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The MC2730 Radioisotopic Thermoelectric Generator: A Development Report

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THE MC2730 RADIOISOTOPIC THERMOELECTRIC GENERATOR:
A DEVELOPMENT REPORT

ABSTRACT

This report presents an overview of the Sandia Laboratories radioisotope thermoelectric generator development program as of August 1973.

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FOREWORD

This report is focused on the development of a milliwatt radioisotopic thermoelectric generator for use in weapon applications. Since it is desirable that this overview of the Sandia radioisotopic thermoelectric generator development effort be made available to all interested parties, it may be obtained through:

U.S.A.E.C.
Technical Information Storage
P. O. Box 62
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A Milliwatt Radioisotopic Thermoelectric Generator for Weapon Applications

A small RTG is being developed for use in a nuclear weapon application.

M. K. Parsons

Introduction

A radioisotope-powered thermoelectric generator, designated the MC2730 RTG (Frontispiece), is being developed as the power source for a nuclear weapon application. The RTG satisfies the requirement of such systems for a power source that will operate continuously for the life of the weapons with which they are used.

In this article, we give an overview of the RTG development program. Development activities are described in more detail in other articles in this report.

Background

Thermoelectric generators operate on the principle that a temperature difference within a material creates an electrical potential difference that would cause current to flow in an external load circuit. Using two materials with different thermoelectric characteristics provides a net potential difference within a circuit so that usable power may be obtained. This principle is widely employed in thermocouples where the electric potentials are used to measure temperature. In RTG's, radioisotopic fuels are used as a heat source.

Prototype RTG power sources for weapon-system applications were developed in the early 60's. These power sources, the Space Nuclear Auxiliary Power (SNAP) 15A and B, developed by the AEC Division of Isotope Development for Lawrence Livermore Laboratory, and the MC2012 thermoelectric generator developed for Sandia Laboratories at Mound Laboratory under AEC Division of Military Applications funding, had a nominal 1-milliwatt power output and were based on wire-thermocouple technology. After the exploratory studies, the power requirement

increased from 1-milliwatt single channel to 25-milliwatt dual channel. As a result semiconductor thermoelectric technology, because of its higher conversion efficiency, was used for the MC2730 RTG.

Chemical batteries appeared attractive for these applications in that their use would preclude problems associated with additional radioactive materials. However, even where space for the power source is not limited, studies of relative cost and effectiveness have continued to decidedly favor the semiconductor thermoelectrics over chemical batteries at this stage in the development of the two technologies. The RTG approach is currently most cost-effective even without consideration of the costs attendant upon annual replacement of the shorter-lived chemical systems.

Design Goals

The design goals for the MC2730 RTG were that it provide, with 0.999 reliability, a minimum of 25 milliwatts of power on at least one channel over an 8-year service life, and that it have a very low probability of posing a significant radiological hazard. These goals present the classic problems of high-reliability, long-life component design:

- It is not economically practical to fabricate and test sufficient RTG's to demonstrate empirically that the reliability goal can be met.
- Development time scales do not permit actual demonstration of the RTG's ability to meet the service-life goal before it is put into use.

Thus, design strategy relies on conservative design choices together with a major emphasis on identifying and under-

standing potential degradation modes. An understanding of the physics of failure mechanisms is emphasized so that accelerated-aging tests can be used in which temperatures and/or partial pressures higher than nominal are traded against time. The accumulated data from accelerated aging tests, together with our inferred degradation models, suggest that the RTG can be credibly designed to have a life equal to that of the using system.

The design goal for the plutonium-238 heat source, consisting of the radioisotope fuel and its encapsulation, is that it be sufficiently well proven in development testing so that no special care or handling will be needed in the field. Also, the additional radiological hazard contributed by the heat source in an abnormal environment is to be less than 10% of that attributable to the associated weapon, so that transportation and storage radiological safety requirements need not be increased. The heat source will be tested as follows to demonstrate safety and to establish design margins: (1) for a 150-m/s impact into hardened tool steel, (2) for a fuel-fire environment of 1000°C for 1 hour at end-of-life helium pressure, (3) in case of detonation of adjacent high explosive, and (4) through accelerated-aging tests.

Special Design Considerations

The 25-milliwatt requirement places the MC2730 between typical SNAP system power levels of 10 to 200 watts and the milliwatt or less required by heart pacemakers and by early prototype power sources for weapon application. Thermopile fabrication problems arise from the extreme aspect ratio (cross-section area to length) required for the individual thermoelements in a 25-milliwatt design. For a thermoelectrically matched system, the aspect ratio, A/ℓ , of the thermoelements is determined by the resistivity, ρ , the Seebeck coefficient, S , the temperature differential, ΔT , the load voltage, V , and the electrical power, P , and can be expressed approximately as:

$$A/\ell = \frac{2\rho P}{S\Delta TV}$$

Note that this aspect ratio is proportional to electrical power.

For powers measured in hundreds of watts, the element cross-sections are in the square-centimeter region, where macroscopic bonding techniques can be used to bond electrode plates to individual thermoelements (there are

life data on such bonds from the AEC Space Nuclear Systems programs). At the submilliwatt extreme, the power requirement is sufficiently low that efficiency is not as important, and the less-efficient but more easily fabricated thermocouple wires could be used. Also for the submilliwatt range, one could use larger than optimum semiconductor elements, accepting inefficiency to maintain fabricability. However, for the intermediate 25-milliwatt power level, the more efficient semiconductor thermoelectrics in an optimized configuration are very desirable. Under these conditions, cross-section dimensions can be as small as a tenth of a millimeter in some design options.

The problem for the 25-milliwatt thermopile design is to fabricate and bond together large numbers of fragile thermoelements and then interconnect them using micro-circuit techniques in such a way that the thermopile will survive the service life at the hot-junction temperature. No significant life data were available in the literature on micro-circuit interconnections at temperatures of interest.

Other factors to be considered in the design are associated with the potentially large production quantities. Although space program RTG's often used much larger amounts of plutonium, there were only a few RTG's in well-defined locations. Radiological safety considerations are complicated in the case of the MC2730 by the likelihood of a significant number of units being widely dispersed. Also, the potentially large numbers of MC2730's make production costs a significant part of total program costs, and production yield becomes a major concern in the choice of materials and fabrication processes.

Description

The MC2730 (Fig. 1) consists of a 6-thermal-watt Pu oxide (80% enriched in the mass 238 isotope) heat source, two mechanically bonded but electrically independent silicon-germanium (SiGe) thermopiles, and silica thermal insulation that maintains a temperature difference of 350°C across the thermopiles. Heat-source thermal contact with the thermopile is maintained by a spring acting through an insulating column. The thermopile is electrically isolated from and thermally connected to both the heat source and the heat sink (baseplate) by boron-nitride disks 0.25 mm thick. Gold ribbons, attached at the cold end, are used to electrically connect the thermopile to thick-film Pt-Au conductors printed on an alumina substrate attached to

Fig. 1 MC2730 radioisotope thermoelectric generator

the output connector. The baseplate contains the output connector, a pumpout tube, and tapped mounting holes. The device fits within a right circular cylinder 7 cm in diameter by 10 cm long, excluding connector and pumpout tube.

Heat Source

The heat source is a nonvented pressure-vessel design having three layers of encapsulation and Pu oxide fuel. Since ^{238}Pu is an alpha-particle emitter, the heat source must either be selectively vented to relieve helium pressure or designed to contain the helium pressure that would be generated in the worst case: exposure to a fuel fire at the end of generator life. The many complications of selectively venting the helium were avoided by designing the heat source as a sealed pressure vessel.

T-111 alloy (90% tantalum, 8% tungsten, 2% hafnium) 1.0 mm thick was chosen for the pressure vessel because of its high-temperature strength and its good impact characteristics. Tantalum alloys, however, are subject to

oxygen attack which, because of resulting embrittlement, compromises their impact resistance. Hence, when used for plutonia containment, T-111 must be protected from both external and internal sources of oxygen. External protection is provided by sealing the pressure vessel within an oxidation-resistant outer container (0.50 mm) of the nickel-base alloy Hastelloy C. Internally two approaches are used to inhibit interaction of the plutonia with the pressure vessel. First, yttrium powder is added to the plutonia in sufficient quantity to reduce the O:Pu ratio from 2 to 1.75, at which ratio interaction with the T-111 has been shown to be negligible. Yttrium is also an effective getter for hydrogen, carbon, and nitrogen, which could conceivably be present as fuel impurities. Second, as an added precaution, a separate sealed T-111 liner (0.50 mm) is included which serves to assure that the pressure-vessel weld will not be weakened by plutonia contamination of the weld zone during welding.

Thermopile

In the thermopile design, fabricability and minimum material complexity are emphasized. They are achieved through the use of relatively lightly doped (2×10^{19} carriers/cm³) 80-20 a/o (atomic percent) SiGe alloy thermoelements bonded into a linear array with a borosilicate glass.

Microcircuit techniques are used to interconnect the 44 thermoelements of each thermopile channel. A 3-micron thin film of tungsten is sputtered over the entire surface of each end of the thermopile. Contact pattern masks, photoresist, and tungsten etches are then used to define the thermoelement interconnections.

Evolution of the thermopile has been characterized by tradeoffs of moderate decreases in efficiency for large gains in fabricability. In early thermopile development for the MC2730, the "standard" SiGe of the thermoelectric literature (doped to about 1.5×10^{20} carriers/cm³) was used, with nearly square thermoelements (80/channel) arranged in a two-dimensional matrix array. This approach required first bonding the thermoelements into rows and then performing a second glass bonding of the multielement rows to each other with a lower viscosity glass. Although assembly feasibility was demonstrated, problems with thermoelement alignment, voids in the glass bonds, shorting between thermoelement rows, and chipping damage to the small corner thermoelements during handling all contributed to low fabrication yields. The practical difficulties with the

square-matrix thermopile design were associated with the second glass bonding of a number of rows of elements.

The obvious way to overcome the difficulties of the matrix thermopile design was to use wide, thin elements so that a square pile would result from only a single row of thermoelements per channel. However, this would have required thermoelements only 0.08 mm thick. A possible solution was implicit in the expression for thermoelement aspect ratio, which contains the term ρ/S . Since the Seebeck coefficient, S , increases more slowly than resistivity, ρ , as carrier concentration is decreased (S varies approximately as $\rho^{1/2}$), it appeared possible to gain some increase in aspect ratio, and hence use fewer but thicker elements, by decreasing the doping level (increasing ρ).

There were three major difficulties with this approach:

- Thermoelectric efficiency would decrease as resistivity was increased from optimum. Inadequate data were available for predicting the amount of this decrease.
- The 0.18-mm SiGe wafers that appeared necessary could not be consistently produced by available slicing techniques.
- Most important, the literature on contact resistance as a function of carrier concentration for Si led one to suspect that parasitic contact resistances would

be excessive at the 2×10^{19} carrier/cm³ concentration of interest.

