DEVELOPMENT OF THERMOELECTRIC DEVICES BASED ON *n*-TYPE *PbTe*/*p*-TYPE TAGS-85 ($(AgSbTe_2)_{0.15}(GeTe)_{0.85}$) AND *n*/*p*-TYPE *Si-Ge* ALLOY

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- *In the present paper we discuss the synthesis of high quality single phase thermoelectric materials (such as n-type PbTe / p-type TAGS-85 ($(AgSbTe_2)_{0.15}(GeTe)_{0.85}$) and Si-Ge alloy) and the issues related with their thermoelectric device fabrication. In the n-type PbTe / p-type TAGS-85 based devices the contribution of contact to the total device resistance is only 3.0%. Devices consists of one p-n leg (each elements having 7.5 mm dia) generated an output power of 0.61 W (at operating current of ~ 17 A) at hot side temperature $T_h = 500°C$ and a temperature difference $\Delta T = 410°C$. The efficiency of developed devices was found to be 6%. For the Si-Ge based devices contribution of contact resistance to the total device resistance is around 50%. Single p-n couple of Si-Ge based device, which operates at hot side temperature of 900ºC (for a temperature difference of 600°C), shows a power output of 0.49 W. Low efficiency of conversion ~ 1.2% of Si-Ge based devices is attributed to high contact resistance.*

Introduction

Thermoelectric power generation i.e. conversion of heat into electricity is becoming more and more of vital importance in terms of global energy strategy because of its incomparable advantages to retrieve waste heat energy emitted by automobiles, factories etc.[1, 2]. Depending on the operating temperature of thermoelectric devices (TED) different kinds of *n* and *p*-type semiconductor materials are currently being used [1, 2]. The key to realizing an efficient TED depends on finding good single phase homogenous thermoelectric materials and very low contact resistance between interconnects and thermoelements. Semiconductor alloys like *n*-type *PbTe* and *p*-type $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ (TAGS-85) and *Si-Ge* alloys are well established for electrical power generation at high temperatures [1, 2]. In the space mission TED such as *n-PbTe*/*p*-TAGS based devices, the contacts between elements and electrodes (nickel stripes) were formed by *Ag-Cu-In* brazing alloys [1-3] whereas in case of *Si-Ge* based devices electrical contacts were formed by tungsten or molybdenum as interconnect and graphite as buffer layer [1, 2, 4]. In literature there are only few reports giving details of fabrication of highly efficient TED based on different materials. In this paper, we report the fabrication and characterization of *n*-type *PbTe*/*p*-type TAGS-85 and *n*/*p*-type $Si_{90}Ge_{10}$ alloy thermoelements and the fabrication of devices using single *p-n* couple. The efficiency of *PbTe*/TAGS-85 based devices was found to be ~ 6%. However for the *Si-Ge* based devices the efficiency ~ 1.2%, which is due to high contact resistance between thermoelements and interconnects.

Experimental details

Single-phase polycrystalline *n*-type *PbTe* and *p*-type TAGS-85 materials were synthesized by vacuum melting in a rocking furnace [1]. In brief, stoichiometric amount of desired material was ground in agate mortar pestle for 1 hour. The homogenously mixed powder was filled in a pre-cleaned quartz ampoule that was sealed under vacuum (~ 10^{-6} mbar) and heated at 900ºC in a rocking furnace for 1 hour. The rocking eliminates segregation of the different components and yields high homogeneity in the melt. The prepared material was ground into fine powder.

The *Si*-*Ge* alloy was synthesized using melt-quench method. Briefly the chunks of *Si* and *Ge* materials (in stoichiometric ratio of *Si* 80 mole% and *Ge* 20 mole%) were kept in a graphite crucible under vacuum (~ 10^{-6} mbar) and subsequently heated at 1350ºC for 10 minutes using induction heating. In the molten state of materials the stirring action is provided by the eddy currents. For preparing the p-type material boron (0.06 mole%) was intentionally added as the dopant (mixed with the initial grinded *Si* and *Ge* materials). The quenching of molten material was done by pouring it into a water cooled copper crucible, which helps in avoiding the segregation of *Si* or *Ge* during the alloy formation. For preparing *n*-type *SiGe* alloy, gallium phosphide (0.63 mole%) and red phosphorus (1.25 mole%) were added as dopants. Final melt ingots were grounded into fine powder in planetary ball mill.

