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COPIES:

SUBJECT

THERMOELECTRIC PERFORMANCE OF SINTERED SILICON-GERMANIUM ALLOYS COMPARED TO ZONE LEVELED ALLOYS

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The DOE-sponsored Improved Thermoelectric Materials program has been concentrating on improving the performance of Silicon-Germanium (SiGe) based materials, while studying other advanced thermoelectric materials at a lower level of effort. Information now in hand is sufficient to conclude that improvement of SiGe by the methods currently under investigation is not possible. The most promising ideas put forth in our proposal for this program have been exhausted and virtually all concepts will likely be exhausted within six months at the current level of effort. The purpose of this note is to describe the important data now in hand in order to motivate criticism of the current analysis, ferret out any further ideas and generally allow planning for future efforts.

The results described here have impact not only on the current DOE program but on virtually all thermoelectric activities in the foreseeable future. It is not my intention in the present note to present a dogmatic, single-minded interpretation of the data but to stimulate thought on the structure of future activities.

SCOPE OF THE EXPERIMENTAL PROGRAM

The experimental data presented covers a variety of materials and preparation techniques. Procedures have been developed to measure the Seebeck coefficient, electrical resistivity, thermal conductivity, carrier concentration and Hall mobility at room temperature with a precision of better than 2%. These characterizations allow analysis of trends in the figure-of-merit with greater reliability than is generally possible with high temperature measurements due to the increased technical difficulties associated with high temperature measurements.

Sixty-seven hot pressed, 2" diameter by 0.5" thick compacts have been prepared and characterized by these techniques and the data on these compacts are listed in Table 1. Detailed descriptions of the samples are available in the ITM monthly reports. The variables studied include: GaP concentration; method of incorporating GaP (i.e. adding GaP directly to the melt compared to mechanical blending procedures); particle size variations; alternate additions such as Al₂O₃, Y₂O₃ Graphite, V₂O₃ and titanium; pressure assisted reaction of silicon and germanium; and hot pressing parameters. One sample of Gas Atomized material has also been characterized to date.

Each compact is sliced in such a manner that the characterizations are all performed on pieces taken from approximately the same relative region of each compact. This minimizes possible variations due to systematic inhomogeneities associated with the hot pressing procedures.

COMPARISON WITH ZONE LEVELED MATERIAL

Work performed in the early 1960's on zone leveled silicon-germanium alloys provides the only systematic study of the effects of doping level, silicon to germanium ratio and temperature on silicon-germanium alloys. The results of these studies should be familiar to anyone working on thermoelectric materials today. (J.P. Dismukes et al, J. Applied Phys., 35 (10) 1964, 2899) These studies provide the data-base for selection of composition and doping levels still used today. The data stands up well to even very close scrutiny. The figure-of-merit depends on temperature, silicon to germanium ratio and carrier concentration. In order to compare new materials to this data base these variables must be properly taken into account.

The ITM program has selected the fixed composition of 80 atomic percent silicon and 20 atomic percent germanium. Characterizations are performed under controlled conditions to allow for the greatest possible precision. In particular, the data discussed below are essentially room temperature values. In comparison to the zone leveled material data-base only the carrier concentration must be taken into account. This is important since the Seebeck coefficient, the electrical resistivity and the thermal conductivity are all strong functions of the carrier concentration.

Note that since room temperature properties only are used, the data discussed here are not sufficient for selection of the optimized material for high temperature applications. Indeed, the room temperature figure-of-merit of N-type zone leveled material increases with decreasing carrier concentration, while the reverse is true of the high temperature figure-of-merit for the same material. Thus, while the data on sintered material is not, in itself, sufficient for selecting an optimized material it is sufficient for indicating the important trends observed.

The figure-of-merit at room temperature, with a fixed composition is a function of the carrier concentration only. The figure-of-merit of a sample of sintered material should be compared to the figure-of-merit of zone leveled material at the same carrier concentration. This can be done as follows. The figure-of-merit of zone leveled material can be described by

$$Z_{ZL}(n) = S_{ZL}(n)^2 \sigma_{ZL}(n) / K_{ZL}(n) \quad \text{Eq. 1}$$

$$Z_{SIN}(n) = S_{SIN}(n)^2 \sigma_{SIN}(n) / K_{SIN}(n) \quad \text{Eq. 2}$$

where Z is the room temperature figure-of-merit,

n is the carrier concentration

S is the Seebeck coefficient

σ is the electric conductivity

K is the thermal conductivity

and the subscripts ZL and SIN indicate zone leveled or sintered material. The ratio of the figure-of-merit of a sintered material to the figure-of-merit of a zone leveled material with the same carrier concentration may be written

$$Z_{SIN}(n) / Z_{ZL}(n) = (S_{SIN}(n) / S_{ZL}(n))^2 (\sigma_{SIN}(n) / \sigma_{ZL}(n)) / (K_{SIN}(n) / K_{ZL}(n)) \quad \text{Eq. 3}$$

The first term on the right hand side of Equation 3, the ratio of the Seebeck coefficient for sintered and zone leveled materials, is expected to be unity. This expectation has been experimentally verified for all sintered materials studied. Even the addition of significant quantities of GaP and the other additives listed above do not significantly effect the relationship between the Seebeck coefficient and the carrier concentration as determined by Hall effect measurements. This data is shown in Figure 1 where the Seebeck coefficient is plotted against carrier SiGe concentration. P-type samples appear in the upper half of the Figure and N-type samples in the lower half. All of the data points in this figure represent quantities measured on GE produced samples. The solid curves represent the RCA data on zone leveled material.

