

High-Performance Half-Heusler Thermoelectric Devices Through Direct Bonding Technique

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Abstract

Solid-state thermoelectric generators (TEGs) are promising solution for waste heat recovery. However, they typically suffer from lower conversion efficiency, lack of reliable high temperature device fabrication process and long-term stability. In order to realize high electrical conversion efficiency (ECE) in TEGs, it is critical that in conjunction with high TE materials figure of merit, zT , there is also a reliable TE module fabrication process. This study demonstrates the TEG fabrication process that results in reduced thermal and electrical contact resistances between metal electrodes and TE legs, even at high temperatures ($>600^{\circ}\text{C}$). The fabrication approach is demonstrated using p-type ZrCoSb -based and n-type ZrNiSn -based half-Heusler TE materials. High temperature brazing material is used as a filler that enables direct bonding of TE legs to the copper electrode without metalizing legs. This technique improves the TEG performance and stability at high temperatures by minimizing the contact resistance and diffusion at TE leg/electrode interface. The fabricated modules exhibit a high power density of $\sim 11.5 \text{ Wcm}^{-2}$ and an ECE of 9.5% at 670°C temperature gradient. The module was exposed to longtime soaking at

550°C in air and was found to exhibit negligible deterioration. These results are highly promising for advancing the TE modules in waste heat recovery applications.

Keywords: Waste heat recovery, Thermoelectric, half-Heusler, Contact resistance, Efficiency, Air stability, Direct bonding, Metallization

1. Introduction

Novel renewable and sustainable alternative energy resources are being developed by harvesting wasted energy [1,2,3]. Thermoelectric generators (TEGs) are promising for directly converting waste heat into electricity and are positioned to play a major role in providing energy harvesting solutions [2,4,5]. In past few decades, both theoretical and experimental research has been conducted on the development of thermoelectric (TE) materials [6,7,8]. TE material performance is evaluated by a dimensionless figure of merit, zT . High zT (≥ 1) has been a benchmark for high-performance TE materials. The maximum conversion efficiency (η) of a TE material is expressed by Equation (1) [9]

$$\eta = \left(\frac{T_H - T_C}{T_H} \right) \frac{\sqrt{1 + (zT)_{avg}} - 1}{\sqrt{1 + (zT)_{avg}} + \left(\frac{T_C}{T_H} \right)} \quad (1)$$

where T_C and T_H are cold- and hot-side temperatures, respectively, and $(zT)_{avg}$ is the average material figure of merit. The first term in parenthesis is the theoretical maximum efficiency, known as Carnot efficiency. Higher $(zT)_{avg}$ and ΔT ($=T_H - T_C$) leads to higher η in a desired temperature range.

Prior investigations have led to fundamental understanding of design principles, identification of promising material systems, and development of suitable synthesis techniques. This has led to demonstration of excellent material performances. For example – peak zT of 2.6 and 2.5 at 650°C has been reported in SnSe single crystal [10] and polycrystalline Na-doped PbTe-

SrTe alloys [11], respectively. (Bi,Sb)Te₃ [12,13,14,15] and Mg₃(Bi,Sb) [16,17,18] systems have been found to be excellent TE materials at low temperatures (-50 to 250°C). In medium temperature range (250 to 550°C), there are multiple options such as Ba₈Ga₁₆Ge₃₀ [19], Mg₂(Sn,Si,Ge) [3,20,21,22], BiCuSeO [23,24], Zn₄Sb₃ [25,26], Cu₂(S,Se,Te) [27,28], GeTe [29,30] and skutterudites [31,32,33,34,35]. In high temperature range (550 to 1000°C), SiGe [36,37,38,39], Yb₁₄MnSb₁₁ [40], and half-Heuslers [7,41,42,43,44,45] are suitable candidates. These material advancements have strengthened the opportunity for design and development of TE devices. However comparatively, the progress in fabricating high temperature TE devices has been limited and there is considerable gap between the reported zT values and device performance. A TE device comprises of several materials in addition to that of TE legs. Thus, a well-performing TE device requires integration of multiple layers with varying thermal expansion coefficients, thermal and electrical properties, and process compatibility. Going forward, it is vital for TE community to demonstrate high temperature and high electrical conversion efficiency (ECE) devices in order to meet the application-oriented metrics.

Recently, half-Heusler (hH) materials have been thoroughly investigated due to their excellent TE properties at high temperature, and high mechanical strength and thermal stability [46,47]. There are some promising compositions in p- and n-type hH TE materials such as ACoSb (A = Ti, Zr, Hf) [48,49] and BFeSb (B = Nb, Ta) [44,50] systems. However, there is scarcity in demonstration of reliable hH TE devices, mainly due to the high contact resistance between the metal electrode (also known as interconnect) and TE leg which is a prominent factor in determining the device ECE. Main challenges in fabricating reliable TEG device is to identify suitable metallization and brazing material in order to obtain low contact resistance [51,52,53,54]. Here we briefly list some important demonstrations in literature. Zhang *et al.* [55] demonstrated 1 kW

