RECENT ADVANCES IN SILICON–GERMANIUM ALLOY TECHNOLOGY AND AN ASSESSMENT OF THE PROBLEMS OF BUILDING THE MODULES FOR A RADIOISOTOPE THERMO-ELECTRIC GENERATOR*

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Summary

This paper reviews the state of the art of silicon–germanium technology and assesses the problems of building thermoelectric modules in Europe, based upon silicon–germanium alloys, for use in a multihundred watt radioisotope thermoelectric generator. The generator developed in the United States for the International Solar Polar mission has been used as a reference system. The essential features of an alternative system, which employs thermocouples fabricated from improved silicon–germanium alloys based upon a design by the Fairchild Space and Electronics Company, is also described.

It is concluded that although the fabrication of reliable electrical contacts will present a major problem, the technology is available in Europe to build thermoelectric modules similar to those developed for the International Solar Polar mission.

1. Introduction

The use of radioisotope thermoelectric generators (RTGs) to provide electrical power in inhospitable and inaccessible environments has been described in the literature [1, 2], and the factors which determine their conversion efficiency exhaustively dealt with [3 - 9]. An RTG consists, in essence, of a number of thermocouples connected electrically in series and thermally in parallel to form a module. Isotopic energy is employed as a heat-source at the module's 'hot end' and electrical energy is extracted at its 'cold end'. Once the operating temperature conditions of a generator have been decided, the conversion efficiency of its module(s) is determined solely by the so-called figure of merit Z of the thermocouple material. Where $Z = \alpha^2\sigma/\lambda$; α is the Seebeck coefficient and σ the electrical conductivity. The

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thermal conductivity, λ, is the sum of a contribution λ_L due to phonons and a contribution λ_e due to charge carriers. All three parameters in the figure of merit vary with carrier concentration and in silicon–germanium alloys Z is optimized at around 10^{26} m^{-3}. At this high carrier concentration λ_L still accounts for more than 75% of λ.

Silicon–germanium alloys have emerged as the most successful thermoelectric materials for use in 'deep space'. They were developed at RCA for use in the U.S. multi-hundred watt generators (MHW) which provide 155 W(e) at an efficiency of 6.5 percent. and a specific power of 1.8 W(e) per pound. The first application of this generator was early in 1976 in the American Air Force LES 8/9 communication satellite, followed in 1977 by the Voyager spacecraft. During the late 1970s silicon–germanium technology encountered strong competition from a new class of thermoelectric materials, the selenides. Developed at the 3M Company, the selenides held out the promise of substantial improvements in material performance. Initial results were encouraging but serious difficulties were encountered in maintaining material stability, and enventually silicon–germanium thermoelectrics were chosen by the American Department of Energy for use in conjunction with the newly developed 'General Purpose Heat Source' (GPHS) to provide on-board power (294 W(e) at an efficiency of 6.7 percent. and a specific power of 2.4 W(e) per pound) for the Galileo and International Solar Polar Missions (ISPM). These missions are planned to be launched from space shuttles. Performance tests on the silicon–germanium thermoelectric converter using an electrical heat source indicate that the mission's power requirements will be met [10].

The main driving force behind developments in thermoelectric material technology and, in particular, that of silicon–germanium is the U.S. Department of Energy's 'Thermoelectric Development Programme for Space Power' [11]. The RTG system's goals for the late 1980s are a specific power of 3.5 W(e) per pound and a system efficiency of >9 percent. The realization of this performance is critically dependent upon improvement in material conversion efficiency and, at present, there are at least two major and one supporting ongoing thermoelectric material development projects in the U.S. which involve silicon–germanium technology. These are located at Syncal Corporation, Sunnyvale, California; Ames Laboratories, Iowa State University; and the General Electric Company, Schenectady, NY. Efforts at Syncal Corporation are directed at investigating improved silicon–germanium alloys, based on the small additions of gallium phosphide (SiGe–GaP), and in fabricating a number of thermoelectric modules from these materials. Ames Laboratories are concerned with evaluating SiGe–GaP alloy and in particular in investigating its stability. The project at General Electric is aimed at the identification and development of promising new high temperature thermoelectric materials, including those based upon the Si–Ge alloy system. In the U.K. a modest research programme has been underway for some time at UWIST, Cardiff, to improve the figure of merit of silicon–germanium alloys through the use of very small grain size material [12].

The European Space Agency (ESA) is actively engaged in space activities, and is responsible for the development of the spacecraft to be employed on the International Solar Polar mission. Craft such as this, which fly remote from the sun, require an alternative to solar cells for their primary electrical power source. There is, therefore, a potential requirement for isotope (or reactor) fuelled generators, and the use of thermoelectric modules is one of the conversion systems being considered for future use, since it has already been used in the past. This paper reviews the current state of Si–Ge alloy technology and assesses the problems in building in Europe the modules for a multi-hundred watt radioisotope thermoelectric generator.

