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Co-Sb- and Zn-Sb-Based Thin-Film Thermoelectric Modules for Temperature Sensors

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Thermoelectric technology has been a focus of many scientists because of its ability to generate voltage from a temperature gradient or vice versa. The generation of voltage from a temperature gradient is due to the Seebeck effect. This effect has been utilized to measure temperatures of a certain object in thermocouple applications. The sensitivity of thermocouples can be described by how fast and how large such voltage generation occurs from a minimal temperature change. Such a parameter can be derived by plotting voltage versus temperature data. The slope of this plot is a Seebeck coefficient. Thus, thermocouples with very large Seebeck coefficients are critical in applications that require very sensitive and accurate measurements of temperature. For this reason, thermoelectric generator (TEG) modules that are typically fabricated to have large Seebeck coefficients can be beneficial. In this experiment, we fabricated thin-film TEG modules based on cobalt-antimonide (Co-Sb) and zinc-antimonide (Zn-Sb) thermoelectric materials for a possible temperature sensor. They showed a reasonably high Seebeck coefficient in a temperature range between 50 and 200 °C, and also good reliability in cyclic temperature measurements, demonstrating their future benefits as thermocouples.

1. Introduction

The recent worldwide issue of global warming has ignited the beginning of enormous effort into discovering alternative energy sources and increasing energy efficiency. In such efforts, thermoelectrics have been attracting attention from many scientific groups mainly because of the Seebeck effect.

The Seebeck effect discovered by Thomas Seebeck in 1821 is created when two dissimilar materials are joined together. When a temperature gradient is applied, for example, in a form of heating, the electrons near the hot side would have a higher kinetic energy than those near the cold side. This induces the diffusion of electrons from the hot side to the cold side, thereby inducing a P-N junction-like behavior in the system. This

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*Corresponding author: e-mail: swhan@kimm.re.kr generates a charge potential gradient, simply known as voltage.(1–3)

Because of this Seebeck effect, we could generate electricity from waste heat, thereby increasing fuel efficiency. The best example would be a thermoelectric generator (TEG) module connected to an automotive engine.(4)

The voltage that we can obtain from the Seebeck effect between two different materials (A and B), V_{AB}, can be derived from eq. (1) below.

$$V_{\mathrm{AB}} = \Delta V_{\mathrm{A}} - \Delta V_{\mathrm{B}} = \int_{T_0}^{T} (\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})\mathrm{d}T \qquad (1)$$

Here, T_0 is the reference temperature, T is the temperature of interest, and α_{A} and α_{B} are the unique Seebeck coefficients of materials A and B, respectively, which depend on T.(5,6)

ΔV_{A} is defined as the voltage gain across the hot and cold ends in material A as shown in eq. (2). The same definition applies to ΔV_{B}.(5,6)

$$\Delta V_{\mathrm{A}} = \int_{T_0}^{T} \alpha \mathrm{d}T \qquad (2)$$

This is valid because we know that α is equal to $\mathrm{d}V/\mathrm{d}T$ from Seebeck's definition. On the basis of the above equations, with the measured ΔV, we can derive ΔT; this is the basic principle behind thermocouples or temperature sensors.(1) Good sensors require a linear behavior with high sensitivity and reliability. In temperature sensors, such sensitivity will largely depend on the two materials because a large difference in α would generate a large "voltage signal" with a small change in temperature. This makes a TEG a good candidate for a temperature sensor because it has a largely different value in N- and P-type legs; they have different signs owing to different charge carriers.(7) Moreover, the possibility of powering such a sensor system with a thermoelectric voltage obtained from a temperature gradient without any external power sources makes this application environmentally friendly.

In this experiment, we fabricated a thin-film TEG module using n-type cobalt-antimonide (Co-Sb) and p-type zinc-antimonide (Zn-Sb) thermoelectric materials. This module was initially targeted to be used in a high-temperature environment. Then, the Seebeck voltages generated from a change in temperature were measured and compared with those of conventional thermocouples. It turned out that our thin-film TEG module showed almost the same sensitivity as type-K thermocouples.(8)

2. Materials and Methods

2.1 *Fabrication of thin-film TEG*

To fabricate a TEG module, silver (Ag) electrodes were first deposited on 4-inch silicon substrates using a chrome mask for patterning. The 99.9%-pure Ag target was sputtered at room temperature via direct current (DC) magnetron sputtering at 71 W for 2 h while the chamber pressure was maintained at 7 mTorr.

