Where There Is Heat, There Is a Way

Thermal to Electric Power Conversion Using Thermoelectric Microconverters

by M. A. Ryan and J.-P. Fleurial

Spacecraft for missions to explore the outer planets of our solar system, that is, planets beyond the orbit of Mars, require a source of electric power which is not dependent on external sources such as solar energy. These spacecraft typically rely on a radioisotope system to provide heat which is converted directly to electric power. Large missions now underway, such as Galileo (launched 1989 to study the Jupiter system) and Cassini (launched 1997 to study the Saturn system) use radioisotope thermoelectric generators (RTG) to provide power. These RTGs use SiGe thermoelectric elements to convert thermal to electric power, with a hot side temperature ~ 1275 K and an efficiency of ~6%. The Galileo spacecraft has an RTG system which provides ~500 W of electric power, and the Cassini mission's RTGs provide ~650 W.

Advances in electronics and electronic devices in the last several years have made it possible to miniaturize spacecraft and their instruments significantly. Miniaturization includes plans to incorporate microdevices such as microsensors and microelectronic controls in spacecraft, and to develop miniature autonomous vehicles carrying microinstruments. Miniaturization brings with it significantly reduced power requirements and a need for distributed power architectures; but it also requires more attention to thermal control. In response to miniaturization, development of energy conversion systems has focused on developing miniaturized power conversion systems, increasing conversion efficiency, and approaches to using power conversion systems in thermal control of instruments, that is, converting heat which would otherwise be rejected into usable electric power. A promising approach to meeting these power conversion requirements is development of micro thermoelectric converters which can operate at moderate (200-500 K) temperatures, often with small temperature differentials.

Fundamentals

Thermoelectric power converters are solid-state Carnot devices based on the Seebeck effect. If a temperature gradient is applied across a conducting element, the charge carrier distribution, which is initially uniform, is disturbed as free carriers at the high temperature end diffuse to the low temperature end. This separation of carriers results in an open circuit voltage, the Seebeck voltage. When the junctions of a circuit formed from two dissimilar conductors (*i.e.* n- and p- type semiconductors) are maintained at temperatures T_{hot} and T_{cold}, the open circuit voltage, V, developed is

$$V = S_{pn}\,(T_{hot} - T_{cold}) \qquad (1)$$

where S_{pn} is the Seebeck coefficient ($\mu V.K^{-1}$) of the p- and n-type materials. A typical Seebeck coefficient for the materials to be discussed here is + (for p-) or – (for n-) 150-200 $\mu V.K^{-1}$.

There are many semiconductor candidates that are used as the elements, or legs, in a thermoelectric device. Selection of a material for a particular application depends primarily on the temperature range and the magnitude of the (dimensionless) thermoelectric figure of merit, ZT. ZT represents the relative magnitudes of electrical and thermal cross-effect transport in materials; a larger ZT signifies more efficient conversion of thermal to electric power. At very large values of ZT, the performance of thermoelectric generators would approach the Carnot cycle efficiency. In state-of-the-art materials, maximum ZT values are close to 1, although there is no theoretical limit on ZT. For the temperature range of interest in microdevice and micro spacecraft applications, 200-500 K, alloys based on Bi_2Te_3, $Bi_{2-x}Sb_xTe_{3-y}Se_y$ alloys, are the best materials.

Generally, a thermoelectric module consists of several n- and p-type legs connected in series electrically and in parallel thermally. The open circuit voltage of the series connected module is the sum of the Seebeck voltage produced at each couple. With thousands of couples, open circuit voltages of several volts can be attained, even with a modest temperature gradient of 10 K.

Solid-state thermoelectric power converters are scalable, as shown in equation 2:

$$P_{el}^{max} = \frac{A}{l}\left[\frac{1}{4}\,\frac{S_{pn}^2\,(T_{hot} - T_{cold})^2}{\rho_{pn}}\right] \qquad (2)$$

where P^{max}_{el} is the maximum electrical output, ρ_{pn} is the electrical resistivity, A is the cross-sectional area, and l is the length of a p-n thermoelectric leg couple.