All three objections have been overcome. Contact resistances have been shown to increase much more slowly than anticipated as resistivity was increased. Also, extensive process development on new slicing equipment resulted in the routine slicing of 0.18-mm wafers. Finally, thermoelectric measurements and calculations, as well as prototype fabrication, indicated that the fuel penalty for the linear thermopile would be less than 10% in return for a great improvement in thermopile yield.

Status

The RTG development program is well into the prototype fabrication stage with 33 units under test, 16 of which have been provided for next-assembly development testing. The oldest unit, built in December 1971, has shown no degradation other than that resulting from fuel decay. The emphasis in the current effort is to gain a better understanding of degradation modes through accelerated-aging studies, and to search for improved fabrication processes.

Mound Laboratory, the heat-source production agency, has fabricated 94 development units for use in the RTG development program. The RTG prototype units, except for the heat source and the output connector, are being fabricated in-house. General Electric Neutron Devices has been assigned the RTG production responsibility.

Silicon-Germanium Processing

Hot pressing has proven effective for producing high-quality SiGe alloys for thermopiles.

R. A. Lefever, G. L. McVay, and R. J. Baughman

Introduction

An alloy of 80% silicon and 20% germanium is used in the thermopiles of the MC2730 RTG. SiGe was chosen because it is a simple two-element alloy with good thermoelectric properties. The simplicity of the alloy facilitated investigation of electrical-contact degradation, which limits RTG life.

To obtain the physical and electrical properties required from the SiGe system to meet RTG requirements, it is necessary to produce a homogeneous high-density alloy. However, the difference between the melting temperatures of the two materials (1410°C for silicon and 940°C for germanium; see Fig. 1) makes compositional uniformity difficult. Also, producing high-density materials under the required high-temperature conditions pushes the capabilities of available presses and furnaces. The use of phosphorus as the n-type dopant in the alloy introduced an additional fabrication problem. The high vapor pressure of phosphorus at SiGe melting temperatures can cause substantial difficulties in achieving the doping levels required in the thermopile. Three alternative processes that have been considered for preparation of SiGe thermoelectric materials

on a commercial scale are zone leveling, the Wacker process, and hot pressing.

Zone leveling, which is done by melting narrow zones of a solid alloy bar progressively from one end to the other, normally produces a polycrystalline sample with a density essentially 100% of theoretical and with excellent compositional uniformity. However, the process is slow and high phosphorus doping levels are difficult to achieve. Furthermore, zone-level material consists of relatively large millimeter-size grains. As a result, samples as thin as 0.18 mm, required for thermopile fabrication, contain grain boundaries that extend from one surface to the other. These boundaries are weak, with the result that samples fracture readily.

In the Wacker process, molten alloy drops are periodically deposited on the hot surface of a vertical cylindrical rod. The molten droplet momentarily melts a thin layer of the rod surface and then solidifies, producing a continuous solid sample. The process is relatively rapid and the quality of the resulting material is good. However, the material has a lower ultimate strength than that produced by hot pressing, and it must be procured from foreign sources.

Hot pressing consists of subjecting powdered samples to high pressures and temperatures for specified times. The powdered samples, contained in a die, are evacuated before pressing to remove gases that would be trapped between particles during compacting. Hot pressing appeared to have the potential for producing material with the best overall combination of physical and electrical properties on a production scale. With this process, densities greater than 99.5% of theoretical, high compositional uniformity, and ultimate strengths twice those of zone-leveled and Wacker materials are now being routinely achieved.

Fig. 1 Silicon-germanium phase diagram

Hot-pressing operations and the properties of the resulting SiGe alloy are described in the following sections.

Hot-Pressing Operations

Producing a hot-pressed ingot consists of three relatively independent steps: preparation of an alloy that is as homogeneous as possible with regard to SiGe atomic ratio and dopant concentration, preparation of a powder suitable for hot pressing, and the hot-pressing operation itself.

Chill Casting

The high temperatures and pressures used during hot pressing produce a considerable degree of compositional homogenization. Nevertheless, it is desirable to start with the most homogeneous material possible. Slow solidification of a SiGe melt produces a solid that varies continuously from pure Si to pure Ge. Slow solidification may also allow phosphorus dopant to be lost by precipitation. To enhance homogeneity and minimize loss of phosphorus, the starting material is produced by a rapid-quenching process known as chill casting.

In this process, Si and Ge are weighed in appropriate amounts and loaded into a fused-silica crucible. The crucible is part of an assembly consisting of an RF induction coil, a graphite susceptor, and appropriate insulating materials. A diagram of the basic assembly is shown in Fig. 2. This apparatus, equipped with a hopper for addition of phosphorus, is contained within a bell-jar vacuum chamber. When the crucible is loaded, the vacuum chamber is alternately evacuated and flushed with argon until the oxygen partial pressure is reduced to a very low value. The chamber is then filled to just under one atmosphere with pure argon.

A melt is produced by coupling 10 kHz RF power from the induction coil to the susceptor. The melt is held at temperature for 5 minutes and then poured into a water-cooled rhodium-plated copper mold. Pouring the melt requires about 5 seconds, and a typical charge of 300 grams solidifies completely in about 1 minute. The 10-kHz frequency couples directly to the melt and produces inductive stirring that eliminates the need for mechanical stirring.

Fig. 2 Schematic diagram of chill-casting equipment

Boron doping to produce p-type material is achieved by adding boron to the original charge of Si and Ge before producing a melt. The n-type dopant phosphorus, because of its high vapor pressure, is not added until 90 seconds before the melt is poured.

Despite relatively rapid quenching, the cast ingots exhibit a wide SiGe composition range. However, analyses for dopant content show that both boron and phosphorus are uniformly distributed throughout the ingots and that any phosphorus loss is below the detection limit. The ingots break easily into small pieces and lend themselves well to powder preparation.

Crushing and Grinding

Reducing the chill-cast material to a powder suitable for hot pressing presents a number of problems. Coarse powders are difficult to press to high densities, while fine powders are hard to handle and tend to form substantial surface oxide layers. Particle-size distribution is also an important factor in producing a high packing density and, correspondingly, a high ultimate density. Finally, the material is very abrasive, making it difficult to maintain low impurity levels.

A wide variety of methods for preparation of powders was evaluated, including grinding with alumina balls in alumina ball mills, tungsten carbide balls in tungsten carbide mills, flint stones in rubber-lined and polyethylene mills, impact milling, and explosive shock. All these processes resulted in unsatisfactorily high contamination levels. The best grinding technique was found to be planetary ball milling with agate vessels and balls. Since the agate balls and vessels are fabricated from high-purity silica, metallic impurities introduced into the powders are negligible.

Our current procedure for reduction of chill-cast ingots to powders suitable for hot pressing consists of several crushing and grinding stages. Coarse reduction is achieved by crushing the chill-cast material in a tool-steel mortar and pestle. The crushed material is sieved and the material that passes through the screen is milled for approximately 4 hours using agate vessels and balls. The result is a powder in which approximately 90% of the particles are less than 37 microns in size.

Grinding time must be adjusted for dopant level since increasing the dopant level increases the time necessary to produce a given average particle size. Silicon-rich material is more difficult to reduce than Ge-rich material. Thus, since the chill-cast ingot is composed of material with a range of SiGe atomic ratios, the coarse particles of powders prepared from these ingots tend to be somewhat rich in Si while the fine particles are Ge-rich. Although diffusion during hot pressing tends to eliminate compositional variations, the effects described above can be observed in electron microprobe tracings on sections of hot-pressed ingots.

Hot Pressing

High-density ingots of SiGe alloys are prepared by vacuum hot pressing from powders produced as described above. The powder to be pressed is placed in a die assembly that is then positioned in an induction coil. A typical die assembly is shown in Fig. 3. The chamber is evacuated to a pressure of less than 10^{-5} torr for 1 hour. When the powder has been evacuated, temperature and pressure are simultaneously increased. The operating conditions of 1295°C (indicated control temperature) and 28,000 psi are reached in 12 minutes and are held for an additional 60 minutes. After the sample has been pressed it is ejected from the die and allowed to cool. Cooling is facilitated by filling the chamber with helium.

Fig. 3 Schematic of hot press die assembly

Hot-pressing conditions were determined by evaluating the effects of pressure, temperature, and time on properties of the resulting material. Inadequate pressure results in low density, high porosity, and non-uniformity of both mechanical and electrical properties. Maximum pressure is limited by the strength of the die at the temperatures employed for pressing. If all other conditions remain constant, an increase in hot-pressing temperature increases density. Temperatures close to the melting temperature of the alloy are used. Hot pressing for periods of a half hour or less results in densities that are somewhat low and variable from sample to sample. Increasing the pressing time improves mechanical and electrical properties until times of about an hour are reached, beyond which no additional improvement is observed.

Material Properties

Density

Densities are determined on the hot-pressed ingots by a liquid displacement method, using Freon. The measurements are estimated to be accurate within about 0.1%. For the conditions outlined above, n-type samples range from about 2.995 to 3.000 g/cm³, while p-type samples show a somewhat greater spread, ranging from 2.980 to 3.000.

Sample density is very sensitive to powder characteristics and maintenance of pressure during hot pressing. Samples with bulk densities lower than 2.980 g/cm^3 are rejected from the thermopile fabrication sequence. The best value for theoretical density of undoped 80/20 SiGe appears from the literature to be $3.000 \pm 0.005 \text{ g/cm}^3$. Thus, disregarding the effects of dopant additions, average densities are greater than about 99.5% of theoretical and the minimum acceptable density is about 99.3% of theoretical.

Composition

X-ray powder patterns obtained from hot-pressed ingots exhibit sharp x-ray lines, indicating that a compact of narrow compositional range has been produced from a powder of wide compositional range. X-ray data on samples obtained from various locations within and on the surface of individual ingots indicate that normal samples are macroscopically homogeneous and that preferential loss of Ge does not occur at the surface during hot pressing. X-ray results have been confirmed by γ -ray attenuation and ion-backscattering studies.

An electron microprobe has been used to provide quantitative compositional information. Selected regions of samples were examined by traversing a focused electron beam 3 microns in diameter in 3-micron steps. The effects of hot-pressing time, temperature, and pressure on compositional homogeneity were examined. Consequent improvements in processing conditions have reduced compositional variations from about $\pm 8 \text{ a/o Si}$, with a few excursions greater than this, to about $\pm 2 \text{ a/o Si}$, with a smaller number of large-scale variations.

During early process development of chill-casting and hot pressing, samples were routinely checked for phosphorus and boron content. Within the limits of analytical error ($\sim \pm 0.009 \text{ wt } \%$ for phosphorus and $\pm 0.004 \text{ wt } \%$ for boron), dopant content in the hot-pressed ingots agreed with amounts added before the ingot was cast.

