [3] deposited thick films (20 µm) of telluride compounds using electroplating for fabrication of thermoelectric coolers where the current and heat flow perpendicular to the film plane (column-type design). They built a thermoelectric microdevice that presented a maximum cooling effect of 2 K, and a dimensionless figure of merit 0.011. The $n$-type Bi$_2$Te$_3$ films exhibited in plane Seebeck coefficients ranging from -30 to -60 µV/K and in plane electrical resistivity of 1x10$^{-5}$ Ω-m. The properties of $p$-type Bi$_{2-x}$Sb$_x$Te$_3$ films were not fully characterized due to poor reproducibility.

Due to parasitic conduction heat transfer between the hot and cold junctions, and the thermal and electrical contact resistances, thin films (less than 1 µm) have not been used in conventional column-type thermoelectric coolers. These problems can be minimized if thicker films (2 to 10 µm) are used. Here, the column-type design of a micro thermoelectric cooler is considered for a wireless vapor sensor application, as shown in Figure 1. The thermoelectric films (Bi$_2$Te$_3$ and Sb$_2$Te$_3$), grown based on the deposition technique of Zou et al. [1], are about 4 µm thick. The goal for the cooler is to lower the temperature of the sensor 10 K below ambient in less than 30 seconds, while using minimal power with a 3 V battery. The device design is based on predictions from a thermoelectric cooler model [4]. Initial results of the device fabrication are presented. The deposition and characterization of the thermoelectric films and the device fabrication steps are described.

![Figure 1: Rendering of the micro thermoelectric cooler used with a micro vapor sensor. The column-type design, and various energy conversion mechanisms (Joule heating and Peltier cooling/heating) and heat transfer paths are also shown.](image-url)
resistive heater, which can maintain a constant substrate temperature of up to 300 °C. A type K thermocouple is placed at a distance of 5 mm from the substrate edge. An additional film thickness monitor is used to measure the overall thickness of the deposited compound.

The pressure during deposition varies from $5 \times 10^{-7}$ torr to $2 \times 10^{-6}$ torr. Bismuth and antimony are deposited at a rate of $1 \pm 0.1 \, \text{Å/s}$. The tellurium deposition rate varies from $2 \pm 0.5 \, \text{Å/s}$ to $3 \pm 0.5 \, \text{Å/s}$. The higher uncertainty for Te is an indication of the difficulty in controlling the sublimation of this element. This uncertainty increases with the depletion of Te inside the evaporation boat, and when it is greater than $\pm 0.6 \, \text{Å/s}$ (films thicker than 4 µm), the deposition process is stopped, limiting the height of the columns.

Since a photoresist (PR) layer is used to pattern the columns, the thermal cycling of the substrate during the deposition is limited to maintain the PR integrity. Due to the low deposition rates, the fabrication of a 4 µm thick thermoelectric film takes a minimum of 4 hours. Depositions with the substrate temperature equal to or higher than 90 °C (controlled by the heater), such as the deposition of film S2 characterized in Table 1, had the PR over hardbaked. In this case, the PR could not be removed without damaging the thermoelectric film. The deposition of the remaining films listed in Table 1 had the heater set to a temperature equal to or lower than 70 °C, though the substrate temperature increased during the deposition due to the heat generated by the resistive evaporation sources. The maximum measured substrate temperature is referred to as $T_{\text{sub}}$, which occurred at the end of the deposition.

Characterization of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ films

A glass substrate was attached to the patterned wafer, so that a sample of the deposited film could be obtained for Seebeck coefficient, resistivity and thickness measurements, as well for x-ray diffraction analysis. A silicon substrate with a thin layer of platinum was also included to allow for stoichiometry analysis of the film cross-section.

Energy dispersive x-ray analysis (EDX) was used to identify the elements present in the films, and their relative concentrations. The atomic ratio between Te and Bi (or Sb), which is listed in Table 1, varied up to $\pm 10\%$ along the film thickness. Note that these are qualitative values, i.e., they must be considered only for comparison. The precision (which depends on the x-ray counts in the peaks of interest) and the accuracy (which depends on a reference, i.e., a standard material of known composition to compare to the unknown), were not investigated.

The orientations of the crystals in the films were characterized using x-ray diffraction. The diffraction patterns for several films are shown in Figure 2. The data agrees with the associated entries in the Powder Diffraction File [5], and the corresponding reflection planes (hkl) are labeled. The results confirm the formation of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ and show that the films are polycrystalline without strong preferential orientation. In Figure 2(a), however, the most intense peak is the (1.0.10) reflection plane for film S3, indicating some preferential orientation. As the amount of Te is increased in films S4 and S6, (015) becomes the strongest peak, which agrees qualitatively with the relative intensities reported in the standard powder pattern for Sb$_2$Te$_3$ [for planes (015) and (1.0.10) the relative intensities are 100 and 35, respectively] [5]. In Figure 2(b) the strongest peak corresponds to the (015) plane. The relative intensities of the reflection planes approach the values reported in the standard powder pattern for Bi$_2$Te$_3$ [100 and 70 for planes (015) and (10.10), respectively] [5], when the atomic ratio between Te and Bi decreases.

