$Si_{80}Ge_{20}$ thermoelectric alloys prepared with GaP additions

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Controlled amounts of GaP and P were added to a $Si_{0.8}Ge_{0.2}$ matrix by a powder-metallurgical technique in order to evaluate the optimum composition for thermoelectric applications. Bulk determination of the gallium and phosphorus content in fully dense, hot pressed compacts was performed by inductively coupled plasma atomic emission spectroscopy. The transport properties of the compacts were characterized by Hall effect measurements at room temperature and by measurements of electrical resistivity, Seebeck coefficient, and thermal diffusivity to 1000 °C. Considerable variation in the electrical transport properties were found to accompany changes in the Ga/P ratio, in the total amount of dopant, and changes in other preparation conditions. Alloys with gallium phosphide additions exhibit carrier concentrations higher than those obtained in alloys doped only with phosphorus. Alloys with a nominal phosphorus content greater than 2.0 at. % were found to be overdoped and those containing less than 0.6 at. % phosphorus were found to be underdoped relative to the material's maximum figure of merit. Room temperature electron mobilities greater than 40 cm^2/V s were commonly obtained in samples with a carrier concentration of 3×10^{20} cm^{-3} or greater. A 300–1000 °C integrated average figure of merit ($Z = S^2/\rho\Lambda$) of 0.93×10^{-3} °C^{-1} was achieved within an optimum composition range of 0.8–1.2 at. % P and 0.6–0.8 mol % GaP, which is 20% higher than current n-type Si-Ge alloys doped with 0.59 at. % P as used in the Voyager, Galileo, and Ulysses missions. © *1995 American Institute of Physics.*

INTRODUCTION

Since Steele and Rosi[1] first demonstrated the remarkably low thermal conductivity of silicon-germanium solid solutions, efforts to better understand and optimize these alloys for use in thermoelectric applications have continued. The early work of Dismukes *et al.*,[2] provided an extensive background of both electrical and thermal properties of heavily doped, silicon-rich alloys and formed the groundwork for subsequent enhancements. Processing methods have since received considerable attention such as the application of hot pressed and sintered alloys,[3] the study of grain-boundary scattering and the use of fine-grained alloys designed to lower the lattice thermal conductivity,[4,5] application of high-temperature heat treatments to alter the microstructure and redistribute dopants,[6,7] and control of second-phase oxygen.[8] Moreover, the effects of gallium phosphide additions, once thought to reduce the thermal conductivity[9] and later identified as a mechanism to increase the solid solubility of phosphorus[10] have had considerable impact on the evolution of high performance Si-Ge thermoelectric alloys. The present state of theoretical modeling of the n-type $Si_xGe_{(1-x)}$ system suggests that the optimum dimensionless figure of merit (ZT) at 1000 °C is in the range of 1.1 ($Si_{0.8}Ge_{0.2}$)[11] to 1.2 ($Si_{0.7}Ge_{0.3}$),[12] without the introduction of artifacts such as inert, nanophase phonon scattering inclusions. Standard zone-leveled Si-Ge n-type alloys, doped only with phosphorus, have a ZT value 17%–20% lower than the theoretical maximum. Recent experimental data on n-type alloys containing small (<5 mol %) additions of GaP indicate that these additions can increase ZT_{max} to values near 1.0. Further improvements require optimization of the Ga/P ratio and control of the resulting microstructure.

Initial studies on the application of mechanical alloying (MA) for the preparation of n-type $Si_{80}Ge_{20}$ were performed on alloys with nominal 1.6 mol % GaP and 3.4 at. % P additions.[8] Analysis of the electrical properties of these alloys showed that while the high carrier concentration (3.5–4.2×10^{20} cm^{-3}) resulted in low electrical resistivities and electrical power factors close to the theoretically predicted maximum of 40–45 $\mu W/(cm$ °$C^2)$ at 600 °C, it concomitantly causes a sharp decrease in power factor between 600 and 1000 °C. This rapid decrease in power factor causes a decrease in Z at the highest temperatures. An alloy having a lower carrier concentration, n, but higher carrier mobility should also provide low resistivity but in addition would possess an enhanced Seebeck coefficient, S, due to the logarithmic dependence of S on n.