Microstructure

Optical microscopy has been used to study microstructure.

Samples are mounted and polished for examination through a metallographic microscope. Deep voids with diameters greater than several microns can easily be identified, but shallower and/or smaller voids are difficult to distinguish from impurity inclusions. This distinction can be made with the scanning electron microscope or the electron microprobe. Samples are also etched to reveal microstructure. Etching has shown that grain-size distribution in the hot-pressed ingot accurately represents particle-size distribution in the powder, indicating little, if any, grain growth during hot pressing.

Selected samples from optical microscopy are further studied in the scanning electron microscope, which allows differentiation between inclusions and voids in surfaces and has demonstrated that process refinements have reduced the number of voids greater than 5 microns in diameter that intersect a surface, from about $50/\text{cm}^2$ to essentially zero. Very few voids are now observed, even in the 0.1 to 1 micron range.

Mechanical Properties

Tensile, modulus, and fracture data have been obtained on rectangular plates of Wacker material, hot-pressed material from outside sources, and Sandia hot-pressed 80/20 SiGe alloys. The Wacker material and hot-pressed samples from outside had yield strengths of about 12,000 psi. Sandia hot-pressed material has a yield strength of 24,000 psi.

Thermoelectric Properties

Data on resistivity and Seebeck coefficient have been obtained on all hot-pressed samples suitable for thermopile fabrication or of special interest from the standpoints of processing or composition. The spread in thermoelectric coefficient values is relatively small. Resistivity measurements from one face of a hot-pressed ingot 4.1 cm in diameter by 1.8 cm thick have a standard deviation of about 1%, and the difference in mean resistivity between the two faces is about 2%. One objective of the present program is to determine electrical and physical properties as a function of alloy composition, dopant level, and fabrication conditions.

Characterization of the Thermoelectric Properties of Silicon-Germanium Alloys

Seebeck coefficient, electrical resistivity, and thermal conductivity have been measured for the SiGe alloy used in the RTG program.

R. D. Nasby and E. L. Burgess

Introduction

At the start of the MC2730 RTG program, many of the pertinent fundamental properties of SiGe thermoelectric alloys, such as the Seebeck coefficient, electrical resistivity, thermal conductivity, mechanical strength, dopant solubility, and impurity concentrations, were either not adequately characterized or were expected to be affected by improved material preparation techniques then being developed. It was necessary to characterize the initial values of those properties. Also, because of the required 8-year service life of the RTG at operating temperatures, theoretical models of aging processes had to be devised or evaluated so that estimates of RTG stability could be made with confidence. Examples of these efforts follow.

Characterization of Initial Thermoelectric Properties

The three physical properties of primary interest in thermoelectric generator design are the Seebeck coefficient S , electrical resistivity ρ , and thermal conductivity κ . The product of the average relative Seebeck coefficient between the two dissimilar thermoelectric elements, and the temperature difference, ΔT , between the hot and cold junctions, yields the open-circuit voltage generated in one thermoelectric couple of a thermopile. The thermopile geometry and the resistivity of the SiGe alloys, together with contact resistances, determine the internal resistance of the generator. Thermopile geometry and the thermal conductivity of the alloys, together with the conductance of the generator thermal insulation, determine the temperature difference across the couples of the thermopile. These three parameters, S , ρ , and κ , are often tabulated as the combination $S^2/\rho\kappa$, referred to as the figure of merit, Z . If one considers a simple model of a thermoelectric couple and calculates its conversion efficiency, this efficiency η depends on these three parameters only through the term Z ,

such that η increases with increasing Z . Although additional effects must be considered in accurately modeling a thermoelectric generator, the above discussion indicates the basic roles that these parameters play in defining couple and thermopile output voltages, internal resistances, power outputs, losses, and conversion efficiencies.

The thermoelectric material chosen early in the RTG program was a hot-pressed 80 atomic percent (a/o) Si silicon-germanium alloy doped with boron or phosphorus to produce the p and n-type thermoelectric elements, respectively. For this material, data on S , ρ , and κ were needed as functions of temperature and dopant concentration. Although considerable data existed in the literature for SiGe alloys doped to carrier concentrations for which Z was maximized ($\sim 10^{20} \text{ cm}^{-3}$), data were scarce for the more lightly doped materials ($\sim 2 \times 10^{19} \text{ cm}^{-3}$) that are of primary interest for the MC2730 application.

Experiment Procedure

S , ρ , and κ were measured as functions of temperature for n and p-type samples with carrier concentrations ranging from $1 \times 10^{19} \text{ cm}^{-3}$ to $\sim 2 \times 10^{20} \text{ cm}^{-3}$. S and ρ were characterized from -150 to 1050°C and κ from 25 to 1000°C. Temperatures greater than those envisioned for the RTG were investigated because the inherent properties of SiGe alloys permit operational temperatures up to 1050°C.

Seebeck coefficients were determined by imposing a small ΔT (approximately 10°C) along the sample length. Two chromel-alumel thermocouples were embedded in the sample. Measurement of the ΔT and Seebeck voltage between the thermocouples allowed S to be calculated relative to the chromel lead used for the Seebeck voltage

measurement. Published data for the absolute S of chromel were used to calculate the absolute S of the alloy.

Electrical resistivities were measured using an alternating-current four-probe technique, a precision method for measuring resistivity. AC measurements were used because small temperature differences in thermoelectric materials produce thermal voltages that are not negligible in comparison to the resistance voltage drop.

Thermal conductivities were determined from measurements of thermal diffusivity and specific heat. Thermal conductivity κ equals the product of thermal diffusivity, specific heat, and density. A laser flash technique was used to measure thermal diffusivity, and specific heat was determined by the use of a differential scanning calorimeter.

Thermoelectric Properties

The above measurements yielded S , ρ , and κ as functions of temperature for various dopant concentrations. These data and Z are illustrated as a function of dopant concentration in Fig. 1 for an n-type material at a temperature representative of the RTG application: 323°C (600°K). Similar results were obtained for p-type materials. To maximize Z , a dopant concentration near 10^{20} cm^{-3} is necessary. However, for the RTG application, carrier concentrations of $2 \times 10^{19} \text{ cm}^{-3}$ are used, primarily to reduce difficulties in thermopile fabrication. Lower values of dopant concentration yield increased S and ρ values, allowing fewer couples of larger cross section to be used in obtaining the desired output voltage, internal resistance, and power. The lower concentrations also reduce the phosphorus precipitation effects discussed in the next section.

S , ρ , and κ data for SiGe samples doped to $\sim 2 \times 10^{19} \text{ cm}^{-3}$ are shown in Figs. 2 through 4 for temperatures up to 600°C . These samples are representative of materials used in the MC2730. Calculations of generator performance incorporating such data agree well with actual performance.

Aging of Thermoelectric Alloys

The primary aging mechanism of the thermoelectric properties of 80/20 SiGe alloys is precipitation of phosphorus, the n-type dopant, from electrically active substitutional sites.

Fig. 1 Seebeck coefficient S , electrical resistivity ρ , thermal conductivity κ , and figure of merit Z at 600°K vs dopant concentration for n-type phosphorus doped, 80 a/o Si hot-pressed SiGe alloys

The ensuing decrease in charge carrier concentration affects the three thermoelectric parameters and increases the contact resistances of the thermopile interconnections. Boron precipitation has also been observed; however, since its effects on generator performance are considerably less than those of phosphorus, it will not be discussed in this article.

Fig. 2 Absolute Seebeck coefficient vs temperature for hot-pressed 80 a/o Si silicon-germanium

Fig. 3 Electrical resistivity vs temperature for hot-pressed 80 a/o Si silicon-germanium

Fig. 4 Thermal conductivity vs temperature for hot-pressed 80 a/o Si silicon-germanium

Phosphorus precipitation can occur during the lifetime of a thermoelectric generator because the carrier concentrations required for maximum thermoelectric efficiency exceed the solubility limits of the phosphorus dopant at most temperatures. Hence the alloy, as typically prepared for thermoelectric applications, is in a supersaturated condition.

A precipitation model developed by Lifshitz and Slyozov has been suggested[†] as reasonably describing phosphorus precipitation in SiGe alloys. This model contains constants that can be evaluated from short-term annealing data. Then, to the extent that the model is valid, long-term aging effects can be predicted. The applicability of this model to phosphorus precipitation in 80 a/o Si silicon-germanium alloys has been confirmed through analysis of both long-term (40,000 hours) life-tested thermoelements and short-term annealing of diverse samples (63 to 80 a/o Si, zone-leveled and hot-pressed) prepared both outside and in-house.

Lifshitz-Slyozov Model

It is assumed in the Lifshitz-Slyozov model that precipitation proceeds by diffusion after nucleation has occurred. This assumption differs from more familiar diffusion-limited theories in two respects: the interfacial surface energy of the precipitate particles is accounted for, and an asymptotic solution is obtained that is valid for long times. The result of considering surface energy is that a critical radius (or size) of precipitate particles can be predicted. If particles are smaller than the critical size, they will redissolve; if greater, they will grow. Knowledge of an initial particle-size distribution is required to completely describe precipitation as a function of time. However, Lifshitz and Slyozov have shown that an asymptotic solution exists for the later stages of the precipitation process that is independent of initial particle-size distribution. The precipitation process is described in terms of the inverse of the degree of supersaturation, X , where:

$$X^3 = At + B \quad (1)$$

$$X = (C_o - C_e) / [C(t) - C_e] \quad (2)$$

$$A = A^* (C_o - C_e)^3 / C_e^2 \quad (3)$$

$$A^* = \frac{4}{9} \left(\frac{\delta RT}{2M} \right)^2 \frac{1}{C_p} \frac{D}{\sigma^2} \quad (4)$$

[†]By L. Ekstrom and J. P. Dismukes in *J. Phys. Chem. Solids* 27, 857 (1968).

where, for the phosphorus-SiGe system,

- B = constant of integration (approximately equal to 1)
- C_0 = initial concentration of dissolved phosphorus
- C_e = equilibrium concentration of dissolved phosphorus
- C_p = concentration within precipitate particle
- $C(t)$ = concentration of dissolved phosphorus at time t
- D = diffusion coefficient
- δ = density of matrix
- R = gas constant
- T = absolute temperature
- M = mean atomic weight of matrix
- σ = interfacial surface energy

Values for D and σ are not available for the phosphorus-SiGe system and C_e is known only above 550°C. Therefore, the theory cannot be immediately applied, and these parameters must be determined experimentally. This may be accomplished by measuring the active dopant concentration as a function of time during short-term isothermal anneal tests.

