SILICON-GERMANIUM: AN OVERVIEW OF RECENT DEVELOPMENTS

Cronin B. Vining and Jean-Pierre Fleurial
Jet Propulsion Laboratory/
California Institute of Technology
M/S 277-212
4800 Oak Grove Drive
Pasadena, CA 91109-8099
(818) 354-9374
(818) 354-4144

Author to whom correspondence should be sent: Cronin B. Vining
                                                  Jet Propulsion Laboratory/
                                                  California Institute of Technology
                                                  M/S 277-212
                                                  4800 Oak Grove Drive
                                                  Pasadena, California
                                                  (:   (818) 354-9374
                                                  FAX: (818) 393-6951
                                                  E-+ :CVINING@DSFVAX.JPL.NASA.GOV

SILICON-GERMANIUM: AN OVERVIEW OF RECENT DEVELOPMENTS

Cronin B. Vining and Jean-Pierre Fleurial
Jet Propulsion Laboratory/
California Institute of Technology
M/S 277-212
4800 Oak Grove Drive
Pasadena, CA 91109-8099
(818) 354-9374
(818) 354-4144

Abstract

Over the last decade an impressive variety of innovative techniques has been applied to prepare silicon-germanium alloys with improved thermoelectric figure of merit values. Today, technologically important improvements appear nearly ready for device-level testing. Some approaches have favored the reduction of the lattice thermal conductivity through smaller grain size or addition of inert particulates to enhance phonon scattering. Other approaches sought to improve the electrical properties of the materials by carrier concentration and mobility enhancement. Although most of the experimental work has been conducted on sintered/hot-pressed materials, more sophisticated and complex techniques have been developed to strive for more control over microstructure and composition. The difficulty of understanding the physical mechanisms involved and of predicting the magnitude of possible improvements has led to the development of theoretical tools based on solid-state physics and physical chemistry. This paper attempts to provide an overview of the experimental and theoretical efforts to improve the thermoelectric properties of silicon-germanium with a particular emphasis on some of the less well publicized results. Future prospects and open questions are also briefly discussed.

INTRODUCTION

Particularly well suited for space power applications, heavily doped silicon-germanium (SiGe) alloys have been the exclusive choice for NASA's radioisotope thermoelectric generator (RTG) needs since the launch of Voyager I and II and has performed with distinction in this role. The development of SiGe thermoelectrics, from the early research efforts at RCA's Princeton Laboratory to use in recent space applications, has been amply and capably reviewed by Rosi (1968), Bhandari and Rowe (1980), Rowe (1987), Wood (1988), Rowe (1989), Cody (1990), and Rosi (1991). Slack (1991) provides a very detailed discussion of the theoretical maximum efficiency of silicon-germanium thermoelectric converters. Equally significant, but beyond the scope of this overview, is the extensive effort on SiGe heterostructures, recently reviewed in (Pearsall 1989). The Voyagers, employing a unicouple thermoelectric device configuration and SiGe prepared by hot-pressing, have established a staggering reliability record criteria of 16 years without a single unicouple failure.

After the launch of Voyagers I and II, advantage was taken of the expected lapse before the next RTG would be needed and an ambitious RTG program was undertaken at 3M which included development of a new class of thermoelectric materials based on selenium. This program, unfortunately, encountered serious technical difficulties and the SiGe manufacturing facilities had already been shut down at RCA's Harrison Laboratories. With the re-establishment of a SiGe manufacturing capability, now at General Electric's Valley Forge Space Center (GE-VF), and the approximately concurrent beginnings of the SP-100 space nuclear reactor program, there began a period of renewed interest in SiGe the United States in the early 1980's.

The unfortunate experience with the selenides and the now proven performance of SiGe encouraged a re-examination of the possibility of achieving further improvements in this trusted material. Over the past 10-15 years a variety of sponsors and programs, mostly concerned with the US space program, have contributed significantly to this effort. There will be no attempt to discuss in detail the various sponsors, goals and programs involved. Nevertheless, there are certain general points to be made.

Through a long-standing arrangement the United States Department of Energy (DOE) has provided the United States National Aeronautics and Space Administration (NASA) with RTG's. As such, DOE has sponsored a variety of RTG and SiGe related development activities. NASA, largely through the Jet Propulsion Laboratory/California Institute of Technology (JPL), also maintains a high level of interest in these areas because JPL utilizes these technologies. DOE, NASA and the Strategic Defense Initiative Office (SDIO) share interests in the development of a space nuclear reactor capability and each contribute to the SP-100 program for that reason. At a somewhat lower level of effort, the U.S. Army Electronics Technology and Devices Laboratory (LABCOM) has also expressed a serious interest in SiGe for terrestrial applications.