Then, n-type $CoSb_3$ legs were deposited by RF magnetron sputtering. A metal mask made of stainless steel was used to produce the necessary patterns. To promote adhesion between the silicon substrate and the n-type element, titanium (Ti) was first deposited. The 99.9%-pure Ti target was sputtered for 15 min at 100 W for a 30 nm thickness. Then, Co and Sb targets, both having purities of 99.9%, were also sputtered. The sputtering power was 60 W for both Co and Sb targets. The sputtering was conducted in vacuum for 2 h while maintaining a chamber pressure of 3 mTorr at room temperature to produce a 2 μm thickness. Previous deposition data were used to determine the exact sputtering time and power for the best result.

After the n-type deposition, p-type Zn_3Sb_4 was deposited using the same metal mask. Likewise, for better adhesion, Ti was first deposited at the same power (100 W) for the same amount of time (15 min). After the Ti deposition, the Sb and Zn were sputtered at 60 and 35 W, respectively. The sputtering was conducted for 3 h at room temperature to obtain the same 2 μm thickness.

Then, the deposited patterns were annealed in a vacuum chamber at 200 °C for 30 min. The patterned products were diced with a diamond saw after annealing so that we only have one P-N junction for a temperature sensor measurement as it is in a thermocouple. The overall fabrication process is described in Fig. 1. The TEG module design is also presented in Fig. 2.

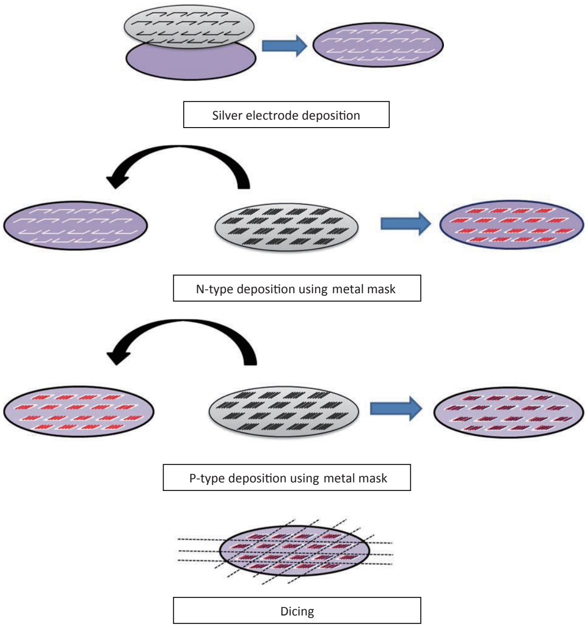


Fig. 1. (Color online) Overall thin-film TEG deposition process. The silver electrode was first deposited using a chrome mask, followed by N- and P-type patterns deposited using the stainless-steel metal masks. The final product was diced into separate modules.

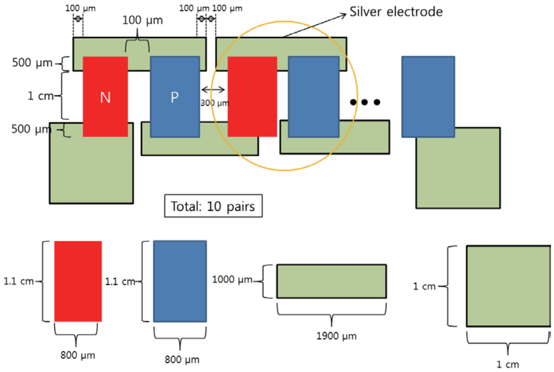


Fig. 2. (Color online) Thin-film TEG module leg design. The yellow-circle highlighted region indicates a cut area for comparison with typical thermocouples. Actual "cut" thermoelectric P-N legs.