Experiment Procedure

SiGe samples varying in Si content from 63 to 80 a/o and prepared by zone leveling and hot pressing were solution-heat-treated (1 hour at 1050°C, then quenched) to dissolve all phosphorus possible. The samples were then isothermally annealed at 700, 600, 500, and 350°C. Total anneal times ranged from 300 hours at 700°C to 2000 hours at 350°C. Anneals were periodically interrupted, samples quenched, and room-temperature electrical resistivities, ρ , or Hall coefficients, R_H , measured. The carrier concentration, n , was determined as a function of the anneal time, either by using ρ and mobility data, where $\rho = n\mu$, μ is mobility, and e is the electronic charge, or

by using the relationship $R_H = 1/ne$. These data represent $C(t)$ of Eq. (1). The $C(t)$ data were then fit to Eq. (1) with C_e , A, and B as fitting parameters. The differences between the sides of Eq. (1) were used in a least-squares routine to fit the data to the theory. In Fig. 5, the experimental data for $C(t)$ are shown as circles for a typical anneal test. After the fitting process, $C(t)$ may be calculated from the theory and the result is shown as the solid line.

Fig. 5 Carrier concentration vs anneal time for a phosphorus-doped 80 a/o Si hot-pressed SiGe alloy at 350°C

Equation (3) was used to calculate A^* , which is essentially the ratio of the unknown parameters D/σ^2 . In Fig. 6, $\log A^*$ is plotted as a function of reciprocal absolute temperature. No significant difference was observed in A^* for different alloy compositions or material preparation techniques. The solid line is a least-squares fit to all the data. Thus, A^* may be represented as $\exp(-Q/kT)$, where Q is an activation energy and k is Boltzmann's constant.

Model Validity

The short-term experimental data can be fit to the theory. The significance of the fitting parameters must now be examined. The fitting parameter C_e is the solubility of phosphorus in the alloy and may be compared with published data. Agreement exists for 63, 70, and 80 a/o Si alloys.

Fig. 6 A^* vs reciprocal absolute temperature for various phosphorus-doped SiGe alloys

The validity of the A^* values, as well as C_e , is confirmed by using them to predict long-term test results. The longest anneal data available are from thermoelectric couples that were life-tested by an outside source for 39,210 and 10,353 hours in a temperature gradient. The resistivity data points shown (Fig. 7) were obtained by measuring room-temperature ρ as a function of position along the elements after completion of the life test. The temperatures that existed at these positions during the life tests were calculated assuming linear temperature gradients between known hot- and cold-junction temperatures. The data thus represent room-temperature ρ as a function of anneal temperature.

The lines were calculated from theory, using A^* and C_e values from the short-term anneal studies. B was assumed equal to unity and ρ was calculated using mobility data. The model predictions are in excellent agreement with experimental data. The maximum resistivity observed in the 10,353-hour data is a result of slower precipitation rates at lower temperatures, which leave that section of the element in a high state of supersaturation. This maximum is closely reproduced by the theoretical curve.

Fig. 7 Comparison of Lifshitz-Slyozov model calculations to resistivity data from life-tested phosphorus-doped, zone-leveled thermoelectric couples

These considerations provide considerable confidence in the application of this model to the prediction of long-term results on the basis of short-term anneal tests. Transmission electron microscopy is being used to further investigate the model on a microscopic level.

Conclusions

The Seebeck coefficient, electrical resistivity, and thermal conductivity were measured for 80 a/o Si silicon-germanium alloys of interest for the RTG program. Calculations of generator performance using these data are in agreement with measured performance of operating generators.

Precipitation of phosphorus in SiGe alloys can be described by the Lifshitz-Slyozov theory. The unknown parameters of the theory have been obtained from short-term anneal tests. These parameters can be used to predict material property changes and associated degradation in SiGe generators as a function of time. In the MC2730, the $2 \times 10^{19} \text{ cm}^{-3}$ dopant level should be stable, based on the model predictions of solubility limits of phosphorus in the 80 a/o Si alloy and low precipitation rates below 300°C.

Glass Bonding of RTG Thermopiles

Glass, which has low electrical and thermal conductivity, is used to bond the thermoelements of the MC2730 RTG.

E. K. Beauchamp, J. Matsko, and C. D. Tuthill

Introduction

The requirement to provide 25 milliwatts of power at 2 volts with the MC2730 RTG is met with a thermopile of 44 alternately arranged p and n SiGe elements. Two thermopile channels are used in each MC2730 to power the two electronics package channels.

The thermopile elements are wafers with dimensions $0.018 \times 0.36 \times 2.5$ cm. Because of the mechanically brittle nature of SiGe alloys, these are individually quite fragile, but when they are bonded together, a rugged structure is formed. The two thermopile channels are also bonded into a single assembly for incorporation into the generator (Fig. 1). The bonding process and its development are discussed below.

Fig. 1 Thermopile assembly

Material Selection

Glass was selected as the bonding material between the SiGe elements of the thermopile and to join the two thermopile assemblies. The choice was based on the following considerations.

A requirement essential to the function of the thermopile is that the bonding material electrically insulate adjacent thermoelements. The electrical isolation achieved generally increases with increasing bond thickness. However, heat loss through the bond, which should be kept to a minimum, also increases with increasing bond thickness. Thus, both low electrical and low thermal conductivity are desirable qualities for the bond. The bonding material and the SiGe must be chemically compatible in the sense that any reaction between the bond and the SiGe must not degrade the thermopile. The expansion coefficients must match well enough so that excessive stresses are not generated by temperature excursions during material processing and RTG operation. The bonding material must have sufficient strength and mechanical stability to withstand thermal and mechanical loading.

A variety of commercial glasses has been developed for sealing tungsten, which has an expansion similar to that of SiGe. As a group, these glasses satisfy the requirements for low electrical and thermal conductivity. Several also satisfy the other thermopile bonding requirements.

The requirement for mechanical stability of the bond is complicated by the plastic-deformation behavior of glass. As glass is heated it does not change rapidly from a solid to a low-viscosity liquid, but changes gradually over wide temperature ranges (Fig. 2). Thus, in general, a glass rigid enough (viscosity $>10^{1.5}$ poise for bonds between elements) to provide mechanical stability at the maximum operating temperature ($\sim 425^\circ\text{C}$) must be heated to above 700°C to obtain the fluidity (viscosity $<10^{7.5}$ poise) necessary for the bonding operation. The absolute upper limit for bonding temperature is the melting point of the SiGe (1280°C). However, as discussed in a later section, there is an undesirable reaction between SiGe and several of the candidate glasses above 900°C . In practice, then, the usable

Fig. 2 Glass viscosity curves

glasses are those with viscosities $<10^{7.5}$ poise in the temperature range 700 to 900°C and $>10^{15}$ poise at 425°C.

The problem of maintaining mechanical stability of the thermopile assembly is further complicated by the requirement to bond two thermopiles into a single assembly. A second bonding step is required, at a temperature low enough so that the first (inter-element) bonds are not distorted. Therefore a glass of lower viscosity must be used for the second bonding operation. The glasses selected for the two bonds are, respectively, the intermediate-temperature Corning borosilicate glasses 7059 and 7052.

Bonding Process Development

To provide a context for discussion of some of the more important aspects of bonding development such as porosity, uniformity of bond thickness, element alignment, and

electrical isolation, the process is represented schematically in Fig. 3. As indicated, the SiGe wafers are coated with a thin layer of glass powder and then bonded into a stack. This stack is sliced into thermopile channels, two of which are bonded together to complete the thermopile assembly.

The procedure for bonding the thermopile is complicated by the scheme used to connect the elements electrically. Connections are made with a tungsten film, initially sputtered onto the end-faces of the pile and subsequently etched to leave pads in the desired areas (Fig. 4). This procedure places two requirements on the bond. First, since the pads are defined by a photolithographic process, the bond and wafer thicknesses must be sufficiently uniform to permit easy indexing of the photolithographic mask with the thermopile end-face. Second, the bond surfaces on the end-faces must be virtually pore-free. Pores, or bubbles, can affect the performance of a pile in two ways. In instances where pore geometry and size are such that the sputtered tungsten does not bridge the gap between elements, high porosity can substantially reduce the electrical conductance of the pad and the power output of the thermopile. On the other hand, it is possible for the tungsten to enter a deep pore in the sputtering operation and not be removed in the etching process because the etchant does not penetrate into the pore. The result could be an electrical contact where none is wanted.

Porosity Control

One approach to controlling porosity in the glass bond is to use a thin sheet of glass. This was tried, and some success was obtained with sheets as thin as 0.010 cm. However, it proved very difficult to produce glass sheets uniformly as thin as the desired 0.0025 cm, either by drawing the glass at high temperature or by grinding it down from thicker sheets. Furthermore, a 0.0025-cm-thick sheet of glass 2.5 cm long is extremely difficult to clean and handle.

A much easier way to produce a thin layer of glass is to deposit glass powder on the SiGe wafers. This, of course, aggravates the problem of producing bonds with low porosity, since the powder must be consolidated in subsequent processing without entrapping gas.

The problem of reducing porosity in the glass layer was solved by vacuum hot pressing. This procedure consists of

Fig. 3 Bonding process flow chart

Fig. 4 Contact pads on thermopile surface

evacuating the gas trapped within the powder layer, raising the temperature, and then applying pressure when glass viscosity is low enough to deform and consolidate the powder particles. However, several difficulties are introduced by earlier processing steps and by reactions between the glass and its surroundings.

One difficulty comes from the use of an organic binder for the glass powder. The binder is essential as a vehicle for deposition and to give the layer of powder sufficient strength for handling. However, before the glass is consolidated, the binder must be completely removed. Not only does the decomposition and oxidation of the organic material produce copious quantities of gas that can contribute to porosity in the glass, but carbonized residues can be left that can produce electrically conducting paths through the glass.

Presently (Fig. 3) the coated elements are heated for 4 hours at 550°C in pure oxygen to remove organics before the stack is assembled for hot pressing. As further insurance against retention of organics or contamination during later storage and assembly, the hot-pressing cycle includes an oxidizing treatment while the temperature is raised. To prevent oxygen entrapment as the glass particles coalesce, the chamber is evacuated at 600°C and held for 30 minutes before the temperature is again increased.

Another difficulty in producing pore-free glass bonds is that in addition to gas physically trapped in the powder layer, gases are adsorbed on and dissolved in the particles. Gases dissolved in commercial glasses generally include water and carbon dioxide, introduced from the atmosphere in a gas-fired furnace during the original melting of the glass. In most applications of commercial glasses, these gases have no effect and are ignored. However, in this program, the dissolved gases are liberated through association of the glasses with SiGe. The gas comes out of solution at ~900°C after the glass has coalesced, and cannot then be pumped out of the bond region.

