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FINAL REPORT FOR
SILICON-GERMANIUM/GALLIUM PHOSPHIDE MATERIAL
IN
HIGH POWER DENSITY THERMOELECTRIC MODULES

Contract Number 4-X20-0520M-1
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Prepared For
Los Alamos National Laboratory
Los Alamos, New Mexico

Prepared By
Synkal Corporation
Sunnyvale, California

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FINAL REPORT FOR
SILICON-GERMANIUM/GALLIUM PHOSPHIDE
IN HIGH POWER DENSITY THERMOELECTRIC MODULES

I. INTRODUCTION

This is the final report of work performed by Syncal Corporation under contract to the Los Alamos National Laboratory on the characterization of an improved silicon-germanium alloy and the fabrication of thermoelectric devices. The improved silicon-germanium alloy makes use of a small addition of gallium phosphide to n- and p-type 80 a/o Si - 20 a/o Ge alloy. The addition of gallium phosphide reduces the thermal conductivity of the material, thereby increasing its figure-of-merit and its consequent potential for conversion efficiency. The thermoelectric devices fabricated by Syncal Corporation as a part of the work performed on the contract include so-called multicouples intended for use in Radioisotope Thermoelectric Generators (RTGs) and ring-type thermoelectric modules intended for use with nuclear reactor heat sources.

This report summarizes the effort in the material as well as the device areas and discusses individual phases of each area in considerable detail. The results obtained on the program, as reported here, are considered significant and hopefully form the basis for further effort.

II. IMPROVED SILICON-GERMANIUM ALLOY

One important aspect of the program was the characterization of the improved silicon-germanium alloy with gallium phosphide additions. The characterization involved the study of the so-called polarity reversal phenomenon previously found to occur in some cases in the p-type alloy, the generation of electrical data for the material as a

function of time and temperature, and the investigation of the sublimation characteristics of the material in high temperature vacuum operation. Additionally, materials work also involved the investigation of the effect of an increased boron concentration in the p-type alloy in an effort to eliminate the polarity reversal phenomenon and the preparation of one inch diameter compacts of the material for the fabrication of unicouples for the General Electric Company. Finally, the characterization of the material involved the preparation and supply of test samples to the Thermophysical Properties Research Center at Purdue University for independent determination of thermoelectric properties.

A. Polarity Reversal Phenomenon

On previous JPL and LANL contracts, Syncal Corporation has developed an improved silicon-germanium alloy by making small additions of gallium phosphide to the material in order to reduce its thermal conductivity. Inasmuch as gallium phosphide appears to dissociate at material preparation temperatures in excess of 1100°C, it has been found that both n- and p-type silicon-germanium alloys with gallium phosphide additions prepared at temperatures higher than 1100°C exhibit n-type conductivity characteristics. This phenomenon is explained by the fact that phosphorus possesses a considerably greater solid solubility than gallium in silicon-germanium alloys and, upon dissociation, gallium phosphide provides an excess of n-type carriers to the material. Annealing of the material at temperatures below 1100°C promotes recombination of the gallium and phosphorus atoms and therefore results in the removal of the excess n-type carriers released during the preparation process.

In view of this, two possible methods exist for the preparation of p-type silicon-germanium alloys containing gallium phosphide. The first involves the preparation of the material at temperatures higher than 1100°C with a subsequent lower temperature annealing step that stabilizes the material at its final p-type electrical resistivity level. The second involves the preparation of the material at temperatures lower than 1100°C.

A major portion of the effort devoted to material investigations on the current contract involved the study of the polarity reversal phenomenon encountered with p-type silicon-germanium alloys containing small amounts of gallium phosphide; it should be noted that in the n-type material, the release of extra carriers from dissociated gallium phosphide further enhances the n-type nature of the material and, therefore, has no deleterious effect on the material. A large number of test samples having the dimensions of 0.5 inch diameter and 0.5 inch height were hot pressed. Each sample represented a different combination of either gallium phosphide concentration or the hot pressing parameters of pressure, temperature and time. In all cases the material consisted of 325 mesh particle size p-type 80 a/o Si - 20 a/o Ge alloy that had been doped with 0.5 atomic percent of boron. Table I shows a listing of the samples prepared, along with values for the pertinent parameters of gallium phosphide concentration or preparation parameters.

Depending on the gallium phosphide concentration and the preparation parameters, the materials shown in Table I exhibited a variety of thermoelectric properties, including both n- and p-type polarities.

TABLE 1

Hot Pressing Parameters

<u>Sample</u>	<u>m/o GaP</u>	<u>Pressure-psi</u>	<u>Temperature-°C</u>	<u>Time-Hours</u>	<u>Comments</u>
3	5.0	30,000	1075	1.0	
4	5.0	30,000	1225	1.0	
6	5.0	30,000	1175	1.0	
8	5.0	30,000	1250	1.0	
9	5.0	30,000	1200	1.0	
11	7.5	30,000	1200	1.0	
12	5.0	30,000	1225	1.0	
14	0	30,000	1225	1.0	
15	1.7	30,000	1225	1.0	
16	3.3	30,000	1225	1.0	
17	5.0	30,000	1125	1.0	
19	6.7	30,000	1225	1.0	
21	5.0	30,000	1000	1.0	
22	5.0	30,000	1200	1.0	
23	5.0	30,000	1150	1.0	
24	5.0	30,000	1100	1.0	
25	5.0	30,000	1100	1.0	
26	5.0	30,000	1050	1.0	
27	5.0	30,000	1025	1.0	
29	5.0	30,000	975	1.0	
31	5.0	30,000	950	1.0	
32	5.0	30,000	950	2.0	
33	5.0	30,000	950	3.0	
36	5.0	30,000	1000	1.0	
37	5.0	30,000	1000	2.0	
38	5.0	30,000	1000	3.0	
41	5.0	20,000	1000	1.0	
42	5.0	25,000	1000	1.0	
43	5.0	35,000	1000	1.0	
46	5.0	30,000	1000	1.0	Anl. 1 Hr./900°C
47	5.0	30,000	1000	1.0	Anl. 1 Hr./950°C
48	5.0	30,000	1000	1.0	Anl. 1 Hr./1000°C