The primary purpose of this overview is to attempt to follow the evolution of the technical ideas to improve SiGe examined in these programs, with special emphasis on less well known results. In some cases, results discussed here may not have appeared elsewhere in print, but every effort has been made to give appropriate credit.

The majority of this overview is organized along the lines of the two main approaches for improving any thermoelectric material: 1) reduce in the thermal conductivity and/or 2) improve the electrical properties. Two contributions warrant particular note due to their influence on subsequent developments. Raag, then at Syncal, initiated work involving gallium phosphide (GaP) additions to SiGe. Generally the notation used to describe this is "SiGe/GaP." This work (Pisharody 1978), which appeared to result in a lower thermal conductivity and a higher figure of merit ($Z = \sigma\alpha^2/\lambda$), has had a major influence on all the following efforts related to SiGe.

A second body of work, which remains a major influence today, is the work of Rowe (1974) and others on the grain boundary scattering of phonons sometimes simply referred to as "fine grain SiGe." More than anything else, the two ideas of "SiGe/GaP" and "fine grain SiGe," have in one way or another dominated all the following work in this area and the story of SiGe technology after the Voyagers is largely the story of these two ideas.

One final comment is in order before proceeding. Several terms, such as "standard SiGe," "SiGe/GaP," and "fine grain SiGe," will be used here in much the same way as they are commonly used throughout the community. "Standard SiGe" means something very like the materials used, say, in the Voyagers. "SiGe/GaP" means it has GaP in it and "fine grain SiGe" means the grains are more or less fine (say, 5 μm or less). Strictly speaking, however, there is no "standard SiGe," for example, only a family of closely related specifications which, religiously executed, produce a product with a narrow range of properties.

The situation is even more obscure for the terms "SiGe/GaP" and "fine grain SiGe," as these terms have been applied to materials prepared by tremendously different methods, and with concomitantly variant properties. Further, they are not exclusive terms. A "fine grain SiGe" may or may not contain GaP, and a "SiGe/GaP" sample may or may not have small grains. And GaP content, grain size, Si/Ge ratio and doping level can vary substantially. Still, with some care, these terms do have some meaning and are convenient for categorization purposes.

THERMAL CONDUCTIVITY REDUCTION METHODS

Grain Boundary Scattering of Phonons

Early work on the effect of grain boundary scattering on the thermal conductivity of fine grain SiGe has been reviewed through 1980 by Bhandari and Rowe (1980), so only a brief discussion will be given here. Goldsmid and Penn (1968) first pointed out that boundary scattering of phonons could be an important effect in the thermal conductivity of alloys at high temperatures, even though the effect is negligible in pure materials. Parrott (1969) extended these calculations and predicted significant reductions in the thermal conductivity of SiGe alloys. Experimental results by Savvides and Goldsmid (1973) on silicon and by Meddins and Parrott (1976) on SiGe alloys tend to support the prediction that fine grain SiGe should have a lower thermal conductivity, particularly in undoped materials.

Rowe, in a series of collaborative papers (Rowe 1974, 1981a,b, Bhandari 1978), has examined the effect of fine grain size and predicted significant improvements in Z. This body of work, both experimental and theoretical, was well known when work on SiGe began to increase in the United States in the early 1980's. Particularly influential was the repeated assertion and widespread expectation that the thermal conductivity could be significantly reduced by fine grain effects, long before any significant reduction in the electrical properties would be observed (Rowe 1974, 1981a,b, Meddins 1976).