Experiments showed that, although the glasses could be vacuum-melted to remove contaminant gases, gases could be easily readsorbed (from ambient air, etc.) by the small particles. Without special techniques for grinding and depositing the powder, there appeared to be no way to prevent recontamination. As an alternative, the bonding process was modified to retard gas release and thereby prevent bubble growth. One modification was to oxidize the SiGe wafers before glass deposition. The resulting thin oxide layer inhibits the glass-SiGe reaction. Eventually, at bonding temperature, the oxide is dissolved by the glass.

Another very effective way of retarding the release of dissolved gas is to keep the bonding temperature as low as possible and thus slow the reactions that promote release. However, lowering bonding temperature also raises viscosity, and as a consequence, bonding pressure must be raised.

The use of high pressure further complicates the bonding process because the fragile SiGe elements must be protected from fracture caused by pressing. The ram faces contacting the outer elements of the stack must be smooth and flat. Also, pressure must be increased gradually so that irregularities in the glass layer can be smoothed and the load

on the elements distributed uniformly while pressure is still low.

Under these constraints, the bonding cycle for the element stack has evolved into that shown in Fig. 5. A similar cycle, with a lower maximum temperature, is used to bond the two thermopile channels into the final assembly. The soak at bonding temperature before application of ram pressure is included to allow temperatures through the stack to equilibrate. Not only does this insure that the glass is soft enough to flow and distribute ram pressure uniformly; it also insures that the glass in all bonds has the same viscosity and hence that the bonds will compress to a uniform thickness. Maintaining ram pressure while the stack cools insures against bubble growth.

Fig. 5 Hot-press bonding cycle

Bond Thickness and Alignment

As stated, the bonding cycle must be controlled to insure uniformity of bond thickness throughout the thermopile. It is also necessary to provide fixturing that keeps elements precisely aligned during pressing. However, the most important factor in controlling bond thickness is initial glass deposition.

Different deposition techniques are used for the two bonds in the assembly. For the first bond, the glass is screen-printed onto the substrates from a fluid slurry. The second bond is applied in the form of a commercially prepared glass tape with an adhesive backing to hold it on the substrate.

Screen printing is commonly used as a technique for depositing thin layers of particulate materials. However, because most applications do not require the precision needed for the MC2730 some improvement in the technique

was necessary. After a brief parametric study, it was concluded that the primary determinants of final bond thickness are screen mesh, wire size, and the volume fraction of glass in the slurry. To obtain the requisite control over screen-printing parameters, the commercial equipment used in this development was modified substantially.

In early program stages, commercial transfer tapes could not be obtained with the required thickness control for the first bond. However, the less stringent requirements on the second bond could be met. Recently precision tapes have become available and are now a viable alternative to screen printing for the first bond.

Low-Resistance Bonds

The most significant type of defect in the thermopiles other than those associated with porosity or bond thickness is the low-resistance bond. Generally, with the high resistivity of the glasses used, bond resistances should be greater than 10^6 ohm. However, about 20% of the thermopile assemblies have at least one bond with isolation resistance below 100 ohms. For such bonds, the effect on electrical output from the two adjacent elements becomes important.

With one exception in which a SiGe particle was found embedded in the glass and in contact with adjacent elements, no source of low resistance has been positively identified. The magnitude of the problem of finding a source can be appreciated when it is recognized that a SiGe rod 4 microns in diameter, extending across the bond, can lower resistance to 100 ohms. For a metal, the filament could be even smaller. An alternative to identifying low-resistance spots in existing bonds is to assume that the source is conductive particulate material introduced during glass deposition, and to attempt to clean up the process to prevent this happening. Some progress has been made with this approach.

Status

Bonding feasibility with adequate yield has been demonstrated under development-shop conditions on a significant number of thermopiles (>100) of the present design. Porosity problems have become manageable partly through improved glass-bond processing and partly through the use of an electrolytic etch technique that is more efficient in dissolving tungsten from pores. Current efficiency in controlling bond and thermoelement thickness is such that a mask covering 6 to 12 thermoelement contacts at a time can be used. This process, which requires multiple exposures, has proved acceptable.

Contacts for RTG's

Tungsten thin-film contacts are used to interconnect thermoelectric elements in the RTG. Alternatively, interconnections can be made by a solid-state reaction of a wire with the thermoelectric material.

J. N. Sweet, G. E. Pike, and P. D. Wilcox

Introduction

Two methods for electrically connecting the thermoelements that make up the thermopile in the RTG are being developed. One involves thin-film techniques similar to those used in microcircuit technology. Another, which may be used in the MC2730 or in second-generation RTG's, combines both glass bonding and a solid-state reaction of an interconnecting wire with the thermoelectric elements in a single elevated-temperature operation.

The thermopile is composed of 22 thermocouples (44 0.018-cm glass-bonded SiGe wafers alternately of n- and p-type conductivity) connected in series to provide a nominal output of 25 milliwatts at 2 volts. The wafers are connected electrically by tungsten thin-film contacts in the first method and by platinum wire embedded in glass in the second. Both connection methods are described in this article.

Tungsten Thin-Film Contacts

In this section the two basic steps for interconnecting the individual n- and p-type thermoelectric elements are described: (1) a blanketing thin-film tungsten deposition followed by (2) a photolithographic etch to remove unwanted tungsten from noncontact areas. Also discussed is the research that has been done to estimate the mechanical and electrical lifetimes of these interconnections.

Most conventional microcircuit metallization schemes are unsuitable for making electrical contacts to thermoelectric semiconductors that operate at elevated temperatures. For example, aluminum, which is widely used in the semiconductor industry for making conductors and contacts on Si integrated-circuit chips, forms a liquid alloy with Si at

577°C. Appreciable solid-state reactions have been found to take place in metal-Si systems at temperatures of the order of 1/2 to 2/3 of the liquification temperature (in °C), and these reactions, if allowed to proceed for long periods, can lead to loss of contact adhesion and to thermopile failure. Experiments have shown that aluminum contacts fail rapidly at 400°C and thus would not be suitable for use in the MC2730, where the thermopile hot-junction temperature can be as high as 425°C.

The lowest liquification temperature for tungsten-Si composites is approximately 1400°C, which is higher than the 1280°C melting point of SiGe and sufficiently above the 425°C maximum operating temperature of the MC2730; consequently tungsten might be expected to be a suitable candidate material for thermopile contact metallization. Tungsten's low resistivity and its low thermal expansion coefficient, which is close to that for SiGe, make it an attractive choice for a contact material. Since bulk-tungsten contacts 1.3 mm thick were used successfully in SNAP generators, which operated at temperatures over 500°C, it was felt that thin-film tungsten contacts might be feasible for the MC2730, which would operate at hot-junction temperatures about 75°C lower. Tungsten, however, has not been widely used in the microcircuit industry because it is more difficult to deposit in thin-film form than materials of lower melting points, such as aluminum and gold. Thus further development of tungsten thin-film contact processes and detailed characterization of tungsten contacts were required.

Contact Process Description

After the thermoelements have been bonded together with glass, the end surfaces are polished smooth. The tungsten

films used to form the contacts are then deposited on the ends of the thermopile by a sputtering process performed in argon at a pressure of 4×10^{-5} atmospheres. For this process the thermopiles are mounted vertically in a heated fixture in the sputtering chamber (Fig. 1). The thermopiles are heated during deposition to form highly adherent films with low internal stress. The sputtering is continued until a layer of about 3×10^{-4} cm of tungsten is deposited.

The next step is photolithographic contact definition. This process, common in the fabrication of semiconductor devices, is readily adaptable to thermopile processing. The end surfaces of the pile are first coated with a negative photoresist solution that forms a highly adherent film after baking. This resist is then rendered insoluble to resist developer after being exposed to light through a mask that is transparent in regions where contacts are desired. After this exposure, the resist is developed and the soluble resist is removed from the areas where tungsten is not desired. The tungsten is removed from these areas by chemical etching. The insoluble resist that remains over the tungsten

in the contact regions protects these areas from the etching solution. When all unwanted tungsten has been etched away, the remaining resist is removed with hot trichloroethylene. Figure 2 shows a section of an early thermopile surface with contacts in place.

A completed thermopile is shown in Fig. 3. The tungsten contacts appear as light strips against a dark background. The gold pads at the bottom of the thermopile are attached by a eutectic "die-bonding" technique and the gold ribbons are then attached by microwelding. These ribbons are welded to a printed circuit board during RTG assembly.

Thermopiles of the type illustrated in Fig. 3 have been electrically interconnected since September 1972. Although problems have been encountered, the average yield of usable thermopiles is about 80%. Most unusable units are rejected because of excessive contact resistance. The units can be reclaimed by etching off the tungsten contacts and repeating the processing cycle. Contact-processing techniques appear to be well defined and characterized.

Fig. 1 Sputtering equipment used in the thin-film contact development program

Fig. 2 Section of thermopile surface with contacts in place (X60)

Fig. 3 Thermopile

Contact-Lifetime Studies

The ability of the contacts to survive extended operation at high temperatures is a major consideration in a thermopile application. Although considerable SiGe contact-life data were generated for tungsten plate contacts in the SNAP program, the thin-film tungsten contacts required in the present application necessitated a thorough test program to ensure that the thin-film contacts would last through 8 years of operation at 425°C. The program has so far included accelerated-aging tests at temperatures above 425°C, as well as diffusion and reaction studies.

In the accelerated-aging tests, the thermopiles were heated in a vacuum at a series of temperatures in the range 550 to 650°C. Periodically, the thermopiles were removed and the resistance of each contact measured. Failure time was defined as the time when average contact resistance had increased to an unacceptable value. These tests have been supplemented with similar accelerated tests of thermopiles installed in RTG's in which electrical heat sources were substituted for isotopic heat sources to achieve higher temperatures. These more realistic tests have confirmed the results found in the original vacuum-aging experiments.

An example of data from accelerated-aging tests for SiGe doped to $1.5 \times 10^{20} \text{ cm}^{-3}$ is shown in Fig. 4. The tests shown were conducted at 550°C (solid line) and 575°C (dashed line). The bars centered at the data points represent a value equal to twice the standard deviation of the resistance value. Two important facts can be deduced from this graph. First, contact resistance is essentially constant for the initial 80% of contact lifetime and then starts to increase quite rapidly, as does the standard deviation. Second, contact lifetime has been reduced from about 1500 hours at 550°C to 530 hours at 575°C, a reduction by a factor of almost 3, caused by a temperature increase of only 25°C. Thus, a very large increase in lifetime might be expected at the maximum design operating temperature of 425°C.

The cause of contact failure is believed to be loss of contact adhesion and ultimately contact unbonding as a result of the formation of a WSi_2 (tungsten disilicide) reaction zone at the contact interface. Silicon from the SiGe alloy diffuses into the tungsten contact to form the reaction layer, creating voids in the SiGe. These voids lead to a decrease in effective contact area and ultimately to decreased adhesion. Contact lifetime can be estimated from an analysis of these diffusion processes.