Figure 1 shows a plot of the Seebeck coefficients of the test samples as a function of electrical resistivity. It is noted in Figure 1 that all of the data lie on a fairly well defined curve that includes both n- and p-type polarities. A curve of the type shown in Figure 1 is typical of doped semiconductors and is known as the so-called thermoelectric-loop. A lot of the test samples depicted in Figure 1 were subjected to vacuum annealing at 900°C and it was found that the characteristics of any given test sample tended to move along the thermoelectric-loop in a counterclockwise direction as a function of annealing time. This means that material exhibiting n-type polarity characteristics in its as-prepared state tends to become less n-type with annealing and eventually reverts to p-type polarity with ever decreasing values of electrical resistivity. After long annealing times, the material asymptotically approaches electrical resistivity values of the order of two milliohm centimeters. This phenomenon is illustrated in Figure 2 in terms of the electrical resistivity of selected test samples as a function of annealing time. The various test samples depicted in Figure 2, represent various material preparation temperatures. It is noted that the higher the preparation temperature, the more n-type the material is in its as-prepared state. With reference to Figure 1, this means that the material has a longer path along the thermoelectric-loop before attaining its final p-type electrical resistivity value. All of the test samples shown in Table 1 that were subjected to annealing at 900°C were periodically cycled to room temperature for electrical resistivity and Seebeck coefficient measurements. The data obtained

Figure 1

Figure 2

on these test samples as a function of time are tabulated in Table 2*; it should be noted that the data in Figure 1 represent a portion of the data tabulated in Table 2. Based on the data shown in Table 2, it is concluded that p-type silicon-germanium alloy with a small addition of gallium phosphide may not initially possess desired characteristics, but that such characteristics are attainable after the annealing of the material. Depending on the preparation parameters of the p-type material, an annealing step may therefore have to be an integral part of material preparation.

B. Annealing Characteristics Of The Material

In order to assess the stability of both n- and p-type silicon-germanium alloy with gallium phosphide additions, a number of test samples of both type alloys were prepared by hot pressing. Samples of each type material were subjected to vacuum annealing at temperatures in the range of temperatures of 500 to 1000°C. Periodically the test samples were cooled to room temperature and measurements of electrical resistivity and Seebeck coefficient were conducted. The results of this procedure are shown in Figures 3 to 6.

Figure 3 shows plots of electrical resistivity as a function of time for the n-type material. The corresponding data for the Seebeck coefficient are shown in Figure 4. The electrical resistivity and Seebeck coefficient data for the p-type material are shown in Figures 5 and 6. It is noted that the n-type material undergoes some change in terms of increased values of Seebeck coefficient and electrical resistivity as a function of time. The change is of an exponential nature and asymptotically appears to approach equilibrium values. The biggest change in the n-type material occurs at the lower end of the temperature range used

*See Appendix

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K·E 10 X 10 TO THE CENTIMETER 18 X 25 CM.
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in the annealing studies. In the p-type alloy, some changes in terms of increased values of electrical resistivity and Seebeck coefficient are also noted. In this case, however, the changes occur at temperatures intermediate to the range of temperatures utilized in the annealing study. In fact, at the highest temperatures, decreasing values of electrical resistivity and Seebeck coefficient were observed. These decreasing values are probably simply a continuation of the results of an annealing process as described in the preceeding section.

Based on the results of the annealing studies, it appears that both the n- and p-type silicon-germanium alloys with gallium phosphide additions are relatively stable as regards their electrical properties. In fact, a comparison to the time behavior of the same properties of standard silicon-germanium alloy indicates that the two materials are not dissimilar in this regard.

C. Alternate P-Type Material

In view of the polarity reversal process discussed in Section A and in view of the fact that the preparation of p-type silicon-germanium alloy with gallium phosphide addition may require a time consuming annealing step, it was decided to investigate the effect of the addition of boron to the material in an effort to eliminate the polarity reversal phenomenon. The rationale for this is that extra boron within the material will neutralize the phosphorus released from gallium phosphide upon the dissociation of gallium phosphide at elevated material preparation temperatures.

As a consequence, three samples were prepared with additional boron over and above that contained within standard silicon-germanium alloy. It should be noted that the standard material contains a nominal concentration of 0.5 a/o of boron. The three samples prepared with the additional boron contained in addition to the boron within the starting material additional amounts of 0.5, 1.0 and 1.5 a/o of boron. This means that the three samples effectively contained 1.0, 1.5 and 2.0 a/o of boron. The samples were prepared by hot pressing at 1000°C according to the standard preparation process. Each of the three samples was subjected to room temperature measurements of electrical resistivity and Seebeck coefficient. The results of these measurements are shown in Table 3.

TABLE 3

Atomic Percent Boron	Electrical Resistivity m Ω -cm		Absolute Seebeck Coefficient μ v/°C	
	Before Anl.	After Anl.*	Before Anl.	After Anl.*
1.0	1.52	0.82	120	91
1.5	1.16	0.53	115	75
2.0	1.27	0.41	111	64

*Annealed for one hour at 1200°C

It is noted in Table 3 that all three samples contain values of electrical resistivity considerably lower than those obtained with material not containing additional boron, even after prolonged annealing of such material. Typically, material not containing additional boron tends to asymptotically approach values of electrical resistivity of about two milliohm centimeters. Based on these results, it is concluded that the addition of boron to the p-type material does

alleviate the polarity reversal process and may simplify p-type material preparation, i.e. it may eliminate the necessity of an annealing step as a part of the material preparation process. It should be noted that annealing of the three test samples at temperatures as high as 1200°C, did not result in the reversal of the polarities of the test samples from p-type to n-type. The addition of boron to the material therefore, appears to truly compensate the extra phosphorus released from gallium phosphide as a result of dissociation. Finally, it is not known why the test sample containing 2 a/o boron exhibits an electrical resistivity value slightly higher than the sample containing 1.5 a/o of boron.