While several studies had achieved Z values in sintered or fine grain materials similar to previous results on zone leveled SiGe (Rosi 1968), none had reported the expected improvements. To address this discrepancy as well as other thermoelectric materials issues, DOE supported the Improved Thermoelectric Materials (ITM) program at GE-VF beginning in 1984 (ITM Final Report 1989). These studies examined a wide variety of hot pressing and particle comminution methods and achieved thermal conductivity reductions in fully dense (>97%) materials of up to 50% (Vining 1991a), as shown in Figure 1. While qualitatively confirming the expected reduction in λ with grain size, the temperature dependence of the reduced thermal conductivity, shown in Figure 2, was not quite as expected from theory and a highly correlated reduction in the electrical mobility resulted in no net improvement in Z compared to similar zone leveled materials, as indicated in Figure 3.
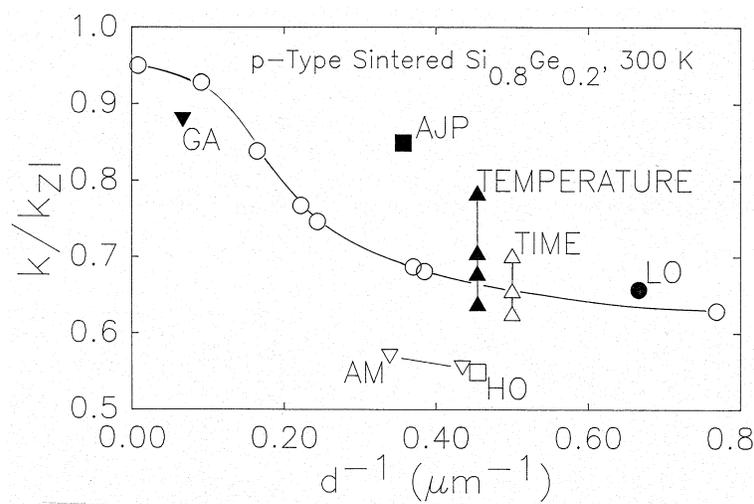

FIGURE 1.   Thermal Conductivity of Sintered, p-type SiGe as a Function of Particle Size, Normalized to Zone Leveled Material. The Labels Indicate Processing Variations, Discussed in (Vining 1991a).
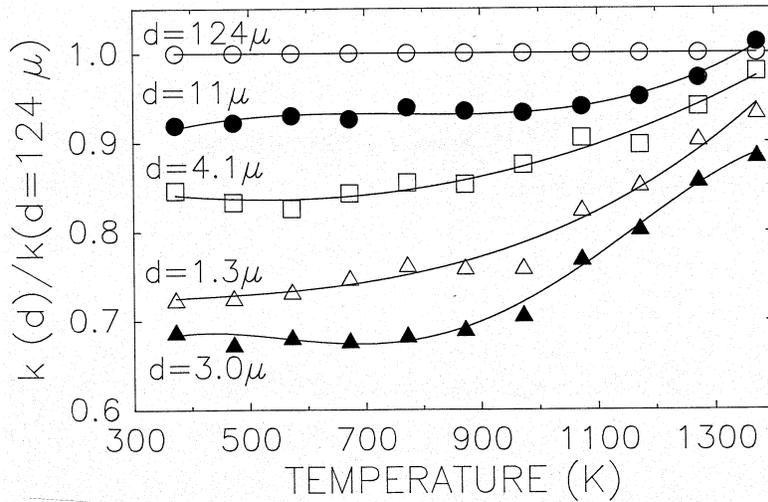
FIGURE 2. Thermal Conductivity for Five Samples of Sintered, p-type SiGe, Normalized to the Thermal Conductivity of the Largest Particle Size Sample (Vining 1991a).
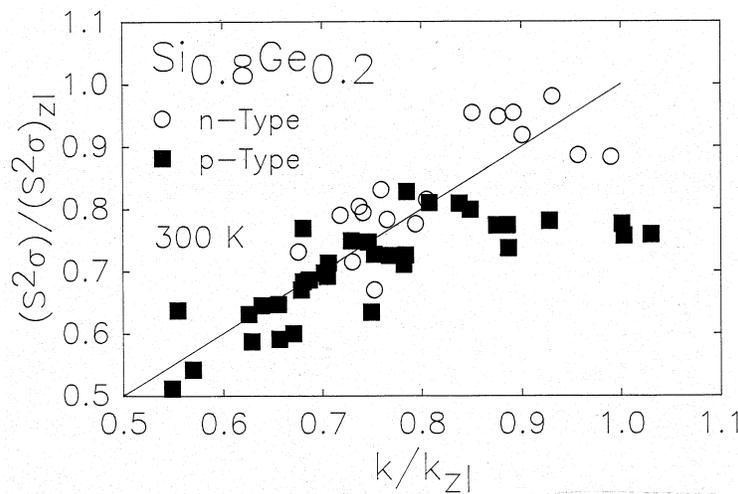

FIGURE 3. Electrical Power Factor as a Function of Thermal Conductivity, Where Each Property has been Normalized to Zone-Leveled Materials. The Solid Line Represents a Figure of Merit Equivalent to Zone-Leveled Materials (Vining 1991a).