Table 1: Deposition conditions and properties of Bi$_2$Te$_3$ (B1 to B6) and Sb$_2$Te$_3$ (S1 to S6) films at room temperature. (*) The heater was set to a temperature equal to 90 °C. The photoresist used for patterning could not be removed after the film growth.

<table>
<thead>
<tr>
<th>Film Designation</th>
<th>$T_{\text{sub}}$ °C</th>
<th>$L_{\text{te}}$, µm</th>
<th>$\rho_e$, µΩ·m</th>
<th>$\alpha_S$, µV/K</th>
<th>$\alpha_S^2/\rho_e$, mW/K²·m</th>
<th>At%Te/At%(Bi or Sb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 / S1</td>
<td>94 / 73</td>
<td>3.7 / 4.2</td>
<td>24 / 32</td>
<td>-84 / 105</td>
<td>0.29 / 0.34</td>
<td>1.2 / 1.6</td>
</tr>
<tr>
<td>B2 / S2*</td>
<td>95 / 90</td>
<td>4.5 / 3.7</td>
<td>30 / 19</td>
<td>-81 / 120</td>
<td>0.22 / 0.76</td>
<td>- / 1.7</td>
</tr>
<tr>
<td>B3 / S3</td>
<td>99 / 74</td>
<td>3.7 / 3.6</td>
<td>54 / 35</td>
<td>-70 / 105</td>
<td>0.09 / 0.32</td>
<td>1.7 / 1.7</td>
</tr>
<tr>
<td>B4 / S4</td>
<td>99 / 77</td>
<td>3.7 / 4.2</td>
<td>48 / 35</td>
<td>-71 / 135</td>
<td>0.10 / 0.52</td>
<td>2.0 / 2.2</td>
</tr>
<tr>
<td>B5 / S5</td>
<td>106 / 76</td>
<td>4.4 / 4.0</td>
<td>31 / 36</td>
<td>-83 / 127</td>
<td>0.22 / 0.45</td>
<td>1.6 / -</td>
</tr>
<tr>
<td>B6 / S6</td>
<td>106 / 96</td>
<td>4.5 / 4.3</td>
<td>40 / 47</td>
<td>-80 / 173</td>
<td>0.16 / 0.64</td>
<td>1.2 / 4.4</td>
</tr>
</tbody>
</table>
The Seebeck coefficient, $\alpha_S$, was measured at room temperature, under vacuum, and the results are presented in Table 1. One end of the film (10-20 mm long and 2-4 mm wide) was thermally connected to a heat sink and the other end to a heater. The temperatures of the hot and cold sides ($T_h$ and $T_c$, respectively) were measured with fine copper-constantan thermocouples. The copper legs of the thermocouples were also used to measure the potential difference, $\Delta\phi$, across the film. The Seebeck coefficient was determined by the ratio between $\Delta\phi$ and ($T_h - T_c$), with an accuracy of $\pm 4\%$.

The electrical resistivity ($\rho_e = R_e A_e / L$, where $L$ is the film length, $A_e$ is the film cross section area, and $R_e$ is the electrical resistance) was obtained by the standard four probe measurement. Fine copper wires were used for the electrical potential measurement, which was performed at room temperature and under vacuum. The film thickness, $L_{th}$, was obtained from four different points of the sample, with an accuracy of $\pm 5\%$, using a surface profiler. The accuracy of the resistivity measurements, which are presented in Table 1, was found to be $\pm 25\%$ (limited by uncertainties in $A_e$ and $L$).

To fully characterize and compare the samples, measurements of the Hall coefficient (for carrier mobility) are planned. The trends observed so far are discussed below. Also note that, low electrical conductivity substrate (glass) is used for property measurements (while in the device, the thermoelectric films are grown on Pt).

For the Sb$_2$Te$_3$ films, as indicated in Table 1, $\alpha_S$ increases with an increase of the Te content (films S3, S4 and S6), and this agrees with the results reported by Kim et al [6]. An increase of the substrate temperature (films S2 and S3) decreases the electrical resistivity, and increases the Seebeck coefficient. Zou et al. [1] have reported a resistivity of $1.04 \times 10^{-5} \Omega$-m and a Seebeck coefficient of $171 \mu$V/K, for a substrate temperature of $230 ^\circ$C maintained during the co-evaporation of the Sb and Te elements. The electrical power factor, $\alpha_S^2/\rho_e$, is equal to $2.80 \times 10^{-3} \text{W/K}^2\text{-m}$, which is almost four times larger than the highest electrical power factor listed in Table 1 for $p$-type films. For the Bi$_2$Te$_3$ films, there is no detectable effect due to the increase in the Te content on the thermoelectric properties, as shown in Table 1. Zou et al. [1] have reported a resistivity of $1.3 \times 10^{-5} \Omega$-m and a Seebeck coefficient of $-228 \mu$V/K ($\alpha_S^2/\rho_e$ equal to $3.99 \times 10^{-3} \text{W/K}^2\text{-m}$), for a substrate temperature of $260 ^\circ$C maintained during the co-evaporation of the Bi and Te elements. Based on these results, in order to maximize $\alpha_S^2/\rho_e$, future designs of the device and the process steps will allow for higher substrate temperature.