D. Sublimation Studies

Sublimation studies conducted on the present program have concerned themselves with both the uncoated silicon-germanium alloys with gallium phosphide additions and such alloys when coated with a thin layer of silicon dioxide. A number of samples of uncoated as well as coated material have been tested for weight loss as a function of time and temperature. The results of all of the sublimation studies are summarized in Figure 7 in terms of weight loss as a function of temperature. Shown also in Figure 7 are the weight loss rates for pure silicon and pure germanium and previously obtained results on standard silicon-germanium alloys at Sandia Laboratories. It is noted that the silicon-germanium alloy with a gallium phosphide addition has a weight loss quite similar to that expected of standard silicon-germanium alloy. It is also noted that coating the material with a thin (0.002 to 0.005 inch) layer sub-

stantially reduces the weight loss of the material. Of the various sublimation rate data shown for the silicon dioxide coated material in Figure 7, the two data points exhibiting the highest sublimation rates represent material in slice form which only had the large surfaces coated with silicon dioxide. Because the edges of the slice were uncoated, a higher sublimation rate due to the sublimation of the bare material may be anticipated. In fact, assuming a negligible loss rate for the material from the two silicon dioxide coated surfaces and assuming a surface area from which sublimation takes place equivalent to that of the edges of the material, a calculation shows that the sublimation of the test samples represented by the two highest sublimation rate data points for the coated material in Figure 7 is quite similar to that of the bare material. It is thus concluded that those particular data points pertain to the sublimation of the uncoated material at the edges of the coated samples. The remainder of the data shown in Figure 7 for the coated material, very likely represent either the sublimation of the coatings themselves or the sublimation of the material through the coatings or a combination of both. It is quite apparent in Figure 7 that a substantial reduction in the sublimation rate of the material can be obtained by the application of a thin silicon dioxide coating to the material.

E. Thermal Conductivity Measurements

At the request of the Department Of Energy, Synkal Corporation prepared n- and p-type 80 a/o Si - 20 a/o Ge alloy with gallium phosphide additions for independent thermal conductivity determinations at the

Thermophysical Property Research Center at Purdue University. The material prepared for these measurements contained five mole percent of gallium phosphide and was prepared from 325 mesh powders. The powders were hot pressed at 1000°C for one hour at a pressure of 35,000 psi. These hot pressing parameters are typical of material with near optimum thermoelectric properties, as determined previously on the present program. Both the n- and p-type samples, having lengths of about 0.7 inch and diameters of about 0.5 inch, were subjected to detailed thermoelectric property measurements at Syncal Corporation. These measurements included determinations of electrical resistivity, Seebeck coefficient and thermal conductivity as a function of temperature from room temperature to about 700°C. The results of the measurements of the electrical properties are shown in Figure 8.

At the completion of the measurements at Syncal Corporation, the two test samples were sliced into 0.020 inch thick discs and two discs of each polarity type material were submitted to Purdue University for independent thermal conductivity determinations. These determinations are made by means of the measurement of thermal diffusivity as a function of temperature by means of a laser pulse technique and the separate measurement of specific heat. The results of the determinations made at Purdue University are shown in Figures 9 and 10 in terms of thermal conductivity as a function of temperature. Superimposed on Figures 9 and 10 are the previously determined thermal conductivity values on the same test specimens at Syncal Corporation. Also superimposed on Figures 9 and 10 are the standard thermal conductivity values for n- and p-type 78 a/o Si - 22 a/o Ge alloy. It is noted in Figures 9 and 10 that

Figure 8

Figure 10

the thermal conductivity determinations at Syncal Corporation very closely approximate those performed at Prdue University. Inasmuch as the two sets of measurements are not only performed at different organizations but also represent completely different measurement techniques, it is believed that the close agreement between the two sets of data is quite significant. A comparison of those data to those of the standard silicon-germanium alloy indicates that the material containing gallium phosphide possesses thermal conductivity values significantly lower than those of the standard material.

F. Preparation Of Large Compacts

On two separate occasions on the present program, the Department Of Energy requested that Syncal Corporation provide silicon-germanium alloy with gallium phosphide addition to the General Electric Company for the fabrication of so-called unicouples. Inasmuch as the unicumple thermoelement dimension is such that it cannot be fabricated from the small one-half inch diameter pellets typically hot pressed at Syncal Corporation, it was necessary to perform the pressing in a bigger die. This was done in a TZM die with an opening such that compacts of one inch diameter result. On each of the two occasions during which material was pressed for the General Electric Company, a total of six n-type and six p-type compacts were hot pressed. In some cases, the difference in the thermal expansion characteristics of TZM and the silicon-germanium alloy resulted in cracks within the compacts. In all cases, however, it was decided that the compacts were usable because unicumple thermoelements could be machined from the

compacts such that there was no interference from the cracks. The material hot pressed for the General Electric Company utilized the same hot pressing parameters as those previously used (See Section E). The only difference between this material and that previously prepared was that the amount of gallium phosphide in the p-type material was reduced from five mole percent to 3.5 mole percent and the boron concentration was increased from 0.5 to 2.0 atomic percent. This change was made in view of the findings that the addition of boron to the p-type material eliminates the polarity reversal process previously observed (See Sections A and C). It must be noted that no detailed thermoelectric property measurements were performed on the material - prepared and submitted to the General Electric Company. It was anticipated that such measurements would be performed at the General Electric Company.

III. MULTICOUPLES FOR ISOTOPIC POWER SYSTEM

A portion of the present program was concerned with the design, fabrication and test of multicouples for radioisotope thermoelectric generators (RTGs). A design of such a multicouple was formulated and submitted to the Department Of Energy for approval. The design was approved and a number of multicouples of that design were fabricated on the present program. The design of the multicouple is shown in Figure 11. It should be noted that Figure 11 gives all the materials of construction and the dimensions of all multicouple components. The multicouple represents a high voltage design in which each multicouple produces in excess of four volts of load voltage when operating at its peak power point of nearly 1.5 watts. These performance values presuppose the

SYNICAL MULTICOUPLE

Height of Multicouple - 0.750"
 Thermoelement Height - 0.394"
 Number of Thermoelements - 42
 Thermoelement Cross-Section -
 0.037" x 0.045"

Cold Side
Shoe Pattern

Hot Side
Shoe Pattern

Figure 11

operation of the multicouple between hot and cold side operating temperatures of 1000 and 300°C, respectively. A unique feature of the multicouple is the total enclosure of the thermoelectric material within silicon dioxide. Based on the results of sublimation studies, it may be anticipated that this reduces sublimation of the thermoelectric material by an order of magnitude.