In a diffusion-controlled process governed by a diffusion constant D , the amount of reaction-layer growth X after a time t is governed by the relationship $X = k\sqrt{Dt}$, where k is a numerical constant. In many cases D has a temperature dependence of the form $D = D_0 \exp(-Q/kT)$, where $D_0 = \text{constant}$, $Q = \text{"activation" energy}$, $k = \text{Boltzman constant}$, and $T = \text{absolute temperature}$. If, at any

Fig. 4 Results of contact accelerated-aging tests

temperature, contact failure occurs after a certain thickness of WSi_2 has formed, then we can use the two formulae above to show that failure time t_F is related to absolute temperature by $\log(t_F) = A(1/T) + B$, where A and B are constants that depend on the other constants described above. Thus, if the log of failure time is plotted against inverse temperature the result should be a straight line if all the assumptions are correct.

A plot of this type is shown in Fig. 5. The solid line is the least-squares fit to the failure-time data points denoted by an X, and the slope of the line corresponds to an activation energy of 3 eV/atom of W reacted. When the line is extrapolated to longer times and lower temperatures, as indicated by the dashed line, the extrapolation intersects the 8-year lifetime line (dot-dashed horizontal line) at a point corresponding to a temperature of 480°C . At 425°C , the extrapolated line yields a predicted lifetime of over 500 years. Thus there appears to be an adequate thermal margin for the thin-film tungsten contacts when they are operated at or below 425°C .

Electrical Characteristics of Tungsten-SiGe Contacts

To provide better understanding of the electrical contact between tungsten and SiGe, research was begun to characterize such contacts by means other than room-temperature resistance. Although there is much information about metal-semiconductor junctions, the RTG contact problem had three features not normally considered: (1) Nearly all previous experience with metal contacts had been with single-crystal semiconductors. However, as a result of our material preparation process, the SiGe used in thermopiles is polycrystalline. This meant that grain-boundary effects at the contact surface needed study. (2) Another phenomenon that affects contact resistance is the presence of a small oxide layer on the SiGe/contact surface before tungsten deposition. As this oxide thickens, resistance increases rapidly beyond the acceptable limit. However, the oxide layer also inhibits the rate of formation of a WSi_2 reaction zone at the interface, and hence increases contact lifetime. There is thus some finite oxide thickness required for optimum thermopile performance. (3) Finally, because of the long-lifetime requirement for these contacts, it was important to know if and how their electrical properties change with time at elevated temperatures.

Our primary method of characterizing the electrical properties of tungsten contacts involved electron tunneling.

Fig. 5 Contact failure time as a function of aging temperature

Figure 6 illustrates the basic ideas that exist regarding tunneling experiments. For general purposes, we consider here the presence of an oxide layer between the tungsten and a sample of heavily doped n-type SiGe. An applied voltage, V , causes a current, I , to flow. We measure I versus V and the differential conductance, $\sigma = dI/dV$, versus V at several temperatures. By carefully analyzing these curves, one can learn how the electrons move from one side of the contact to the other. Figure 6b shows an energy-level diagram for the junction region when it has been cooled to nearly absolute zero. The shading indicates the range of electron energy levels along the length of the junction. Electrons are permitted above these regions, but they must receive additional energy to get there. At higher temperatures, for example, some electrons absorb energy from the vibrating lattice of atoms and partially populate the upper regime. Below the line labeled E_c (the conduction band edge) in the semiconductor is the energy-band gap in which no electrons are permitted. Also in the diagram are two potential energy barriers. The largest arises from the band gap of the insulating oxide, while the parabolic barrier is a "Schottky" barrier (a simple electron barrier that occurs when metal is in contact with a semiconductor) that is present even when the oxide is absent. Classically, electrons in the semiconductor would be blocked from transferring to the metal (or vice versa) until they had sufficient energy to completely surmount the oxide barrier. However, a

Fig. 6 Tunneling process in SiGe semiconductor

well-known prediction of quantum mechanics is that a few electrons will penetrate or tunnel through these barriers. Such a process is illustrated in Fig. 6b, where we also show the semiconductor electrons gaining a small amount of energy from the battery. At low temperatures, tunneling is the dominant process of electron transport. We can extract information about the barrier region by examining curves of differential conductance versus applied voltage. Information about the energy distribution of electrons in SiGe is also revealed by these data.

Typical data are given in Fig. 7 which show differential conductance $\sigma = dI/dV$ versus V at several temperatures. The solid curves were measured on a sample just after it had been removed from the sputtering chamber with a fresh contact of tungsten. The small conductance values, especially at low temperature, indicate that a thin oxide layer is present in the contact. The location, temperature dependence, and width of the sharp dip in σ near zero voltage indicates the presence of defects in the oxide layer. After these measurements were completed, the sample was heated in a vacuum for 16 hours at 500°C. Remeasurement of electrical properties yielded the set of dashed curves. The large increase in conductance shows that electrons no longer see the same barrier. Further heat treatments at 500°C for up to 50 hours do not change the characteristics. The curves after heat treatment look like simple metal-semiconductor contacts that still have the parabolic Schottky barrier. This indicates that the oxide has either developed microcracks or has been modified chemically by impurities diffusing in so as to provide an intimate metal/semiconductor contact.

Thus far our characterization and measurement of the

reaction of tungsten contacts to SiGe have yielded results that give confidence in their ability to perform electrically throughout device lifetime. We first find that the SiGe grain boundaries do not adversely affect electrical-contact characteristics. Second, we find that at least a thin oxide layer in the junction does not seriously degrade the contact because its initial low conductance can be annealed away. Finally, we find that (except for initial changes) none of the junction's electrical characteristics are altered by heating and aging.

Wire-Intraconnected Thermopiles

A review of fabrication problems with the early MC2730 thermopile led to a method for interconnecting thermopile elements that combines both the glass bonding and the electrical interconnections into a single elevated-temperature

Fig. 7 Differential conductance vs bias voltage

operation. The advantages of the method are that it provides:

- Compatibility with a broader choice of contact materials, some of which are expected to withstand higher operating temperatures and oxidizing environments.
- Simplicity of fabrication and rapid start-to-finish times.

In this section are described the physical assembly, key fabrication processes, and general characteristics of wire-intraconnected thermopiles as they are known at this time. (A patent application covering this process has been filed by the AEC with the US Patent Office.)

In the wire-intraconnected thermopile the thermoelements are connected electrically by contact with a wire embedded in the glass rather than by tungsten thin films. During assembly, the wire has a solid-state reaction with the wafers above and below, connecting one end of an n-type wafer electrically with the same end of a p-type wafer. Such a connection alternates from one end of the stack to the other, forming a number of two-element thermocouples connected electrically in series (Fig. 8). The stack can be assembled from wafers of sufficient area so that it can be sliced into several 0.36-cm-wide thermopile channels.

Fabrication Processes

The electrical intraconnection for this thermopile is made simultaneously with the glass bonding operation. An assembly of parts including all wafers, wires, and powdered-glass layers is placed in a hot-press cavity. In the hot-pressing operation the glass melts and wets the adjacent parts, pressure is applied causing the thermoelectric wafers to come into contact with the wires, and the wafers react with the wires to form compounds of low electrical resistivity and low contact resistance.

The hot-pressing operation produces good electrical contact and a strong monolithic structure but requires careful pressure and temperature control throughout the process. A typical cycle, determined experimentally for each combination of materials, takes about 20 hours. During

Fig. 8 The physical arrangement of a wire-intraconnected thermopile stack

this time the temperature is increased slowly at first in an oxidizing gas to remove organic binders from the glass layer, then more rapidly in nonoxidizing argon gas, until the melting point of the glass is reached. At this point a constant-temperature soak is maintained for about an hour. The assembly is then cooled. During the cycle, pressure on the assembly is increased to about 70 psi by the time the soak temperature is reached. Argon is permitted to flow through the chamber at one atmosphere of pressure.

After cooling, the thermopile stack is sliced into individual units. A second glassing bonds two channels together before the thermopiles are lapped to final dimensions. Output leads are then attached and the unit is ready for testing and service without the polishing, sputtering, and photolithography required with the thin-film intraconnecting process.

General Characteristics of Wire-Intraconnected Thermopiles

Many wire and glass compositions can be used with SiGe wafers. Platinum was first used with Corning 7052 glass. Then the temperature capability was increased by using

platinum-rhodium (Pt-Rh) alloys and Corning 7059 glass, which has higher viscosity at a given temperature. Figure 9 illustrates the temperature dependence of hot pressing for a particular Pt-Rh alloy and shows the latitude in temperature and time that can be used to achieve a given reaction at the contact. It is necessary that the viscous properties of the glass under hot-pressing conditions be compatible with the rate of diffusion and reaction of the particular wire being used. Early results show that metals or alloys of iridium, platinum, rhodium, and ruthenium will yield thermopiles operable to temperatures of 500 to 700°C. However, appropriate glasses, ceramics, or glass-ceramics must be developed for higher temperatures.

During hot pressing, diffusion occurs and numerous compounds are formed in the contact region when the wire reacts with the wafer. With Pt wires, Pt_2Si and Pt_2Ge_3 are dominant but $\text{Pt}_3\text{Si}_3\text{Ge}$ is also observed. The characteristics of the contact arise from a variety of compounds whose formation is dependent on the starting materials and the hot-pressing conditions. For example, if the temperature is greater than 830°C, a eutectic liquid of Pt and SiGe may form. Thus, the physical properties and electrical resistance are a result of the complex reactions that occur during hot pressing.

Fig. 9 Time and temperature dependence of reaction products at the wire/wafer interface in wire-intraconnected thermopiles

Contact resistance varies considerably between different wire-intraconnected thermopiles, and this remains a major area of study. The lowest specific contact resistance to date is about 1 milliohm-cm* for a Pt-wire-intraconnected thermopile with Corning 7052 glass. More commonly, initial specific contact resistance is near 100 milliohm-cm and falls to 10 to 40 milliohm-cm after annealing, which is as good as or better than the sputtered-tungsten contacts currently being used.

Studies of aging in early Pt/7052 glass thermopiles at elevated temperatures indicated that resistance changes were likely caused more by flow or yield of the 7052 glass than by diffusion and reaction at the contact.

These accelerated-aging results have prompted the use of the higher-temperature glass, Corning 7059. While glassing or hot pressing temperatures with 7059 glass must be greater than 830°C (Pt-Si eutectic), successful thermopiles have been made using alloys of Pt and Rh. These thermopiles have higher contact resistance than pure Pt but also appear to age more slowly. At this time an 8-year life appears reasonable, based on the requirement that contact resistance be less than 120 milliohms-cm at end of life.