A study was initiated to investigate the effects of the relative amount of gallium and phosphorus on the electrical and thermal properties of $Si_{80}Ge_{20}$ alloys and to improve the performance of the material in the 600 to 1000 °C range, while maintaining the high power factors observed near 600 °C in the overdoped alloys. This article summarizes efforts to identify the variables associated with the optimization of n-type $Si_{80}Ge_{20}$ alloys containing GaP and P as prepared by MA and hot pressing.

EXPERIMENTAL DETAILS

Silicon-germanium alloys doped with gallium phosphide and phosphorus were prepared by a solid state reaction between stoichiometric quantities of elemental silicon, germanium, gallium phosphide, and phosphorus in a hardened tool-

TABLE I. Sample identification and nominal compositions.

Sample ID	at. %	at. % Ga	Ga/P
A90	1.25	0.50	0.40
A91	2.00	1.00	0.50
A92	1.88	0.63	0.33
A93	2.50	1.25	0.50
A94	1.60	1.60	1.00
A95	2.75	1.25	0.45
A96	3.00	1.25	0.42
A97	2.20	1.08	0.50
A98	1.90	0.80	0.42
A99	3.00	0.75	0.25
STD-1	1.10	0.00	0.00
STDM-4	3.40	0.00	0.00

steel vial under a high-purity helium environment using a Spex 8000 high-energy vibratory mill. The Si and Ge were mixed in an 80:20 ratio and varying amounts of GaP and P were added to each charge. Table I lists the nominal dopant additions along with the nominal Ga/P ratios. The sample designated A94 was prepared with GaP only, in order to observe the amount of dissociation occurring between the gallium and phosphorus during preparation. Once the reaction was completed, as verified by x-ray diffraction, the powder was transferred to a graphite-lined die under helium and hot pressed at 1130 °C with an applied pressure of 140 MPa (22 ksi) under a vacuum of 1×10^{-7} Torr. The hot pressing time was typically 45 min, although some of the alloys (which are discussed separately below) were hot pressed for longer times in order to evaluate the impact of grain growth.

Samples for studies of Seebeck coefficient, electrical resistivity, Hall effect, thermal conductivity, and metallographic and chemical analysis were cut from each hot pressed compact. Some of the samples were measured in an "as-pressed" condition after furnace cooling to ambient, while others were subjected to a thermal "reset" treatment at 1050 °C for 20 min followed by air cooling. This temperature roughly corresponds to the point of maximum solubility of phosphorus in $Si_{80}Ge_{20}$ and facilitates comparisons between electrical resistivity and carrier concentration from sample to sample.

The room temperature carrier concentrations and Hall mobilities were measured on thin (0.1 cm) disks using the van der Pauw method[13] with four point contacts equally spaced around the perimeter. The procedure described by Ndlela and Bates[14] was used in this study. A magnetic field of 1 T was applied during which time a minimum of four voltage readings were obtained and subsequently averaged

for each of the four current directions. The field was reversed and the voltage samplings repeated. The intermediate Hall coefficients were averaged and the carrier concentration was determined from the relation $n = (R_H e)^{-1}$. The accuracy of this technique is estimated at better than 1% of the true value. The electrical resistivity and Seebeck coefficient measurements were performed by a standard dc four-point probe technique[15] and by determination of the slope of the thermal emf versus temperature plot,[16] respectively. Both properties were measured simultaneously on the same sample in a vacuum chamber ($\sim 10^{-7}$ Torr) in the temperature range of 25–1000 °C by a computer-controlled data acquisition system. A fifth-order polynomial regression was used to calculate the integrated power factors in the temperature range of 300–1000 °C. The thermal diffusivity of a 1.27 cm diam by 0.1 cm thick disk of the A92β sample was measured from 300 to 1000 °C by a standard laser flash diffusivity technique described in a previous publication.[17] Briefly, both faces were coated with a thin (30 μm) layer of graphite and the sample was mounted in a low thermal conductivity holder machined from low density ZrO_2. The sample was placed in the center of a BN tube which was wound with Ta wire. This heater assembly was positioned inside a vacuum chamber such that a pressure of better than 10^{-7} Torr was maintained during the characterization. The front surface of the sample was irradiated by a pulse from a ruby rod laser. The zirconia sample holder minimized conductive heat losses from the material and the thermal transient was measured using an InSb detector. Corrections for finite pulse width and heat loss were applied using an in-house computer program. Thermal diffusivity values were calculated for each 5% rise in temperature between 5% and 95% of the maximum value. An average thermal diffusivity was then determined from these values. The thermal conductivity was determined from the product of the thermal diffusivity, density, and specific heat. Published data[18] were used for for the thermal expansion coefficient and heat capacity.