2. Silicon–germanium alloys

Recent developments in silicon–germanium alloy technology make it necessary to distinguish between established "unmodified" silicon–germanium alloys and "modified" silicon–germanium alloys. In the latter the thermoelectric properties of the material have been altered through the use of small grain size or the introduction of small amounts of Groups III and V elements. The preparation of unmodified silicon–germanium alloys by both single crystal [13, 14] and hot pressing methods [15 - 19] is well documented, as is the behaviour of their thermoelectric properties under operating conditions and over long periods of time. Information is also available on the preparation of small grain size material [20] and of SiGe–GaP [21]. There is a limited amount of information, however, on the thermoelectric properties of these modified materials and on their sublimation behaviour. The temporal behaviour of thermoelectric materials under device operating temperature conditions is of particular importance as it enables predictions to be made of the end-of-life performance of generators deployed in deep space missions. Two of the principal factors which limit the long-term performance of unmodified silicon–germanium alloy thermocouples are dopant precipitation and material sublimation.

The figure of merit of silicon–germanium alloys optimises at carrier concentrations which exceed the solid solubility of phosphorus and boron, the elements normally employed as n- and p-type dopants [22]. In order to approach the optimum Z value it is found necessary in practice to dope the alloys to concentrations at the solid solubility limit of the dopant in the alloy. The solid solubilities of phosphorus and boron possess retrograde characteristics that are strongly temperature dependent [23]. It is found that over the temperature range of operation of thermoelectric generators based upon Si–Ge technology (600 - 1300 K) the amount of dopant in solution at a particular temperature can exceed the solubility limit at that temperature and consequently precipitate out of solution as a function of time [24]. The Seebeck coefficient and electrical resistivity are strong functions of carrier concentration and, hence, of the amount of dopant in solid solution. A comprehensive investigation of precipitation effects in heavily doped silicon–germanium alloys has indicated that substantial changes in α and σ accompany long term heat treatment [25 - 28]. The rate of precipitation and, hence, of change in properties is greatest in n-type material over the temperature range 600 - 900 K, while in p-type alloy its maximum is at the higher temperature range 1000 - 1200 K. A good fit has been obtained between long term experimental data and a precipitation model due to Lifshitz and Slyozov [29], and the effect of precipitation on the electrical conductivity (σ) and Seebeck coefficient (α) has been predicted up to a 12 year period. Significant changes in σ and α also result from relatively short periods of heat treatment [30 - 32] and it has been demonstrated that the precipitation effects are reversible and that the materials can be rejuvinated by suitable annealing. The Lifshitz–Slyozov model is unable to explain short term precipitation effects in p-type alloys although a satisfactory explanation has been obtained using soliton theory [33].

Changes in the thermal conductivity accompany heat treatment at high temperatures. Researchers at Syncal Laboratory report that the changes are significant at 900 K in both n-type and p-type alloy, with an increase in temperature leading to a greater change. They conclude that the changes in thermal conductivity reflect changes in the lattice of the materials rather than being a consequence of dopant behaviour, and that the observed decrease in thermal conductivity with time is consistent with enhanced alloying [26]. Workers at UWIST, Cardiff, however, report that the precipitation of dopant phosphorus has a profound effect on the thermal properties and conclude that when the concentrations of dopant in solid solution in the alloys is very high, not only is the electronic contribution to thermal conduction appreciable, but, more important, the phonon–electron scattering process is responsible for the very high lattice thermal resistivity [34].

In the multi-hundred watt (GPHS) generator 576 thermocouples are arranged in 16 circumferential rows of 36 couples. The couples are made in unicouple assemblies as shown in Fig. 1. The legs are of silicon–germanium alloy and are fabricated from 78 at.% silicon alloy with a thin section of 63.5 at.% alloy segmented at the cold end. The n-type leg is doped with phosphorus and the p-type leg with boron. The alloys are initially vacuum cast, then crushed, vacuum hot pressed and sliced. The n- and p-type legs are equal in size. At the hot end the unicouple legs are bonded to a Si–Mo (85 at.% silicon) "hot-shoe". Electrical insulation between the unicouple legs is provided by astroquartz (SiO_2) fiber, while a multifoil insulator consisting of alternate layers of molybdenum foil and astroquartz provides thermal insulation [35].