Conclusion

Two interconnection processes have been developed for the small thermoelectric elements that are characteristic of 25-milliwatt RTG power levels. Sufficient understanding of the nature of the contact and its degradation modes has been achieved to give confidence that lifetime goals can be met with the tungsten thin-film process. Also, a wire interconnection process in which the thermoelectric elements are bonded and contacts are formed in a single step is being investigated. It is expected that continued development of the wire interconnection process will result in 25 milliwatt monolithic thermopiles capable of long-life operation at temperatures of 500 to 700°C.

*Total contact resistance equals contact resistance in milliohm-cm divided by the length of the contact.

The Application of Helium-Ion Backscattering to Electrical Contact Studies for the RTG

Ion backscattering is used to analyze the aging processes at the interface between the contacts and the thermoelements of the RTG.

J. A. Borders and J. N. Sweet

Introduction

To predict the service lifetime of the RTG, one must know the possible failure modes and their time and temperature behavior. Because chemical reactions between the metal electrode and the bulk semiconductor are common problems with semiconductor devices, we must define such reactions and determine that they will not adversely affect the RTG during its opening lifetime.

Sputtered-tungsten films are the prime material for the high-temperature contacts in the RTG. These contacts form the interconnections between the "hot" ends of the p- and n-type wafers that make up the thermopile. To determine contact lifetimes at the nominal operating temperature of 380°C, we subject the contacts to higher-than-normal temperatures (500 to 700°C) where reactions are speeded up (accelerated aging). Behavior observed at these temperatures is then extrapolated back to operational temperature. Electrical resistance measurements on thermopiles subjected to accelerated aging have indicated that RTG lifetime would be limited by a phenomenon that caused a sudden increase in contact resistance after a time that was dependent on the accelerated-aging temperature. Also, tungsten contacts that had been aged at very high temperatures (600 to 700°C) showed a decrease in mechanical bond strength between the tungsten contact and the SiGe-alloy semiconductor, and eventually fell off. Extrapolation of this behavior to a temperature of 380°C indicated that a lifetime well in excess of 8 years could be achieved. To provide confidence in these predictions, understanding of the physical mechanism that caused the degradation was necessary.

A technique that can resolve atomic composition in depth is necessary for nondestructive analysis of the reaction

taking place at the metal-semiconductor interface.

Analytical techniques have been developed in recent years to study surface and near-surface properties. For the most part, however, these techniques are sensitive either to only the first layer of atoms on the sample surface, or they measure an average over several thousand atom layers. Thus depth information can be obtained with these techniques only by the laborious technique of physically stripping a layer from the sample and remeasuring the properties of the newly exposed surface. This, however, destroys the sample.

Energetic helium-ion backscattering is an analytical technique that allows the study of surface layers up to about 1 micron (10^{-6} m) thick. It yields information on the depth distribution of atomic composition with a depth resolution of about 100 to 200 Å (1 to 2×10^{-8} m). The technique is nondestructive so that repeated analyses can be made progressively as a sample ages. The results can be obtained quickly and are quite easily interpreted. This paper reviews the fundamentals of ion backscattering and presents results of a study of sputtered-tungsten films on SiGe alloys that were used to simulate high-temperature electrical contacts on the RTG.

The Physics of Ion Backscattering

Ion backscattering uses two types of interactions between an energetic ion and a target to provide mass and depth information about the target atoms. In the energy region of interest (0.1 to 3.0 MeV), the incident ion can penetrate the electron cloud of a target atom and come sufficiently close to the nucleus to be elastically scattered. The energy of the scattered ion, E_{scatt} is related to its incident energy, E_0 , by

$$E_{\text{scatt}} = kE_0$$

where the constant k is dependent only on the incident ion mass, the target atom mass, and the scattering angle. If, for example, we use a beam of helium ions and detect the backscattered ions at a discrete scattering angle, the energy of these scattered ions is a function only of target atom mass. The ions scattering from the heaviest atoms in the target will have the largest energy after scattering.

The foregoing deals only with elastic ion-atom scattering events at the surface. Most incident ions do not come close enough to the nuclei to interact at the surface, but penetrate the target and lose energy by electronic excitations. This energy loss can be characterized by

$$\frac{\Delta E}{\Delta x} = -N \mathcal{E}(E)$$

where N is the atomic density (number of atoms per unit volume) of the target, and $\mathcal{E}$ is the "stopping" cross section, which is usually a slowly varying function of energy over the region of interest. Thus, ions elastically scattered from an atom below the surface lose energy both before and after they interact with a nucleus, and will be detected at a lower energy than those scattered from similar atoms on the surface. Since $\mathcal{E}(E)$ can be experimentally measured, it is therefore possible to correlate the energy of the backscattered ion with the depth from which it was scattered.

The ideal scattering spectra from targets containing two species of atoms A and B, with A heavier than B, are shown in Fig. 1. Figure 1a shows the spectrum from an infinitely thin target containing equal numbers of atoms of the two species. The spectrum from a thin-film target of the same atomic composition, of the order of $1000 \text{ \AA}$ (0.1μ) thick, is seen in Fig. 1b. Figure 1c shows the spectrum from a "thick" target of the same material. The difference in the height of the scattering peaks for A and B atoms results from the backscattering cross sections, which are proportional to the square of the number of protons in the target nuclei. Thus, ion backscattering for heavy elements is more sensitive than for lighter elements.

Application to Layered Targets

Ion-backscattering studies can be particularly useful when applied to substances in which the atomic composition varies

with depth. The case of a thin film of a heavy element on a substrate whose atoms are light is a good example. The ideal scattering spectrum from such a target is shown in Fig. 2a. A chemical reaction may take place between the film and the substrate such that a new phase is formed that comprises both heavy and light atoms. This situation is shown diagrammatically on the left side of Fig. 2b, with the ideal scattering spectrum for such a sample shown on the right. Thus, ion backscattering permits analysis of reactions taking place at an interface thousands of angstroms (several 0.1μ 's) below the surface without destroying the sample. This is very useful for examining electrical contact behavior on semiconductor devices.

Analysis of Electrical Contacts to the RTG

Ion backscattering was employed to observe chemical reactions taking place at the tungsten-SiGe interface during accelerated aging. The experimental apparatus is diagrammed in Fig. 3. An incident beam of 1.5 MeV

Fig. 1 Ideal scattering spectra from targets containing two species of atoms A and B

Fig. 2 Ideal scattering spectrum; thin film of heavy element on substrate of light atoms, before and after thermal reaction

helium ions was used. The beam is generated and accelerated in a Van de Graaff accelerator, is bent in a magnetic analyzer and, after passing through a series of collimators, hits a target. Ions that are scattered at some angle θ are detected in a silicon surface-barrier detector and the resultant pulses, after suitable amplification, are stored in a multichannel pulse-height analyzer. The backscattering spectrum from a SiGe target covered with a 1200-Å (0.12 μ) layer of sputtered tungsten is shown in Fig. 4. This spectrum was taken before aging. The figure shows the strong, narrow scattering peak caused by the tungsten film, the scattering edges caused by the Si and Ge, and the "gap" between the low-energy side of the tungsten peak and the scattering edge caused by the Ge in the SiGe alloy. The Si and Ge backscattering yields correspond to 80 a/o Si and 20 a/o Ge.

Fig. 3 Ion-backscattering experiment arrangement

Fig. 4 Ion-backscattering spectrum; silicon-germanium target covered with 1200-Å layer of sputtered tungsten

The specimen was aged at 675°C for 20 hours in vacuum, and the backscattering experiment was repeated. The results, which typify the behavior of many aged samples, are shown in Fig. 5. The most obvious feature of the spectrum is the step in the low-energy side of the tungsten peak. This was caused by the presence of atoms in the film which are much lighter than tungsten atoms and which contribute to the slowing of helium ions in the film, but not to scattering in this energy region. The well-defined level of the step indicates that a compound layer has probably formed. The energy gap between the tungsten and the Ge edges is about as wide as before aging. From this observation we can say that there has been little intermixing of Ge and tungsten atoms; therefore the layer is not a tungsten-Ge compound.

The changed position of the Si edge indicates that Si has moved into the tungsten, and measurements of the relative yields from tungsten and Si atoms in the mixed region show that there are two Si atoms per tungsten atom. Thus, it is apparent that a layer of WSi_2 has been formed between what was the metallic tungsten contact and the SiGe semiconductor.

The positive slope of the scattering-yield-versus-energy curve immediately behind the Ge edge in Fig. 5 is somewhat unusual. Normally, yield curves decrease with increasing energy because of the energy dependences of elastic-scattering cross-sections and inelastic stopping cross-sections in this energy region. The positive slope

Fig. 5 Ion-backscattering spectrum; silicon-germanium target with tungsten film after aging

means that the amount of Si in the SiGe alloy, near the original interface, has been reduced. The depth of this depleted region is about 1000 Å (0.1 μ) and the average Ge content at the interface has been increased to about 25 a/o from 20 a/o. Owing to the very low diffusivity of Si in the SiGe alloy, it is very difficult for Si atoms to come from deep within the alloy to replace the surface Si atoms that have migrated into the WSi₂ layer.

The interpretation of what happens during high-temperature

aging is that Si in the SiGe alloy at or near the interface with the tungsten film diffuses into the tungsten and forms WSi₂. Loss of Si from the alloy can lead to void formation in the SiGe near the contact interface, and a reduction of contact area. This reduces the adhesion of the contact to the semiconductor and increases the electrical resistance of the contact. Scanning electron micrographs (SEM) confirm this interpretation. Samples of SiGe with a 3-micron-thick tungsten film were subjected to accelerated aging to the point of contact failure. After electrical and mechanical failure, the surfaces of the SiGe that had been in contact with the tungsten films were analyzed with the SEM. Surface features included many microscopic voids and "wormholes" caused by Si depletion.

Ion backscattering and scanning electron microscopy have supported the hypothesis that contact failure is a result of void formation at the interface when, at high temperatures, Si leaves the SiGe alloy and enters the tungsten film to form a WSi₂ reaction layer. This mechanism qualitatively explains the changes in both electrical resistance and mechanical bond strength. The backscattering data also have facilitated the quantitative determination of reaction-zone thickness for a given aging time and temperature. This information is important to interpret the results of accelerated-life-test electrical measurements made on actual thermopile samples with 3-micron-thick tungsten contacts, and to assure a service lifetime in excess of 8 years at operating temperature.

Heat-Source Development for the MC2730 RTG

A radioisotopic heat source, for which safety and long life are prime considerations, supplies thermal power for the RTG.

P. D. O'Brien and G. J. Jones

Introduction

Thermal power for the MC2730 RTG is produced by the alpha decay of ^{238}Pu , which is encapsulated in the MC2893 heat source in the form of ceramic particles. Requirements for the heat source are that:

- It must provide the thermal power (~6 watts) necessary to maintain a 25-milliwatt/channel output over the 8-year service life of the generator.
- Throughout its service life, it must be capable of surviving an accident during transportation, handling, or use without creating a significant radiological hazard.