2.2 *Voltage-gain measurement*

The thermoelectric "junction" that was cut from a thin-film thermoelectric module was placed halfway on a heating pad and halfway on a stage to generate a temperature gradient across a sample. The exact temperatures of the heating pad and stage were measured using a FLIR A-300 infrared camera. Then, the DC voltage generated from such a temperature gradient was measured using a FLUKE 287 TRUE RMS digital multimeter connected to two gold probes. The voltages were measured while the temperature of the heating pad was increased from room temperature to 400 °C and decreased from 400 °C to room temperature to see how it behaves in a cyclic experiment. The experimental setup is shown in Fig. 3.

3. Results

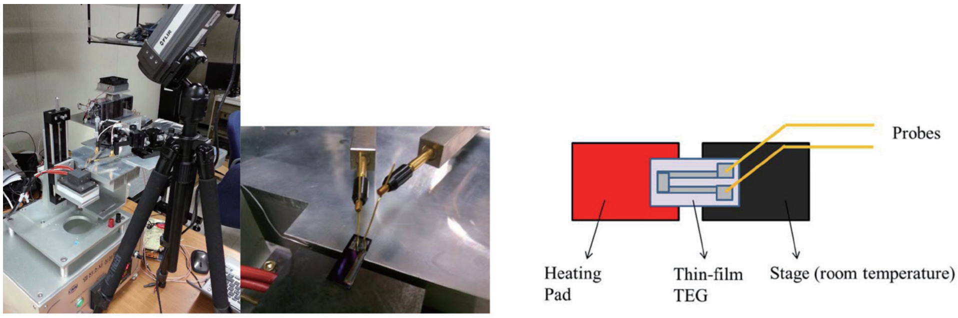
3.1 *Thermoelectric material property measurement*

To identify at which power and for how long the sputtering should be carried out, preliminary experiments on depositing various compositions of Co-Sb and Zn-Sb were conducted.

Primarily, the power factor was the main concern; the higher the power factor, the better the Seebeck effect. The Seebeck coefficient of each material was also measured for further analysis. Both Seebeck coefficients and power factor data of as-deposited N and P materials are shown in Fig. 4.

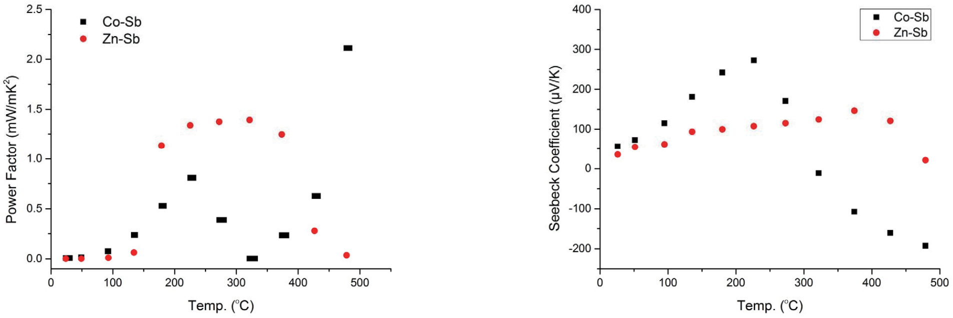
3.2 *Fabricated thin-film TEG module*

The finally produced thermoelectric modules are shown in Figs. 5(a) and 5(b), whose dimensions are 37.9 × 21.0 and 1.9 × 12.0 mm^2, respectively. Figure 5(b) shows a P-N junction that was cut from the original thin-film TEG module to make it resemble thermocouples.



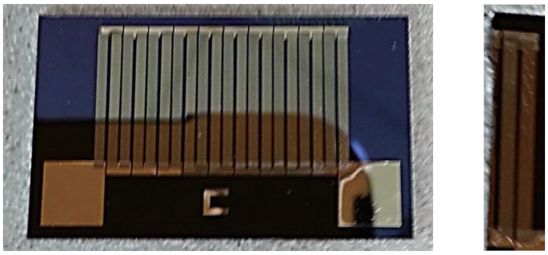
(a) (b) (c)

Fig. 3. (Color online) (a) Overall experimental setup where the temperature gradient between the heating pad and the stage is measured by an infrared camera, and the generated voltage by a digital multimeter. (b) Two gold probes measure the voltage generated at the open end. (c) Close-up top view of overall experimental setup.