Silicon–germanium alloys are operated with a hot junction temperature of up to 1300 K. At this temperature significant material sublimation and reaction takes place. Loss of material results in erosion of the hot shoe and a decrease in the cross-sectional areas of the thermocouple legs, both of which tend to increase the thermal resistance of the couple which, in turn, results in an increase in temperature which further aggravates the situation. Sublimate of the evaporate material deposits on the thermal insulation and

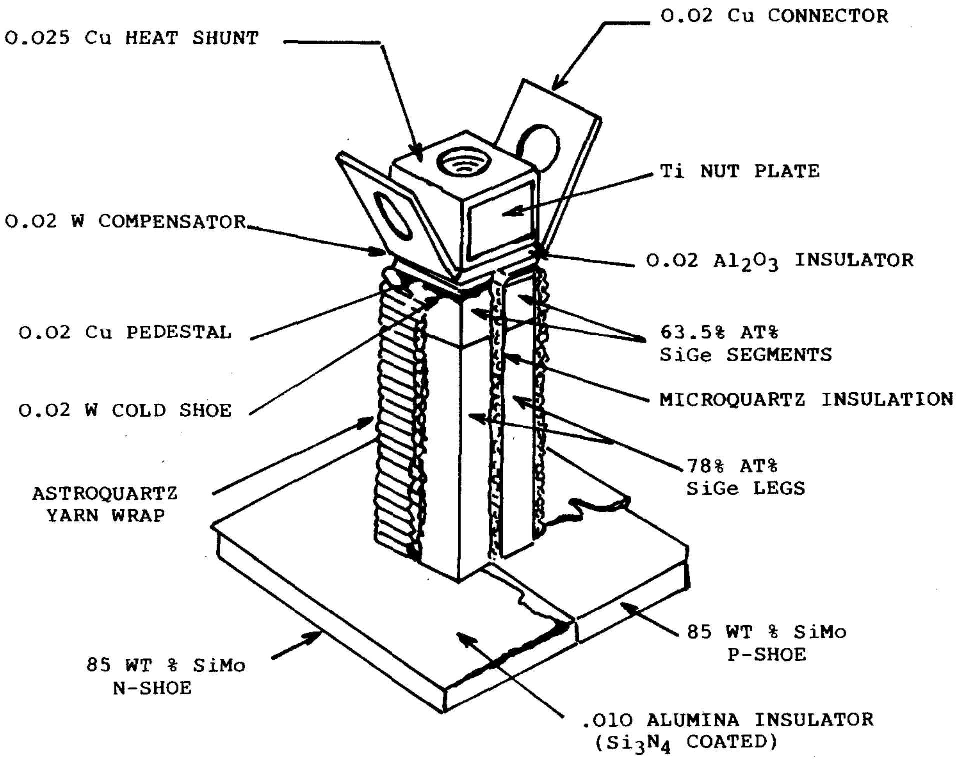

Fig. 1. Multi-hundred watt silicon–germanium unicouple. (Courtesy U.S. Department of Energy.)

reduces its effectiveness; in addition the sublimate reacts with the fibrous insulation and ultimately leads to a complete loss of power output.

A variety of methods has been employed in an attempt to reduce material sublimation: coating the hot shoe with carbon; the use of graphite hot shoes; SiO_2 leg barriers coating the thermocouple legs with Al_2O_3; use of SiO_2 hot shoe spacers, and coating the hot shoe and legs with Si_3N_4 [35]. Sublimation from the free surface is minimized by coating with Si_3N_4, but, even so, the longevity of the coating is limited by its reaction with the CO which originates from a number of sources within the generator [36].

3. Improved silicon–germanium alloys

The relatively low figure of merit of silicon–germanium alloy is attributed to its high thermal conductivity. In semiconductors, even when heavily doped, the lattice component of the thermal conductivity predominates and attempts have been made to reduce the lattice thermal conductivity through the introduction of further disorder in the lattice. A variety of methods has been tried, such as: addition of impurity atoms, creation of vacancies at lattice sites, introduction of defects and increasing the weight of the lattice components. Usually these methods result in an increase in the electrical resistivity. Thus any reduction in thermal conductivity must overcompensate for the increase in electrical resistivity if the figure of merit of a material is to be improved. Two methods have been developed which preferentially reduce the lattice thermal conductivity. (i) The addition of small amounts of Groups III and V elements; (ii) the use of very small grain size material.

Significant reductions in the thermal conductivity of silicon–germanium alloys accompany the addition of small amounts of Groups III and V elements. The symbolic notation for p-type material, for example, being $|p\text{-}Si_xGe_{1-x}|$ (III–V). Gallium phosphide is isostructural and isoelectronic with silicon–germanium alloys and it has a lower value of vapour pressure that other Group III–V compounds at high temperatures. Consequently, attention to date has concentrated on this material. The reduction in lattice thermal conductivity is greater when the GaP content is varied between four and eight molecular percent. [37]. The thermal conductivity of n- and p-type 80 at.% Si–20 at.% Ge alloy to which an unspecified amount of gallium phosphide has been added is displayed in Figs. 2 and 3 as a function of temperature. Evidently, reductions in thermal conductivity of up to 50% compared with unmodified alloy have been obtained. Generally, the electrical resistivity of SiGe–GaP is higher than unmodified alloy when in the as-prepared state. High temperature annealing, however, significantly reduces the electrical resistivity, which after long annealing times (~5000 h) attains values comparable with ummodified alloys. Peculiar effects have, however, been noted during the annealing of boron-doped SiGe–GaP alloy. Upon prepara-