RESULTS AND DISCUSSION

The total bulk phosphorus and gallium contents of several hot-pressed compacts were determined by inductively coupled plasma—atomic emission spectroscopy (ICP-AES) and the results are summarized in Table II. Total phosphorus loss consistently exceeded that of the gallium so that the actual Ga/P ratio was greater than the nominal value. This was not unexpected due to the high vapor pressure of phosphorus over silicon and germanium and the likely formation of a small amount of phosphorus vapor during MA. Based on

TABLE II. Results of ICP-AES determination of P and Ga contents of several $Si_{0.8}Ge_{0.2}$ alloys.

Alloy ID	Nom. Ga (%)	Nom. P (%)	Nom. Ga/P	Actual Ga (%)	Actual P (%)	Actual Ga/P	Ga/P diff. (%)
A90α	0.50	1.25	0.40	0.49	1.10	0.45	11
A91α	1.00	2.00	0.50	0.93	1.56	0.60	19
A91γ	1.00	2.00	0.50	0.93	1.43	0.65	30
A92α	0.63	1.88	0.34	0.59	1.28	0.46	38
A93α	1.25	2.50	0.50	1.16	1.87	0.62	24

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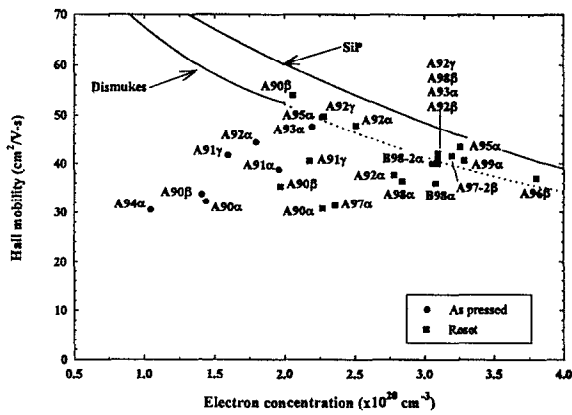
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FIG. 1. Room-temperature Hall mobility as a function of measured carrier concentration. The mobility of phosphorus-doped Si is indicated by the solid line labeled SiP. The mobility of zone-leveled $Si_{0.8}Ge_{0.2}$ (Ref. 2) is indicated by the solid line up to $n=2\times10^{20}$ cm^{-3}, which has been extrapolated to higher carrier concentration values, as indicated by the dashed line.

these and previous results a difference of 40% between the nominal Ga/P ratio and the measured value appears to be an upper limit.

As the amount of excess phosphorus (i.e., above the solubility limit) is increased, there is a greater probability that partial liquefaction of SiP may occur during hot pressing, thereby increasing the rate of grain growth through liquid-phase sintering. According to the equilibrium phase diagram, SiP melts at 1131 °C, which is within temperature-measurement error of the point at which these alloys were consolidated. Parallel studies on alloys doped only with phosphorus show strong correlation between grain size after hot pressing and the amount of phosphorus present in the bulk. Similar results are observed in these alloys although the presence of GaP complicates the comparisons. Of the alloys hot pressed for 45 min, the material with the smallest grain size, 0.5–1.0 μm, (A90α) contains 0.61% P and 0.49% GaP (Ga/P=0.45). Significantly larger grains, on the order of 10 μm, are found in the A93α alloy, which contains 0.71% P and 1.16% GaP (Ga/P=0.62). Consideration of the remaining alloys indicates that the A96 and A99 materials have the largest grain size, on the order of 20–25 μm each.

Hot pressing time can also have a strong influence on microstructure. To illustrate this effect, three compacts were prepared from the initial A92 charge. One each was hot pressed for 45, 60, and 75 min with a corresponding grain size progression of 0.5–1.0 μm, 5–10 μm, and 15–25 μm, respectively. As will be shown, microstructure can play an important role in the electrical transport of these alloys due to the existence of electrical potential barriers at the grain boundaries.