output power at $\Delta T=550^{\circ}\text{C}$ using 400 hH TEGs where each TEG consisted of 28 unicouples. Each unicouple produced a power density of 5.26 Wcm^{-2} with respect to TE leg area at ΔT of 500°C . Fu *et al.* [56] fabricated a hH device comprising of 8 unicouples which showed a maximum device power density of 2.2 Wcm^{-2} and a conversion efficiency of 6.2% at $\Delta T=655^{\circ}\text{C}$. Yu *et al.* [57] built a hH module comprising of 8 unicouples which showed a power density of 2.11 Wcm^{-2} with respect to the total device and a conversion efficiency of $\sim 8.3\%$ under a temperature difference of 655°C . Bartholomé *et al.* [58] fabricated a hH module comprising of 7 unicouples with a peak power density of 1.1 Wcm^{-2} with respect to the total device and 3.2 Wcm^{-2} with respect to the TE material at $\Delta T=527^{\circ}\text{C}$. Joshi *et al.* [53] reported hH unicouple which showed a peak power density of $\sim 8.9\text{ Wcm}^{-2}$ with a conversion efficiency of $\sim 8.9\%$ at a temperature difference of 678°C .

In order to enhance the performance of a TE device, in addition to high ΔT and $(zT)_{\text{avg}}$, device design is critical towards minimizing the thermal and electrical contact resistances at the junction of metal electrode and TE leg (semiconductor). The main source of thermal contact resistance is roughness of contact surfaces that can be minimized by finely polishing the surfaces to increase the effective contact area for thermal conduction [59]. Thermal paste can also be used to improve the thermal conduction by filling the gaps between two surfaces. The metal/semiconductor electrical contact can have Schottky (rectifying) or ohmic (non-rectifying) behavior. In TE devices, an ohmic contact behavior is crucial to provide easy conduction of electrical charges and reduce the Joule heating [31,52,53,59]. Introducing a limited diffusion barrier at the junction of Cu electrode and TE legs is a practical way to minimize atomic diffusion, control chemical reaction with TE materials and maintain conductive electrical contact [60]. However, such barriers can also generate contact resistance which can be amplified at high temperature. In general, diffusion barrier material, brazing technique and material, and difference

in coefficient of thermal expansion between TE legs and electrodes can result in high contact resistance [61], deterioration in TE properties due to the extended diffused layer and reacted TE materials at high temperature [53], and crack generation and propagation at the junction during thermal cycling [62,63].

In order to overcome the problems listed above and provide superior ECE, we demonstrate a direct bonding technique that does not require metallization of TE legs. We successfully fabricated and characterized a high temperature hH TE module comprising of nanostructured p-type ZrCoSb [64] and n-type ZrNiSn [65] legs which can withstand a hot-side temperature of $\sim 700^{\circ}\text{C}$ in vacuum. By reducing the specific contact resistances of both p- and n-type legs through the direct bonding technique, a 30% improvement in power density is achieved compared to the best reported data [53], with a thermal to electrical energy conversion efficiency of 9.5% at 670°C temperature gradient, which to the best of our knowledge is the highest reported efficiency for a single stage hH device made using similar p- and n-type TE materials and properties.

2. Results and Discussion

2.1. Half-Heusler Thermoelectric Module Fabrication

A thin diffusion barrier layer is commonly utilized for enabling the brazing of TE legs to metal electrodes. This is achieved by metallizing the top and bottom surface of the TE materials with a conductive metal such as gold, silver or nickel. Figure 1-a and b show common techniques for growing diffusion barrier layer. One of the methods is based upon thin film deposition techniques (Figure 1-a) such as electroplating [66], electroless plating [67,68], sputtering [69], and electron-beam evaporation [70,71]. Thin film deposition provides low contact resistance and high-temperature stability, but it is expensive process, requires long time, and there is a possibility of peeling off the metalized film. Another method is through simultaneous sintering of diffusion

barrier metal (or alloy) onto TE materials via spark plasma sintering (SPS) (Figure 1-b). Although the SPS process is convenient, it can generate extra contact resistance at the interface [72,73]. Different materials have been used as a diffusion barrier in TE modules, such as Ni in Bi₂Te₃-based modules [66,70], Mo [74]; Ti-Al [75] in skutterudite-based modules; Fe, Ni, Co and Nb-based alloys in PbTe-based modules [76,77]; and Ti in hH-based modules [53]. Even though the diffusion barrier might have a good electrical contact at room temperature, it can be a source of contact resistance at high temperature [76] that deteriorates the output power and efficiency of the TE module. Another issue that can reduce the device performance and increase the TEG fabrication cost is partial or total peeling off the metalized layer from the legs during the dicing process.

The direct bonding technique provides a sophisticated solution for the metallization of TE materials (Figure 1-c). Figure 1-d and e show the schematic and the actual fabricated uncouple TEG module made of p- and n-type hH legs, respectively. Different components of the uncouple include direct bonded copper (DBC) substrates made of copper and aluminum nitride (AlN) for top and bottom headers. AlN is a hard ceramic with high thermal conductivity and electrical insulation properties. It is used to efficiently conduct the heat from heat source to TEG as well as maintain the mechanical rigidity of the TEG. Cu electrode provides electrical conduction between TE materials. A pair of p- and n-type TE materials are connected thermally in parallel and electrically in series. Brazing material is used to provide a reliable connection between TE legs and Cu. The brazing material should have a high wettability, minimum interfacial diffusion in TE legs and high electrical and thermal conduction. Direct bonding technique enables brazing of TE legs to Cu electrode without metallizing legs. This technique reduces the module fabrication complexity, fabrication time, defects at the junction, and interfacial resistances.