A number of multicouples of the design shown in Figure 11 were fabricated on the present program. The fabrication sequence consisted of the slicing of n- and p-type silicon-germanium alloy with gallium phosphide addition into slices having thicknesses equal to the width of one side of the final thermoelement width, the bonding of the slices by means of layers of silicon dioxide, the slicing of the bonded composite slices in directions perpendicular to the individual slices and the bonding of the composite slices by means of layers of silicon dioxide. Boron doped silicon contact pads were bonded in an alternating manner on the two faces of the finished thermopiles such that all of the thermoelements within the thermopile are electrically connected in series. In the case of the two end-most thermoelements, the silicon contact pads on the cold side extend slightly beyond the edges of the thermopile. It is to this portion of the cold side contact pads that lead wires are attached. A molybdenum heat receptor plate is bonded through a layer of silicon dioxide to the hot face of each thermopile. Another molybdenum plate, slightly bigger than the thermopile cross-section, is bonded to the cold side of the thermopile. A box-like stress relief structure is brazed to the latter molybdenum plate. The stress relief structure is subsequently attached by means of a bolt and nut arrangement to a radiator cooling plate. It should be noted that

the molybdenum plates at the hot and cold faces of each thermopile possess brazed tungsten transition members that are placed adjacent to the thermopile. The reason for the transition member is the desire to match the thermal expansion coefficient of the thermopile to the metal to which the thermopile is bonded; the thermal expansion coefficients of silicon-germanium alloy and tungsten are very closely matched.

Initial testing of the first three multicouples indicated difficulties with the test set-up because when the multicouples were heated to hot side temperatures of 1000°C, it was found that their cold sides attained temperatures considerably higher than those intended. Rather than the 300°C design cold side temperature, the multicouples operated at cold side temperatures of about 600°C. In view of this, the test set-up was redesigned such that better cooling of the cold sides of the multicouples is possible. When the test was restarted, it was noted that at the design hot side temperatures of 1000°C, the cold sides of the multicouples operated reasonably close to the desired temperature of 300°C.

The results of the multicouple testing are shown in Figures 12 and 13 in terms of the performance parameters of open circuit voltage, internal resistance and power output and the hot and cold side temperatures as a function of time. It should be noted that the indicated temperatures are measured with thermocouples located at the center of the molybdenum heat collector and the inside surface of the cold side stress alleviation member. As such, the difference between the indicated temperatures is greater than the temperature difference across the active thermoelectric material within the multicouples. It is estimated that temperature drops of the order of 20 to 30 degrees Centigrade exist between the thermocouple locations and the hot and

cold junctions. It is noted in Figures 12 and 13 that the performance of the multicouples is fairly stable, except for an initial adjustment in internal resistance and open circuit voltage. This adjustment is similar to that seen for the bulk material in Figures 3 to 6 and very likely represents a form of dopant precipitation previously noted for plain silicon-germanium alloys. The several discontinuities in the data represent heater replacement, following heater burnout. It should be noted that Kanthal wire heaters were initially used and it was found that heaters of that type are subject to frequent failure. In view of this, the heaters were replaced with those using high temperature molybdenum wire and heater failure became considerably less frequent towards the end of the total test time of the more than 5000 hours on the present program.

It is noted in Figures 12 and 13 that the performance of the multicouple is quite stable. Although slight differences exist in the performance of the three multicouples, these differences can be ascribed to differences in operating temperatures. It should be noted that inasmuch as all three multicouples are heated by the same heater, it has not been possible to individually adjust the temperatures of the three multicouples such that they would all operate at the same temperatures. A normalization of the data, however, indicate a close correlation between the performances of the three multicouples.

In order to compare the performance of the three multicouples against their predicted performance on the basis of material properties, the conversion efficiency of each multicouple was calculated as a function of the temperature difference across the multicouple when the multicouple operates at a hot junction temperature of 1000°C. The actual measured temperature differentials across the three multi-

couples were corrected for the extraneous temperature drops at the hot and cold sides of the multicouples. The correction was based on analytically estimating the extraneous temperature drops. It was found that the correction is fairly small, being of the order of 20°C at both the hot and the cold sides. The analytically predicted conversion efficiency of the multicouple and the actual results for the three multicouples being tested are shown in Figure 14. Also shown in Figure 14 is the calculated conversion efficiency of a multicouple based on standard silicon-germanium alloy. It is noted not only that the addition of gallium phosphide to silicon-germanium alloys is analytically predicted to possess a higher conversion efficiency, but that the conversion efficiencies of the three multicouples are fairly close to those analytically predicted. The slight deviation of the calculated curve and the actual results may be ascribed to a combination of several factors. For example, the extraneous temperature drop at the hot and cold sides of the multicouple may be slightly greater than analytically determined. If this were the case, the actual data points shown in Figure 14 would be shifted closer to the analytical curve. It is also possible that the material within the three multicouples possesses properties slightly different from the properties used to generate the analytical curve.

In addition to the three multicouples initially fabricated and tested, a number of other multicouples were also fabricated with the intent of testing these additional multicouples in four-multicouple test modules in order to establish the conversion efficiency of the multicouples in an actual test device. The four-multicouple test structures consist of three inch cube boxes made of aluminum. Four multicouples are placed on the inside of the test structure such that they are attached to four adjacent sides of the

Figure 14

structure. A heater is placed in the center of the test structure. All of the void volume within the test structure is filled with multifoil insulation consisting of alternating layers of molybdenum foil and quartz cloth. Thermocouple wires and heater leads are taken out of the test structure through penetrations in the multifoil insulation at the top of the structure. The first such structure to be fabricated on the present program was subjected to performance tests.