The heat source and its development are described below.

Description

The MC2893 heat source (Fig. 1) incorporates 15 grams of PuO_2 , generates 6 watts of thermal power, and operates at a nominal temperature of 425°C . The fuel is contained within three layers of encapsulation, each a deep-drawn cylinder with a flat end-cap TIG* welded in place. The heat source is 2.3 cm in diameter and 2.3 cm long, and has a mass of 70 grams.

Fuel

The fuel is plutonium dioxide (plutonia) enriched to 80% in the ^{238}Pu isotope. It is used in the form of irregular

*Tungsten inert gas.

Fig. 1 MC2893 heat source

ceramic shards with a size range of 53 to 500 microns. This fuel was selected for the following reasons:

- Its relatively long half-life (88.4 years) minimizes thermal power degradation over the service life of the RTG.
- Its high specific power (0.4 watts/gram) and power density (2.22 watts/cc) permit a compact heat-source configuration.
- Its low rates of neutron and gamma emission minimize personnel exposure and radiation damage to nearby electronic components.

In other heat sources, ^{238}Pu has been used in the form of the metal and as a cermet (plutonia in a metal matrix), as well as in the form of a ceramic. The metal is unsuitable for the RTG because it melts at 641°C and, when molten, is extremely reactive with containment materials. Cermets have been used in large heat sources where high thermal conductivity is necessary to maintain acceptably small fuel temperature gradients. For small heat sources like the MC2893, the ceramic fuel form is preferred because of its relatively high specific power.

The primary decay mode of ^{238}Pu is alpha emission; the alpha particles are captured within the fuel material itself, producing heat and forming helium atoms. The radiation that escapes the heat source consists primarily of gamma photons that accompany alpha decay and neutrons produced in (α, n) interactions with oxygen and other light-element impurities in the plutonia. Cross sections for (α, n) interaction are much higher for ^{17}O and ^{18}O than for ^{16}O and, although the higher isotopes are present to the extent of only about 0.25% in atmospheric oxygen, neutron production in the fuel can be reduced from about 14,000 n/gm-sec to 3500-4000 n/gm-sec simply by "exchanging" the oxygen in the plutonia. This is accomplished by passing ^{16}O -rich oxygen through a bed of hot shards. With oxygen-exchanged fuel, the dose rate at the surface of a 6-watt heat source is about 1500 mrem per hour, of which roughly 1000 are from neutrons and 500 from gammas. Oxygen exchange has been specified for production heat sources.

During encapsulation, the fuel is mixed and reacted with elemental yttrium to reduce the stoichiometry of the fuel, producing an oxygen-to-Pu ratio of 1.8. This is done to improve compatibility with the encapsulation materials.

Encapsulation

The heat source design incorporates three layers of encapsulation with welded closures: an outer cladding, a strength member, and a liner. The outer cladding is designed to protect the inner layers from external contaminants, especially oxygen. Hastelloy C, a nickel-base alloy frequently used in chemical reaction vessels, was selected as the cladding material because of its high-temperature strength and stability, its corrosion resistance, and its formability and weldability.

The strength member is located between the cladding and the liner. The strength-member material must have good high-temperature creep resistance to withstand the effects of the high internal helium pressure that can be generated at fire temperatures, and sufficient ductility to survive high-velocity impact at the normal operating temperature. Refractory metal alloys, especially those based on tantalum and molybdenum, are the logical candidates. A tantalum alloy, T-111 (90% Ta, 8% W, 2% Hf), was chosen because of its superiority over molybdenum alloys in impact resistance.

The liner provides a physical barrier between the plutonia and the strength member and guarantees that the strength member weld will not be contaminated and weakened by plutonia during welding. T-111 was chosen as the liner material to minimize the number of different materials and therefore the number of potential material interactions.

Material Compatibility Tests

All materials were chosen on the basis of their beginning-of-life properties; material choices are valid, then, only as long as those properties do not change significantly. Therefore, it is necessary to assure that no detrimental interactions will occur either between materials or from external contaminants during service life. For this reason, compatibility testing constitutes a major part of the heat-source development activity.

Table I lists the compatibility test programs undertaken to date. Two of them, discussed below, illustrate the nature of the problems involved.

Min-K Outgassing

Min-K TE 1400 was chosen as the thermal insulation that encloses the heat source within the RTG because of its good insulating properties and its freedom from contaminants. Unlike most fibrous insulators, it contains no binders. However, because of its very large surface area, it can adsorb up to 2 wt % of water. Studies show that a much more vigorous bakeout than recommended by the manufacturer is required to remove the water, and that exposure to air following bakeout cannot be tolerated. The dried thermal insulation was found to readsorb a significant fraction of water from low-humidity ambient air in less

than an hour. In the sealed RTG, water from improperly baked-out Min-K could seriously degrade the thermopile by oxidizing the tungsten contacts. Also, reaction of the water with the heat-source cladding could cause hydrogen embrittlement of the T-111, reducing the impact resistance of the heat source. A Min-K bakeout procedure was developed to assure that water is removed that otherwise would be released at normal RTG operating temperatures. This procedure has been used since the first MC2730 RTG was built in 1971.

Fuel/T-111 Compatibility

A test program was designed to verify that reducing the stoichiometry of the plutonia is effective in inhibiting interactions between the fuel and the liner. In an earlier test conducted by Mound Laboratory, capsules containing plutonia fuel and yttrium powder were exposed to a temperature of 1200°C for long periods of time. Results were compared with those for control capsules in which no yttrium was used. The T-111 in the control capsules became embrittled from reacting with oxygen from the plutonia while the capsules containing the yttrium powder were virtually unaffected.

On the basis of this preliminary experiment, a test matrix was developed for the purpose of studying the kinetics of fuel/T-111 interactions in the temperature range 500 to 1100°C and the effect of fuel stoichiometry on these interactions. The matrix consists of seven different combinations in which sample configuration, amounts of yttrium, and time-at-temperature are varied. The tests involve 120 test samples and cover aging times from 60 days to 2 years.

Early data indicated that the effect of the yttrium was less than desired. This was traced to the fact that yttrium develops an oxide coating from exposure to air which subsequently inhibits the plutonia/yttrium reaction at the operating temperature of the heat source. Therefore fuel reduction is too slow to provide adequate protection for the T-111 liner. To overcome this problem, a pretreatment process was developed that drives the plutonia/yttrium reaction to completion. In this process, the capsules are heated to 1350°C in a vacuum for 1 hour. The PuO₂ reacts with the yttrium so that the ratio of oxygen to Pu averages about 1.75. The heat sources are pretreated before the cladding is added, since Hastelloy C

TABLE I. MC2893 Compatibility Programs

Test	Purpose	Results
1. Min-K TE 1400 outgassing	To determine adsorption characteristics of Min-K	Adsorption determined to be a critical matter. High-temperature bakeout specified.
2. Min-K TE 1400 Hastelloy-C/T-111	To determine material interactions	Effectiveness of high-temperature bakeout verified.
3. Hastelloy-C/T-111; Ni/Ta	To determine material interactions	No problems found. Analysis of diffusion data in process.
4. Yttrium outgassing	To determine existence of contaminant residues	None found.
5. Yttrium oxidation	To determine extent and rate of oxidation	Determined low-temperature (<1000°C) oxidation rates.
6. PuO ₂ outgassing	To determine extent of contaminants and volatile oxides	Tests planned.
7. T-111/fuel	To provide definitive data on heat-source safety and insights into oxygen-transport mechanisms	Effectiveness of reducing stoichiometry of plutonia for inhibiting material interactions verified. Tests continue.
8. External contaminants	To determine effects and sources of O ₂ , N ₂ , and H ₂	Leak checks introduced to control O ₂ and N ₂ ; determination of H ₂ effects in process.
9. H ₂ /T-111	To determine effect of H ₂ on T-111 between 300 and 500°C (cladding does not protect against H ₂)	In process; method of control determined if needed.

melts at about 1300°C. Although longer-term confirmatory tests are still in process, it is believed that pretreatment will prevent degradation of the T-111 liner and strength member for times well beyond the design life of the heat source.

Safety Evaluation

Evaluation of the heat source to assure that it meets safety requirements involves material compatibility (as discussed above), resistance to rupture from internal helium pressure in an accidental fire, and ability to survive impact during transport, handling, and use.

A fundamental design requirement is that the heat source be able to withstand the effects of the maximum helium pressure that could exist in an end-of-life heat source exposed to a 1000°C fire for 1 hour. To demonstrate this capability, 25 strength members, without liners or cladding, were subjected to stress-rupture tests. The strength members were pressurized with high-purity helium and heated to 1000°C, where they were held until rupture occurred. The tests indicate that the heat-source design is adequate. Additional tests to better define burst-pressure variability and to provide an assessment of the temperature dependence of rupture pressure are in process.

The requirement to survive impact has been translated into a specification that no release of fuel should result from a 150-m/sec impact against a hardened tool-steel surface of the bare heat source in any attitude and at its normal operating temperature. Impact tests were performed in air gun facilities at Mound Laboratory, LASL, and Sandia. After preliminary tests to establish the most damaging impact angles, 15 heat sources, loaded with thorium shards to simulate the fuel, were tested at impact velocities up to 300 m/sec. Lowest capsule-rupture velocities resulted from side-on impacts. A small amount of fuel simulant was

released from capsules in the 90°, 203 m/sec and 45°, 296 m/sec impacts (Fig. 2). Three plutonia-fueled capsules were tested at impact velocities up to 150 m/sec at the LASL hot impact facility; there was no release of fuel. The heat sources were returned to Mound Laboratory for determination of the weight fraction of fuel that had been reduced to respirable size (<3.4 microns) by the impact.

Pelletized plutonia is being evaluated as an alternative fuel form. The evaluation consists primarily of particle-size analysis after impact, vibration, and aging. Pellets would replace shards only if it were demonstrated that pellets offer a safety advantage; i.e., if significantly fewer respirable particles would be released in an accident. Preliminary test results indicate that this is not the case.

It is also required that the heat source not contribute more than 10% to the radiological hazard in the event of an accidental detonation of nearby high explosive. Experiments are now underway to develop shielding to be added at the external surface of the RTG. No modification of the heat source itself is being considered for this purpose.

Although some compatibility test data will continue to be generated into FY 76, the success of the pretreatment concept has greatly reduced concern about long-term material compatibility. By October 1973, both the pressure-rupture and impact-test programs will have been completed. On the basis of present test data, the mechanical design of the heat source appears satisfactory. The final heat source configuration will be established on a schedule compatible with present production plans.

Fig. 2 Heat sources after impact tests

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