A wide variety of powder metallurgical processes were examined in this study, including pulverization in a shatter box, gas atomization from the melt, planetary ball milling in various media, attrition milling, and air jet pulverization. Experiments were designed to both increase and decrease the oxygen content of samples in order to examine the role of oxygen. A fine grain sample (labeled LO in Figure 1) prepared with special attention to keep the oxygen content (0.23 wt. %) comparable to large grain size material (typically 0.2 wt. %), still showed a substantial thermal conductivity reduction, but no improvement in Z.

Each method produces distinct particle size and shape distributions as well as variations in the amounts and types of impurities introduced. Generally, smaller particle sizes produce smaller thermal and electrical conductivities. But virtually every other processing variable can also result in changes on the same order of magnitude. Particles produced by different methods or hot pressed

under different conditions result in different thermoelectric properties, even when of nominally the same size. Increasing the hot pressing temperature, for example, by only 45 K resulted in a 2% increase in density (from 97% to 99% dense), but a 20% increase in thermal conductivity.

An important result from this study is the need for tight control over virtually all of the experimental variables and the need to measure all the thermoelectric properties on a single sample. These effects are expected to be superposed on any other study involving sintered SiGe and can easily obscure the primary intention of the experiment. It seems clear that straightforward variations of hot pressing conditions alone offers little overall advantage in terms of Z. But equally important is the conclusion that over a wide range of preparation conditions, excellent Z values essentially identical to zone leveled values can be achieved, in spite of large changes in the individual thermoelectric properties.

While several of the particle comminution methods examined under the ITM program have distinct advantages, one process developed at General Electric's Corporate Research and Development (GE-CRD) center deserves particular note. The gas atomization process, described by Miller (1983), has several advantages as applied to SiGe. This rapidly quenched process can readily produce industrial quantities of highly uniform particles of doped SiGe on the order of 15 μm in diameter directly from the starting elements. Actually, significant compositional segregation occurs within these particles, but on a length scale that allows complete homogenization during ordinary hot pressing. These powders can then be hot pressed without any further processing.

Mechanical Alloying

Mechanical alloying, which produces homogeneous sub-micron SiGe alloys at room temperature, has been studied at Ames for both n-type (Cook 1989) and p-type (Cook 1991, 1993 and Harringa 1992) materials. In addition to very fine microstructures which may produce low thermal conductivity values, this unique process may be suitable for incorporating fine dispersals of inert additions or for incorporating volatile materials difficult to handle by other methods. While reductions in thermal conductivity were reported for both n-type materials (which also contained GaP) and p-type materials, Z values for the n-type materials were similar to previous results while the p-type materials appear to be up to about 10% improved. In this case, however, the improvement may be due to the higher doping level of the mechanically alloyed samples compared to standard materials, rather than the lower thermal conductivity values.

A very similar method of preparation has been reported by Gogishvilli (1990). This study emphasizes the advantages for preparing homogeneous materials by a low temperature process, avoiding the unpleasant consequences of the SiGe phase diagram. No transport properties were reported.

GaP Additions - Indications of λ Reductions

The first efforts to incorporate GaP into SiGe were performed under a JPL sponsored program at Syncal Corporation under Raag (Pisharody 1978). In this report, the thermal conductivity of both n-type and p-type SiGe/GaP is reported to be 40-50% lower than materials without the GaP. A significantly enhanced Z was reported in spite of some increase in electrical resistivity.

Pisharody's paper on SiGe/GaP was extremely influential on future work on SiGe. Eventually, several independent measurements seemed to support these results. Samples of SiGe/GaP, prepared by Syncal, were sent to the Thermophysical Properties Research Laboratory (TPRC) at Purdue University for thermal conductivity measurements (Taylor 1980) and Ames Laboratory, USDOE (Ames) for Seebeck coefficient and electrical resistivity measurements (Raag 1984). This data set, widely referred to as the "Ames/Purdue" data, appears to confirm the lower thermal conductivity and

higher resistivity and suggests an overall improvement in SiGe/GaP compared to standard SiGe of about 23% in Z. See Schock (1983) for the only open publication of these data.

