Vertical Self-Defined Thin-Film Thermoelectric Thermocouples by Angled Co-Evaporation for Use in μTEGs

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This paper reports the development of a novel thin-film thermocouple structure and associated thermoelectric films for use in micro-thermoelectric generators. The proposed structure enables thermocouple length to be independent of film thickness in vertical thin-film μTEGs, allowing greater thermal resistances with thin-film designs while maintaining fill factor. In the presented structure, thermoelectric thin-films are evaporated over the sidewalls of high aspect-ratio columns. Thermocouple length is thus set by the height of the columns rather than the thickness of the deposited film. The process takes advantage of the shadowing of these columns to form N & P thermocouples on the left and right side of the columns. Also reported is development of thermally co-evaporated thin films Bi$_2$Te$_3$/Sb$_2$Te$_3$ onto vertical surfaces for use. Integration into proof of concept design TEG structure is briefly detailed.

1. Introduction

Micro-thermoelectric generators (μTEGs) provide a small but robust power source using environmental thermal gradients. They are well suited for remote sensing and IoT applications where there exists high deployment and servicing costs or an inhospitable environment for batteries. In particular, thin-film based μTEGs are attractive due to their scalability and low material usage. However, in the traditional vertical configuration [Fig. 1A], the hot-cold junction is separated only by the thickness of the film[1]. This thermal short reduces the temperature across thermocouple and limits power output. In contrast, lateral designs [Fig. 1B], while capable of large thermal resistances, suffer from greatly reduced fill factor and substrate conduction [2]. Thick film deposition, such as electroplating [3] and screen printing [4] are capable of good thermal resistances and fill factors but suffer from increased material usage and poor material properties compared to thin-films [5].

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P_{\text{TEG}} = \left( \frac{\alpha_s^2}{2\rho} \right) \left( \frac{\Delta T_{\text{total}}}{R_{\text{th,couple}}} \right) \left( \frac{R_{\text{th,couple}}}{R_{\text{th,total}}} \right)^2 \frac{A_{\text{leg}} N_{\text{legs}}}{L_{\text{leg}}} \tag{1}
\]

The power output of an idealized single film TEG is given in equation 1 above. The first set of terms represent the power factor of the thermocouple material; $\alpha_s$ is the Seebeck coefficient, $\rho$ is electrical resistivity. The second set represents the temperature across the thermocouple; $\Delta T_{\text{total}}$ is the available temperature difference in the environment, $R_{\text{th,couple}}$ is the thermal resistance across the hot-cold junctions of the thermocouples and $R_{\text{th,total}}$ is the total thermal resistance of the TEG system. The last set represents the electrical component of the thermocouple geometry. $A_{\text{leg}}$ represents the cross-sectional area of the thermocouple perpendicular to heat flow, $N_{\text{legs}}$ is the number of legs and $L_{\text{leg}}$ represents the length of the
thermocouple parallel to the hot-cold junction. $A_{\text{leg}}$ multiplied by $N_{\text{legs}}$ normalized by device area represent the fill factor of the TE material.

Additionally, $R_{\text{th,couple}}$ is impacted by the thermocouple geometry. Longer thermocouples and smaller fill factors increase thermal resistance, though at the cost of increased electrical resistance. The optimal length to fill factor ratio is dependant on the ability of the TEG system to reject heat. The simplified equation for an ideal vertical TEG is given by equation 2 below. $\kappa$ is the thermal resistivity of the TE film and $R_{\text{th,other}}$ is the sum of all other thermal resistances in series the thermocouples. For Bi$_2$Te$_3$ based generators, this implies an optimal thermocouple length of approximately 30 μm for a fill factor of .2 and an $R_{\text{th,other}}$ of 10 K/W.

$$R_{\text{th,couples}} = \frac{\kappa L_{\text{leg}}}{A_{\text{leg}} N_{\text{legs}}} = R_{\text{th,other}}$$  \hspace{1cm} (2)

2. High Aspect Thermocouples

We report a new thin-film thermocouple structure capable of achieving >25 μm thermocouple lengths utilizing thin films while maintaining moderate fill factors. The structure is based on thin-films conformally deposited over the vertical surfaces of thermally insulating columns. In this design [Fig. 2], the column defines thermocouple length rather than film thickness, decoupling the two. This allows for high thermal resistance while maintaining the material and fabrication advantages of thin-films. By utilizing the sidewall surfaces, this approach doubles the available area for TE legs, increasing fill factor.