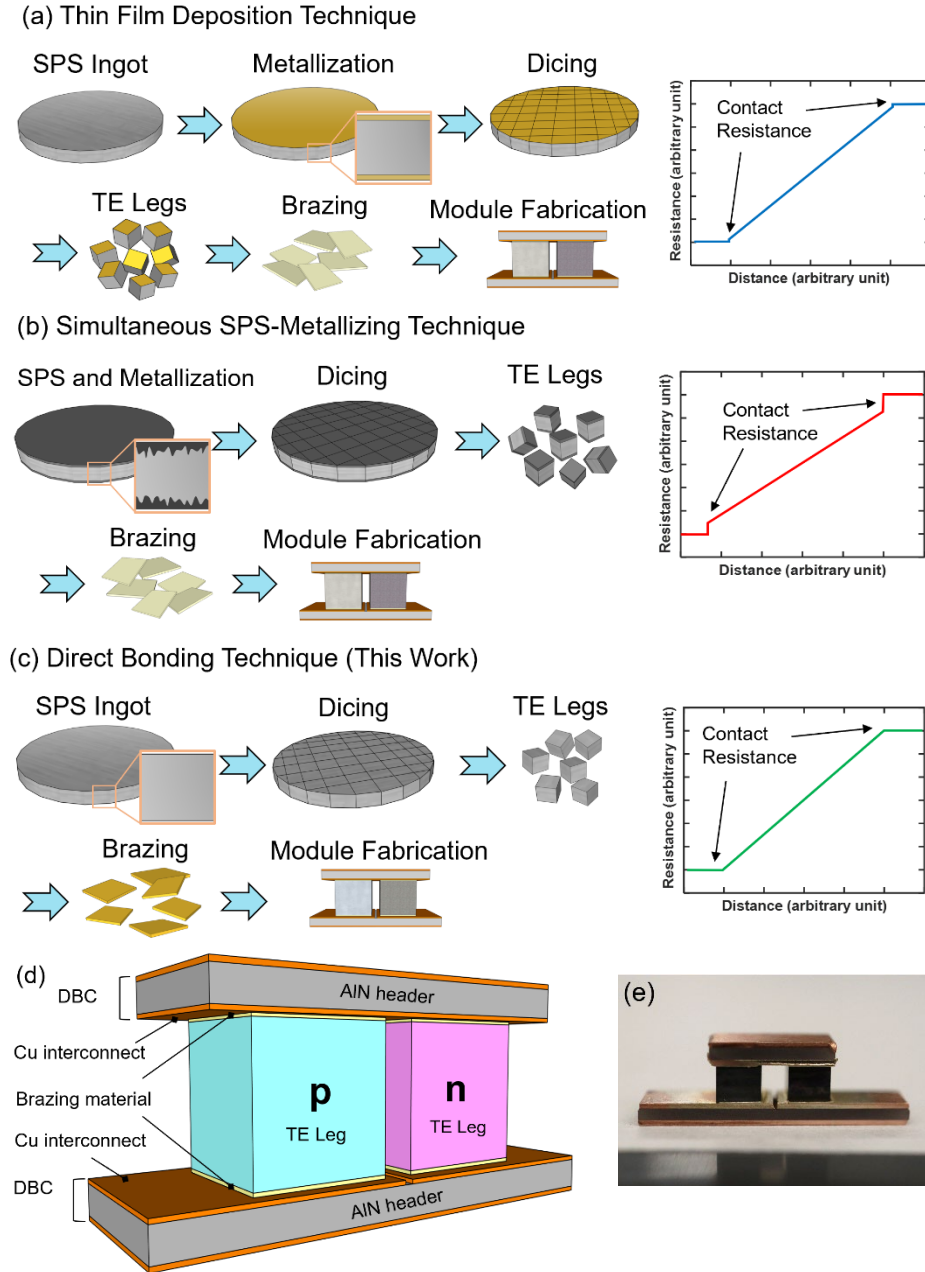


Figure 1: Schematic diagram of fabrication process for TE modules using common techniques to grow metallized (diffusion barrier) layer (a) thin film deposition technique, and (b) simultaneous sintering and metallization by SPS. Dicing the legs may peel off metallized layer in (a) and (b). (c) Fabrication process flow for direct bonding demonstrated in this study. (d) The schematic diagram and (e) actual picture of the fabricated hH TEG uncouple. More pictures on fabrication process for the module are provided in Figure S1.

2.2. Half-Heusler Thermoelectric Module Characterization

TE properties of synthesized nanostructured p-type ZrCoSb and n-type ZrNiSn are shown in Figure S2. The average zT of p- and n-type materials from 100°C to 700°C are 0.54 and 0.71, respectively. In order to verify the performance and reliability of the fabricated TE devices, two parameters are critical to measure: (i) the electrical contact resistance at the junction of TE leg and Cu interconnect, and (ii) the thermal to electrical conversion efficiency. These parameters are separately measured by home-built setups.