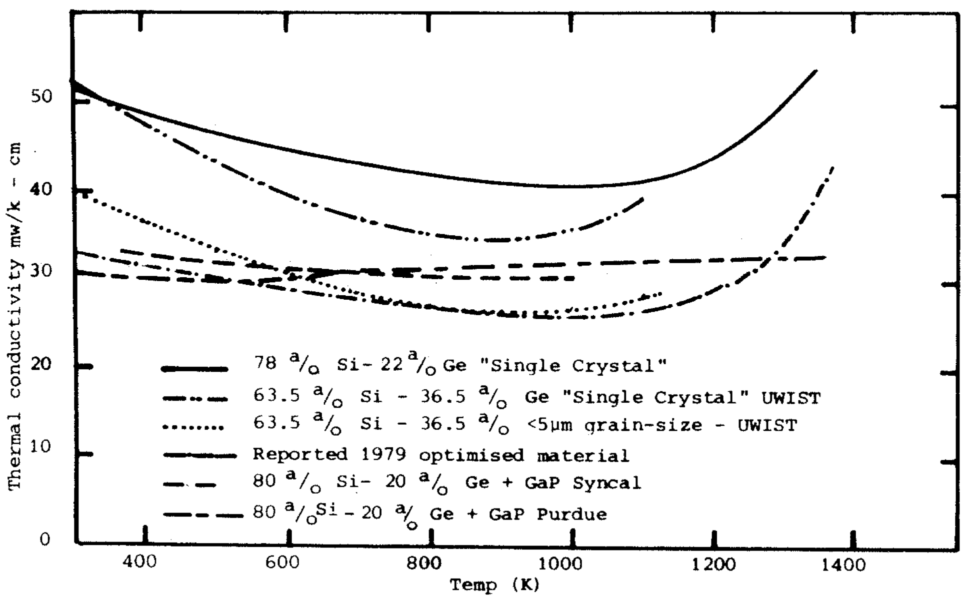

Fig. 2. Thermal conductivity of n-type Si–Ge materials as a function of temperature.

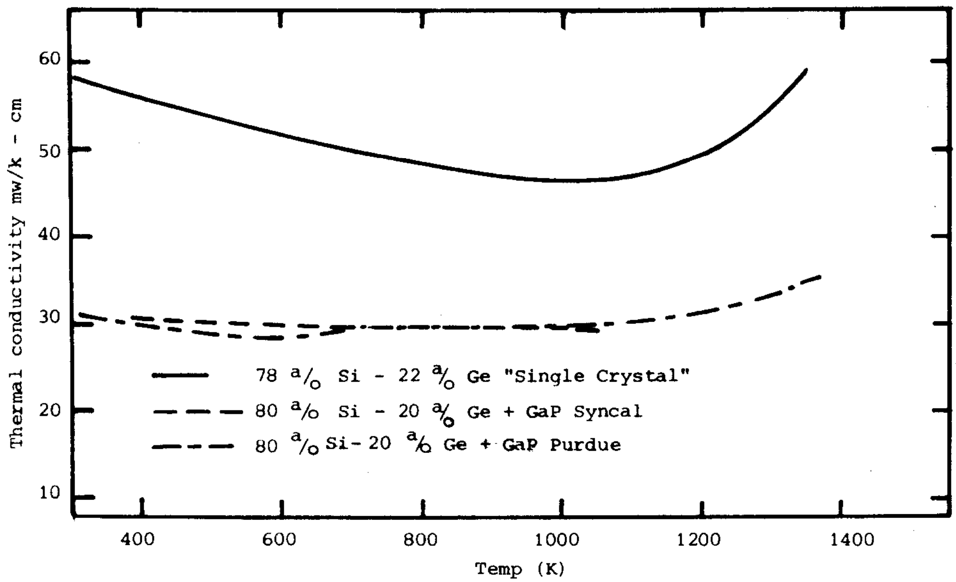

Fig. 3. Thermal conductivity of p-type Si–Ge materials as a function of temperature.

tion at ~1400 K the modified alloy exhibits n-type Seebeck polarity which vanishes, typically, after annealing for about 400 h. Further annealing slowly restores its expected p-type character. The anomalous behaviour is attributed to cross-doping effects. A comprehensive examination of the properties of SiGe–GaP material, as well as theoretical studies of phenomena such as cross-doping, is underway at Syncal Laboratory [38].

Sublimation rates of SiGe–GaP material when coated with SiO_2, have been investigated at the Jet Propulsion Laboratories [39]. Gallium phosphide dissociates in silicon–germanium and gives rise to numbers of donors (P) and acceptors (Ga). Because phosphorus is more soluble in silicon–germanium than in gallium the net result is an introduction of donors and, consequently, a cross-doping of the p-type material; this reduces the carrier concentration to below the value which optimises the thermoelectric figure of merit. The effects of two other Group III–V compounds, namely, gallium antimonide and boron phosphide on the thermoelectric properties of silicon–germanium have been investigated [40]. The dissociation of these two materials should be self-compensating and result in a relatively unchanged carrier concentration.