To fabricate *n*-type *PbTe* elements (7.5 mm dia. and 8 mm height), powder of *PbTe* was filled in a stainless steel (SS) die with interface layers of *Fe* and (50% *PbTe* + 50%*Fe*) as shown in Fig. 1 (*a*). The SS die had a thin graphite liner to avoid reaction with thermoelectric materials. This layered structure was then pressed in a vacuum hot press at temperature of 600ºC and load of 700 kgs. The fabrication of *p*-type TAGS-85 elements was carried out in a similar way to that of *n*-type *PbTe* using *SnTe* and *Fe* as interface materials as shown in Fig. 1 (*b*). As the diffusion of *Fe* into TAGS-85 is reported to result in rapid degradation of the contacts [1, 5], *SnTe* was used as a diffusion barrier. For fabrication of *Si*-*Ge* thermoelements the grinded material was filled in graphite die set with a thin layer of carbon at the top and bottom end. This layered structure was then pressed in a vacuum hot press at 1050ºC and load of 700 kgs.

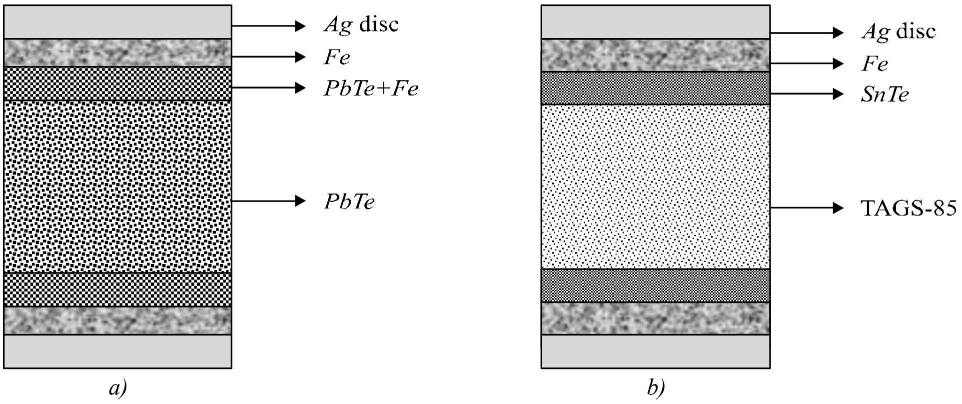
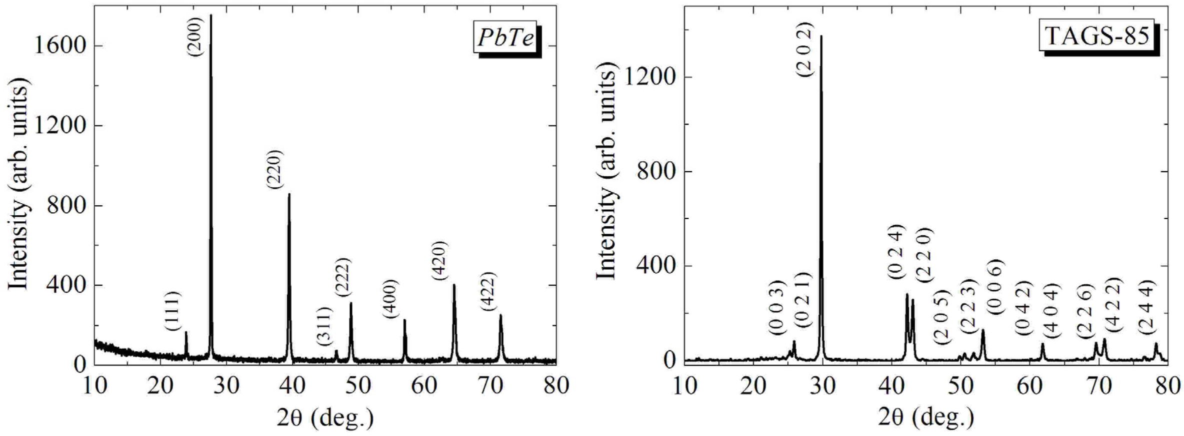


Fig. 1. Schematic diagram showing the sequence of materials inside the die set for fabrication of (a) n-type (PbTe) and (b) p-type (TAGS-85) thermoelements.