The relationship between the device ZT (with uppercase Z) and the material zT (with lowercase z) is given by Equation (2) [78],

$$(ZT)_d = (zT)_m \left(\frac{L}{L + 2R_c\sigma} \right) \quad (2)$$

where $(ZT)_d$ and $(zT)_m$ are device and material figure of merit, respectively, L is the length of the TE leg, R_c is the electrical contact resistance, and σ is the electrical conductivity of the TE material. $(ZT)_d$ is always less than $(zT)_m$; in an ideal case that $R_c=0$, $(ZT)_d$ is equal to $(zT)_m$. For a highly doped TE material with high electrical conductivity ($\sim 10^3 \text{ Scm}^{-1}$), $(ZT)_d$ deteriorates with thin legs and higher R_c . Hence, according to Equation (2), in order to have a maximized device performance, R_c must be negligible. This relation validates the importance of TE device design and contact resistance. R_c is mainly controlled by the quality of contact metallization of the TE materials, soldering/brazing material, material and surface preparation of electrodes, and device fabrication process [54,79].

The effect of contact resistance is more crucial when the electrical conductivity of the TE legs is high [79]. Therefore, TE materials with high electrical conductivity requires a better contact to minimize the contact resistance. The contact resistances of both legs were analyzed using an automated scanning four-probe technique (Figure 2-a and b). The resistances of both p- and n-leg

increase linearly with distance and neither diffusion nor notable contact resistance at the interfaces are observed (Figure 2-c and d). The results show an ultra-low ohmic contact resistance between the Cu electrode and the TE legs. The specific contact resistance of p- and n-type TE legs is $<1\mu\Omega\cdot\text{cm}^2$, which is among the lowest contact resistances in different TE materials [53,80,81]. This is also the lowest reported contact resistance in hH modules, which enables the power output and efficiency improvement [56,58]. The low contact resistance minimizes Joule heating at the interface of TE leg/Cu electrode resulting in a more efficient thermal to electrical energy conversion. The reduced contact resistance at the junction also resulted in a very low overall unicouple internal resistance of $\sim 4\text{ m}\Omega$ at room temperature.

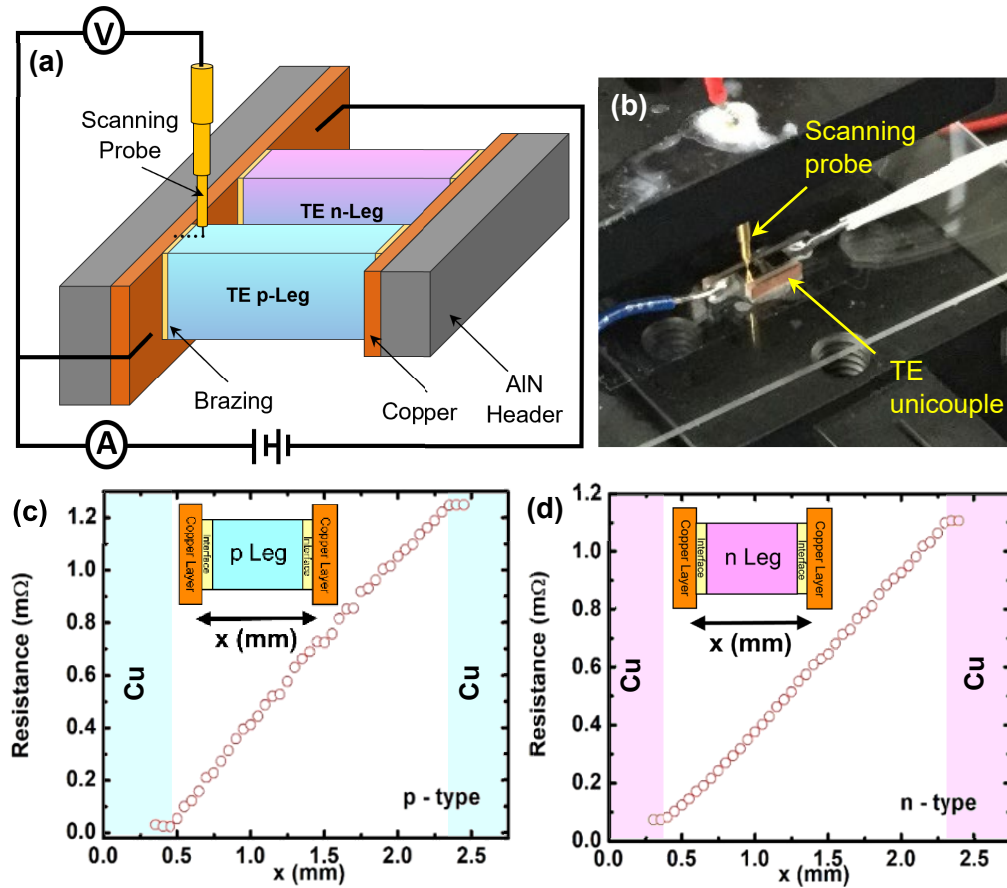


Figure 2: (a) The schematic diagram and (b) actual picture of home-made four-probe contact resistance measurement system. The contact resistance plots for (c) p-type, and (d) n-type legs.