As a consequence of the performance test, it was found that when the hot sides of the multicouples were heated to the 1000°C design temperature, the cold sides operated at considerably higher temperatures than 300°C. More specifically, if the four-couple test modules were operated under conditions such that the center of the heat collector of each multicouple was at an effective temperature of 1030°C, it is estimated that the average hot junction temperatures of the multicouples were 1000°C. Under these conditions it was found that the outer aluminum case operated at about 475°C. This means that the average cold junction temperatures of the multicouples were about 500°C. Under these conditions, each multicouple produced approximately 0.7 watts of electrical power and the total heat input to the four-couple module was in the range of 80 to 90 watts. The overall conversion efficiency of the module was therefore of the order of 3.0 to 3.5 percent. This range of conversion efficiencies is only about half of the theoretical efficiency of the multicouple operating under these conditions. The reason for it is that the relative area of thermal insulation to that of the thermoelectric material within the module is excessive and even with the best thermal insulation it is not possible to reduce heat losses to less than 50 percent of the total heat input to the module. It is, therefore, the configuration of the four-couple module

itself that prohibits the performance of accurate efficiency measurements. It should be noted that the very high cold side temperature of 475°C noted for the outer case of the four-couple module results from the relatively low emissivity of the aluminum used for the material of the outer cases. If the emissivity of the outer case were artificially enhanced, the cold sides would operate at lower temperatures. For a given heat input, however, the hot side operating temperatures would be correspondingly lowered. If it were desired to maintain the hot side temperatures at 1000°C , greater amounts of input power would be required. The net result would be a somewhat greater power output of the device. The efficiency of the device would also be slightly greater, but it would still only represent about 50 percent of the theoretical efficiency because the relative amounts of heat flowing through the thermoelectrics and those flowing through the thermal insulation would not be appreciably affected. The conclusion made by Syncal Corporation on the basis of its experience with four-couple modules on the current program is essentially identical to that previously formulated by JPL on the Multi-Hundred-Watt program.

In order to illustrate the difference between measured efficiency of multicouples in a four-couple module and the theoretical efficiency, Figure 15 shows a plot of the conversion efficiency of standard silicon-germanium alloy and the alloy with gallium phosphide additions as a function of the temperature difference across the material, when the material operates at a hot side temperature of 1000°C . Figure 15 shows the conversion efficiency of a four-couple module in two instances. First, shown for a 500°C temperature difference is the uncorrected conversion efficiency of a four-couple module. Second, the conversion efficiency of a four-couple module operating across the same temperature

differential is shown when the data are corrected for heat losses through the thermal insulation. It is noted that in the first case, the conversion efficiency is quite low. In the second case, the conversion efficiency is only slightly below the theoretical curve for the material. This demonstrates the difficulty of obtaining accurate conversion efficiency measurements from four-couple test modules. It should be noted that the 500°C temperature differential applies to the case of the four-couple test module operating at a cold side temperature such that the individual cold junctions of the multicouples are at average temperatures of 500°C.

In view of the finding that accurate conversion efficiency measurements are not possible with four-couple test modules, it is suggested that such measurements be performed in the future in a calorimetric test set-up in which heat flow can be closely monitored. Such a test set-up is, for example, represented by a comparative thermal conductivity apparatus in which heat flow is carefully controlled. If such a test set-up is used for efficiency measurements, it will not be possible, however, to utilize a multicouple test structure such as fabricated on the present program. This structure cannot possess a heat receptor plate and a flexible stress relief member if it is desired to maintain axial heat flow during measurement and thereby eliminate radial heat losses.

IV. THERMOELECTRIC MODULES FOR REACTOR POWER SYSTEM

The design of a conductively coupled thermoelectric module to a heat pipe in a reactor power system underwent various design iterations on the present program before the formulation of a final design. It should be recalled that on a previous program, the module design involved compressive loading of various component interfaces. On the present

program the design utilizes all metallurgically bonded interfaces. The design assumes a molybdenum heat pipe to which is bonded a corrugated molybdenum stress relief member. Bonded to the stress relief member is a molybdenum insulator backing. The insulator is plasma sprayed alumina which is attached to the insulator backing. Thermocouples made of n- and p-type thermoelements are bonded to the alumina insulator through a thin layer of silicon dioxide; the thermoelectric material used in the thermocouple is n- and p-type 80 a/o Si - 20 a/o Ge alloy with a small addition of gallium phosphide; legs are interconnected at the hot side by means of a boron doped silicon contact pad. On the cold side of the thermocouple are boron doped silicon pads that do not interconnect the two thermoelements, but rather contain output lead wires. The cold side of the thermocouple is bonded to a radiator heat pipe through a thin layer of silicon dioxide.

A number of bond tests were conducted between the various interfaces of the all metallurgically bonded thermocouple in order to assess the feasibility and quality of the various interfaces. It was discovered that the use of molybdenum adjacent to the thermoelectric material resulted in the cracking of the thermoelectric material and for this reason it was proposed that molybdenum in such locations be replaced with tungsten. Additional tests indicated that this material replacement effectively eliminated cracking problems. The final thermocouple design therefore uses a tungsten insulator backing and a tungsten transition member between the thermocouple cold junction and the molybdenum cold side radiator heat pipe.

Detailed performance analyses were conducted for the performance of the all metallurgically bonded thermoelectric

module. These analyses included those pertaining to temperature distribution within the module. The results of the analyses are shown in Figures 16 to 20 in terms of module performance and temperature distribution as a function of heat pipe operating temperature. Figure 16 shows plots of module power output and load voltage as functions of heat pipe operating temperature. It should be noted that the data shown in Figure 16 presuppose the operation of the module under a load condition in which the load resistance is 1.2 times the internal resistance of the module. It should be noted that this approximately corresponds to the maximum efficiency operating point of a thermoelectric device. The total heat input to the module as a function of the heat pipe operating temperature is shown in Figure 17. The conversion efficiency of the module, which represents the quotient of the power output curve in Figure 16 and the heat input curve in Figure 17, is shown as a function of heat pipe operating temperature in Figure 18. It should be noted that the design operating temperature of the heat pipe in Figures 16 to 20 is 1127°C.

