Practical Contact Resistance Measurement Method for Bulk Bi₂Te₃-Based Thermoelectric Devices

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The impact of contact resistance on thermoelectric (TE) device performance grows more significant as devices are scaled down. To improve and understand the effects of contact resistance on bulk TE device performance, a reliable experimental measurement method is needed. There are many popular methods to extract contact resistance, but they are only well suited for measuring metal contacts on thin films and do not necessarily translate to measuring contact resistance on bulk TE materials. The authors present a measurement technique that precisely measures contact resistance on bulk TE materials by making and testing stacks of bulk, metal-coated TE wafers using TE industry-standard processes. An equation that uses the Z of the stacked device to extract the contact resistance is used to reduce the sensitivity to resistivity variations of the TE material. Another advantage of this technique is that it exploits realistic TE device manufacturing techniques and results in an almost device-like structure. The lowest contact resistivity measured was $1.1 \times 10^{-6} \Omega \text{ cm}^2$ and $1.3 \times 10^{-6} \Omega \text{ cm}^2$ for *n*- and *p*-type materials, respectively using a newly developed process at 300 K. The uncertainty in the contact resistivity values for each sample was 10% to 20%, which is quite good for measurements in the $10^{-6} \Omega$ cm² range.

Key words: Thermoelectrics, bismuth telluride, contact resistance

INTRODUCTION

The cooling power density quantifies the capacity of a thermoelectric (TE) device to pump heat. Highwatt-density devices can dramatically change the historical standards of cost per watt of heat pumped. The maximum cooling power density per unit area for a single element (Q_{max}) is derived by differentiating the total heat flux (Q) for Peltier cooling¹ and is given by Eq. 1.

$$Q_{\max} = \frac{1}{2L} \left[\frac{\alpha^2 T_{\rm c}^2}{\left(2\rho + \frac{4\rho_{\rm c}}{L}\right)} - k\Delta T \right], \tag{1}$$

where L is the device leg length, ρ_c is the contact resistivity, ρ is the bulk resistivity, k is the thermal

conductivity, T_c is the cold-side temperature, and α is the Seebeck coefficient.

From Eq. 1, the cooling power density is inversely proportional to the leg length, L, of the device; therefore, the cooling power density can be increased by reducing the leg length. Bulk material is currently the predominant commercial option to obtain the required performance because of the high cost of thin-film material processing and limitations on film thickness. Micro-TE coolers, i.e., bulk TE coolers with very small element lengths, are becoming the norm in the telecommunications industry, where the TE cooler stabilizes the temperature of laser diodes that send optical signals through fiber-optic cables.² The impact of contact resistance on micro-TE cooler performance is quite significant for devices with element length of 200 μ m or less.

One of the requirements to quantify the effects of contact resistance on a micro-TE cooler is to develop a reliable experimental method to determine contact

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resistivity on bulk TE materials. In the case of low-resistance ohmic contacts, the fraction of the voltage drop across the interface is small compared with the voltage drop across the bulk TE material. In addition, the distribution of the current density across the contact area and into the semiconductor is nonuniform. Correct extraction of contact resistivity is difficult, especially below $10^{-6} \ \Omega \ cm^2$. There has been a considerable amount of work done on the characterization of ohmic contacts to Si and GaAs, ³⁻¹⁰ but not much work has been reported on the measurement of metal contacts to bulk Bi₂Te₃-based TE materials.

To quantify the electrical contact resistance on bulk Bi_2Te_3 TE material, the authors have devised a device-like structure (DLS) utilizing numerous layers of TE material soldered together in a single reflow process and subsequently diced as shown in Fig. 1. The control consists of a single wafer with a thickness approximately the same as the total length of the TE material in the DLS stack. The resulting test samples are measured for device Z. By comparing the Z values of the stack and the control samples, the electrical contact resistance can be calculated from the drop in Z-values due to the added number of interfaces.

The advantages to this method are plentiful. Firstly, this testing technique allows measurements on bulk TE materials. Secondly, since the measurements are made on a DLS formed using fabrication steps similar to those used for a TE cooler, the resulting contact resistance should be representative of an actual TE cooler. Finally, the DLS can be cross-sectioned and inspected thoroughly to determine the actual thickness of each layer of the structure, thus minimizing errors due to uncertainties in structure geometry.

