Pulsed-light surface annealing for low contact resistance interfaces between metal electrode and bismuth telluride thermoelectric materials

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Pulsed-light surface annealing for low contact resistance interfaces between metal electrode and bismuth telluride thermoelectric materials

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Abstract:

Traditional deposition methods of electroplating, sputtering and evaporation can produce weak and inconsistent interfaces between the electrode contact and Bi_2Te_3-based nanostructured thermoelectric (TE) materials. Electrode contact layers with low bonding strength are mainly due to severe damage of the top layer of the TE material during surface preparation. We report a novel and cost-effective method for surface preparation of thermoelectric materials (Bi_2Te_3) using pulsed light annealing prior to nickel electroplating. Short duration high-energy light absorption at the surface of the TE material causes reflow and annealing of surface structures which enhance the electrical and thermal flow across the interface through more consistent and stronger bonding between the electrode metal and TE material. An electrical contact resistance reduction on the order of 5 $\mu\Omega$-cm^2 and pull strength of around 8 MPa was reproducibly measured for both p-type ($Bi_{0.5}Sb_{1.5}Te_3$) and n-type ($Bi_2Te_{2.7}Se_3$) compositions compared to electroplated nickel samples that did not receive pulsed light annealing. This novel technique for surface preparation prior to metallization is applicable to a range of TE materials, and will lead to significant improvement in the performance of TE modules and devices.

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Keywords: thermoelectrics, contact resistance, Pulsed-Light annealing, cooling, power generation, high ZT.

1. Introduction

Thermoelectric (TE) devices are well-known options for power generation and cooling applications ranging from electrical power generation for space vehicles, [1] waste heat and solar energy harvesting into electricity , [2, 3] and thermal cyclers for polymerase chain reaction (PCR) [4]. Bi_2Te_3 and its alloys with Sb_2Te_3 and Bi_2Se_3 have demonstrated peak thermoelectric performance around room temperature and are widely recognized as the best option for cooling applications and power generation from low-grade waste heat. [5, 6] Progress continues to be made in improving the thermoelectric figure-of-merit (ZT) of Bi_2Te_3 based alloys through nanostructure engineering [7-14] but the development of strongly bonded contact metal layer with very low contact resistance on nanostructured Bi_2Te_3 has been challenging and has hampered fabrication of stable thermoelectric modules prepared from these materials.

The bonding strength and electrical contact resistance between the electrode and thermoelectric materials are key factors in the fabrication of highly-efficient and reliable thermoelectric modules. An optimized module should have maximized bonding strength and minimized electrical contact resistance between the TE materials and electrodes. The contact resistance R_c between the electrode and thermoelectric elements decreases the effective $<ZT>_D$, with $ZT = S^2\sigma T/k$ (S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity and T is the absolute temperature) of thermoelectric devices according to equation 1, [15, 16]

$$<ZT>_D = \frac{(L)}{(L + 2R_c\sigma)} <ZT>_m \tag{1}$$

where L is the length of the thermoelectric leg, R_c is the contact resistance, and $<ZT>_m$ is the effective ZT of the thermoelectric material between the hot side (T_h) and cold side (T_c). For a typical Bi_2Te_3 device, L ~ 1 - 2 mm and, $\sigma \sim 10^5$ S/m, R_c should be much less than $L/2\sigma \sim 10^{-4}$ Ω-cm^2. Ideally, the contact resistance should be less than 1 $\mu\Omega$-cm^2.

Traditional metallization methods used in the fabrication of Bi_2Te_3-based thermoelectric devices include electrochemical deposition, sputtering and evaporation of nickel (Ni) which prevents interlattice diffusion of Cu from the electrode [17, 18] or solder/brazing material into the thermoelectric material. [19, 20] Ideally, the contact layer would consist of high pull strength (> 10MPa) and contact resistance ~ 1$\mu\Omega$-cm^2. Reported bonding strength and contact resistance values are inconsistent and range between 1 – 10 MPa and 5-100 $\mu\Omega$-cm^2 respectively using conventional metallization techniques on nanostructured Bi_2Te_3 and these attributes have hampered efforts to incorporate the nanostructured TE materials in cooling and power generation modules [16].