The lattice thermal conductivity of silicon–germanium alloys can also be reduced by employing small grain size compacts, an effect attributed to phonon–grain boundary scattering. In semiconductor alloys whose constituent elements have large differences in atomic masses the short wavelength phonons are scattered by alloy disorder, resulting in the heat being carried by phonons of long wavelength. These longer wavelength phonons are effectively scattered by grain boundaries [41]. In a Si–Ge alloy compact with a grain size of ~5 μm a reduction in the lattice thermal conductivity of ~28% [42] compared with equivalent single crystal alloy is observed. At 1000 K this reduction is almost 35% [43]. Preliminary measurements of electrical resistivity and Seebeck coefficient indicate that these properties do not change with grain size over the range indicated. The thermoelectric figure of merit and conversion efficiency is substantially higher in small grain size materials, as shown in Figs. 4 and 5. Information on the long term behaviour of small grain size materials is scant. Preliminary measurements at UWIST indicate that some grain growth accompanies an extended period of heat treatment at high temperature although, in very heavily doped samples, grain growth appears to be inhibited by precipitated dopant. It has also been reported that the addition of GaP to Si–Ge alloy reduces grain growth [44]. In any event, at the present time the implication is that providing there are no unforeseen technological problems associated with the fabrication of thermocouples from these materials, the performance of a thermoelectric generator would be significantly improved through the use of small grain alloy [45].

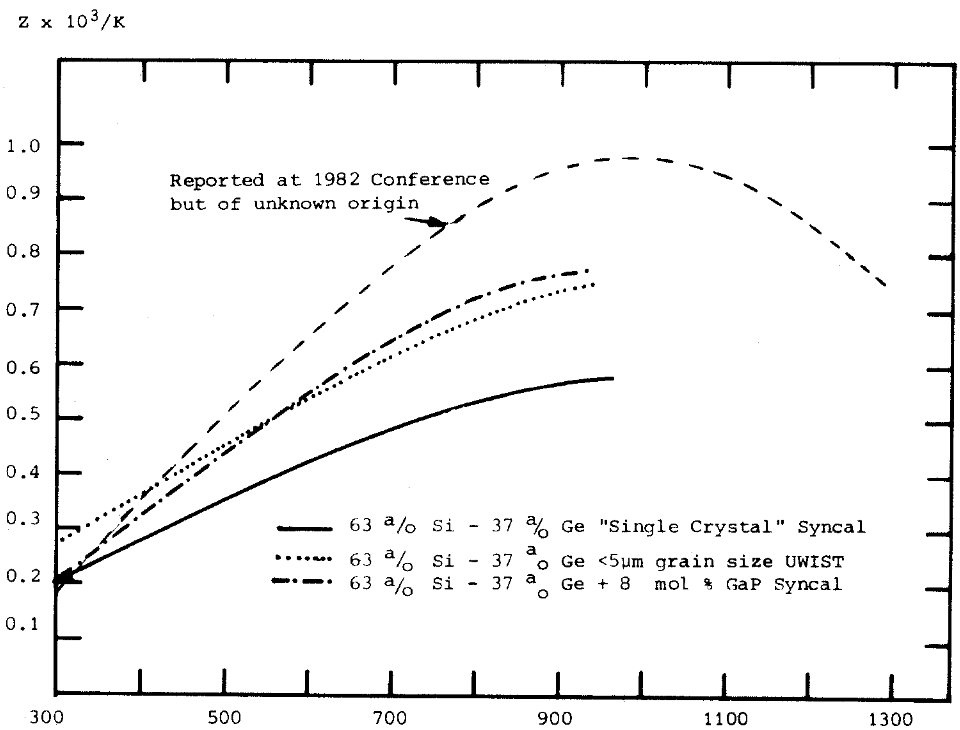

Fig. 4. Figure of merit for Si–Ge materials as a function of temperature.

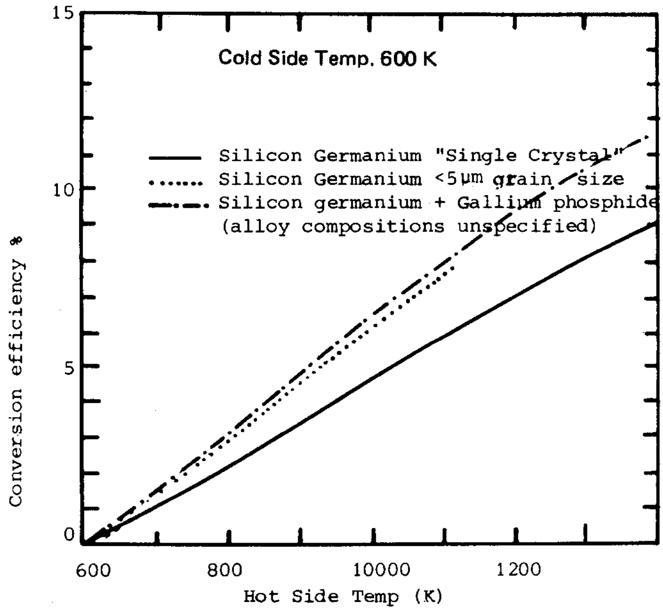

Fig. 5. Conversion efficiency of silicon–germanium materials.