The maximum electrical output, P^{max}_{el} is directly proportional to A/l, the leg geometric aspect ratio, making power density inversely proportional to leg length. The electrical output voltage of a thermoelectric power converter is directly proportional to the number of elements connected in series and to the temperature difference between the hot and cold sides of the device.

Device Optimization

Because maximum power in a thermoelectric converter is proportional to A/l, the specific power (W/cm^3) of a converter can be increased significantly if the thermoelectric elements can be reduced to several tens of µm height while maintaining the aspect ratio of legs in a larger device. Figure 1 shows the specific power of a thermoelectric power converter as a function of leg

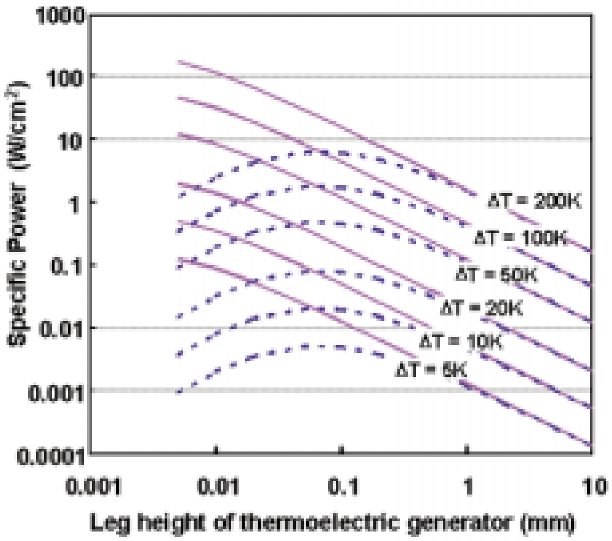


FIG. 1. Calculated specific power of a thermoelectric power converter as a function of leg height, ZT = 0.9, T_{cold} = 300K and contact resistance $R_c = 1x10^{-6}$ W cm^2. The dotted line (.....) shows data for a low thermal conductivity substrate (1 mm alumina), and the solid line (-----) for a high thermal conductivity substrate (0.25 mm diamond).

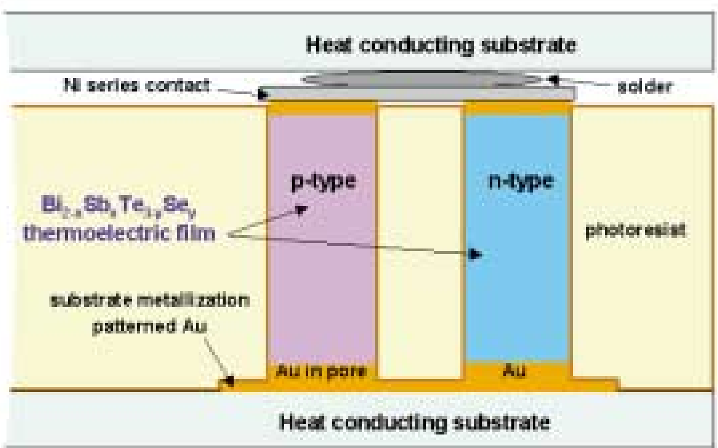


FIG. 2. A thermoelectric microconverter is built up from a metallized substrate by electrodeposition of contact and thermoelectric materials in 10 µm x 50 µm pores made by photolithography in thick photoresist.

height. Highest specific power can be achieved with leg heights of several tens of µm, where thousands of couples can be fit into a small volume. This scaling law also applies to the heat source, which makes devices thinner than 10 µm difficult to operate, as very high heat flux densities (1 kW/cm^2 or higher) would be required. Another interesting aspect of thermoelectric device miniaturization is the possibility of fabricating microgenerators where several thousand couples are connected in series electrically, so that an output voltage approaching 1 V per degree can be achieved.