EXPERIMENTAL PROCEDURES

Process steps for fabrication of stacked devices using *n*- and *p*-type Bi_2Te_3 wafers are shown in Fig. 2a-d. Bi_2Te_3 wafers were lapped to 0.25 mm thickness. The composition of the *n*-type material is

approximately (Bi2Te3)0.9(Bi2Se3)0.1 and that of the *p*-type material is $(Sb_2Te_3)_{0.75-0.80}(Bi_2Te_3)_{0.25-0.20}$. After lapping, the wafers went through surface preparation and metal deposition. Au was deposited on the top on the metal contacts to prevent oxidation of the surface and also to make the surface wettable for soldering. After metal deposition, a wafer was placed on a specially designed fixture. Solder was applied on it manually with a ceramic strip, ensuring flatness and smoothness. Then, a second wafer was placed on the first and pressed down gently to force excess solder out. The process continued until all wafers were stacked on top of each other as shown in Fig. 2c. Ten wafers were stacked together and joined with tin-antimony-based solder. The clamped stack was reflowed in a BTU Paragon 70 reflow furnace. Several test runs were performed to ensure uniform solder reflow and repeatability. After the reflow process, the stacked-up device was diced into $3.8 \text{ mm} \times 3.8 \text{ mm}$ squares. Cu tabs were soldered on each end of the stacked device along with thermocouples and current lead wires. For control purposes, a single wafer approximately 2.5 mm tall was sliced from an adjacent portion of an ingot to achieve high uniformity of TE properties. The controls and the stacked devices were mounted on a Z-test stand for testing as shown in Fig. 1. Thermoelectric property measurements were carried out from 260 K to 340 K using an in-house built state-of-the-art measurement system at Marlow Industries.

CONTACT RESISTANCE MODEL

To calculate the contact resistivity of bulk Bi_2Te_3 wafers, the authors used an in-house built test fixture to measure the sample and control device Z values using the modified Harman technique.^{11,12} The system also provides the Seebeck coefficient, α , and electrical resistivity, ρ . This measurement system is well calibrated using production materials, and experimental error is within 2%.



Fig. 1. Schematic of sample mounted on a Z-test stand for (a) control sample and (b) stack sample. (c) Picture of sample mounted on an actual Z-test stand.





The control consisted of a single wafer approximately 2.5 mm tall as discussed in the "Experimental Procedures" section. The Z of the control is represented by Eq. 2.

$$Z_{\text{control}} = \frac{\alpha^2}{\left(\frac{\rho L}{A} + \frac{2\rho_c}{A}\right)\left(\frac{kA}{L}\right)},\tag{2}$$

where L is the overall height of the control sample, and A is the cross-sectional area.

The stacked sample was prepared with ten wafers approximately 0.25 mm thick as discussed in the "Experimental Procedures" section. The Z of the stack is represented by Eq. 3.

$$Z_{\text{stack}} = \frac{\alpha^2}{\left(\frac{\rho N t}{A} + \frac{2N\rho_c}{A}\right)\left(\frac{kA}{Nt}\right)},\tag{3}$$

where N is the number of stacked wafers, and t is the average thickness of the wafers in the stack.

To compare the Harman results for the control and the stacked sample, a new variable, Z_{ratio} , is defined by Eq. 4.

$$Z_{\rm ratio} = \frac{\overline{Z_{\rm control}}}{\overline{Z_{\rm stack}}},$$
 (4)

where $\overline{Z_{\text{control}}}$ and $\overline{Z_{\text{stack}}}$ are the averaged Z values from multiple samples tested on the Harman test fixture.