The copper-silver (Cu-Ag) based alloy is used as brazing material to connect hH legs and copper electrode. Figure 3 shows the scanning electron microscopy (SEM) image along with elemental energy-dispersive X-ray spectroscopy (EDS) mapping for p- and n-type legs at the junction of TE leg with Cu electrode. Higher magnification SEM image and morphology of the interface are shown in Supplementary Information (Figure S3). The interface is uniform and there is no trace of any structural defect at the junction (Figure 3). Elimination of diffusion barrier resulted in limited diffusion of the brazing material into the TE legs (intermetallic layer), on the order of $<20\text{ }\mu\text{m}$ in p- and n-leg, which is significantly lower than the reported values for the same material system [53]. Thus, TE material properties do not deteriorate at the junction of TE leg and Cu electrode, which is a common problem in TE device fabrication due to the high temperature processing. This result matches with the contact resistance data that shows ohmic contact with negligible resistance at the junction of the TE leg/Cu electrode. Since the brazing temperature is higher than the operational temperature, the small diffusion layer helps in creating a strong intermetallic compound (mainly made of Cu, Ag and Sn) that benefits stable bonding and limits further diffusion of Cu into the legs, thereby, stabilizing the device performance.

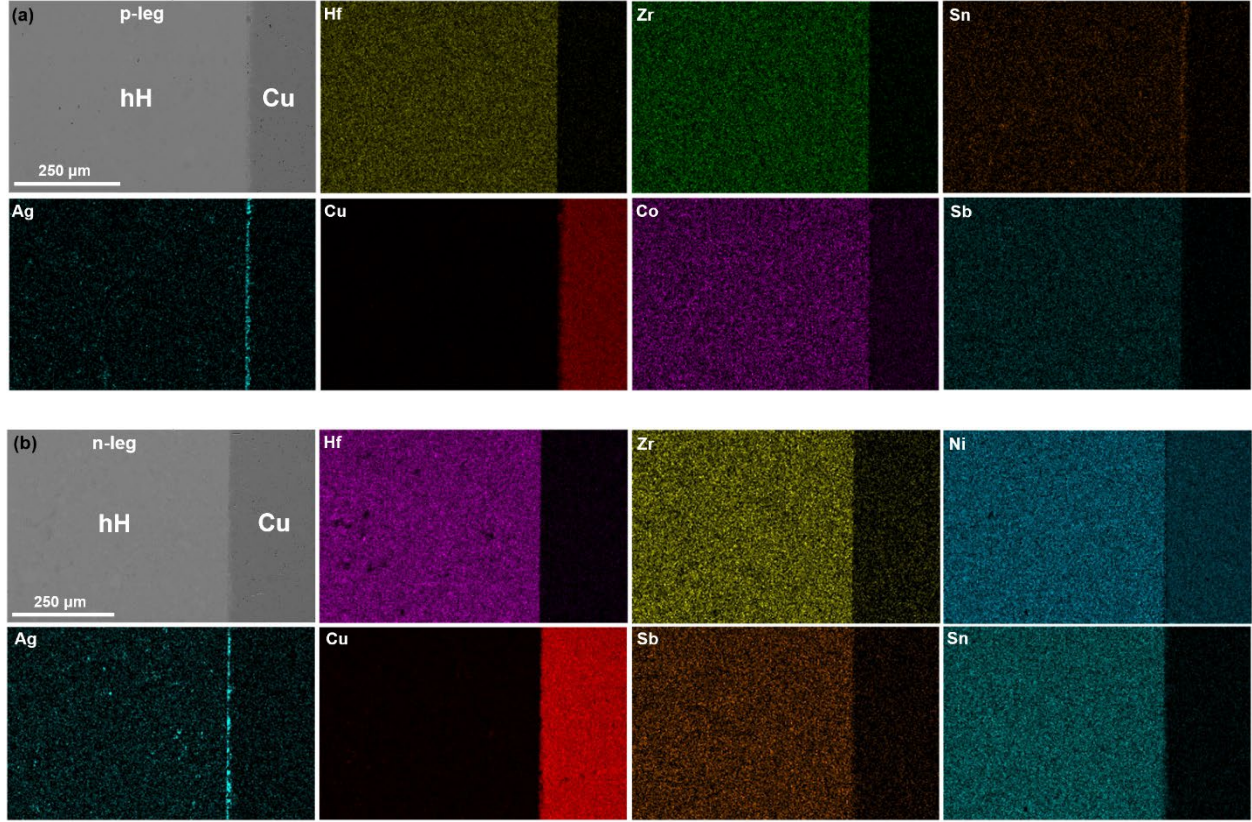


Figure 3: SEM image and EDS mapping of Cu-Ag brazing material at hH/Cu interface for (a) p- and (b) n-type hH thermoelectric legs.