Figure 1 shows that specific power is maximized when the leg height is ~0.05 mm, taking heat transfer limitations of low thermal conductivity substrates into account. Machining bulk materials to such a sizes is a difficult and expensive task. Miniature thermoelectric power converters have been made using bulk material machined to dimensions of a few hundreds of µm.[1,2] Machined thermoelectric legs can be made with heights of ~200 µm, but attaining an aspect ratio (A/*l*) which allows a high maximum power (see Eq. 2), is difficult using machined materials. Actual devices based on bulk fabrication technology are typically limited to a few hundred couples due to thermal and mechanical stress issues, thus resulting in high current intensity, low voltage characteristics.

Approaches to fabrication which do not rely on machining, but use a more direct method of deposition make fabrication of micro thermoelectric power converters possible. Electrochemical deposition is a relatively inexpensive approach to deposition which allows variation in substrate design and deposit thickness and is versatile enough to allow the composition of deposited materials to be varied. The values of x and y in $Bi_{2-x}Sb_xTe_{3-y}Se_y$ alloys determine whether a material is n- or p-type and has an effect on the magnitude of the Seebeck coefficient. There is a large body of literature on electrochemical deposition of compound semiconductors containing selenium and tellurium, particularly II-VI compounds.[3-5] At the Jet Propulsion Laboratory (JPL), we have taken advantage of this literature as well as work in depositing compound semiconductors for thermoelectric applications[6-8] to synthesize Bi_2Te_3 and related materials for thermoelectric elements.[9-11] By using a combination of electrochemical deposition and integrated circuit processing techniques, it is possible to make micro power converters with legs 50 µm tall and 10 µm in diameter. A sketch of one couple in a thermoelectric micro converter is shown in Fig. 2. A power converter with this size of thermoelectric element will have a specific power as high as 0.5 W/cm^2 for a 10 K temperature gradient. With 10,000 couples connected in series, the open circuit voltage will be 15.0 V for a 10 K gradient.

$Bi_{2-x}Sb_xTe_{3-y}Se_y$ compounds were deposited at room temperature or at slightly elevated temperature (~40°C) at constant potential in a standard three electrode configuration. The working electrode was a high thermal conductivity substrate (*e.g.* diamond, Si/SiO_2) which had been metallized with Au in a pattern to allow series connection of thermoelectric couples. The cell had a Pt counter electrode and a saturated calomel electrode (SCE) reference. Regions for deposition on the substrate were defined using a thick photoresist mask patterned with wells several tens of µm deep and a few µm in diameter. Thermoelectric legs were deposited in the wells from solutions containing dissolved elemental metals with a concentration on the order of 10^{-3} M in aqueous 1 M HNO_3 (pH = 0). Solutions containing Sb or Se use chelating agents such as citrate, tartrate or ethylene diamine tetraacetate (EDTA) to allow higher concentrations of the less soluble elements at pH 0.

Successive processing steps were used to build up a thermoelectric microconverter. After depositing p-type legs in wells formed in photoresist, the substrate was re-patterned with wells for n-type legs, followed by re-patterning to deposit electrical interconnects from Au and Ni. Use of IC processing techniques makes it possible to design a microconverter with many thousands of couples connected in series. Figure 3 shows a view of Bi_2Te_3 legs that have been grown at a density of 90,000 legs/cm^2. Figure 4 shows a microdevice with 122 legs connected in series. Resistance measurements of the string show that it is possible to create structures with contact resistivity as low as 10^{-8} Ω cm^2.

The performance of a thermoelectric microconverter made in this manner is projected to be similar to the performance of a macro-scale converter, provided a suitably concentrated heat source can be used. The materials properties are similar to those of bulk materials, and thermal-to-electric conversion efficiency is expected to be in the 5-6% range, as it is with macro scale systems.