4. Status of radioisotope thermoelectric generators based upon silicon–germanium technology

It has been confirmed [11] that an improved design Multi-Hundred Watt (MHW) Radioisotope Thermoelectric Generator (RTG) using unmodified silicon–germanium alloy thermocouples will be employed in the scheduled March 1986 International Solar Polar Mission (ISPM). The generator designated GPHS/RTG is so named because it is designed for use with the general purpose heat source (GPHS). The American Department of Energy's objective of reaching an RTG system efficiency of 9% by the late 1980s already appears to be well on the way to being achieved. The Fairchild Space and Electronics Company have produced an RTG design which incorporates the modular GPHS, "modified" silicon–germanium alloy thermocouples and an advanced thermoelectric module concept. Designated the "Modular Isotopic Thermoelectric Generator" (MITG), its principal distinguishing feature is its total modularity [46]. The generator, in essence, consists of a number of identical units, each unit consisting of one GPHS module surrounded by eight thermoelectric modules as well as standardised sections of thermal insulation; housing, radiator fins and electrical circuits. Each unit produces approximately 24 W at 28 V. The basic design is adaptable to a wide range of power levels, since the output power can be scaled in 24 W steps by varying the number of standard generator units. This scalability represents a significant advance over early RTG designs. Although power levels can be changed in the MHW/GPHS generator, this generally involves major changes in the thermoelectric couples and circuits to maintain the same output voltage. Design analysis of the generator predicts that a 12 unit 282 W(e) MITG will operate at a conversion efficiency of 9.4% and, having a weight of 60 pounds, has a specific power of 4.7 W(e) per pound.

The components of the thermoelectric module are shown in Fig. 6 [11]. Hot and cold junction temperatures of 1300 K and 600 K are essentially the same as the silicon–germanium generators used at present. The leg assembly forms a nearly cubic block of 0.36 in. edge length. The hot shoes consist of diffusion-bonded, doped silicon wafers and the cold shoes of a sputtered tungsten coating. The thermoelectric elements, the hot and cold shoes, and the electrical terminal leads are completely enclosed by a SiO_2 glass coating. The 2 in. square heat collector and the cold end mounting stud are made of molybdenum and tungsten. The heat collector possesses a central tungsten pedestal for the attachment of the thermopile and has a tapered cross-section that decreases from the thickness of the central pedestal of 0.60 in. to a thickness of 0.002 in. at the edges. The threaded molybdenum mounting stud is bonded to a 0.02 in. thick tungsten plate which serves as the attachment to the thermocouple. The terminal leads are nickel wires whose ends are brazed into axial holes at the cold ends of the first and last thermocouple legs. Syncal Corporation has been contracted to fabricate six thermoelectric module test devices, each consisting of eight of the

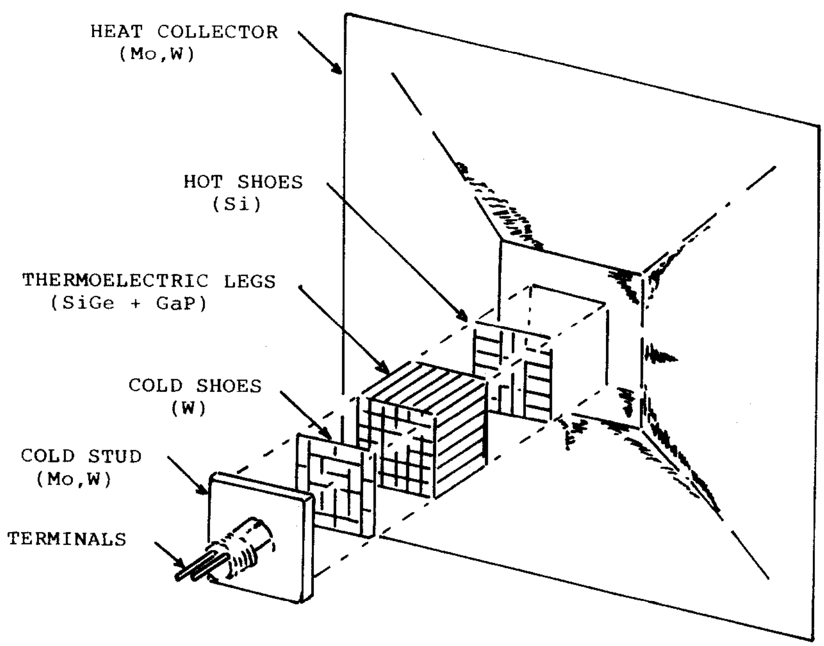

Fig. 6. Exploded view of multicouple thermoelectric generator utilising SiGe–GaP thermocouples (courtesy U.S. Department of Energy).

silicon–germanium multicouple arrangements described. Two of the six test modules utilize the unmodified silicon–germanium alloy material used in the MHW thermoelectric generator, and the remaining four utilize the 'modified' silicon–germanium alloy material.