Based partly on these results, a unique device geometry called a 'bicouple' was developed at GE-VF and the new SiGe/GaP material was tested at the device level (Cockfield 1984), considered a more definitive test than direct thermoelectric property measurements. Four bicouples were built at GE-VF from SiGe/GaP prepared by Thermo Electron Corporation (now called, and hereafter referred to as, TTC) (SiGe RTG Report 1984) and four more bicouples were built from a type of fine grain SiGe then being developed at GE-VF. It should be emphasized that the fine grain SiGe was "expected to exhibit both Seebeck and electrical resistivity no different than standard SiGe, but to have a thermal conductivity reduced by 18%" (Cockfield 1984), but had not been fully characterized. This assumption, though reasonable at the time, is hardly consistent with the studies on fine grain SiGe discussed above.

These eight bicouples were tested simultaneously at Fairchild Space and Electronics Company (Fairchild), as reported by Cockfield (1984). Analysis of the results required estimates of the temperatures at the device junctions, which are different for the two types of devices, and this in-turn required certain assumptions about material and junction properties. The electrical properties of the fine grain SiGe devices varied considerably amongst themselves and a few of the test fixture thermocouple readings were judged unreasonable and had to be disregarded. The various assumptions and analyses of these tests have been extensively discussed in the community, some of which is documented in a contract monthly report (SiGe RTG Report 1984), but most of which appears to be entirely undocumented.

The most widely known analysis is due to Eck (1984) and is widely regarded as an excellent analysis of the available data. Among Eck's conclusions regarding this test are: 1) both the fine grain SiGe and SiGe/GaP bicouples produced less electrical power than expected, probably due to higher electrical and thermal contact resistances within the devices; 2) the SiGe/GaP has a distinctly lower thermal conductivity and a distinctly lower electrical power factor ($\sigma\alpha^2$) than the fine grain SiGe; 3) based on preliminary inferential calculations, the Z of the SiGe/GaP material appeared to be 23% higher than that of the fine grain SiGe. Some of these conclusions will be discussed in the summary in context with more recent results.

The combination of the Syncal (Pisharody 1978), the Ames/Purdue (Taylor 1980, Raag 1984) material test results and the bicouple device test results (Cockfield 1984, SiGe RTG Report 1984, Eck 1984) resulted in a concerted effort to determine the precise mechanism by which GaP additions resulted in a lower thermal conductivity. Another consequence of these results was the adoption of n-type SiGe/GaP for the MOD-RTG program (MOD-RTG Program 1991), an advanced, multicouple oriented RTG development program based on a Fairchild design (Schock 1983). A type of fine grain SiGe was adopted for the p-type materials due to concerns over the stability of p-type SiGe/GaP.

It should be pointed out that the processing specifications for n-type SiGe/GaP adopted by the MOD-RTG program result in thermoelectric properties no better than standard n-type SiGe (deduced from data in ITM Program Final Report 1989). Indeed, atomic concentrations of Ga and P had to be changed drastically to insure reliable manufacturing of SiGe/GaP material with improved Z values using the MOD-RTG process (Vandersande and Fleurial 1992a). Even today further effort is required before SiGe/GaP with improved Z can be manufactured with sufficiently reproducible performance for a flight program. Nevertheless, by building and testing devices manufactured from a current generation SiGe/GaP material, the MOD-RTG program will presumably resolve any bonding or materials compatibility issues which may arise.

GaP Additions - l Reduction Mechanism Studies

A significant impetus had developed, therefore, to determine the precise mechanism by which GaP additions lower the thermal conductivity of SiGe. The ITM program at GE directed considerable effort in this direction, much of which was aimed (at least initially) at reproducing the microstructure observed in SiGe/GaP samples produced by TTC and used in the bicouple tests described above. These efforts were successful in that the microstructures of the GE samples did resemble the TTC samples, and the GE samples did exhibit reduced thermal conductivity values, although the Z values were not improved.

A variety of measurements were performed on these low thermal conductivity GE samples. Extended X-ray absorption fine structure (EXAFS) measurements on the GE samples indicated that the bonding environment of the Ga atoms in the n-type material is identical to the bonding environment of Ga atoms in GaP, while in the p-type material, Ga was bonded in an entirely different (and as yet undetermined) way (ITM Program Final Report 1989). Transmission electron microscopy (TEM) performed on these samples at the University of Virginia (Owusu-Sekyere 1989) revealed a rich microstructure with a distinct bimodal distribution of grain sizes. Fine grains (0.1 to 1.5 μm), not readily observable with optical techniques, were found to occupy as much 55% of the sample. The remainder of the materials were composed of coarser particles (1.5 to 10 μm).