Miniaturizing a thermoelectric power converter makes it possible to provide milliwatts of power at several volts for MEMS devices and other microinstruments. Microconverters can also be used to convert rejected heat to electric power, providing electric power and passive cooling simultaneously.

Recent Results

Recent studies have shown that it may be possible to improve conversion efficiency by manipulating electrical and thermal transport on the nanoscale.[12,13] Calculations have shown that low dimensional structures such as superlattices (2D) and nanowires (1D) will show increased ZT owing to decreased lattice thermal conductivity, improved carrier mobility, and/or creating a high density of states just above the Fermi level. Most of the studies have focused on electron transport in plane or along the

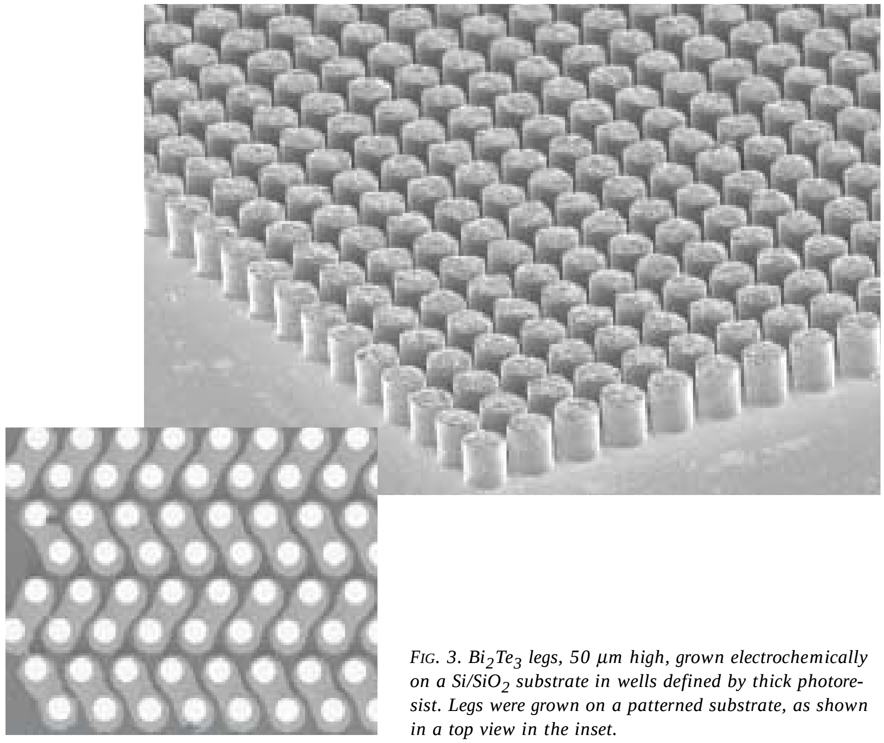
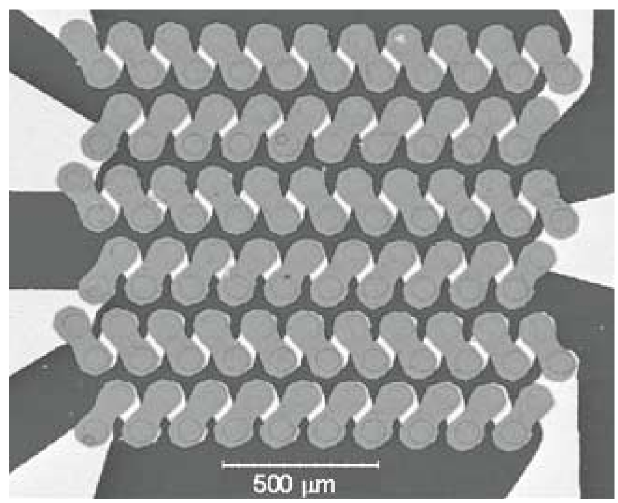


FIG. 3. Bi_2Te_3 legs, 50 µm high, grown electrochemically on a Si/SiO_2 substrate in wells defined by thick photoresist. Legs were grown on a patterned substrate, as shown in a top view in the inset.