(a) (b)

Fig. 4. (Color online) (a) Power factor data. (b) Seebeck coefficient data obtained for each N ($CoSb_3$) and P (Zn_3Sb_4) material under an as-deposited condition.



(a) (b)

Fig. 5. (Color online) (a) Thin-film TEG module deposited as described in Fig. 1. (b) Cut P-N junction, resembling thermocouple applications.

The apparent quality of the TEG module was checked with an optical microscope. It showed that none of the legs overlapped with each other. Also, the electric current flowed without any problem when checked with a multimeter. The cut sample was checked with the same procedure, and no problem was found.

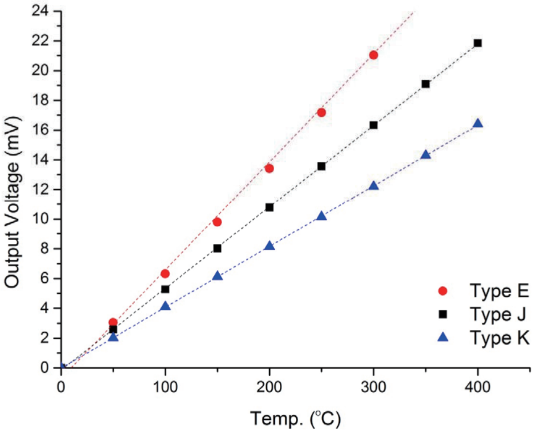
3.3 *Comparison with commercially available thermocouples*

The typical commercially available thermocouple output voltage vs temperature data up to 400 °C are presented in Fig. 6. The data were obtained from ref. 8. The data points were linear-fit to obtain approximate Seebeck coefficients (slopes). The resultant linear-fit values are tabulated in Table 1. The results of multimeter readings of our sample are shown in Fig. 7. The data were then linear-fit to mainly obtain the slopes; the results of fitting are shown in Table 2.

4. Discussion

We selected Co-Sb ($CoSb_3$) and Zn-Sb (Zn_3Sb_4) thermoelectric materials because they are known to produce good thermoelectric properties between an intermediate temperature range and a high temperature range. Our primary focus was to determine whether we could utilize thermoelectric materials as temperature sensors, thereby providing a future way to run such sensors powered by TEGs.

As shown in Fig. 4, when powers of 60 and 44 W were applied to Co and Sb, respectively, the highest power factor, almost 2 mW/mK^2 at approximately 500 °C, was obtained. For Zn-Sb, sputtering powers of 60 and 35 W were found to produce the highest power factor, approximately1.5 mW/mK^2 near 300 °C. Thus, these powers were



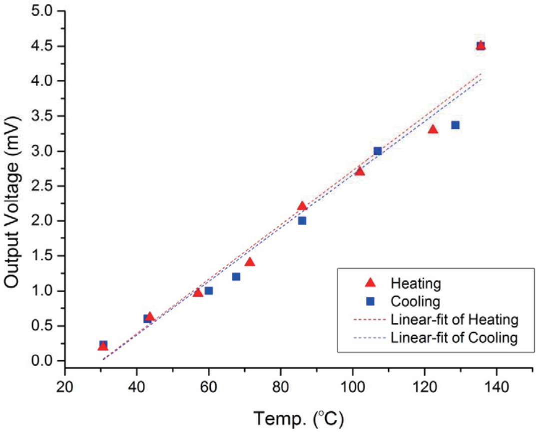


Fig. 6 (left). (Color online) Commercially available thermocouple output voltage vs temperature data with linear fitting.

Fig. 7 (right). (Color online) Multimeter reading results of our thin-film TEG.

Table 1
Linear-fit results of commercial thermocouples.