FIGURE 4. Thermal Conductivity of SiGe/GaP, Normalized for Carrier Concentration Effects, as a Function of Ga Content and Preparation Method.

Several calculations performed independently in the mid-1980's suggested GaP alone should not lower the thermal conductivity. Rosi's calculations (the only result published) indicate addition of 5% GaP to $Si_{0.8}Ge_{0.2}$ should <u>increase</u> the thermal conductivity by about 8% (Rosi 1991). In retrospect, the reason for this is simple: SiGe has a low thermal conductivity due to the large difference in mass between Si and Ge. But the masses of Ga and P are both <u>between</u> the masses of Si and Ge, so any addition of GaP actually decreases the average mass difference. This is not in discord with either the EXAFS results, which indicate (at least for n-type) that the GaP was not in solution in any case or the TEM results, which provided ample microstructural reasons for the low thermal conductivity.

Further experiments at GE involved preparation of samples with various amounts of GaP. Some samples were prepared by blending powders of SiGe with powders of GaP and hot pressing the mixtures. Others were prepared by adding GaP directly to a melt of SiGe (in an effort to get more GaP in solution), followed by pulverization and hot pressing. Although widely discussed in programmatic reviews in the mid-1980's, these results are not documented in the open literature, and the raw data must be extracted from Appendix A of the ITM program final report (1989).

Figure 4 shows the effect of additions of GaP on the thermal conductivity, normalized by the thermal conductivity of a comparable zone leveled sample (λ_{zl}) to account for variations in doping level. Four variations of preparation conditions are considered. Most of the thermal conductivity reduction observed in this study is due to grain size effects. Indeed, except for the very highest concentrations studied (where the normalizations used may be less reliable), the normalized thermal

conductivity actually increases with increasing GaP content, in qualitative agreement to the theoretical calculation of Rosi discussed above.

An important point regarding Figure 4 is that a quite different conclusion might be reached if the normalization is neglected. Typically, adding more GaP results in higher carrier concentrations due to the higher solubility of P compared to Ga. Higher carrier concentrations result in lower thermal conductivities, as is well known (Rosi 1968). Also, the processes generally used to prepare SiGe/GaP tended to produce much finer grain sizes than had previously been studied, which, as discussed above, certainly lowers the thermal conductivity.

Thus, it seems clear today that the mechanisms responsible for the lower thermal conductivity of SiGe/GaP materials are the fine grain size and high carrier concentration, both of which are a natural consequence of the processes adopted to introduce GaP, as first suggested in (Amano 1987). In a sense, then, GaP works, but not by the mechanisms originally supposed. In analogy to the fine grain studies, it might be expected that GaP additions would not improve Z, at least compared to similar zone leveled materials.

P-Type Materials: Boron and III-V Additions

Several early SiGe/GaP results had raised concerns about the stability of the p-type materials, which required additions of large quantities of boron to overcompensate for the inherent n-type tendencies of GaP additions. Studies were directed at the cross-doping effects (Gunther 1982) and after the SiGe/GaP bicouples (SiGe RTG Report 1984) experienced relatively rapid degradation with time (presumably associated with the p-type SiGe/GaP materials), much of the experimental efforts shifted focus to n-type SiGe/GaP.

One small program involving LABCOM, TTC and JPL examined the effects of additions of BP, GaP and GaSb on p-type SiGe (McLane 1986). At the time, the mechanism by which GaP lowers the thermal conductivity was still in serious question. It seemed plausible that regardless of how GaP additions worked, other III-V compounds might function similarly and one needed only to avoid poisoning the p-type electrical properties. Preliminary results seemed encouraging, but reproducibility of the initial measurements proved difficult and no real improvement seems to have been achieved by this approach.