(a)



(b)

FIG. 4. (a) A microdevice with 122 legs (61 couples) connected in series on Au metallization on a Si/SiO_2 substrate; (b) side view of microdevice, showing Ni contacts between thermoelectric legs in a couple.

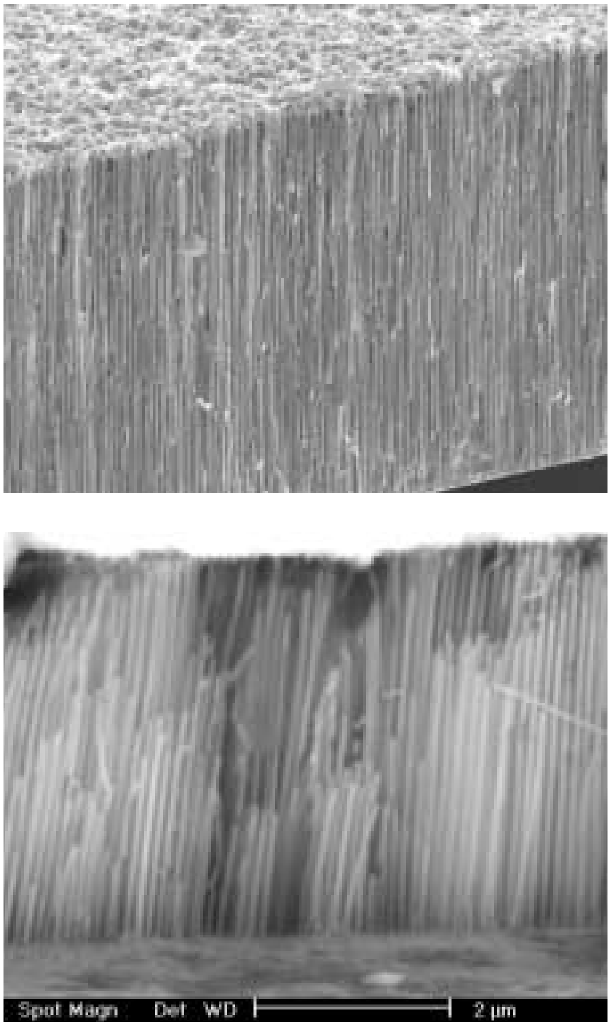


FIG. 5. (a) Bi_2Te_3 nanowires grown in 200 nm pores, 50 µm tall; (b) Bi_2Te_3 nanowires grown in 40 nm pores, 5 µm tall.

nanowire axis (quantum well and quantum wire), cross-plane electron transport (superlattices), and phonon engineering (size effects in superlattices and nanowires). In the last few years, experiment has shown a decrease in lattice thermal conductivity in superlattices,[14] and carrier mobility effects consistent with theoretical band structure models in Bi nanowires.[15] ZT is predicted to increase by a factor of 2.5–3 in nanoscale devices. One of the most successful approaches so far has been to use a Bi_2Te_3/Sb_2Te_3 superlattice with phonon reflective interfaces and very small band edge offset for electron transmission (but no quantum effects) to increase ZT up to 2.4 near room temperature.[16] Even stronger transport effects are predicted in nanowires due to their increased surface/interface area.[17]

Nanowire-based devices are attractive from a fabrication standpoint because the wires can be left in the template in which they are grown to provide structural support. At JPL, we have focused on synthesizing nanowires of n- and p- type $Bi_{2-x}Sb_xTe_3$ in alumina templates. Wires as small as 40 nm diameter have been grown, as shown in Fig. 5, but 40 nm is still too large to show a quantum effect. Work continues to fabricate alumina templates with 10-20 nm diameter pores, 30-50 µm thick. The very large aspect ratio provided by 10 nm diameter wires 50 µm long will result in a large ΔT, even with a low heat flux. Low-dimensionality is expected to result in an increased Seebeck coefficient and reduced thermal conductivity, and thus a significant increase in ZT and conversion efficiency.