The impact of doping and microstructure on carrier mobility is shown in Fig. 1. The data points shown in Fig. 1 correspond to all samples prepared for this study, regardless of prior thermal history. The solid line labeled "Dismukes" represents the mobility of zone-leveled $Si_{0.8}Ge_{0.2}$ for samples doped with phosphorus up to about 2×10^{20} cm^{-3} (Ref. 2), and the dashed line represents an extrapolation of those results to higher doping levels. The alloys near the upper right

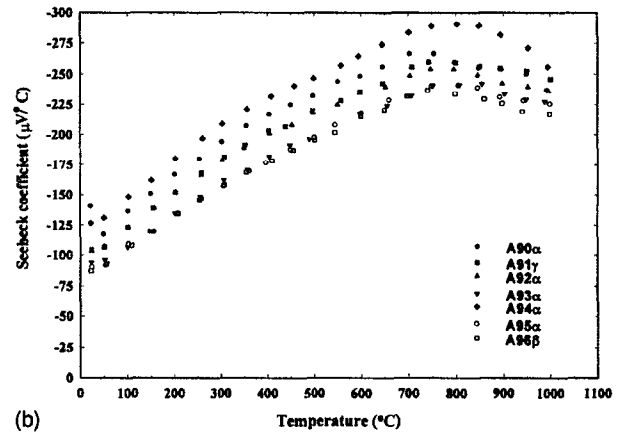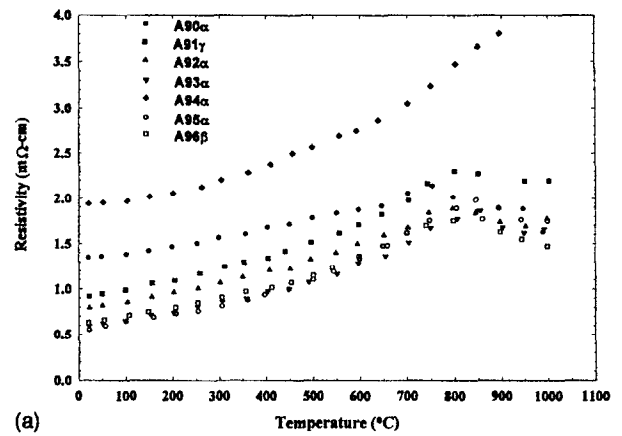FIG. 2. (a) Resistivity and (b) Seebeck coefficient of selected as-pressed $Si_{0.8}Ge_{0.2}$ alloys containing various amounts of GaP and P.

hand corner of Fig. 1, i.e., toward higher values of n and μ, tend to have a larger grain size than those with lower carrier concentrations, and this is believed to be a key factor as to why they have superior mobility. X-ray diffraction analysis indicates that the actual ratio of silicon to germanium was within 3% of the nominal 80:20 value based on lattice parameter determination.

That longer hot pressing times have a significant effect is seen by comparing the A92-alloys A92α, A92β, and A92γ in reset condition (■), all corresponding to the same composition. Alloy A92α (■, 2.8×10^{20}, 37.7) corresponds to a 45-min hot pressing time while alloys A92β (■, 3.08×10^{20}, 40.0) and A92γ (■, 3.10×10^{20}, 42.1) correspond to 60- and 75-min hot pressing times, respectively. The latter two points lie on the dashed line, corresponding to the highest mobility expected in $Si_{0.8}Ge_{0.2}$ for a given carrier concentration. In fact, several combinations of composition and hot pressing conditions are seen to yield points on the extrapolated Dismukes mobility curve. However, as mentioned previously, alloys with an excessively large carrier concentration will tend to have low Seebeck coefficients and less than optimal electrical power factors (S^2/ρ). For example, the A96β alloy (■), with 1.75 at. % P and 1.25 mol % GaP is overdoped,
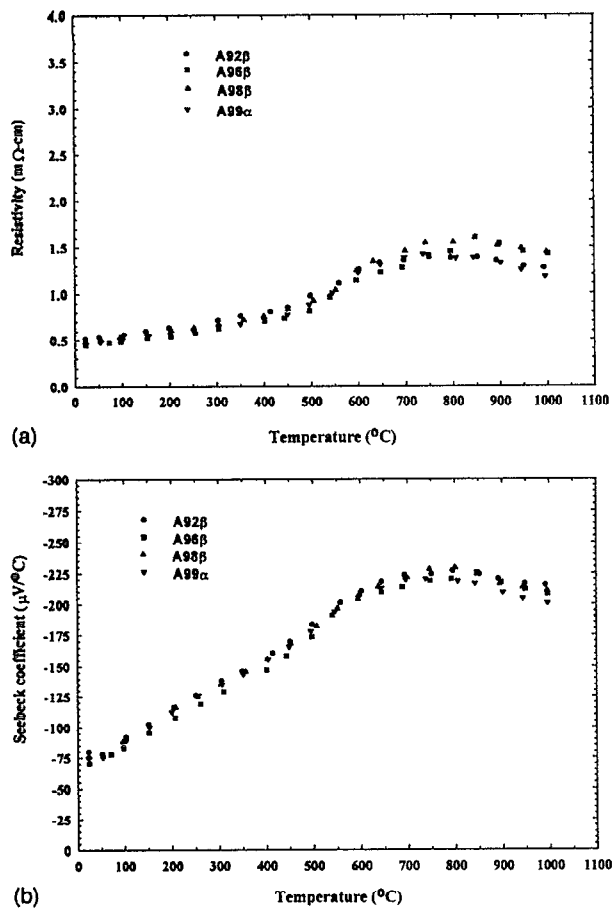
FIG. 3. (a) Resistivities and (b) Seebeck coefficients of selected $Si_{0.8}Ge_{0.2}$ alloys containing various amounts of GaP and P and thermally treated ("reset") for 20 min at 1050 °C prior to measurement.