The temperature distribution within the module as a function of heat pipe operating temperature is shown in Figure 19 in terms of the heat pipe, the hot junction, the cold junction and the cold side heat pipe surface temperatures. It should be noted that the temperature distribution values shown in Figure 19 are based on the assumption that the cold side heat pipe surface always operates at 520°C. Moreover, it is assumed that the radiator operates at a temperature of 500°C and that a 20°C temperature differential exists between the radiator and the cold side heat pipe surface for all hot side heat pipe operating temperatures. Although it is noted in Figure 19 that the bulk of the total

K&S 1/4" x 1/4" x 1/4" INCHES 1/4" x 1/4" x 1/4" INCHES
16 X 25 CM. KEUFFEL & ESSER CO. MADE IN U.S.A.

Power Output - watts

1500

1000

500

150

100

50

Voltage

Power

Load Voltage - volts

Heat Pipe Temperature - °C

Figure 16

K&E 10 X 10 TO THE CENTIMETER 40 1310
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

Heat Input - watts

25,000

20,000

15,000

10,000

5,000

900

Heat Pipe Temperature - °C

1000

39

1100

1200

Figure 1

K·E 10 X 10 TO THE CENTIMETER 40 131U
18 X 25 CM.
MADE IN U.S.A.
KEUFFEL & ESSER CO.

Conversion Efficiency-percent

10
9
8
7
6
5
4
3
2
1
0

1000

1100

1200

Heat Pipe⁴⁰ Temperature-°C

Figure 12

K&E 10 A 10 TO THE CENTIMETER 40 131U
18 X 25 CM. MADE IN U.S.A.
KEUFFEL & ESSER CO.

Temperature - °C

1300
1200
1100
1000
900
800
700
600
500
900 1000 1100 1200

Heat Pipe Temperature - °C

Heat Pipe

Hot Junction

Cold Junction

Cold Side Heat Pipe

Figure 1

1/2" 16 X 25 CM. KEUFFEL & ESSER CO. MADE IN U.S.A.

Temperature Drop - °C

Figure 21

temperature differential between the hot and cold side heat pipe surfaces occurs across the thermoelectric material, finite temperature drops also occur across the hot and cold side passive members. The bulk of such drops are across the hot and cold side insulators and across the stress compensator on the hot side. This is best seen in Figure 20 which shows the insulator and stress compensator temperature drops as a function of hot side heat pipe operating temperature. Although the biggest temperature drop occurs across the stress compensator, fairly sizable drops also occur across the various hot and cold side insulators. In view of this, effort will be undertaken in order to minimize the various temperature drops. It is believed that the stress compensator temperature drop can be reduced in half and that the hot and cold side insulator drops can be minimized by reducing or possibly totally eliminating the temperature drops due to the silica layers. This may be possible if the alumina insulators are replaced with other types of insulators that may be bonded to the silicon electrical conductors of the thermocouples within the modules.

In a meeting with cognizant LANL and DOE personnel, it was decided that prior to the building of a complete all metallurgically bonded ring module on a heat pipe, it would be more prudent to build and test isolated test structures containing a single thermocouple. Moreover, it was concluded that the test structures should contain hot and cold side calorimeters such that efficiency measurements would be possible on the thermocouples. Accordingly, a design of such a test structure was formulated. The thermocouple consists of n- and p-type silicon-germanium alloy legs with gallium phosphide additions. The two legs are separated from each other and totally encased in a 0.003 inch thick layer of silicon dioxide and are electrically interconnected by

means of silicon hot and cold shoes. The output from the thermocouple is obtained by 0.020 inch diameter niobium wires which are silver eutectic brazed into the cold shoes. The thermocouple with its hot and cold side insulators and a hot side stress relief member is bonded to a molybdenum heater block and a niobium heat sink. The heater block and the heat sink possess protrusions having the same cross-sections as the thermocouple hot and cold sides. These protrusions serve as calorimeters for the determination of heat flowing into and out of the thermocouple; it should be noted that the thermocouple possesses a wedge-shaped configuration typical of thermocouples in the cylindrical SPAR module concept. The heater block and the heat sink are connected on their peripheries with a heat shield that also serves to contain fibrous thermal insulation that surrounds the thermocouple and the calorimeter sections of the device. Tungsten/niobium thermocouples are placed on the two calorimeter sections and also in various places along the length of the thermocouple structure and associated members between the heater block and the heat sink. The thermocouples exit from the test device by means of two-hole alumina ceramics that extend through the niobium heat sink. Thermocouple output leads exit similarly from the test device. Figure 21 shows a schematic representation of the test device.

It should be noted that the test device is patterned after a comparative thermal conductivity measurement apparatus in which heat flow through the material or device undergoing test is determined by the known geometry and measured temperature differences across calorimeter sections on two sides of the material/device being tested. This method has been extensively used at Synkal Corporation and elsewhere for accurate heat flow measurements. It is estimated that the accuracy of the method is better than five percent at temp-

eratures up to about 800°C and better than ten percent at temperatures up to 1000°C. For example, heat flow and thermal conductivity measurements with an apparatus based on this principle have been performed on materials identical to those having been measured by totally different methods and it has been found that excellent agreement usually exists. It is thus concluded that the test device will not only enable the determination of the electrical performance of the thermocouple, but will also provide a good indication of the heat flowing through the thermocouple. This, in turn, enables a good assessment of the efficiency of the thermocouple. Additionally, the measurement of temperatures at various places within the thermocouple structure enables the determination of temperature drops across extraneous members of the device. Inasmuch as all of the extraneous members of the device represent the dimensions and materials of the SPAR thermoelectric module, it is anticipated that the data obtained from the test device will be directly applicable to the SPAR module.

A number of thermocouples for the test devices were fabricated. The thermocouples in their as-fabricated state consist of wedge shaped n- and p-type thermoelements that are bonded to each other through a layer of silicon dioxide. Silicon dioxide layers also cover all four sides of the thermocouple. The n- and p-type thermoelements are interconnected at the hot side by means of a high silicon content silicon-germanium alloy electrode having a thickness of 0.040 inch. Electrodes having the same thickness and consisting of the same high silicon content alloy are individually bonded to the n- and p-type thermoelements at the cold side. The lateral faces of both the hot and cold side electrodes are covered with silicon dioxide, as is the space separating

the two cold side electrodes. This means that the thermoelectric material within the thermocouple is totally isolated from its environment and it is only the external faces of the hot and cold side electrodes that are exposed in the as-completed thermocouple. When each thermocouple is bonded into the final test device, even these exposed hot and cold side electrodes will be isolated from the environment because it is these faces that are bonded to other components within the test device.