The fabricated thermoelements were characterized for phase identification, microstructures, interface analysis, temperature dependence of Seebeck coefficient (*S*) and power output. The total device resistance was measured using a standard four-probe measurement technique. To measure it a constant current was sent to the sample by Keithely source meter (model 2400) and corresponding voltage was recorded by Keithley nanovoltmeter (model 2182). The Seebeck coefficient (*S*) was measured using seesaw method, in this two identical platinum heaters were mounted on the two ends of the sample [6]. The two ends of the sample were alternately heated and generated Seebeck voltages were averaged, so that any spurious voltage is cancelled. The temperature difference across the sample was measured using a chromel-alumel (*K*-type) differential thermocouple, which is fixed on the sample using thermally conducting cement. For measuring temperature dependence of *S* the entire assemble along with sample was placed in a furnace having a uniform temperature zone. The *S* measurements have an error of ± 2%. From sample to sample the variations in these measurements are less than ± 5%.

Results and discussion

PbTe and TAGS-85 based devices: Figure 2 shows *X*-ray diffraction (XRD) patterns of the synthesized compounds. These show single phase *PbTe* (with *NaCl* structure with lattice parameter of 6.463 Å) and TAGS-85 materials [6 – 8]. TAGS-85 is found to have hexagonal structure with *a* and *c*-axis lattice parameters of 8.34 Å and 10.66 Å respectively [8].



a) *b)*

Fig. 2. X-ray diffraction pattern of (a) PbTe and (b) TAGS-85 materials.

The temperature dependence of Seebeck coefficient (*S*) for *PbTe* and TAGS-85 rectangular bar shaped sample (size 7 mm × 3 mm × 1 mm) without any metal contacts on the ends are shown in Fig. 3. The absolute value of *S* increases with increasing temperature. The *S* values at 500°C are found to be 282 μV/K for *PbTe* and 140 μV/K for TAGS-85 and comparable to the best reported values of 300 and 170 μV/K respectively [1, 6 – 8].

For fabrication of the devices, thermoelements were packed in an asbestos housing that provides an enclosure to hold them and being an insulator, reduces direct flow of heat between hot and cold surfaces. Subsequently, silver stripes were placed on the top and bottom side the thermoelements. The entire assembly was vacuum hot pressed (vacuum of 2×10^{-5} Torr) and optimized bonding temperature of 400°C. In order to characterize the devices, they were placed in a home made testing set up having a spring-loaded hot surface and water-cooled copper base. The temperature of hot surface and water- cooled surface was determined by thermocouple attached to them by thermally conducting cement. In order to estimate the power output from the device a known load resistance (R_L nearly equivalent to the four-probe resistance of the device) was connected at the output leads. R_L was made by copper wire and its value was determined using four-probe method. The voltage V_L developed across the load resistance gives an estimate of the current I_L flowing through the device and electrical power generated by device as $V_L \times I_L$. For measurement of load resistance and voltage developed across it, we have done measurement using high precision Keithley make nano-

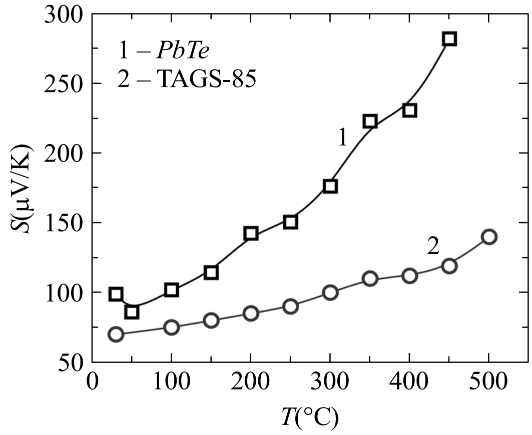


Fig. 3. Temperature dependence of absolute Seebeck coefficient (S) for PbTe thermoelement and TAGS-85 materials.