Substituting Eqs. 2 and 3 into 4, recognizing that $Nt \sim L$, and solving for ρ_c results in Eq. 5.

$$\rho_{\rm c} = \frac{\rho L}{2} \left[\frac{Z_{\rm ratio} - 1}{\frac{L}{t} - Z_{\rm ratio}} \right]. \tag{5}$$

As shown in Fig. 3a, average values of Z were extracted from the measured values of Z as a function of temperature for the stack and control samples. These values were used to calculate Z_{ratio} as a function of temperature. Similarly, the average



Fig. 3. Example plot showing how the contact resistivity was extracted from the *Z* measurements of the stack device and control: (a) plot of *Z* as a function of temperature for stack and control samples, and (b) plot of electrical resistivity, ρ , as a function of temperature for control samples.

value of ρ as a function of temperature was extracted as shown in Fig. 3b. Then, the contact resistivity, ρ_c , was calculated from Z_{ratio} and ρ as a function of temperature using Eq. 5. To decrease experimental errors, as standard practice we used the average of five stack samples and three control samples; therefore, we are averaging the contact resistance of 100 interfaces for each experiment. Due to the dominant effect of contact resistance to

Temperature (K)	<i>p</i> -Type/Process 2		<i>p</i> -Type/Process 1		<i>n</i> -Type/Process 2		<i>n</i> -Type/Process 1	
	$Z_{ m ratio}$	$ ho_{\rm c} \ (\mu \Omega \ {\rm cm}^2)$	$Z_{ m ratio}$	$ ho_{\rm c}~(\mu\Omega~{\rm cm}^2)$	$Z_{ m ratio}$	$ ho_{\rm c} \ (\mu \Omega \ {\rm cm}^2)$	$Z_{ m ratio}$	$ ho_{c} \ (\mu \Omega \ cm^2)$
260	1.095	1.02	1.255	2.89	1.078	0.94	1.225	2.31
280	1.092	1.14	1.246	3.22	1.078	1.04	1.225	2.53
300	1.092	1.30	1.239	3.59	1.077	1.12	1.222	2.74
320	1.094	1.50	1.235	3.99	1.074	1.16	1.218	2.93
340	1.098	1.77	1.233	4.43	1.068	1.17	1.213	3.10

Table I. Summary of contact resistivity data for measurements carried out on n- and p-type Bi₂Te₃ for processes 1 and 2

Table II. Uncertainty in ρ_c calculated from variation in Z_{stack} from multiple samples tested

Wafer Type	Etching/Metal Deposition	Z _{stack} Standard Deviation at 300 K (%)	$ ho_{c} ext{ at 300 K} \ (\mu \Omega ext{ cm}^{2})$	$\Delta ho_{\mathbf{c}}$ (%)
p-Bi ₂ Te ₃	Process 1	3.65	3.59	19.36
$p-Bi_2Te_3$	Process 2	1.61	1.30	19.62
<i>n</i> -Bi ₂ Te ₃	Process 1	1.96	2.74	11.13
$n-\operatorname{Bi}_2\operatorname{Te}_3$	Process 2	1.23	1.12	17.59

the overall drop in Z stack, the thermal effects of the solder layers have not been incorporated in our calculations.

RESULTS AND DISCUSSION

Contact resistance measurements for metal contacts to n- and p-type Bi₂Te₃ using two different surface preparation processes were carried out, and the results are presented in Table I. The contact metal/diffusion barrier was deposited using Marlow proprietary processes: Process 1 is a standard process, and process 2 is a newly developed one using different surface preparation and cleaning. The contact resistance model explained in detail above was used to extract the specific contact resistivity from the Z ratio of the stacked device and its control. As shown in Table I, the contact resistivity values using process 1 were $3.6 \times 10^{-6} \ \Omega \ cm^2$ and $2.7 \times 10^{-6} \ \Omega \ \mathrm{cm}^2$ for p- and n-type Bi₂Te₃, respectively. For process 1, the accuracy of the measured contact resistivity values is consistent with models and measurements of the performance of actual TE coolers with leg length of 0.45 mm. Initial results for process 2 show a beneficial drop in the contact resistivity at 300 K to $1.1\times10^{-6}\,\Omega\,\text{cm}^2$ and $1.3 \times 10^{-6} \,\Omega \,{
m cm}^2$ for *n*- and *p*-type materials, respectively. The uncertainty in the contact resistivity measurements was calculated from the variation in the device Z values of multiple measured devices, as presented in Table II and plotted in Fig. 4. The maximum uncertainty was measured for *p*-type devices using process 1, being less than 20%,