There is some scatter in the Seebeck or carrier concentration data at the lowest carrier concentrations. In the region of interest, however, the agreement with the zone leveled data is quite good. With the simplification that the Seebeck coefficient depends only on the carrier concentration, the first term in Equation 3 becomes unity and we may write

$$Z_{\text{sin}}(n)/Z_{\text{z1}}(n) = (\sigma_{\text{sin}}(n)/\sigma_{\text{z1}}(n)) / (K_{\text{sin}}(n)/K_{\text{z1}}(n)) \quad \text{Eq. 4}$$

To evaluate the relative improvement in the figure-of-merit one need compare only the reduction in the electrical conductivity, normalized for the effect of doping, to the reduction in thermal conductivity, also normalized for the effect of doping. This procedure requires determining the carrier concentration for a given sample and estimating the electrical and thermal conductivities of zone leveled material for that carrier concentration, taking into account the differences between N- and P-type dopants. The RCA data-base has been utilized and these estimates have been made for 67 compacts to date. The results of this comparison are shown in Figure 2.

If Equation 4 is greater than unity an improvement is indicated and if Equation 4 is less than unity performance degradation is indicated. The normalized thermal conductivity is plotted against the normalized electrical conductivity in Figure 2. The lower right corner of this figure represents a reduction in thermal conductivity greater than the reduction in electrical conductivity, and therefore, an improvement in overall performance. The upper left corner represents the opposite, a greater reduction in electrical conductivity than thermal conductivity and a loss in overall performance. The solid line indicates compensating electrical and thermal effects. The two dashed lines represent 5% error bars.

Note in Figure 2 that no sample shows more than about 5% deviation from the solid line in the direction of improved performance, while a great many samples fall beyond this line in the area of degraded performance. Within the cumulative experimental errors sintered materials perform as well as but no better than zone leveled materials. Thermal conductivities as low as 57% of zone leveled material value have been produced, however, a nearly exactly compensating reduction in the electrical conductivity has been observed.

This data make it clear that the mechanism by which the thermal conductivity has been lowered to date has a compensating effect on the electrical properties such that no net gain in the figure-of-merit is obtained. This is true regardless of whether GaP is present in any form or not.



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SUMMARY

There is no longer any motivation for selecting doping levels or compositions differing in any way from the previous compositions. Material performance equal to but not superior to zone leveled material performance can be achieved with relative ease in sintered material. Moreover, the experimental indications that SiGe can be improved which motivated the ITM program no longer exist. Certain ongoing activities on SiGe in the ITM program should be continued, such as the advanced processing studies and the high temperature characterizations already planned. These activities will leave very little room for doubt, if any exists now. Beyond these activities, which are unlikely to take more than six months at the current level of effort, no additional activities on SiGe seem justified, barring some surprise or inspiration in the near future. I consider the chances of improving SiGe significantly beyond the performance of the zone leveled material unlikely and I have no more ideas capable of achieving same.

Now is the time to consider our options and decide our future course. I am currently reviewing the literature in more depth than I have previously and hope to be able to suggest alternate materials for study. At the minimum the ITM program will need restructuring.

CBV

TABLE 1 (cont'd.)

N	5.52	0.56	4.96	-159.56	1.356	76.80	0.600	3400	
N	5.45	0.62	4.83	-147.68	1.218	73.33	0.700	3287	
N	5.39	0.68	4.71	-138.11	1.109	70.45	0.800	3193	
N	5.33	0.74	4.59	-130.18	1.021	68.01	0.800	3112	
N	5.29	0.80	4.49	-123.47	0.949	65.89	1.000	3041	
N	5.24	0.85	4.39	-117.70	0.887	64.03	1.100	2978	
N	5.20	0.91	4.30	-112.67	0.835	62.38	1.200	2922	
N	5.17	0.96	4.21	-108.23	0.789	60.90	1.300	2871	
N	5.14	1.01	4.13	-104.28	0.749	59.96	1.400	2825	
N	5.11	1.06	4.05	-100.73	0.714	58.34	1.500	2783	
N	5.08	1.11	3.97	-97.52	0.683	57.23	1.600	2743	
N	5.05	1.16	3.90	-94.60	0.654	56.19	1.700	2707	
N	5.03	1.20	3.82	-91.92	0.629	55.24	1.800	2674	
N	5.00	1.25	3.75	-89.46	0.605	54.35	1.900	2642	
N	4.98	1.29	3.69	-87.19	0.584	53.52	2.000	2613	
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Theoretical Minimum, G. Slack 0.1									
	3.83	0.84	2.39	-119.35	0.9	65	1.07	3.0058	4133
									54.57