Type	Slope (mV/°C)	Intercept (mV)	R^2 value
E	0.073	−0.701	0.99
J	0.054	−0.141	0.99
K	0.040	−0.015	0.99

Table 2
Linear-fit results of our thin-film TEG sample measurements.

Type	Slope (mV/°C)	Intercept (mV)	R^2 value
Heating	0.038	−1.153	0.961
Cooling	0.038	−1.162	0.973

selected for the best performance. The appropriate deposition times required to produce a 2-μm-thick thin film for Co-Sb and Zn-Sb were also derived empirically (2 h for $CoSb_3$ and 3 h for Zn_3Sb_4).

We aimed to obtain a thicker TEG module because the Seebeck coefficient of a thin film, $S_{T,F}$, increases as the film thickness increases according to the effective mean free path model for the polycrystalline thin film suggested by Tellier, as shown in eq. (3).(9,10)

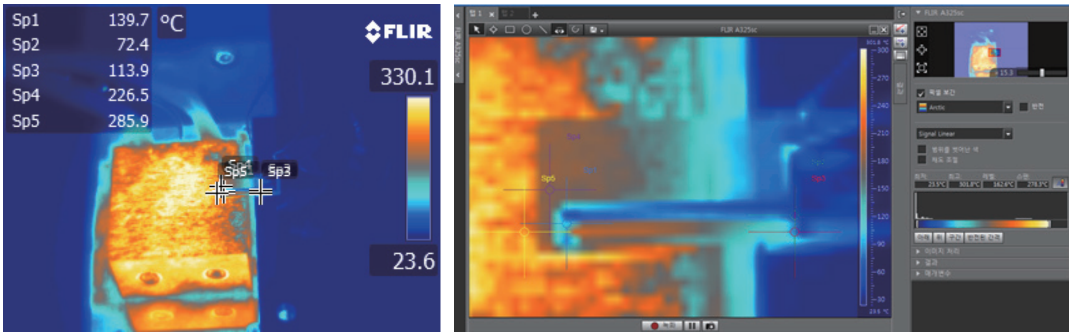
$$S_{T,F} = S_g[1 - \frac{3}{8t}(1 - p)l_g\frac{U_g}{1 + U_g}] \quad (3)$$

Here, $S_g = \frac{\pi^2 k^2 T}{3eE_F}(1 + U_g)$ and $U_g = (\frac{d ln l_g}{dE})E_F$. S_g is the bulk Seebeck coefficient, k is the Boltzmann constant, e is the electron charge, E_F is the Fermi energy, p is the specularity parameter, l_g is the bulk-form effective mean free path, and t is the film thickness. It was indeed shown in Kim *et al.*'s work that the thermopile sensor sensitivity increased with increasing film thickness in Sb-Te- and Bi-Te-based TEGs.(11)

Although the Seebeck coefficient of $CoSb_3$ is supposed to be negative because we planned to use it as an n-type material, it stayed positive up to approximately 275 °C. This sign change could be attributed to the heat treatment effect induced by increasing the measurement temperature. It removes lattice strain and lattice defects, thereby helping in the formation of a "correct" $CoSb_3$ phase in an originally amorphous material.

When measuring the voltage generated across the thin-film TEG, we measured the temperatures using an infrared camera. The temperatures of the heating pad, substrate, top electrode, and N- and P-legs on the stage were measured, as shown in Fig. 8. Sp 1 measured the temperature of the top silver electrode, whereas Sp 2 measured that of the P-leg, Sp 3, the N-leg, Sp 4, the substrate on the heating pad, and Sp 5, the heating pad itself.

The heating pad itself was heated by applying a predetermined amount of current through joule heating, and thus the temperature of the pad could be set by us. It could reach 400 °C at most. However, owing to air convection and the thermal loss between



(a) (b)

Fig. 8. (Color online) (a) Infrared camera image showing the temperatures of interest when the heating pad was maintained at 350 °C. (b) Magnification of the infrared camera shown on top.

the Si substrate and the pad, the temperatures of the elements placed on top of the pad were significantly lower than the intended heating pad temperature. Such temperatures evaluated at each point when the temperature was increased from 50 to 400 °C at 50 °C intervals are shown in Fig. 9.