TABLE III. Integrated average power factors $(S^2\rho)$ between 300 and 1000 °C of n-type $Si_{80}Ge_{20}$ alloys prepared with varying amounts of GaP and P. (Hot pressed 45 min except where noted.)

Sample ID	Thermal history	$\langle\rho\rangle$ (mΩ cm)	$\langle S\rangle$ (μV/°C)	$\langle PF\rangle$ (μW/cm °C²)
A96β	As pressed	1.394	−209.5	31.9
A95α	As pressed	1.434	−213.6	32.7
A94α	As pressed	3.034	−262.0	23.1
A93α	As pressed	1.368	−213.7	34.0
A92α	As pressed	1.538	−229.4	34.5
A91γ	As pressed	1.834	−234.3	30.4
A91α	As pressed	1.652	−217.6	29.1
A90α	As pressed	1.844	−242.7	32.0
A99α	Reset	1.132	−195.0	34.3
A96β	Reset	1.151	−193.9	33.4
A95α	Reset	1.212	−203.3	35.1
A93α	Reset	1.171	−205.5	36.6
A92α	Reset	1.375	−205.6	31.3
A98β (60 min)	Reset	1.229	−198.6	32.9
A92β (60 min)	Reset	1.167	−200.5	34.7
A92γ (75 min)	Reset	1.236	−201.0	33.0
A92γ (75 min+20 h heat treatment at 1225 °C)	Reset	1.443	−212.6	31.6
STD1-1	As pressed	1.556	−226.4	33.1
STDM-4	As pressed	1.43	−222.2	34.8

having a room temperature carrier concentration of 3.8×10^{20} cm^{-3}.

The effect of the 20-min thermal treatment at 1050 °C is clearly observed in Fig. 1. For instance, alloy A92α in the as-pressed condition (which means the sample was cooled from the hot pressing temperature to ambient at the natural cooling rate of the furnace) is represented by a solid circle (●), while the same sample following the thermal "reset" treatment is represented by a solid square (■). Another example is illustrated by the transformation of the A93α sample from the as-pressed condition (●) to the thermal reset (■) condition. In general, we have observed that this type of thermal reset shifts the carrier concentration along a path roughly parallel to the extrapolated Dismukes mobility curve.

It is also observed that there is a significant amount of dissociation between the gallium and the phosphorus from the GaP additive during processing, as is seen by examining the sample A94α. This alloy was prepared with 1.6 mol % GaP and no elemental phosphorus, in order to observe the degree to which dissociation takes place. If no dissociation of the GaP had occurred, the observed carrier concentration would be dominated by trace impurities in the starting materials, perhaps on the order of 10^{15}–10^{16} cm^{-3}. However, since phosphorus is much more soluble than gallium in Si-

Ge, dissociation of the GaP is expected to result in an n-type doping due to the phosphorus going into solution. In particular, sample A94α has a room-temperature carrier concentration of 1.1×10^{20} cm^{-3}, which corresponds to roughly 15% dissociation of what is estimated to be the actual GaP content of the compact (taking losses into account).