Due to the small grains and brittle nature of nanostructured BiTe-based materials, the surface gets damaged during the preparation process which leads to poor performance behavior of the contact layer. In this study, a novel approach for surface preparation of $Bi_{0.5}Sb_{1.5}Te_3$ (p-type) and $Bi_2Te_{2.7}Se_3$ (n-type) using pulsed light annealing prior to the metallization step (electroplating) is explored. We measured low contact resistance on the order ~ 5 μΩ-cm^2 and bonding strength of ~ 8 MPa reporducibly for both p- and n-type TE materials. The low contact resistance and good bonding strength is attributed to the formation of a thin recrystallized layer on the TE surface after pulsed light annealing which enhanced the electrical transport as well as mechanical bonding strength typically observed for ingot-based materials. Pulsed light annealing was demonstrated to have a marked impact on the performance of nanostructured $Bi_{0.5}Sb_{1.5}Te_3$ (p-type) and $Bi_2Te_{2.7}Se_3$ (n-type) materials prepared by ball milling commercial ingots and hot pressing into TE elements, and suggest that rapid light annealing of hot-pressed elements prior to metallization may provide significant TE module performance benefits.

2. Experimental details

Nanostructured materials were synthesized by ball milling 1-5 hrs of commercial ingots of compositions $Bi_{0.5}Sb_{1.5}Te_3$ (p-type) and $Bi_2Te_{2.7}Se_3$ (n-type) and hot pressing in to ½” disks at T = 300 – 500 °C under 60 MPa uniaxial pressure. The pressed disks were then polished using silicon carbide powder and cleaned with acetone/ isopropyl alcohol/ and deionized water in combination with ultrasonication. Cleaned TE disks were annealed using a Novacentrix’ PulseForge 1300 with pulsed energy densities between 9.0 J/cm^2 and 20 J/cm^2. The optimization of pulse energy density was performed by varying (a) pulse voltage, (b) pulse width, and (c) exposure time to obtain best possible results. Furthermore, using the PulseSim calculation software, temperature vs. time profiles were simulated using different pulse energies to maintain peak temperatures of 600 – 1200 °C to sufficiently heat and recrystallize the top few micrometers of the disks. Clean TE disks and TE disks exposed with the PulseForge of both types of materials were electroplated with nickel (Ni) using a custom Ni solution bath. The Ni plated disks were then diced into 2.5 mm × 2.5 mm x 1.75 mm TE elements using a precision dicer [Dicing Saw ADT] to avoid chipping and cracking at the edges. The TE elements (p & n) were soldered with bonding pads and connected to copper wires to enable measurement of the voltage across the interfaces between the TE material and Ni using a custom four-point scanning probe technique illustrated in (Figure 1). [16] For these measurements, a constant current of 100 mA was applied to the TE element during the voltage measurement. The bonding strength of the Ni layer was measured using a commercial pull tester (Mark-10 Manual Force Meter, Cole-Parmer). The microstructure of the interface was studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM, JEOL-6340F). The simultaneous measurement of electrical resistivity and Seebeck coefficient was conducted with a commercial system (ZEM-3, ULVAC). The TE elements were then assembled into unicouple devices with copper electrodes. Power output was measured using a custom Nanohmics' power generation system at temperature differentials up to 200 ^{o}C.