Fig. 4. Uncertainty in contact resistivity values for $\mathit{n}\text{-}$ and $\mathit{p}\text{-}\text{type}$ Bi_2Te_3 at 300 K.

which is quite good for measurements in the $10^{-6} \Omega \text{ cm}^2$ range. As the contact resistivity decreases, the calculated ρ_c value becomes more sensitive to device Z variation from sample to sample. Therefore, for measurements in the $5 \times 10^{-7} \Omega \text{ cm}^2$ range, more devices need to be tested to reduce the standard deviation of the measured value of Z. One of the many advantages of this method is that values of contact resistivity can be extracted for a wide

range of temperatures, and Table I presents a lowering of the contact resistivity as the temperature is decreased. The variation with temperature of the contact resistivities, roughly mirroring the temperature dependence of the bulk resistivities, is consistent with constriction effects.¹³

CONCLUSIONS

We have developed a method that can precisely measure the contact resistance on bulk TE materials via processing stacks of bulk, metal-coated TE wafers using TE industry-standard processes. This technique incorporates realistic TE device manufacturing techniques and results in an almost DLS. therefore producing a realistic value for the electrical contact resistance in a bulk TE device. The contact resistivity using process 1 was measured to be $3.6\times 10^{-6}\,\Omega\ \text{cm}^2$ and $2.7\times 10^{-6}\,\Omega\ \text{cm}^2$ for *p*- and *n*-type Bi_2Te_3 , respectively, and the accuracy of these values is supported by the performance of TE coolers with leg length of 0.45 mm. For a new etching/metal deposition process, we measured a drop in the contact resistivity at 300 K to $1.1 \times 10^{-6} \ \Omega \ cm^2$ and $1.3 \times 10^{-6} \ \Omega \ cm^2$ for *n*- and *p*-type materials, respectively. The uncertainty in the contact resistivity values for each process/ material combination was 10% to 20%, which is considered good for measurements in the $10^{-6} \ \Omega \ cm^2$ range. Work is in progress to apply this technique to other material systems.

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REFERENCES

- 1. H.J. Goldsmid, *Electronic Refrigeration* (London: Pion, 1986), p. 9.
- A.S. Arnold, J.S. Wilson, and M.G. Boshier, *Rev. Sci. Instrum.* 69, 1236 (1998).
- 3. S.L. Zhang, Microelectron. Eng. 70, 174 (2003).
- V. Narayanan, Z. Liu, Y.M.N. Shen, M. Kim, and E.C. Kan, IEDM Tech. Digest 87 (2000).
- S.P. Zimin, V.Š. Kuznetsov, and A.V. Prokaznikov, *Appl. Surf. Sci.* 91, 355 (1995).
- K. Yamada, K. Tomita, and T. Ohmi, *Appl. Phys. Lett.* 64, 3449 (1994).
- Z.Z. Chen, Z.X. Qin, Y.Z. Tong, X.D. Hu, T.J. Yu, Z.J. Yang, X.M. Ding, Z.H. Li, and G.Y. Zhang, *Mater. Sci. Eng. B* 100, 199 (2003).
- A. Katz, S. Nakahara, W. Savin, and B.E. Weir, J. Appl. Phys. 68, 4133 (1990).
- M.O. Aboelfotoh, C.L. Lin, and J.M. Woodall, Appl. Phys. Lett. 65, 3245 (1994).
- R.P. Gupta, K. Xiong, J.B. White, Kyeongjae. Cho, H.N. Alshareef, and B.E. Gnade, J. Electrochem. Soc. 157, H666 (2010).
- G.S. Nolas, J. Sharp, and H.J. Goldsmid, *Thermo-electrics:* Basic Principles and New Materials Developments (Berlin: Springer, 2001), p. 99.
- R.J. Buist, New Material for Testing Thermoelectric Materials and Devices. http://www.tetech.com/publications/pubs/ ICT92RJB.pdf (accessed 10 July 2011).
- W. Manners and B. Gholami, *IEE Proc.-Sci. Meas. Technol.* 152, 161 (2005).