The temperature dependences of the electrical resistivity, ρ, and Seebeck coefficient, S, of these alloys are shown in Figs. 2 and 3. The figures distinguish those samples which were measured in the as-pressed condition [Figs. 2(a) and 2(b)] from those which were thermally reset prior to measurement [Figs. 3(a) and 3(b)]. Table III lists the integrated average resistivity, Seebeck coefficient, and power factor of these alloys between 300 and 1000 °C. The resistivities of all alloys to which elemental phosphorus had been added show a characteristic decrease with temperature above 800 °C. While this might seem to be due to thermal excitation of electron-hole pairs, a simple calculation of the density of thermally activated electrons in the conduction band of a semiconductor with an energy gap of 1.1 eV yields a value of $\sim10^{18}$ cm^{-3} at 1000 °C, which is on the order of 1% of the density of ionized impurity carriers. Thus, the "turn-down" at high temperatures is due to the effects of increasing solubility of phosphorus.

Complicating the interpretation of these results is the inherent "metastability" of heavily doped Si–Ge alloys with time at elevated temperature due to the tendency for dopant precipitation. Each curve represents the combined effects of ionized impurity scattering, which is a thermally activated process, and dopant precipitation. The measurements of electrical resistivity and Seebeck coefficient were performed simultaneously on each sample and required 6–7 h for a complete excursion from room temperature to 1000 °C. In measurements of the dependence of carrier concentration on
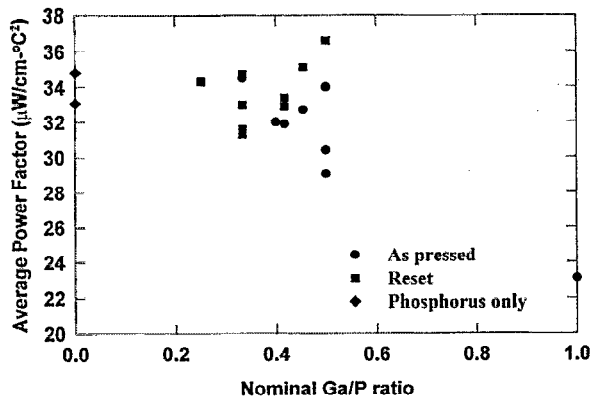
FIG. 4. Power factor (averaged between 300 and 1000 °C) as a function of nominal ratio of gallium to phosphorus for SiGe alloys with GaP (solid symbols) and for alloys doped only with phosphorus (diamonds).

FIG. 6. Optical metallography of two alloys with different nominal doping levels but similar electron concentrations. (left: A95α prepared with 2.75 at. % P and 1.25 at. % Ga; right: A90α prepared with 1.25 at. % P and 0.50 at. % Ga) (1000X).

time at temperature, we have found that similarly doped samples show a decrease of 40% in carrier concentration after only 70 min at 600 °C and approach a limiting decrease of 74% after 4000 h. The electrical resistivity and Seebeck coefficient of the samples that had been thermally reset tend to lie in a much narrower range than for those samples which were measured following a furnace cooling; in those samples significant dopant precipitation would have occurred.

The electrical power factor (S^2/ρ) of these alloys is expected to depend on the total amount of dopant added and on the Ga/P ratio, which is a measure of the amount of GaP in a sample. These effects are illustrated in Figs. 4 and 5. Figure 4 shows the average power factor as a function of Ga/P ratio. The data do not follow any simple trend, which illustrates that the amount of GaP added to Si-Ge may not by itself be a strong predictor of a high power factor. Other factors must also be considered. Indeed, two samples of Si-Ge containing no gallium at all exhibit power factor values not much lower than the highest values obtained in this study.

In Fig. 5 the average power factor is plotted as a function of the average Seebeck coefficient. Again, the results do not follow any simple relationship, indicating that additional fac-

tors such as processing variations and measurement errors may be significant. But the Seebeck coefficient is directly related to the carrier concentration, and is therefore expected to provide an indication of the total amount of dopant in solution. And in spite of considerable scatter in the results, Fig. 5 nevertheless indicates that Si-Ge with GaP additions can achieve significantly higher carrier concentration values (as indicated by the lower Seebeck values) compared to doping with phosphorus alone. This is particularly true for samples which have been thermally reset. Figure 5 also suggests that the power factor decreases with average Seebeck values below about 205–210 μV/°C, which is consistent with theoretical expectations.