Acknowledgment

The research reported in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration. Part of this work was supported by the U.S. Office of Naval Research and the U.S. Defense Advanced Research Projects Agency. ■

References

1. V. A. Semeniouk, T. V. Pilipenko, G. C. Albright, L. A. Ioffe, and W. H. Rolls, *Proceedings of the 13th International Conference on Thermoelectrics,* AIP Conf. Proc. 316, 150 (1995).
2. V. A. Semeniouk and J.-P. Fleurial, *Proceedings of the 16th International Conference on Thermoelectrics,* IEEE Catalog No. 97TH8291, 683 (1997).
3. R. K. Pandey, S. N. Sahu, and S. Chandra, *Handbook of Semiconductor Deposition,* M. Dekker, New York (1996).
4. M. Paunovic and M. Schlesinger, *Fundamentals of Electrochemical Deposition*, Wiley Europe, West Sussex, England (1998).
5. M. Schlesinger and M. Paunovic, *Modern Electroplating, 4th Edition,* Wiley Europe, West Sussex, England (2000).
6. M. Muraki and D. M. Rowe, *Proceedings of the Xth International Conference on Thermoelectrics,* Cardiff, Wales, UK, 174 (1991).
7. M. Takahashi, Y. Katou, K. Nagata, and S. Furuta, *Thin Solid Films,* **240,** 70 (1994).
8. P. Magri, C. Boulanger, and J. M. Lecuire, *Proceeding of the XIIIth International Conference on Thermoelectrics*, B. Mathipraksam, ed., Part I, 1994.
9. J.-P. Fleurial, *et al.*, *Thermoelectric Materials 1998*, T. M. Tritt, M. G. Kanatzidis, H. B. Lyon, and G. D. Mahan, eds., MRS Volume 545 (1998).
10. J.-P. Fleurial, J. A. Herman, G. J. Snyder, M. A. Ryan, A. Borshchevsky, and C.-K. Huang, *Thermoelectric Materials 2000,* T. M. Tritt, M. G. Kanatzidis, G. Nolas, and G. D. Mahan, MRS 2000 Spring Meeting Symp. Proc. (2000).
11. J.-P. Fleurial, G. J. Snyder, J. A. Herman, M. Smart, P. Shakkottai, P. H. Giauque, and M. A. Nicolet, *Proceedings of the 34th Intersociety Energy Conversion Engineering Conference*, 99-2569 (1999).
12. L. D. Hicks, T. C. Harman, and M. S. Dresselhaus, *Appl. Phys. Lett.*, **63**, 3230 (1993).
13. X. Sun, Z. Zhang, and M. S. Dresselhaus, *Appl. Phys. Lett.*, **74**, 4005 (1999).
14. R. Venkatasubramanian, *Phys. Rev. B*, **61**, 3091 (2000).
15. J. Heremans, C. M. Thrush, Y.-M. Lin, S. Cronin, Z. Zhang, M. S. Dresselhaus, and J. F. Mansfield, *Phys. Rev. B,* **61**, 2921 (2000).
16. R. Venkatasubramanian, E. Silvola, and T. Colpitts, *Nature*, **413**, 597 (2001).
17. S. G. Volz and G. Chen, *App. Phys. Lett.*, **75**, 2056 (1999).

About the Authors

M. A. RYAN *is a Principal Member of the Technical Staff at the Jet Propulsion Laboratory, California Institute of Technology, and works in thermal to electric energy conversion and in chemical sensing.*

J.-P. FLEURIAL *is Technical Group Supervisor for the Materials and Device Technologies Group at the Jet Propulsion Laboratory, California Institute of Technology and works in development of thermoelectric devices.*