voltmeter and source meter, so the errors associated with power measurement are less than ± 2%. Characteristics for a typical single *p-n*-couple device as function of load resistance are shown in Fig. 4 for hot end temperature of 500ºC and temperature difference of 410ºC. The device showed an open circuit voltage of 68 mV and maximum output power of ~ 0.61 W (with load voltage of 34 mV and current of 18 A). Based on the measured Seebeck coefficient of *PbTe* and TAGS-85 for a temperature difference of 410ºC and average temperature of 295ºC, we estimate the open circuit voltage of device as ~ 50 mV. The difference between actual (~ 34 mV) and estimated value could be due to the loss of heat at silver metal stripes and iron electrodes as a result the temperature difference across the thermoelectric material may have a lower value. Fabrication of silver ended thermoelements (as shown in Fig. 1) was done by hot pressing at 600ºC. Being a silver (from stripes) and silver (from the end of the thermoelements) bond, these contacts can withstand high temperature > 400ºC. Operating the device at 500ºC in atmosphere did not show any change in the output characteristics for a period more than 8 months. The internal resistance R_{int} of a device (see Fig. 1) has two contributions. First contribution is due to material resistance R_m contributed by (*a*) *PbTe* (R_{PbTe}) and TAGS (R_{TAGS}) cylindrical shaped layers, (*b*) *SnTe* (R_{SnTe}) or *PbTe* + *Fe* ($R_{PbTe+Fe}$) and *Fe* layers (R_{Fe}) in TAGS/*PbTe* elements and (*c*) silver discs and strips (R_{Ag}). Second contribution is combined contact resistance (R_c) of all the interfaces in each element. Contributions to R_m were determined by measurement of four probe resistivity of each material and for a two legs device were found to be, $R_{PbTe} = 1.1$ mΩ, $R_{TAGS} = 0.75$ mΩ, $R_{SnTe} = 45.4$ μΩ, $R_{PbTe+Fe} = 5$ μΩ, $R_{Fe} = 0.87$ μΩ and $R_{Ag} = 9.82$ μΩ yielding a total materials resistance of $R_m = 1.92$ mΩ. The resistance of single leg device (having two elements) was measured to be 1.98 mΩ. This yields average contact resistance for each element to be 26 μΩ·cm^2 (13 μΩ·cm^2 for each contact). From thermoelectric conversion point of view the acceptable value of electrical contact resistance for material interfaces within TED should be less than 100 μΩ·cm^2 [1]. Contribution of contact resistance to total device resistance is found to be 3%. Efficiency of the device was directly measured as ratio of electrical power output to heat flow through the device. For determination of heat flow through device elements, radiation loss from heater and heat flow through asbestos housing were first determined using thermally insulating material and plain asbestos sheets. For these single leg device, heat flow was found to be 10 W, yielding a typical device efficiency of ~ 6%. The durability of the devices was investigated by their continuous operation under $T_h = 500$ºC and $\Delta T = 410$ºC in air. Three devices have operated continuously for a year without any measurable degradation.

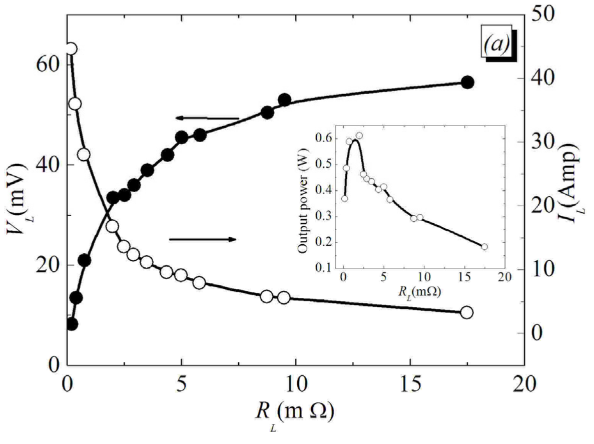


Fig. 4. (a) The load voltage V_L and current I_L as a function of load resistance R_L for single couple PbTe/TAGS-85 based device. Inset shows output power of device as a function of R_L.

Si-Ge alloy based devices

The *X*-ray diffraction pattern for synthesized *Si-Ge* alloy is shown in Fig. 5 (*a*). It shows a single phase *Si-Ge* materials. The sample taken from different portions of the melt cast ingot shows similar pattern. The inset of the figure shows the enlarged view of (111) peak, which appears at 28.6 degree. This peak is usually taken as a marker to show whether the alloy is formed or not. The presence of single (111) peak at 28.6 degree corresponds to the formation of homogenous *Si-Ge* alloy formation [1]. For the comparison purpose, in Fig 5 (*b*) we have plotted the XRD data for just normally melted and slowly cooled sample (no quenching of the melt), it shows that (111) peak is actually corresponds to independent (111) peak for *Si* and *Ge* indicating that there is no alloy formation. The energy dispersive *X*-ray analysis (EDX) shows that the melt-quench sample has $Si_{89}Ge_{11}$ composition. It may be noted that although our starting *Si*:*Ge* ratio was 80:20 but after alloy formation the final material has *Si*:*Ge* ratio as 89:11, which might be due to the evaporation of some germanium from the melt due to its high vapor pressure at 1350ºC.