69a, three castings combined into one batch of powder. See W.L. 06185-384-4,5,6
 75b, three castings combined into one batch of powder. See W.L. 061785-384-4,5,6

W.M.=Wet Milled, Acetone
 S.H.=Shatter Boxed Only
 AJP=Air Jet Pulverized
 Insitu=Elements reacted in Hot Press; Pressure Assisted Reaction Sintered
 Blend=GaP mechanically blended with SiGe feed powder to hot press
 Melt=GaP added directly to the SiGe melt, during vacuum casting
 G.A.=Gas Atomized (GE-CRD)
 Osprey=Rapid quenched
 DM=Shatter Box + 4 hours Dry Milling
 81,82 are open ITM numbers

FIGURE 1

80% Si-20% Ge Alloys, Room Temperature

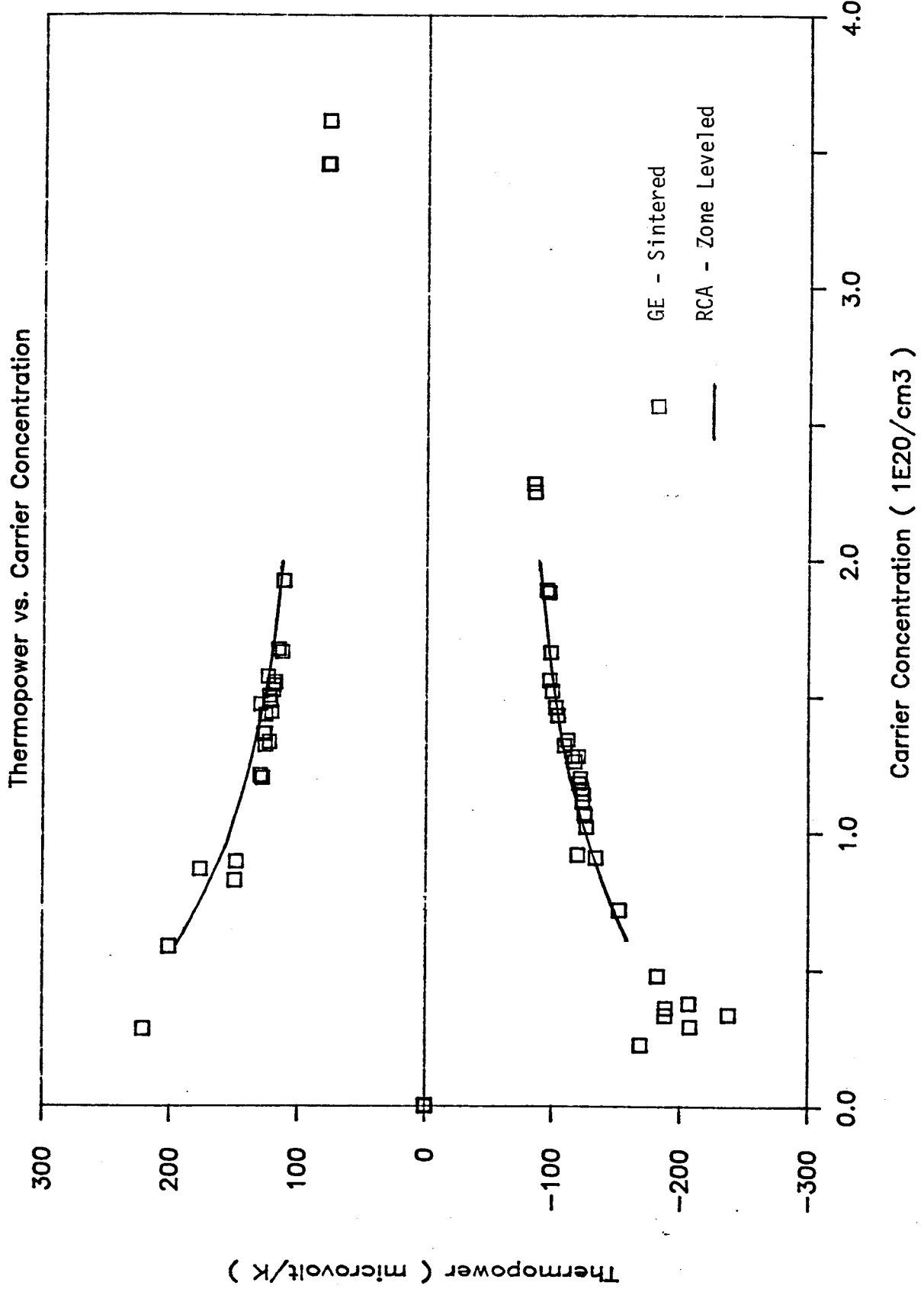


FIGURE 2

80% Si-20% Ge Alloys, Room Temperature