A generator designated (Ql-A) and representative of MHW silicon–germanium technology has been completed in the U.S.A. and has been tested for 20 000 h [47], but there is still little, if any, information available about how the ends were achieved in a number of significant areas. There is no information on the material properties which leads to optimization of the thermoelectric figure of merit and to the maximization of the generator module efficiency and lifetime. The preparation of heavily doped silicon–germanium alloy starting material which possesses homogeneity in alloy composition and carrier concentration is an essential step in the production of well characterized compacts. Achievement of high alloy densities requires that the material be vacuum hot pressed very close to the alloy solidus temperature. Both these stages in alloy preparation, although not major problems, are difficult, and require considerable experimental skill. Further, there are two principal causes of material degradation: precipitation of dopants and materials sublimation. The precipitation of dopant in silicon–germanium alloys has been investigated in the U.K. to some depth, but little work has been reported on sublimation and a considerable development effort would be required in this area to implement preventive measures reported.

It is very difficult to bond metal contacts to silicon–germanium alloys. A variety of methods has been reported in the literature [12] but the only ones which have proved reliable involve advanced technology, the details of which have not been published. The technique used to achieve the grading in the alloy composition of the thermocouple from 78% Si at the hot end to 63% Si at the cold end has also not been revealed.

It has been reported, however, that development of the multicouple approach has been hampered by some difficult fabrication and process requirements [48], and an alternative method utilizing current technology to obtain an improvement in specific power has resulted in the fabrication and testing of bicouples [49]. The bicouple is similar in design and construction to the multi-hundred watt unicouple, but has four legs, comprising two n–p couples of silicon–germanium alloy. The advantage of a bicouple configuration is that it can provide double the voltage or double the current of a unicouple similar in construction, depending upon whether connections are made in series or in parallel. Bicouple assemblies have been fabricated using both SiGe–GaP and fine grained Si–Ge and their performance has been tested at General Electric and by Fairchild Industries. During the ingradient testing, some of the fine grained bicouples revealed high internal resistances, while the SiGe–GaP bicouples showed only a 3% spread, which suggests sound bonding. It has also been reported that the electrical performance of the SiGe–GaP bicouple was 81% of that expected, while the fine grained Si–Ge bicouple measured 90% of its expected power.

5. Conclusions

Recent advances in silicon–germanium material technology have resulted in the development of modified alloys with substantially reduced thermal conductivities. The major research effort has concentrated on reducing the lattice thermal conductivity through the addition of small quantities of gallium phosphide. Although some uncertainty exists regarding the electrical behaviour of p-type SiGe–GaP, thermocouples have been fabricated from this material. The reported reduction in lattice thermal conductivity which accompanies the use of small grain-size material, although not as dramatic as observed in SiGe–GaP, does not appear to be accompanied by additional problems in material stability. There is little, if any, information, however, on the long-term behaviour of either of these modified silicon–germanium alloys and the fabrication of reliable electrical contacts still presents a major problem.

It is concluded that, although the fabrication of reliable electrical contacts to unmodified silicon–germanium will present a major problem, the technology is available in Europe to build thermoelectric modules similar to those developed for the International Solar Polar Mission.

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References

1 D. M. Rowe, *Proc. Inst. Electr. Eng., 125* (IIR) (1978) 1113 - 1136.
2 D. M. Rowe and C. M. Bhandari, *Modern Thermoelectrics*, Holt, Rinehart and Winston, London, 1983.
3 A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, INFOSEARCH, London, 1957.
4 I. B. Cadoff and E. Miller (eds.), *Thermoelectric Materials and Devices*, Reinhold, New York, 1959.
5 P. J. Bateman, *Contemp. Phys., 2* (1960) 302 - 311.
6 H. J. Goldsmid, *Applications of Thermoelectricity*, Methuen Monograph, London, 1960.
7 R. W. Ure and R. R. Heikes (eds.), *Thermoelectricity; Science and Engineering*, Interscience, London, 1961.
8 F. D. Rosi, *Solid State Electron., 11* (1968) 833 - 868.
9 D. A. Wright, *Metall. Rev., 15* (1970) 147 - 160.
10 C. E. Kelly and G. R. Ambrose, *Proc. 17th IECEC, August 1982, Los Angeles, CA*, 1382 - 1386.
11 P. A. O'Riordan, *Proc. 4th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 10 - 12, 1982*, pp. 15 - 25.
12 D. M. Rowe, *Proc. 4th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 10 - 12, 1982*, pp. 96 - 103.