A second program involving the same laboratories examined the effects of really large additions of boron to SiGe, up to 20 atomic percent boron, again based on encouraging preliminary results (Vining 1988). Figure of merit improvements were not immediately forthcoming, mostly due to the formation of relatively high thermal conductivity second phases. But these experiments did serve to emphasize that very low resistivity values could be achieved by boron additions alone due to the high solubility of boron. Although even the earliest SiGe studies indicated boron is sufficiently soluble to achieve greater than optimum hole concentrations (Rosi 1968), only recent studies appear to confirm that standard SiGe is in fact under-doped. Improvements in Z of 10-15% have been reported merely by increasing the atomic boron concentration from 0.23 at% (used in the Voyager RTGs) to 0.6-1.3 at% (Bajgar 1991, Loughin 1993, and Fleurial 1993a).

Column IV Additions: Sn and Pb

An attractive idea that recurs from time to time is the question of alloys of Si and/or Ge with one of the other column IV elements: C, Sn or Pb. From the point of view of lower lattice thermal conductivity, one desires the greatest difference between the masses of a two-component alloy as possible and generally heavier masses. Assuming the only difference between a Si-Pb and a Si-Ge alloy were the mass of the atom, for example, a recent calculation suggests the Si-Pb material would

have twice the figure of merit (Vining 1990) of the SiGe material. It seems natural, then, to investigate alloys involving the heavy elements Sn and Pb.

A patent (Duncan 1985) has been granted for Sn and Pb additions to SiGe which indicates a major reduction in thermal conductivity and improvement in Z, as described in (Duncan 1989). Unfortunately, more recent results (Elsner 1990) strongly suggest some measurement error in the original data. Recent thermodynamic calculations of several Si-Ge-Metal systems (Fleurial 1990c) have shown that the maximum solid solubilities of Sn and Pb in $Si_{80}Ge_{20}$ are about 0.12 at% and less than 0.001 at% respectively. In this case, neither Sn nor Pb are soluble enough in either Si or Ge to have any observable decrease in the thermal conductivity of a SiGe alloy.

Neutral Donor Scattering

White (White 1990, 1992) has examined theoretically the effect of neutral impurities on the lattice thermal conductivity. Shallow, neutral impurity states perturb the electronic structure in the vicinity of the impurity, which strains the lattice and results in phonon scattering. This contribution to phonon scattering is estimated to lower the thermal conductivity by about 8% at high temperatures, which may be observable in some cases. Unfortunately, further increases in this phonon scattering mechanism appear to be ineffective at lowering the thermal conductivity at high temperatures in these heavily doped alloys.

Inert Particulates

For some years it has been recognized that alloying is effective at scattering short wavelength phonons and free carriers (and/or grain boundaries) are effective at scattering long wavelength phonons. A substantial amount, perhaps the majority, of the heat is therefore attributable to a range of intermediate wavelength phonons with (relatively) low scattering rates. A scattering mechanism directed at these intermediate wavelength phonons might, therefore, be quite effective at lowering the thermal conductivity.

One possible scattering mechanism is to introduce a fine, randomly distributed dispersion of very small (say, 50-100 Å) particulates into an otherwise undisturbed single crystal. This general idea has been recognized as early as 1966 and is described in a Monsanto patent (Henderson 1966), summarized in Sittig's (1970) review of the patent literature. This report claimed to improve Z of SiGe by additions of aluminum oxide, calcium oxide, boron nitride, and a long list of other additions. Up to 14% of particulates were added to SiGe, with particulate sizes ranging from 50 to 500,000 Å and inter-particulate distances from 50 to 500 Å. Z values as high as 1.1×10^{-3} K^{-1} were reported.

Serious experimental and theoretical investigations are more recent and still active. Slack, under the ITM program, has attempted to grow suitable particulates in-situ by precipitation of boron (ITM Program Final Report 1988). An SDIO sponsored program with JPL and Los Alamos pursued a plasma deposition process with similar goals, but encountered difficulties before the concept could be verified. This same program examined the possibility of producing extended defects by neutron radiation (Vandersande 1990a,b). While not strictly particulates, the neutron induced defects were supposed to cluster in a manner which would scatter intermediate wavelength phonons. Reductions in thermal conductivity were in fact observed, but the effect annealed out rather quickly with time and the reduction of the electrical mobility was greater than the reduction of the thermal conductivity. Still, this is an important result because the properties rapidly returned to their pre-radiation values, demonstrating the radiation resistance of SiGe.

The most substantive effort on particulate additions is currently underway at TTC, with support from JPL. Calculations performed by Klemens (1991), White (1990, 1992), Vining (1991b), and Slack (1991) suggest significant improvements in Z (10-40%) may be possible by incorporating fine

particulates in SiGe. Slack (1991) discusses the importance of achieving a large grain size in the final material in order to avoid degradation of the electrical conductivity.