At the completion of the fabrication of two thermocouples for the test device, five 0.023 inch diameter holes were drilled on one side of both thermocouples. These holes will be used for instrumentation lead wires in the final test device. Two of the holes are located in the hot and cold side electrodes. The three remaining holes in each thermocouple are located within the thermoelectric material, with two of the three holes very close to the opposite extremities of the thermocouple and the third in their middle. The placement of temperature sensing thermocouples within these holes will enable the measurement of the temperature distribution within the thermocouple when it is operating in the test device. It will also be possible to determine the temperature drop, if any, across the bond interface between the thermoelectric material and the hot and cold side electrodes.

LANL made available to Syncal Corporation the components that were to be supplied by LANL for the test device. These components include the hot side molybdenum heater block, the stress relief member and the hot and cold side alumina insulators. In their as-received condition, the components had been coated with a thin layer of titanium in order that they can be diffusion bonded into the final test assembly. The first diffusion bonding attempt involved the diffusion bonding of the stress relief member, a tungsten

backing plate and the alumina insulator into a composite structure. The diffusion bonding was done in vacuum at 1100°C under a pressure of the order of 100 psi. It was found that practically no bonding at all occurred at any of the interfaces between the various components. On the possibility that there was some contamination on some or all of the interfaces, the bonding cycle was repeated with new components after each component had been carefully cleaned with various solvents. Once again, little, if any, bonding occurred at any of the interfaces. These interfaces are identified in the schematic shown in Figure 22.

Discussions were held with cognizant LANL project personnel regarding the lack of diffusion bonding of the various hot side interfaces. Utilizing the same components, a diffusion bonding experiment at LANL confirmed the lack of bonding at the interfaces. Inasmuch as a previous bonding test at LANL had resulted in good interface bonds, it was a little unclear as to the negative result found by SynCal Corporation and subsequently confirmed by LANL. One possible explanation for the finding is that the titanium coatings applied to the test device components represented two different coating applications. It is conceivable that some contaminant was present in the second application, thereby inhibiting the formation of diffusion bonds. Bonding of the cold side components was also attempted on the test device. The cold side components involve a niobium calorimeter section, an alumina insulator and two tungsten transition pieces. The cold side of the thermocouple is to be subsequently brazed to the tungsten transition pieces. Figure 23 shows a schematic of the cold side components of the test device. The first diffusion bonding attempts also indicated a lack of bonding between the various components. Apparently, whatever inhibited the formation of diffusion bonding between the hot side components is also responsible for the lack of

SPAR Test Device Hot Side Assembly

Figure 22

SPAR Test Device Cold Side Assembly

Figure 23

bonding between the cold side components. As a consequence of difficulty encountered in the diffusion bonding, it was decided to insert 0.001 inch thick titanium shims at the various interfaces and to repeat attempts at the diffusion bonding of the various hot and cold side components. It should be noted that the test device can, in effect, be separated into three sub-assemblies. The hot side sub-assembly, shown in Figure 22, consists of a molybdenum heater block and calorimeter, a stress relief member made of molybdenum foil, a tungsten backing plate and an alumina insulator. The cold side sub-assembly, shown in Figure 23, consists of a niobium base and calorimeter, an alumina insulator and two tungsten electrodes to which test device output leads are connected. The third sub-assembly of the test device, of course, includes the n- and p-type thermoelements, along with a hot side silicon contact that interconnects the thermoelements and two cold side silicon electrodes.

In the diffusion bonding of the components of the hot side sub-assembly, titanium shims were placed on either side of the stress relief member and in between the tungsten backing plate and the alumina insulator. The diffusion bonding was performed in vacuum at a temperature of 1100°C under a pressure of the order of 100 psi. The pressure was obtained by the static loading of the individual components in the arrangement shown in Figure 22. A special diffusion bonding fixture was utilized in order to assure alignment of the various parts. At the completion of the diffusion bonding cycle, it was found that good bonding resulted between the various components.

The diffusion bonding of the components of the cold side sub-assembly was done by placing titanium shims on either side of the alumina insulator. The diffusion bonding was done in the hot press under vacuum at a temperature of 1100°C with a static loading of about 400 psi. Once again,

it was found that satisfactory bonding resulted. On the basis of this finding, it was concluded that the reason for failure to achieve diffusion bonds was very likely an insufficient amount of titanium at the component interfaces. This conclusion was arrived at because in the bonding done, use was made of the titanium coated components previously supplied by LANL that were found not to bond when no use of the additional titanium shim was made. Had contamination been a factor in the lack of bonding, it may be expected that no bonding would have also resulted with the additional titanium shim. As already mentioned, this, however, was not the case.

At the completion of the preparation of the hot and cold side sub-assemblies for the test device, it remained to combine the sub-assemblies with the thermocouple sub-assembly in order to complete the test device. It will be recalled that the thermocouple sub-assemblies had been fabricated previously. The intended sequence of the combining of the three sub-assemblies is the bonding of the hot side sub-assembly to the thermocouple sub-assembly through a layer of silicon dioxide. The cold side sub-assembly is attached by brazing it to the tungsten electrodes with silver. Inasmuch as the silicon dioxide bond to the hot side sub-assembly is effected at 1100°C and the cold side braze is done at 980°C, it is obvious that the final test device assembly must be accomplished in two separate operations. First, the thermocouple sub-assembly is bonded to the hot side sub-assembly. This is followed by the brazing of the cold side sub-assembly.

Three thermocouple sub-assemblies were successfully bonded to three hot side sub-assemblies through a layer of silicon dioxide. This bonding operation was performed in vacuum at 1100°C with a load of about 100 psi. Subsequent

attempts to braze the cold side sub-assembly to the cold side contacts of the thermoelectric couple were, however, unsuccessful. An inspection of the bond area indicated that bonding did not result because of an apparent lack of wetting between the silver and the tungsten. As a consequence of this finding, a concerted effort was devoted to the development of an alternate braze material.