The main compartments of the home-built test setup to measure the conversion efficiency of a unicumple TEG include a high temperature compatible heater assembly to provide uniform hot-side temperature, a TEG unicumple connected to power supply and voltmeter to accurately apply a load and measure voltage difference, a Q-meter to measure the heat flow at a certain distance, a water-cooled heatsink attached to the bottom of the Q-meter to maintain the cold-side temperature constant and dissipate the heat coming from the heat source (Figure S4). The temperature gradient along the Q-meter is measured with several K-type thermocouples with specific equal distances (Figure S4). The efficiency calculation equations are presented in the supplementary information. The output power and efficiency measurements were performed up to 700°C in vacuum while the cold-side temperature was maintained at ~20°C using a cooling water circulation system.

Conductive silver paste was applied at the junction of heater/top header, and thermal paste (OMEGATHERM™) was applied at the junction of bottom header/cooler to minimize the thermal contact resistance on the hot- and cold-side, respectively. Upon increasing the hot-side temperature, output voltage, resistance, power and efficiency increased, as shown in Figure 4.

The open circuit voltage (V_{OC}) increases linearly with temperature and reaches to a maximum of 231.4 V at $\Delta T=670^\circ\text{C}$ (Figure 4-a). The device resistance (R) increases from 8.8 m Ω at $\Delta T=182^\circ\text{C}$ and reaches to 11.1 m Ω at $\Delta T=670^\circ\text{C}$ (Figure 4-b). Device voltage (V_d) shows a linear trend versus current (I) under different ΔT 's (Figure 4-c), and at $I=0$ A it is equal to V_{OC} . Power density was calculated by knowing R , V_{OC} , V_d , cross-sectional area of the thermoelectric legs, and the current (Figure 4-d). At each temperature, the maximum power is obtained from Figure 4-c or simply calculated by $P_{max} = V_{OC}^2/4R$. Figure 4-e shows the temperature dependent power density compared with the literature values. Power density reaches 11.5 Wcm $^{-2}$, which is the highest output power densities among similar TE modules with similar material zT , in the same temperature range [53,55,57,58]. The maximum conversion efficiency of ~9.5% was achieved in the fabricated uncouple which is the highest efficiency to date in this temperature range in hH single stage modules (Figure 4-f) [55,56]. Dash line is the calculated maximum theoretical conversion efficiency for comparison. The theoretical efficiency is higher than experimental values in all temperature ranges. The difference is due to several reasons including the difference between the hot-side temperature and actual leg temperature and heat losses through the TE legs due to radiation. According to this result, low contact resistance at the interfaces is a crucial factor that can significantly improve power and conversion efficiency. Table S1 compares the specification and properties of the hH uncouple investigated in this study with similar hH based TEG devices reported in the literature.