3. Results and Discussions

The impact of pulsed light annealing of hot-pressed thermoelectric material on the surface micromorphology, contact resistance, bonding strength, and TE power generation performance was evaluated. Figure 2 shows X-ray Diffraction (XRD) patterns illustrating the impact light annealing had on the surface of $Bi_{0.5}Sb_{1.5}Te_3$. As evidenced in Figure 2, the material phase composition was not altered by pulsed light annealing, rather, diffraction peak intensity increased as a result of surface recrystallization (top curve). This was an indication that the surface micromorphology became more crystalline which led to improved electrical contact interface after deposition of the electrode. These results were confirmed by high resolution SEM imaging as illustrated in Figure 3. Surface grain reflow observed after pulsed light annealing was shown to lead to marked increase in grain size, in the range of 10 µm (Figure 3b), as compared to non-annealed samples which had an average grain size much less than ~1 µm (Figure 3a). Figure 3c, a cross section image of pulse light annealed surface, shows that the reflowed grain thickness is around 2-3µm and the nanoscale grains are preserved below the reflowed surface which is essential for better thermoelectric properties. [7] The pulse light annealing process was initially optimized by changing pulse energy densities through pulse (a) voltage (700 – 800 V), (b) exposure time (2 – 4 milliseconds), and (c) frequency (pulse width: 10 – 30 µs). Figure 4 show the SEM images of different combination of voltage, exposure time and frequency and corresponding energy densities. It is clearly seen from Figure 4 that the surface reflow increases with pulse energy densities and eventually cracks the top melted surface (Figure 4f). The optimized pulse energy density is found to be in the range of 12-15J/cm^2.

To study the effect of pulsed light annealing on the interfacial electrode contact resistance, TE elements (with and without light annealing) were electroplated with nickel (Ni), diced in to 2.5 mm × 2.5 mm elements, and characterized by scanning the electrical properties of the interface between the TE material and Ni layer using the measurement system shown previously in Figure 3. Figure 5 shows the measured voltage of Ni-metallized n-type (a) and p-type (b) elements across the respective length in which voltage measurement across metal and TE elements are straight lines with slopes providing their respective resistivities while the jump on voltage at interfaces quantifies the contact resistance between TE materials and metal (Ni). The voltage change across the interface was significantly lower for samples subjected to pulsed light annealing compared to samples that did not received pulsed light treatment. The calculated value of contact resistance determined by the change in voltage across the interface for both types of materials is presented in Table 1. Pulsed light annealing not only reduced the contact resistance but also led to improvements in the bonding strength between the metal layer and TE elements. Pull test characterization performed on the TE elements, with and without pulsed light annealing, demonstrated much improved and consistent bonding strength (~ 8MPa) compared to elements without pulsed light annealing (~ 1-5 MPa). Moreover, pulse light annealing helped to make uniform contact resistance across two interfaces of the n-type TE elements which was asymmetric before light pulse annealing. P-type elements have shown uniform contact across both interfaces of TE elements with or without light pulse annealing.

TE devices were fabricated using pulsed light annealed elements to improve the performance of the devices. Figure 6 shows the modeled and experimental output power density of uni-couple devices having two different contact resistance values. The power density was calculated using a fixed cold-side temperature (T_c) = 25 ^oC and a variable hot-side temperature (T_h) up to 225 ^oC. The device fabricated using a 13.9 J/cm^2 pulsed light anneal produced 25% higher electrical power output compared to the device comprising TE elements that were not exposed to pulse light annealing. Overall, the measured power densities are within 15% of the modeled values corresponding to their contact resistance. A power density of about 1 W/cm^2 was measured from a uni-couple fabricated using pulsed light annealed $Bi_2Te_{2.7}Se_{0.3}$ (n-type) and $Bi_{0.5}Sb_{1.5}Te_3$ (p-type) elements. The results illustrated that application of the novel pulsed light annealing process before electrical contact metallization can lead to effective TE surface modification in a low-cost and rapid method. Furthermore, pulsed light annealing is amenable to high throughput manufacturing methods which would enable new TE device geometries that are amenable to all types of TE materials used in high-temperature power generation and cooling applications.