Figure 6 shows the typical microstructure of two alloys which were found to have nearly identical room temperature carrier concentrations: A90α, with an average grain size of 1 μm, and A95α, with an average grain size of 25–30 μm. Since the mean free path of carriers at 25 °C is estimated to be on the order of 10 nm, one might expect little effect of grain size on mobility unless the material were truly "nanostructural." However, as Fig. 1 clearly shows, this is not the case, as there is nearly a 37% reduction in mobility, apparently due to the fine grain size of the A90 material. In general, this study found that samples with lower mobility values tend to have small grain sizes that are nevertheless considerably larger than the estimated mean free path.

Slack and Hussain[12] considered the effect of electrical potential barriers at grain boundaries using the approach of Murota and Sawai.[19] They concluded that a significant (i.e., 20%–40%) reduction in mobility could be expected to accompany a decrease in grain size from that of an infinitely large-grained crystal to 1 μm. Indeed, applying the Murota and Sawai relationship between grain size, L, effective width of the grain boundary, W (composed of two parts, that of the disordered region and that of the charge depletion region on each side of the boundary), the magnitude of the electrical resistance at the boundary, R_b, and the resistivity of a similarly-doped crystal of infinite grain size, $\rho(\infty)$, given by

$$\rho = \rho(\infty)\left(\frac{L}{L-W}\right) + R_b\left(\frac{L}{(L-W)^2}\right),$$

one finds that the observed mobility values in this study are consistent with a grain boundary potential barrier of $\sim 2.0 \times 10^{-8}$ Ω cm^2. This value assumes a $\rho(\infty)$ of 5.6×10^{-4}
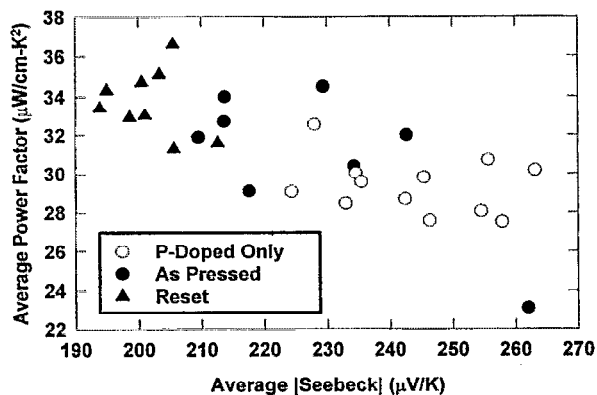

FIG. 5. Power factor as a function of Seebeck coefficient (both averaged between 300 and 1000 °C) for SiGe alloys with GaP (solid symbols) and doped with phosphorus only (open circles).
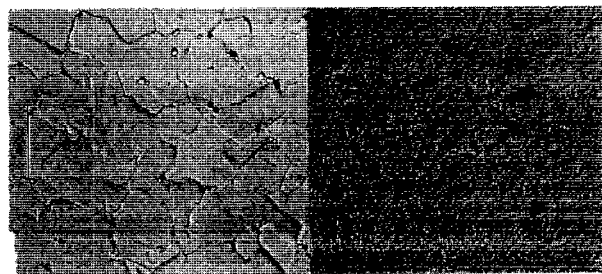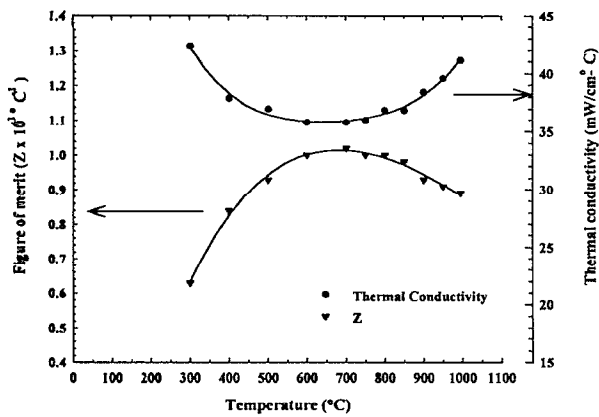
FIG. 7. Thermal conductivity (circles) and figure of merit (triangles) of A92β. (Nominal composition: 0.63 mol % GaP and 1.25 at. % P).