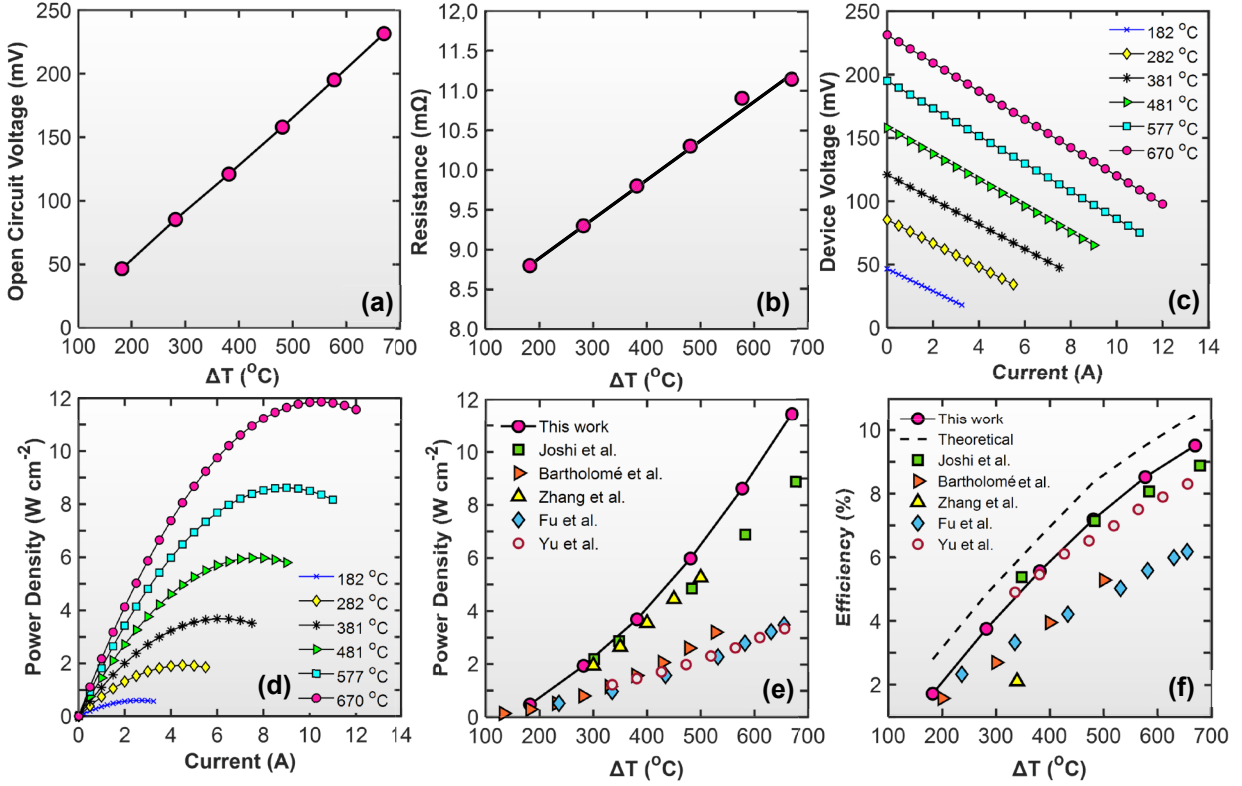


Figure 4: (a) Open circuit voltage versus ΔT , (b) resistance versus ΔT , (c) device voltage versus current (I) under different ΔT , and (d) power density of the fabricated hH unicouple versus I under different ΔT . Comparison of (e) power density with respect to the TE material, and (f) efficiency obtained in this work with hH based TEG modules reported in literature [53,55,56,57,58] as a function of ΔT .

A module comprising of 6 couples (inset of Figure 5-a), i.e., 12 n- and p-type hH legs, was fabricated and tested under similar condition in air to confirm the performance of the single couple on a larger scale. The 6 couples are electrically connected in series. Figure 5-a shows that the six-couple module produces close to 6X more power than the unicouple. This result confirms the capability of scaling this method into large-scale modules for a waste heat recovery application. One of the main obstacles to the widespread usage of TEGs is high temperature stability in a severe environment. High temperature enhances the diffused layer at contacts (the junction of leg and

headers) that degrades the overall performance of the TEGs. An oxidizing environment at high temperature also enhances the degradation rate of the TEGs by oxidizing the TE legs and deteriorating the leg/header junction. While TEGs show better performance when they are tested under vacuum in the lab environment, their practical application requires proof of operation under high temperature in-air and long-term stability. In order to validate the air stability of the modules, the unicouple was tested at a hot-side temperature of 500°C and 550°C in the air. The test setup is shown in Figure S5. No significant degradation in voltage and power was observed after more than 20 hours of operation in the air at 500°C (Figure 5), which demonstrates the high stability of the fabricated hH module in a severe environment. After 20 hours of testing at 550°C, the degradation rate is only ~2.7%. It should be noted that the small variation between V_{OC} and power in Figure 4 and Figure 5 is due to the difference in test conditions where usage of a large plate as a hot-side enhances radiation and convection effect that reduces ΔT across the TE leg.