4. Conclusions

A novel and cost-effective method to prepare the surface of thermoelectric materials has been evaluated using pulsed light annealing prior to electroplating of the metal electrical contact layer. The pulsed light annealing method was demonstrated to rapidly inject Joules of light radiation to induce reflow of the top surface morphology of hot-pressed, nanostructured TE material. Surface annealing not only enhanced the electrical and thermal conductivity across the electrode-TE interface, but also made for a homogenous and stronger bond between the metal and thermoelectric materials. Contact resistances ~ $5\mu\Omega\text{-cm}^2$ and pull-test determined bonding strength of around 8 MPa was consistently measured for the electrode interface of both p- ($Bi_{0.5}Sb_{1.5}Te_3$) and n-type ($Bi_2Te_{2.7}Se_3$) compositions. This novel technique of surface preparation for metallization is applicable to a broad number of TE materials to improve TE module performance over a wide range of applications in both power generation and cooling.

5. Acknowledgements

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Figure and Table captions:

Figure 1. Schematic illustration of the contact resistance scanning probe measurement device.

Figure 2. XRD pattern of the surface of p-type bismuth antimony telluride ($Bi_{0.5}Sb_{1.5}Te_3$) with (top curve) and without (bottom curve) pulsed light surface annealing.

Figure 3. SEM images of the surface of p-type $Bi_{0.5}Sb_{1.5}Te_3$ before (a) and after (b&c) pulsed light annealing process.

Figure 4. SEM images of different combination of light pulse voltage (700 – 800 V), exposure time (2 – 4 milliseconds), frequency (pulse width: 10 – 30 μs), and their corresponding energy densities.

Figure 5. Measured voltage across the length of Ni electroplated on (a) n-type and (b) p-type TE elements. The measurements were accomplished by creating a cross-section of the layer structure after dicing and scanning the voltage across the interfacial layers using the probe measurement system of Figure 1.

Figure 6. Modeled power density curve for two different contact resistance values of 10% and 20% for p-type ($Bi_{0.5}Sb_{1.5}Te_3$) and n-type ($Bi_2Te_{2.7}Se_3$) elements with $T_c = 25\ ^oC$ and variable T_h (up to 225 ^oC). Experimental power density measurements for p-type ($Bi_{0.5}Sb_{1.5}Te_3$) that had been subjected to pulses light annealing (filled circles) and without pulsed light annealing (open circles) are also shown and compared favorably with the predicted values.

Table 1. Calculated contact resistance from the voltage vs. distance data (Figure 5).

Figures:

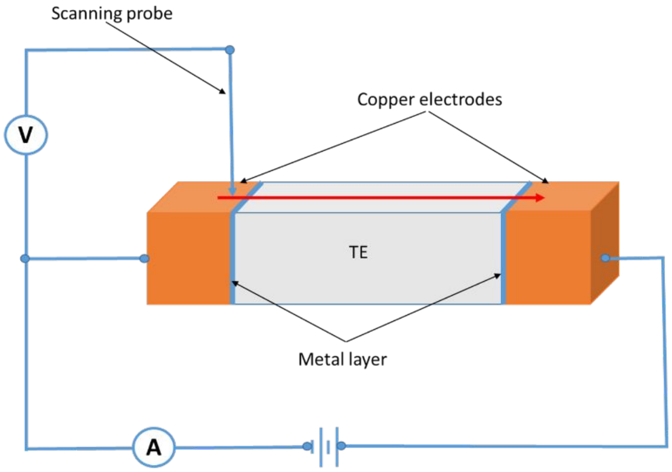

Figure 1. Joshi *et al.*

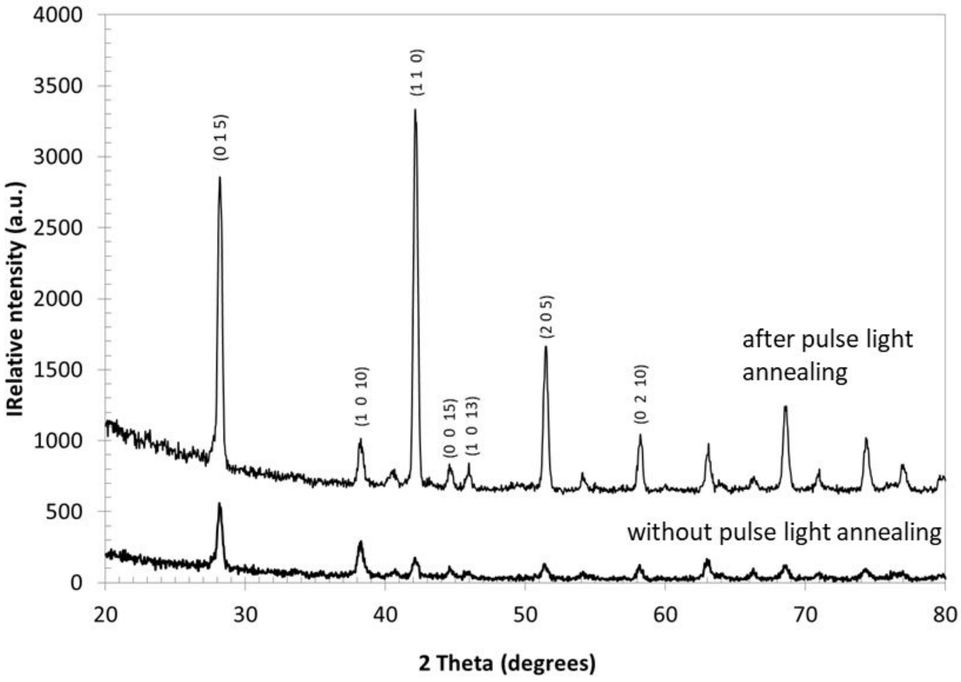

Figure 2. Joshi *et al.*

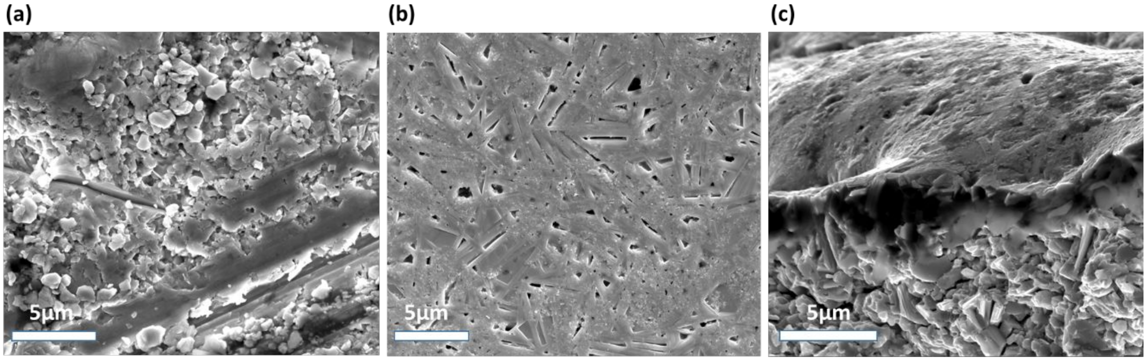

Figure 3. Joshi *et al.*

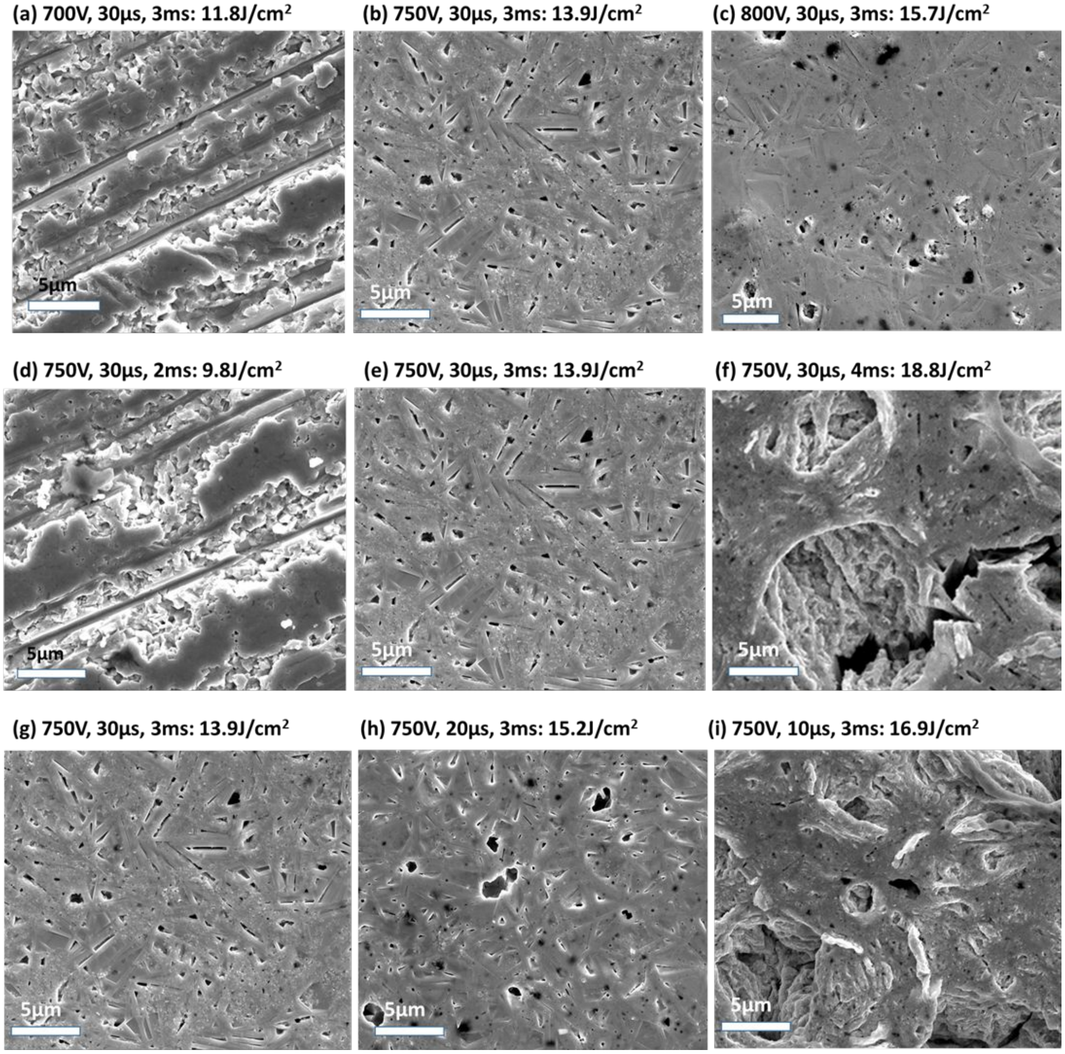
(a) 700V, 30µs, 3ms: 11.8J/cm²
(b) 750V, 30µs, 3ms: 13.9J/cm²
(c) 800V, 30µs, 3ms: 15.7J/cm²
(d) 750V, 30µs, 2ms: 9.8J/cm²
(e) 750V, 30µs, 3ms: 13.9J/cm²
(f) 750V, 30µs, 4ms: 18.8J/cm²
(g) 750V, 30µs, 3ms: 13.9J/cm²
(h) 750V, 20µs, 3ms: 15.2J/cm²
(i) 750V, 10µs, 3ms: 16.9J/cm²