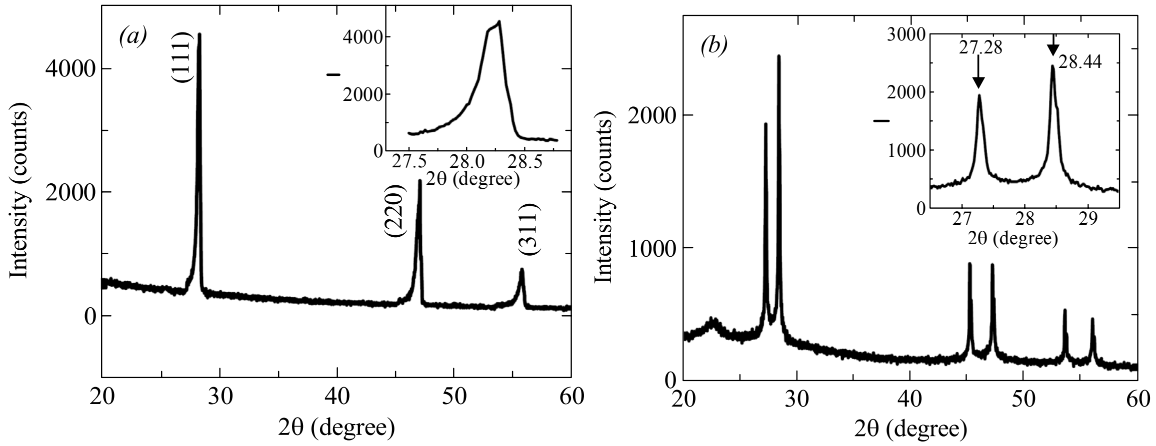


Fig. 5. X-ray diffraction pattern of Si-Ge alloy materials (a) prepared by melt quench method. (b) prepared by melt and slow cooling.

The temperature dependence of Seebeck coefficient (*S*) for n and *p*-type *Si-Ge* rectangular bar shaped sample (size 7 mm × 3 mm × 1 mm) without any carbon layer at the ends are shown in Fig. 6. Both *p* and *n*-type *Si-Ge* alloy shows nearly same Seebeck coefficient and its value at 900°C was found to be 180 μV/K, which is comparable to the best reported value of *S* (~ 210 μV/K) for the optimized *Si-Ge* materials [1, 2, 11].

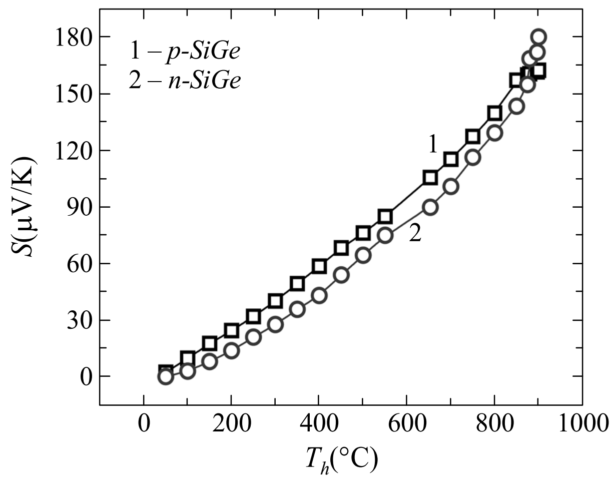


Fig. 6. Temperature dependences of absolute Seebeck coefficient (S) for n /p-type Si-Ge alloy.

Fig. 7 (*a*) shows the schematic diagram for the fabrication of single *p-n*-couple *Si-Ge* based devices. Here *n*- and *p*-type thermoelements having carbon layer at the ends were placed in an asbestos housing and joined using molybdenum (*Mo*) strip and *Ag*-disc as brazing material. The carbon layer serves two purpose: (i) it is effective in absorbing thermal stress caused by a mismatch of thermal expansion between *Mo*, *Ag*-disc and *Si-Ge* alloy (ii) it avoids the direct reaction between *Ag* and *Si-Ge* thermoelements, which otherwise leads to very high contact resistance [10]. The entire assembly was vacuum hot pressed (vacuum $\sim 2 \times 10^{-5}$ Torr) at optimized bonding temperature of 1050ºC. The photograph of fabricated device is shown in Fig. 7 (*b*).