Ω cm (corresponding to a similar doping level) and a conservative estimate of 10 nm for the width of the grain boundary region, W.

The value of $R_b = 9.6 \times 10^{-8}$ Ω cm^2 used by Murota and Sawai and by Slack and Hussain corresponded to oxygen-free silicon, and one would expect a lower potential barrier in such materials. An increasing amount of second-phase oxygen would be expected to increase the electrical barrier potential, thereby decreasing the mobility for a given grain size. Formation of scattering sites as a result of the second-phase oxygen is expected to be a relatively minor contribution to the carrier scattering. The total oxygen content of these alloys is estimated as 0.6–0.8 at. %, based on the results of neutron-activation analyses performed on similar samples prepared from the same starting materials. The room-temperature Seebeck coefficients of the aforementioned alloys were found to be similar, as expected: −90.4 μV/ °C for the A95 material and −88.4 μV/ °C for the A90 sample. The results of this study tend to confirm Slack and Hussain's contention that large-grained, low-oxygen alloys are more desirable for thermoelectric applications at high temperature than fined-grained materials.

Since the mobility of many samples in this study approach the mobilities extrapolated from zone-leveled samples, it is unclear how much additional improvement in mobility (if any) would result by further reductions in the oxygen level. However if the trend established for the more heavily doped n-type alloys applies here, an additional improvement of 5%–10% in power factor should be possible by using float-zoned silicon as the starting material, which would translate to an average power factor of 38 μW/(cm °C^2) between 300 and 1000 °C. This value would agree with most theoretical models, which predict an optimum power factor near 40 μW/(cm °C^2) for the silicon-germanium system.

The thermal diffusivity of an alloy showing one of the highest power factors in this study, A92β, was measured from 300 to 1000 °C. The thermal conductivity, Λ, calculated using the density, measured diffusivity and extrapolated specific heat values, is shown in Fig. 7. The integrated average thermal conductivity between 300 to 1000 °C was deter-

mined to be 37.5 mW/(cm °C), which, when combined with the electrical data, gives an integrated average figure of merit ($Z = S^2/\rho\Lambda$) of 0.94×10^{-3} °C^{-1} and a maximum ZT of 1.1 at 1000 °C. The figure of merit curve for this material is also shown in Fig. 7. Not only is the average Z higher than that for the more heavily doped samples discussed in the introduction, the rate at which Z drops off near 1000 °C is not as severe. Due to the lower carrier concentration of the A92β composition, the ratio of the electronic to the phonon component of the total thermal conductivity at 1000 °C is expected to be less than that of the more heavily doped material. Moreover, the rate at which the Seebeck coefficient falls off near 1000 °C is also much lower than what has been observed on more heavily doped alloys; this low rate is primarily responsible for maintaining the comparatively high power factor between 800 and 1000 °C.

A composition near that of the A92 material, i.e., containing 1.25 at. % P and 0.63 mol % GaP, is apparently close to the optimum for n-type Si$_{0.8}$Ge$_{0.2}$ alloys prepared by MA and hot pressing. However, it is likely that some of the beneficial effects of optimizing dopant concentration in a given alloy system may be offset by subsequent high-temperature diffusion bonding processes applied during device fabrication and, as mentioned, by the tendency for dopants to precipitate out of solid solution during long-term applications.

CONCLUSION

Nearly optimized electrical properties can be obtained in n-type Si$_{80}$Ge$_{20}$ alloys prepared by mechanical alloying and hot pressing having a nominal GaP content of approximately 0.6 mol % and a Ga/P ratio of 0.25–0.50. The primary effect of the GaP additions appears to be an enhanced carrier concentration, as previously reported.[10] Duration of the hot pressing sequence has a pronounced effect on the microstructure and hence the electrical properties. Alloys with an average grain size ≥5–10 μm and room-temperature values of carrier concentration ≥2×10^{20} cm^{-3} had mobilities at or near the best values observed in zone leveled materials. Integrated average power factors of 34–35 μW/(cm °C^2) between 300 and 1000 °C were obtained by several combinations of composition and preparation procedure. A maximum value for the dimensionless figure of merit, of $ZT = 1.1$ was obtained at 1000 °C. The integrated average figure of merit of an alloy having the highest power factor was determined to equal 0.94×10^{-3} °C^{-1}. Microstructure was shown to have a significant effect on carrier mobility through grain boundary potential scattering.

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