Figure 4. Joshi *et al.*

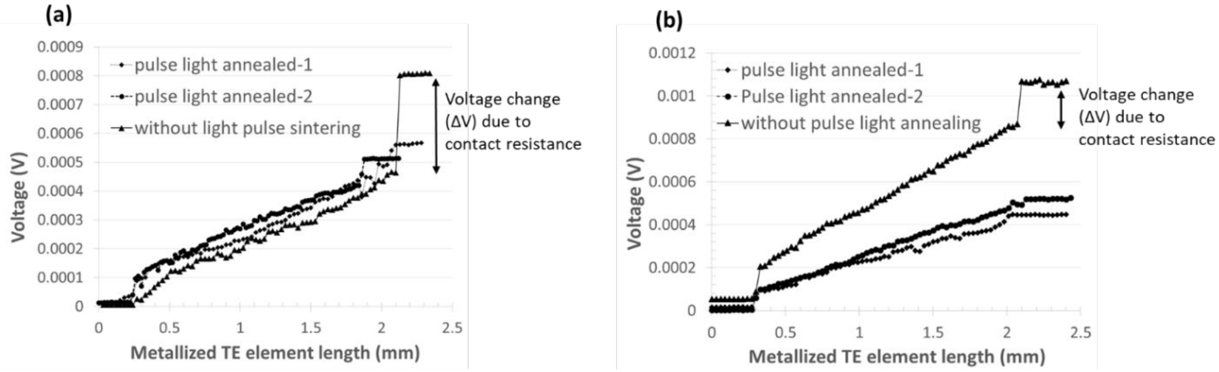

Figure 5. Joshi *et al.*

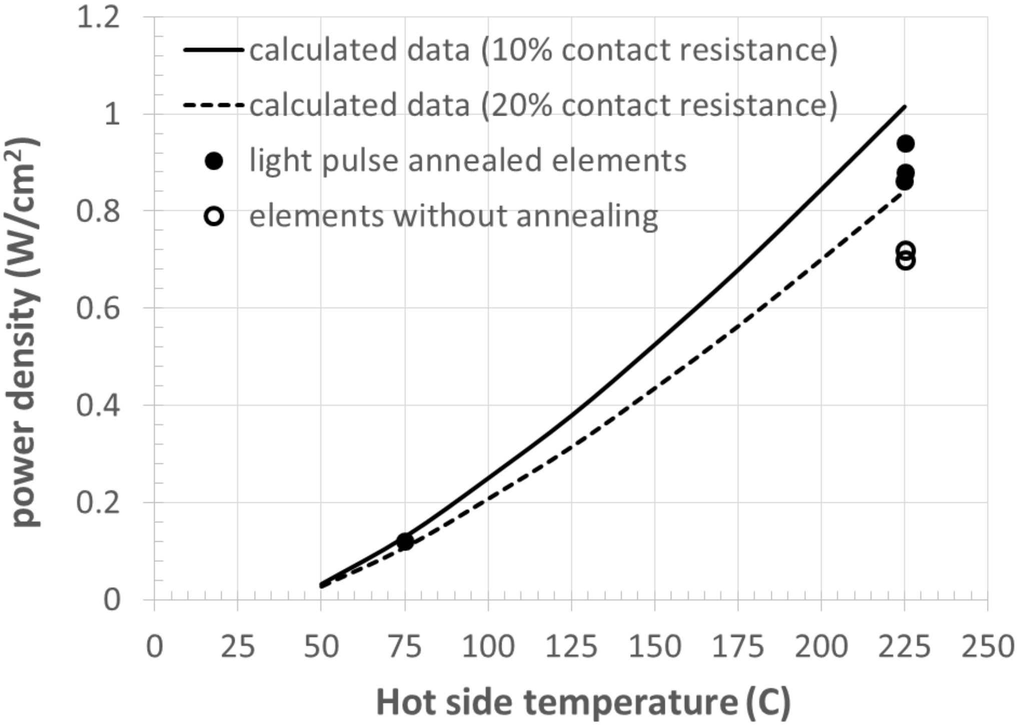

Figure 6. Joshi *et al.*

Table 1. Joshi *et al.*

Type of materials	Contact resistance in μΩ-cm^2	
	Without pulsed light annealing (average of two samples)	With pulsed light annealing
n-type ($Bi_2Te_{2.7}Se_{0.3}$)	30	7.7
p-type ($Bi_{0.5}Sb_{1.5}Te_3$)	20.3	5.2

Table of Content

Pulse light annealing process improves the efficiency of bismuth telluride based thermoelectric devices by reducing the contact resistance significantly.