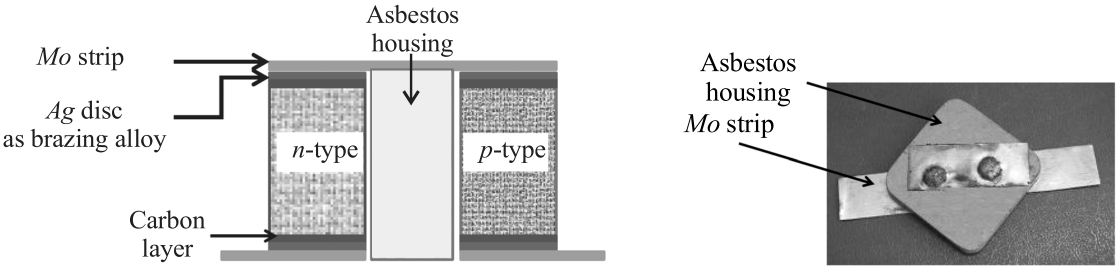


Fig. 7. Schematic diagram and photograph showing the packing and interconnection between elements in singe leg n/p-type Si-Ge based device.

The four probe resistance of the device was found to be 58 mΩ. In order to characterize the devices, they were placed in a home made testing set up having a spring-loaded hot surface and water-cooled copper base. The temperature of hot surface and water-cooled surface was determined by thermocouple attached to them by thermally conducting cement. The device was sandwiched between hot and cold surface. The testing setup along with the device was kept in a vacuum chamber evacuated to 4×10^{-3} mbar of vacuum. After achieving the vacuum, argon gas was introduced in the chamber through the needle valve maintaining a dynamic argon pressure of 500 mbar and heating of the device was started. Characteristics for a typical one leg device as function of hot side temperature are shown in Fig. 8 (*a*). For hot end temperature of 900ºC and temperature difference of 600ºC, the device shows an open circuit voltage of 230 mV and maximum output power of ~ 0.2 W (with load voltage of 120 mV and current of 1.74 A). Heat flow for this device is found to be 16 W, hence the working efficiency of the devices ~ 1.2%. Contributions to R_m were determined by measurement of four probe resistivity of each material and for a one leg device was found to be, $R_{n\text{-}SiGe} = 7$ mΩ, $R_{p\text{-}SiGe} = 11$ mΩ, $R_{Mo} = 12$ mΩ, $R_{carbon} = 0.1$ mΩ, and $R_{Ag} = 0.0006$ mΩ yielding a total materials resistance of $R_m = 30$ mΩ. The difference between device resistance (58 mΩ)) and the material resistance R_m yields average contact resistance for each element to be 6.5 mΩ·cm^2 (3.25 mΩ·cm^2 for each contact). For *Si-Ge* based single leg devices the contribution of contact resistance to total device resistance was found to be 50%, hence these devices shows low efficiency (~ 1.2%). Further efforts are being made to reduce the contact resistance.

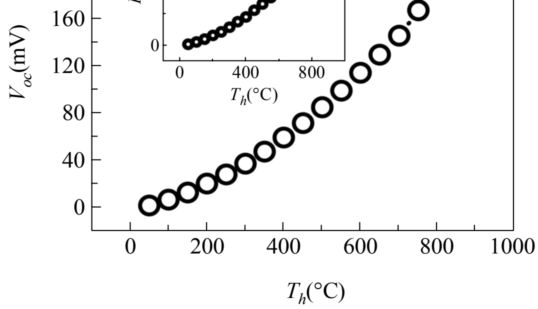


Fig. 8. Open circuit voltage of the single leg Si-Ge device as a function of hot side temperature. Inset shows the current generated by the device (load resistance ~ 58 mΩ) as function of hot side temperature.

Conclusions

In conclusion we have demonstrated a process for the fabrication of thermoelectric devices based on *n*-type *PbTe*/*p*-type TAGS-85 and *n/p*-type – type *Si-Ge* thermoelements. The average electrical contact resistance for each contact in the *PbTe*/TAGS-85 devices was found to be $\leq 35\ \mu\Omega\cdot cm^2$. SEM images and EDX analysis of electrode and thermoelectric materials interfaces revealed chemically sharp interfaces even after long period of operation of devices. For hot end temperature of 500°C and temperature difference of 410°C, single *p-n* leg devices exhibited typical output power of ~ 0.6 W (at current of 17 A) with a working efficiency of 6%. The devices have been continuously operated for a year without any degradation.

For *n*/*p*-type *Si-Ge* alloys based devices, thermoelements were joined using molybdenum as interconnects, and the contribution of contact to the device resistance is 50%. For hot end temperature of 900°C and temperature difference of 600°C, single *p-n* leg devices exhibited an output power of ~ 0.2 W (at current of 1.75 A) with a working efficiency ~ 1.2%.

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