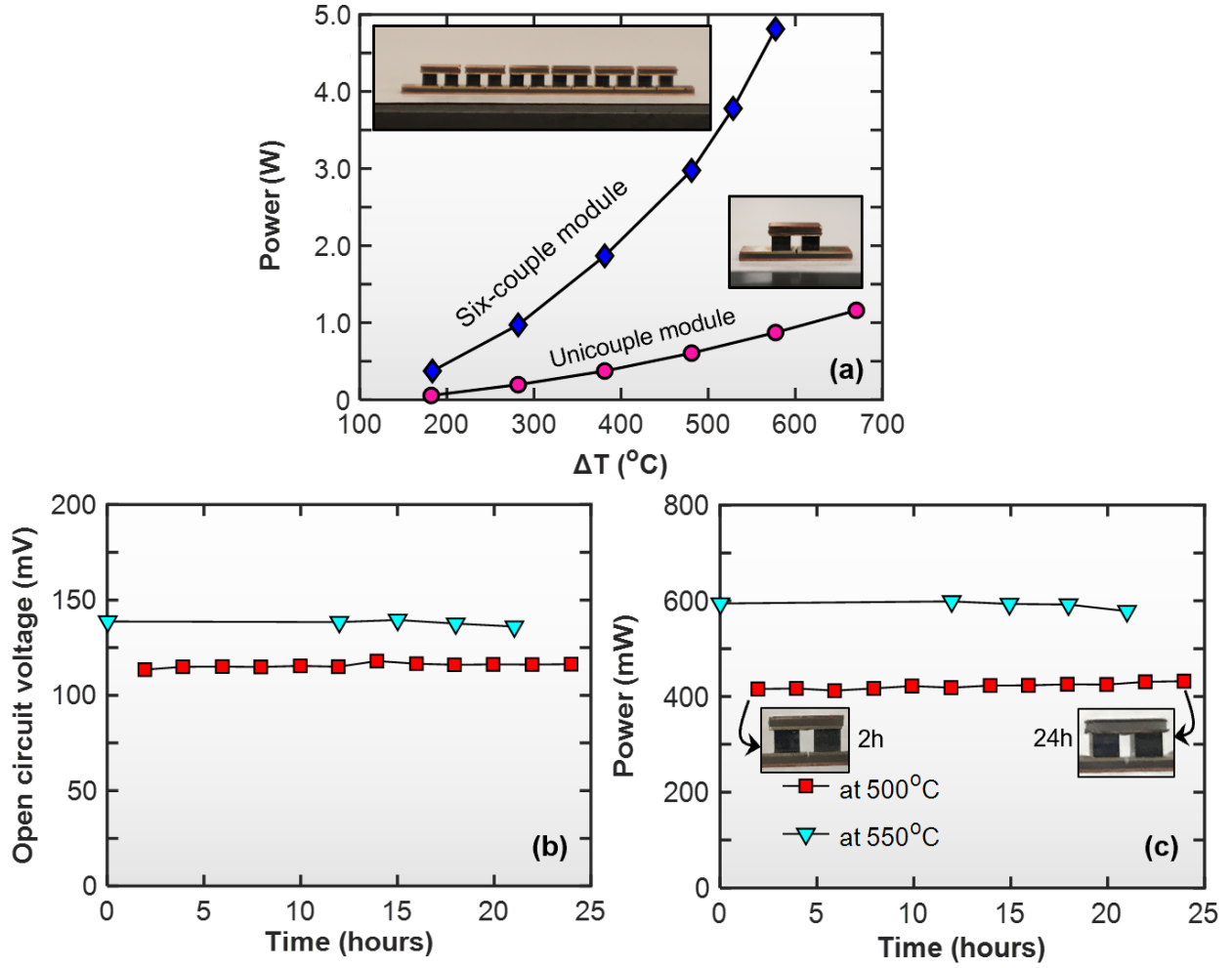


Figure 5: (a) Output power of the fabricated hH unicouple and six-couple modules versus ΔT . The inset shows the actual picture of the modules. Time dependent (b) open circuit voltage (V_{oc}), and (c) output power of the unicouple module tested at 500 and 550 $^{\circ}\text{C}$ in air. The inset shows the actual picture of the modules.

Conclusion

A thermoelectric device was fabricated from nanostructured ZrCoSb (p-type) and ZrNiSn (n-type) half-Heusler materials using a high temperature fabrication process. The joining technique successfully enabled direct bonding between TE legs and Cu electrode without leg metallization. This technique minimizes the diffusion barrier layer inside the TE leg with specific contact

resistance $<1 \mu\Omega\cdot\text{cm}^2$ at the junction of leg/interconnect at room temperature. The results demonstrate the lowest contact resistance reported so far through a suitable brazing material that eliminates the time-consuming and expensive metallization process for TE legs. The peak power density of $\sim 11.5 \text{ Wcm}^{-2}$ and conversion efficiency of 9.5% at a temperature difference of $\sim 670^\circ\text{C}$ was achieved, which is the best performing data in rigid single stage hH alloys with similar materials to date. These results confirm the importance of the module fabrication technique to achieve low contact resistance half-Heusler TE modules. The air stability test results showed very stable performance up to 550°C , opening the opportunity to use thermoelectric generators for high temperature heat recovery application.

Experimental Section

Materials synthesis: High-purity elements of zirconium slug (Zr, 99.9%), hafnium piece (Hf, 99.9%), cobalt pieces (Co, 99.9%), nickel slug (99.995%), antimony shot (Sb, 99.999%), and tin wire (Sn, 99.95%) were used to fabricate p-type $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ (ZrCoSb) and n-type $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.99}\text{Sb}_{0.01}$ (ZrNiSn) half-Heusler alloys. The alloys were synthesized by induction melting under argon atmosphere followed by high energy ball milling using SPEX mixer/mill (Model 8000D, SPEX). The synthesized p- and n-type powders were then consolidated in a cylindrical graphite die with an inner diameter of 12.7 mm (half inch) at different temperatures using spark plasma sintering (SPS) to obtain nanostructured ingots with 12.7 mm diameter and ~ 2 mm height. Thermoelectric properties of the synthesized materials are presented in Figure S2.

Unicouple fabrication: Nanostructured ZrCoSb (p-type) and ZrNiSn (n-type) based half-Heusler ingots were polished to a thickness of ~ 1.92 mm using a MULTIPREP[®] Allied High Tech polishing system and then diced into $2.3 \text{ mm} \times 2.3 \text{ mm}$ (p-type) and $2.2 \text{ mm} \times 2.2 \text{ mm}$ (n-type) legs. The module was fabricated via a direct bonding technique to bond TE legs to copper (Cu)

electrode without metallizing legs using a Cu-Ag based brazing material. The legs were brazed to Cu electrodes by a reflow process using a vacuum reflow technique in an argon environment above 700°C.

Unicouple characterization: The internal resistance of the unicouple was measured using a four-probe meter (MTI Corporation). The contact resistances of the fabricated unicouple was then measured by a home-made four probe technique. The output power and conversion efficiency were measured using a home-made efficiency testing setup [82]. The system was evacuated to a pressure of $\sim 10^{-4}$ mbar. Once the pressure was stabilized, the measurements were started. At a set temperature, open circuit voltage (V_{OC}) and device voltage (V_d) were obtained simultaneously using a voltmeter (KEITHLEY) and a power supply (KEITHLEY 2200-20-5). The internal resistance (R_i) and peak power of the unicouple were calculated using V_{OC} and V_d . The air stability test was performed at different temperatures in air (Figure S5). The microstructure and elemental line scan were studied by a field emission scanning electron microscopy (FESEM, FEI Verios), equipped with an energy-dispersive X-ray spectroscopy (EDS, Oxford Aztec).

Supplementary Information

Supplemental figures, tables and equations can be found in supplementary information.

Notes: The authors declare no competing financial interest.

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