A number of precious metal braze alloys were obtained from WESGO, including various gold, silver and platinum alloys. Prior to their use, it was established that excellent brazes can be made with copper. Because of the extremely high diffusion rate of copper in silicon, it was decided, however, that the use of copper can result in the degradation of the thermoelectric properties of the thermoelectric material and all further consideration of the use of copper was abandoned. Of the various precious metal alloys, it was found that the most satisfactory results in brazing silicon to tungsten were obtained with an alloy consisting of 95 percent silver and five percent aluminum. In view of this finding, it was decided to proceed with the brazing of the cold side sub-assemblies to the rest of the test devices.

The first cold side sub-assembly was brazed in vacuum at a temperature of 950°C under a static load of about 100 psi. Although a satisfactory braze resulted, subsequent handling of the test device resulted in its breakage. The breakage occurred through the thermoelectric material of the thermocouple and was traced to the torque imposed on it by the inevitable flexing of the test device during normal handling as a result of the relatively massive hot and cold side sub-assemblies. In view of this, prior to the brazing of the cold sides of the remaining two test devices, it was decided to eliminate the molybdenum heater block from the

test devices in order to reduce the amount of torque imparted to the thermocouple in the completed test device. This was done by the separation of the molybdenum heater block from the calorimeter by machining; these two components were originally machined from one piece of molybdenum. Discussions with cognizant LANL project personnel indicated the acceptability of this procedure. It was decided that a separate heater block would be placed on top of the test device after its installation in the test facility at LANL. The heater block would be diffusion bonded to the hot side calorimeter by means of a titanium shim during the heat-up phase of the testing.

The cold end brazing of the remaining two test devices was successful and no difficulties were encountered during subsequent handling of the test devices. The test devices were delivered to LANL for instrumentation and evaluation. As mentioned above, all of the components of a third test device were also delivered. The stated intention of cognizant LANL project personnel is to perform the brazing of this device at LANL in order to gain experience in the overall area of thermoelectric device assembly.

The two complete test devices and the components for a third test device were delivered to LANL. Recommendations on the bonding of the components of the third test device were made to cognizant LANL project personnel in regard to the temperature and pressure of the bonding of the thermocouple structure to the hot side components and the brazing of the thermocouple structure to the cold side components. Namely, it was suggested that the former bond be effected at 1100°C for 60 minutes in vacuum under a static load of 100 psi. It was also recommended that the cold side braze utilize an alloy of 95 percent silver and five percent aluminum and that the bond be effected at 950°C for 60 minutes

in vacuum under a static load of 100 psi. The hot side bond should be effected before the cold side bond because of its higher bonding temperature.

APPENDIX

Table 2. Annealing Characteristics Of P-type Silicon-Germanium Alloy With Gallium Phosphide Additions

<u>Annealing Time</u>	<u>Polarity</u>	<u>Electrical Resistivity $m\Omega\text{-cm}$</u>	<u>Seebeck Coefficient $\mu\text{V}/^{\circ}\text{C}$</u>
0	P	54.2	172.2
90	P	33.1	171.8
180	P	29.3	179.4
281	P	21.4	176.3
358	P	15.7	183.7
500	P	11.8	175.0
572	P	10.3	171.5
651	P	6.62	166.6
721	P	5.03	160.8
778	P	4.47	158.9
894	P	4.11	147.2
960	P	3.89	153.1
1032	P	3.77	148.0
1129	P	3.39	143.3
1250	P	3.14	140.5
1370	P	2.96	141.7
1538	P	2.75	139.0
1659	P	2.69	137.1
1730	P	2.62	130.3
1852	P	2.68	134.6
1952	P	2.47	131.2
2071	P	2.45	136.0
2146	P	2.36	135.8
2202	P	2.49	130.7
2272	P	2.34	132.9
2480	P	2.18	137.1
2650	P	2.23	129.8
2818	P	2.28	132.5
2990	P	2.11	133.6
3255	P	2.04	129.1
3515	P	2.09	137.2

[illegible]

<u>Annealing Time</u>	<u>Polarity</u>	<u>Electrical Resistivity $m\Omega\text{-cm}$</u>	<u>Seebeck Coefficient $\mu\text{V}/^\circ\text{C}$</u>
0	n	0.91	105.3
72	n	4.14	179.7
151	n	21.9	208.3
221	n	127.2	108.9
278	p	538.7	15.4
394	p	198.8	133.8
460	p	81.6	155.2
532	p	45.3	164.5
629	p	28.1	168.0
750	p	17.1	171.3
870	p	11.2	168.6
1038	p	6.88	166.0
1159	p	5.60	157.1
1230	p	4.77	154.6
1352	p	4.39	149.9
1452	p	3.77	146.8
1571	p	3.36	140.7
1646	p	3.42	141.3
1702	p	3.33	140.4
1772	p	3.05	133.2
1980	p	2.81	135.7
2150	p	2.63	134.7
2318	p	2.54	130.1
2490	p	2.60	137.9
2755	p	2.37	132.4
3015	p	2.28	131.6
3250	p	2.13	128.2
3557	p	2.11	125.9
3938	p	2.02	130.7
4242	p	1.98	131.8
4594	p	2.05	130.4

[illegible]

[illegible]

[illegible]

[illegible]

#13

[illegible]

[illegible]

[illegible]

[illegible]

#17

[illegible]

[illegible]

#21

[illegible]

[illegible]

[illegible]

[illegible]

#25

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

#33

[illegible]

[illegible]

Seebeck Coefficient- $\mu\text{V}/^{\circ}\text{C}$

#41

[illegible]

1

1

#43

[illegible]

[illegible]

#47

Annealing TimePolarityElectrical Resistivity $m\Omega\text{-cm}$ Seebeck Coefficient $-\mu\text{V}/^{\circ}\text{C}$

0

p

2.33

132.4

144

p

2.29

131.3

307

p

2.28

133.5

448

p

2.21

127.2

636

p

2.03

131.0

800

p

1.95

130.6

#48

[illegible]

END

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