2.1 Bi$_2$Te$_3$ and Sb$_2$Te$_3$ Film Deposition

Bi$_2$Te$_3$ was deposited using co-evaporation of Bi and Te sources, as previously reported by our group [6]. The self-shadowing effect of the columns themselves was used to form each individual thermocouple. Bi and Te sources were placed 30° from the wafer normal facing right (Fig. 3). Due to the line-of-sight nature of evaporation, the columns block film deposition on the left facing sidewall surface, forming an N-type thermocouple only on the right sidewall. At the 30° angle, the thickness of the sidewall film is roughly equal to the thickness of film deposited on the planar surfaces on top of the column and in the valley between columns. To help compensate for non-uniformity due to a lack of substrate rotation during deposition, Bi$_2$Te$_3$ was formed under Te rich conditions, with a deposition rate of 1 Å/s for Bi and 3 Å/s for Te. At our substrate deposition temperature of 260°, elemental tellurium re-evaporates from the surface faster than it deposits, leaving only Bi$_2$Te$_3$ behind in a Bi limited system.
To form the P-type thermocouple, Sb and Te sources were placed facing left. Thus, after deposition, a N & P leg pair is created on each column (Fig. 4). At the adjoining planar surfaces, a Bi$_2$Sb$_5$Te$_7$ composite forms. This composite material serves as the basis for electrical contact between the legs. When the N & P legs are deposited separately, the resulting junction is highly resistive at $10^{-5}$ Ω-m² as measured by cross-bridge kelvin structures. However, when both films are deposited simultaneously, the connecting material is ohmic and has an upper limit of $10^{-7}$ Ω-m². In comparison Bi$_2$Te$_3$ to Au were previously measured by our group to have a resistivity of $2\times10^{-9}$Ω. Simultaneous deposition required adjustments to the deposition ratios due to extra tellurium re-evaporation from the substrate due to the dual Te sources. Bi:Te and Sb:Te rates were set to 2:3 Å/s and 1.5:3 Å/s respectively. At the 30° angle, a ratio greater than 1:1 between column pitch and height is required to ensure linkage of the N & P type films, limiting column density. Reducing the deposition angle can also increase column density, but increases extraneous material on top of the pillar. Due to the current flow of this generator, this extraneous material on top does not contribute to the power output.

### 2.2 Film Properties

XRD showed film growth on vertical substrates to be isotropic in orientation, compared with normally C-oriented planar films. Grain structure was also different on vertical films, forming thin rod-like columns with a 30° angle away from the surface at 260° C (Fig. 8B). This angle has been found to be temperature dependent but unrelated to the angle of the sources. Under the same conditions, films on
planar substrates exhibit an initial 1 μm seed layer (Fig. 7B) before columnar growth. Planar films also do not exhibit the voids between the grain columns as seen in the vertical films (Fig. 8C).

![Figure 7. Front(A) and side(B)(C) view of Bi$_2$Te$_3$ co-evaporated on a planar surface. Figure 2B shows development of the initial seed layer while 2C shows columnar grain growth afterwards.](image)

![Figure 8. Front(A), side(B), and isometric (C) view of Bi$_2$Te$_3$ co-evaporated on a vertical oxide surface.](image)

Due to difficulties in measurement in the vertical direction, only the lateral properties of the vertical films could be measured. While film properties were poorer than planar films deposited under the same conditions, power output of the TEG structure was modeled to be 55 μW/K²/cm² (Fig 9). It is theorized the poorer film properties are the result of the isotropic film orientation and the presence of voids in the Bi$_2$Te$_3$ films.

| Film  | Orientation | Dep. Temp. (°C) | Seebeck (μV/K) | Resistivity (μΩ-m) | Power Factor (mW/K²/m) |
|-------|-------------|-----------------|----------------|-------------------|------------------------|
| Bi$_2$Te$_3$ | Sidewall | 260 | -160 | 20-50 | .5 – 1.3 |
| Bi$_2$Te$_3$ | Planar | 260 | -240 | 20 | 2.9 |
| Sb$_2$Te$_3$ | Sidewall | 240 | 120 | 30 | .5 |
| Sb$_2$Te$_3$ | Planar | 240 | 180 | 30 | 1.3 |

3. Proof of concept Integration

A proof of concept vertical μTEG was fabricated to demonstrate functionality of the thermocouple structure. Bi$_2$Te$_3$ and Sb$_2$Te$_3$ were co-evaporated onto polyimide columns, forming N/P leg-pairs. Au was placed in the valleys and tops of pillars to reduce contact resistance between the legs. The cap die was glued into place due to oxidation issues of the Au/Sn eutectic. The resulting device was functional but exhibited poor voltage output. Electrical resistance was 620 Ω and voltage output was 6.3 mV/K, giving a FoM of .64 μW/K²/cm². The large discrepancy between expected and measured performance is thought to be caused by primarily by poor thermal and thermal loss between the TE columns and the cap wafer due to the bonding method as well as conduction through the glue.
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