Fabrication of Micro TE Cooler Device

The silicon wafer used for the device fabrication is also the micro cooler heat sink. To provide electrical insulation for the device, a 850 nm silicon dioxide layer is grown on the Si wafer. PR is spun cast defining a lift-off pattern for the hot (bottom) connectors and electrical connectors (pads). These connectors are Cr/Au/Ti/Pt layers grown by E-Beam evaporation. The Au and Pt layers are 200 nm and 20 nm thick, respectively. The Cr and Ti are 20 nm thick seed layers.

The Pt, which has an electrical resistivity about 5 times larger and a thermal conductivity about 5 times smaller than Au, is used for its good adhesion to the columns, while preventing the diffusion of Au. Each column of the thermoelectric element is patterned consecutively before evaporation using an AZ9245 PR mold, which is where the $n$-type (or $p$-type) thermoelectric element will be formed. Once the thermoelectric film is deposited, the PR is removed, leaving only the columns on top of the hot connectors, as illustrated in Figure 3(a). The Sb$_2$Te$_3$ and Bi$_2$Te$_3$ thermoelectric elements deposited on the hot connector pattern are shown in Figures 3(b) and 3(c). Micro thermoelectric coolers with up to 300 pairs of columns with cross-sectional areas equal to or larger than $7 \mu$m x $7 \mu$m are being fabricated.

Figure 3: Bi$_2$Te$_3$ and Sb$_2$Te$_3$ films deposited on Cr/Au/Ti/Pt hot (bottom) connectors. The cold (top) connectors are not shown. (a) Sketch showing approximate thickness of the films. (b) Image from Scanning Electronic Microscope (SEM) showing a top view of the fabricated structures. This image is the enlarged section A indicated in the part (c), top right. (c) SEM of a device with 50 thermoelectric pairs.

Current yield limitations are due to the deformation of the PR patterns (which define the thermoelectric elements) during the long exposure time of the PR to temperatures ranging from 70 °C to 106 °C. In some cases, mainly in devices with large column cross-sectional area (e.g., 30 µm x 30 µm), a shifted column can reach the bottom connector next to it, or even the other column of the pair, leading to the device failure. Also, over hardbaked PR is left at the borders of the columns, affecting the subsequent PR patterning. The use of a
high temperature PR and an alternative method for patterning the columns (such as shadow mask) are being explored. The steps needed to complete the fabrication process, which is underway, are presented in Figure 4. A contact area is defined on top of each thermoelectric element [Figure 4(a)]. After developing and hardbaking the PR, a thin Cr/Au layer (20 nm/20 nm) is deposited by sputtering. This metallization is necessary to avoid the exposure of the PR in the subsequent photolithography process [Figure 4(b)], which is required to define the area where Au (the metal that forms the cold connectors and closes the electrical circuit of the thermoelectric cooler) will be deposited [Figure 4(c)]. This structure will be bonded to a load. Using Ti/Cu and Cu for these last two metallizations (hot connector) resulted in a large increase in the total electrical resistance of the device with time, which might be due to Cu oxidation. Also, the PR thickness on top of the columns varies with the height of the thermoelectric elements (a difference as large as 0.8 µm between the n- and p-type thermoelectric elements has been observed). The PR has been overexposed to ensure a clean electrical contact opening.

![Figure 4](image-url)  
**Figure 4:** Schematic outlining the strategy for fabrication of the cold (top) connectors. (a) Contact opening for Cr/Au. (b) Contact opening for Au. (c) Structure that will be bonded to the vapor sensor.

A preliminary result of the cold connector fabrication is shown in Figure 5, where the PR layers [indicated in Figure 4(b)] were successfully removed with lift-off in acetone. However, the cold connector process needs to be improved to avoid residual materials on top of the connectors (i.e., to ensure good thermal contact with the load), increase the yield, and allow for the fabrication of a complete electrically connected device.

**Conclusion**

Bi$_2$Te$_3$ and Sb$_2$Te$_3$ films have been deposited by co-evaporation of the elements, and the Seebeck coefficient and electrical resistivity were measured. The thermoelectric films with the highest electrical power factor, $\alpha^2/\rho$, have $\alpha_s$ and $\rho_e$ equal to -84 µV/K and 2.4 x 10$^5$ Ω-m ($n$-type film deposited with a maximum substrate temperature of 94 °C), and 120 µV/K and 1.9 x 10$^5$ Ω-m ($p$-type film deposited with a maximum substrate temperature of 90 °C). For the Sb$_2$Te$_3$ films, an increase of the substrate temperature increases $\alpha^2/\rho_e$, and an increase of the Te content increases $\alpha_s$. In the device fabrication, complete pairs (electrically connected $n$- and $p$-type thermoelectric elements) are produced. Future designs will focus on the implementation of higher substrate temperatures and yield improvements.

*Figure 5:* SEM showing the cold connector fabricated on top of the $n$- and $p$-type thermoelectric elements.

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**References**