Sp 1, the temperature of the top silver electrode on the heating pad, is what our thin-film TEG actually measures, being T in eq. (1). Although this is significantly lower than the intended temperature, increasing it further was not possible because of the heater power capacitance limit. These Sp 1 values were considered to obtain Fig. 7.

As shown in Fig. 7 and Table 2, the experimental results matched well between the heating and cooling cases. This means that our results are reproducible and our sample can withstand cyclic operations as most commercial thermocouples would do. Also, the voltage gains were directly proportional to temperature changes, showing good linearity.

The slope was approximately 0.038 mV/°C in both cases. This corresponds to the slope of type-K thermocouples, indicating that its sensitivity is comparable to that of type-K thermocouples. Our initial assumption was that the slope of our module should exceed that of type-E thermocouples. Type-K thermocouples are typically made of nickel-chromium and nickel-aluminum, while type-E thermocouples are composed of nickel-chromium and copper-nickel. It is known that type-K thermocouples can measure a temperature from –200 to 1250 °C, and type-E thermocouples from –200 to 900 °C with the highest voltage change per degree known to date.(12)

As seen in eq. (1), a large difference in Seebeck coefficient (α) between two materials should generate a high ΔV; typical TEG modules utilize two dissimilar materials, N- and P-type semiconducting materials. N-type materials have a negative α, while P-type materials have a positive α. Therefore, the $\Delta\alpha$ in eq. (1) must be significantly large.

However, our result did not show a significantly high change in voltage because the N- and P-type thermoelectric materials used in our thin-film TEG did not show a large difference in α in the actual measurement temperature range of 20 to 150 °C, as presented in Fig. 4. It could be possible because our thin-film TEG was initially targeted

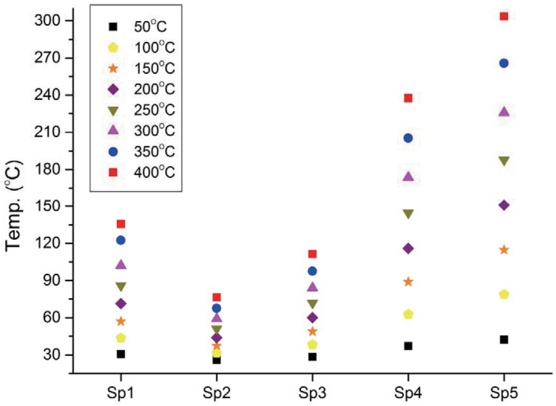


Fig. 9. (Color online) Temperatures of interest when the pad was controlled from 50 to 400 °C at 50 °C intervals.

to be used in a temperature range between 350 and 600 °C. We actually could observe a high power factor and a large difference in α in that range in Fig. 4. Thus, if we had allowed our measurement temperature, Sp 1 in our case, to reach above 350 °C, we would have been able to observe a very high sensitivity in $\frac{\mathrm{d}V}{\mathrm{d}T}$. However, reaching such a high Sp 1 temperature would require more heating power, which was not possible with our current heating system. Future work will be carried out to analyze and upgrade our current system to realize such a high-temperature environment.

Moreover, doping the N and P elements in a TEG to enhance the difference in Seebeck coefficient would increase the voltage output of thermocouples in turn, thereby improving the overall sensitivity and linearity.

5. Conclusions

The Seebeck effect is the basis of thermocouple applications. Good thermocouples should be highly sensitive to changing temperature, and such sensitivity largely depends on the difference in Seebeck coefficient between two dissimilar materials. Because TEGs utilize N- and P-type semiconducting materials with Seebeck coefficients of different signs, they could be used as highly sensitive temperature sensors. Moreover, it could power itself without using external power sources. In this experiment, we fabricated Co-Sb- and Zn-Sb-based thin-film TEG modules. Their sensitivities in terms of voltage gain to a change in temperature were tested and compared with the available data of commercially available thermocouples. It turned out that our module had sensitivity as high as those of type-K thermocouples in a temperature range between 20 and 200 °C.

Acknowledgements

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