13 J. P. Dismukes and L. Ekstrom, *Trans. Metall. Soc. AIME, 233* (1965) 672 - 680.
14 H. W. Dietz and H. A. Herrmann, *Krist. Tech., 4* (1979) 413 - 421.
15 H. Schreiner and F. Wendler, *Z. Metallk., 52* (1961) 218 - 223.
16 M. Piper, *Proc. UKAEA–ENEA, Int. Symp. on Industrial Applications for Isotopic Power Generators, 1966, Harwell,* UKAEA, pp. 349 - 359.
17 R. A. Lefever, G. McVay and R. J. Baughman, *Mater. Res. Bull., 9* (1974) 863 - 872.
18 D. M. Rowe and R. W. Bunce, *J. Phys. D, 10* (1977) 941 - 948.
19 N. Savvides and H. J. Goldsmid, *J. Mater. Sci., 15* (1980) 594 - 600.
20 D. M. Rowe, *Proc. 5th Int. Round Table Conf. on Sintering, Portoroz, Yugoslavia, 1981,* paper 3.5.
21 R. K. Pisharody and L. P. Garvey, *Proc. 13th IECEC, August, 1978, San Diego, CA,* pp. 1969 - 1983.
22 C. M. Bhandari and D. M. Rowe, *Contemp. Phys., 21* (3) (1980) 219 - 242.
23 F. A. Trumbore, *Bell Systems Tech. J., 39* (1960) 205 - 233.
24 L. Ekstrom and J. P. Dismukes, *J. Phys. Chem. Solids,* (1966) 857 - 863.
25 V. Raag, *Proc. 10th IECEC,* IEEE, New York, 1975, pp. 156 - 159.
26 V. Raag, *Proc. 11th IECEC,* IEEE, New York, 1976, pp. 1527 - 1530.
27 V. Raag, *Proc. 2nd Int. Conf. on Thermoelectric Energy Conversion, Arlington, TX,* pp. 5 - 10.
28 D. M. Rowe and N. Savvides, *J. Phys. D, Appl. Phys., 12* (1979) 1613 - 1619.
29 I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids,* (1961) 19, 35 - 50.
30 N. Savvides and D. M. Rowe, *J. Phys. D, Appl. Phys., 14* (1981) 723 - 732.
31 V. S. Shukla and D. M. Rowe, *Phys. Status Solidi A, 66* (1981) 243 - 248.
32 V. S. Shukla and D. M. Rowe, *Appl. Energy, 9* (1981) 131 - 137.
33 N. Savvides, *J. Appl. Phys., 54* (5) (1983) 2402 - 2406.
34 N. Savvides and D. M. Rowe, *J. Phys. D, Appl. Phys., 15* (1982) 299 - 304.
35 C. E. Kelly, *Proc. 10th IECEC, August, 1975, Newark, DE,* pp. 880 - 886.
36 G. Stapfer and V. C. Truscello, *Proc. 11th IECEC, September, 1976, State Line, NV,* pp. 1533 - 1538.
37 N. Gunther, *Proc. 4th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 10 - 12, 1982,* pp. 89 - 95.
38 N. Gunther, *Proc. 4th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 10 - 12, 1982,* pp. 104 - 114.
39 V. Shields and L. Noon, *Proc. 18th IECEC, August, 1983, Orlando, FL,* pp. 235 - 239.
40 G. McLane, C. Wood, J. Vandersande, L. Danielson and V. Raag, *Proc. 6th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 12 - 14, 1986,* pp. 11 - 15.
41 H. J. Goldsmid and A. Penn, *Phys. Lett. A, 27* (1968) 523 - 524.
42 D. M. Rowe, V. S. Shukla and N. Savvides, *Nature (London), 290* (5809) (1981) 765 - 766.
43 D. M. Rowe and V. S. Shukla, *J. Appl. Phys., 52* (12) (1981) 7421 - 7426.
44 B. J. Beaudry, T. Takeshita and K. A. Gschneidner, Jr., *Proc. 5th Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 14 - 16, 1984,* Paper VI-3.
45 D. M. Rowe, *Rep. on Non-Conventional Energy Activities, No. 1. A collection of contributed papers to the 2nd Int. Symp. on Non-conventional Energy, 14 July - 6 Aug., Miramare, Trieste, 1982,* pp. 75 - 84.
46 A. Schock, *Publication No. FSEC-ESD-217-81/180B,* April, 1981.
47 G. Stapfer, *Proc. 3rd Int. Conf. on Thermoelectric Energy Conversion, Univ. Texas at Arlington, March 12 - 14, 1980,* pp. 70 - 74.
48 A. Schock, *Proc. 18th IECEC, August, 1983, Orlando, FL,* pp. 1083 - 1092.
49 R. D. Cockfield and P. D. Gorsuch, *Proc. 19th IECEC, San Francisco, CA, August, 1984,* pp. 2229 - 2234.