TTC has developed a remarkable spark erosion preparation method (Beaty 1990) to produce ultra-fine particles of inert, phonon scattering centers, introducing them into B-doped SiGe and evaluating their thermal conductivity after processing. For this effort, conducted under a JPL/TTC program, particles of SiGe 20 to 120 Å in size were produced and methods were developed for handling, mixing, hot-pressing and heat-treating these powders (Beaty 1991a). After demonstrating Z values typical of standard p-type SiGe/B using appropriate high temperature heat-treatments, attempts were made to introduce inert scattering centers. Suitable scattering center materials were to be electrically, thermally and chemically inert, but electrically conductive enough to be spark eroded.
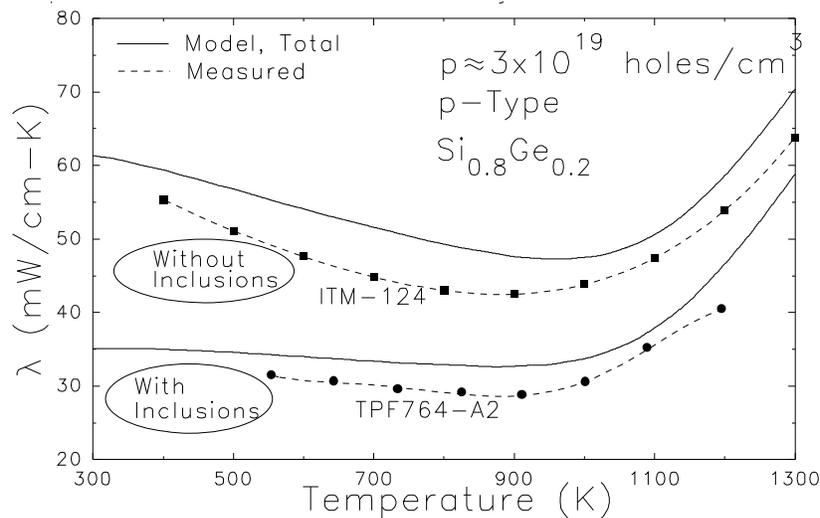
FIGURE 5. Thermal Conductivity for SiGe With and Without Particulates. Solid Lines Were Calculated as Described in (Vining 1991b). Dashed Lines Represent Data From (ITM Final Report 1989) and (Beaty 1991b).

Several materials have been investigated to date (JPL/TTC Workshop 1991): 1) SiO_2, which dissociated within the SiGe matrix; 2) aluminum oxides, which proved to be only metastable when formed by spark erosion; 3) Si_3N_4, which reacted with the B dopant to form BN, and 4) BN which appeared stable within the SiGe matrix. Samples prepared with Si_3N_4 and BN particles exhibited much lower thermal conductivities than standard SiGe, even after several high temperature anneals. Figure 5 shows the good agreement between experiment and theory for the change in thermal conductivity (at equivalent doping level) due to particulate scattering centers (Beaty 1991b). TEM analysis of several such samples showed particles containing B and ranging in size from 50 to 200 Å were embedded in the SiGe grains (Vandersande 1992b). Several samples with BN inclusions succeeded in improving Z up to 0.7×10^{-3} K^{-1} but reproducible results have been hampered by difficulties in the manufacturing process.

Minimum Lattice Thermal Conductivity

Common to all of these thermal conductivity reduction concepts is a limiting principle proposed by Slack (1979) and recently reviewed by Cahill and Pohl (1991). This principle is the idea of a minimum thermal conductivity. In simplistic terms, a phonon is a wave-like disturbance of the atoms in a crystal. If phonon scattering rates became too large, conventional perturbation theory will eventually break down. One way around this breakdown is to impose a lower limit on the phonon mean free path. A natural cutoff is to require the phonon mean free path to be greater than one

interatomic distance. Slack proposes a somewhat more restrictive limit to cutoff the scattering distance at one wavelength, arguing that one cannot really speak of a phonon until it travels at least one wavelength.

Recent estimates now place the minimum lattice thermal conductivity for Si at about 10 mW/cm-K (Cahill 1989). Slack has estimated that if the thermal conductivity of SiGe could be reduced to the minimum value, the Z would more than double over current values, as shown in Figure 6 (ITM Final Report 1989).
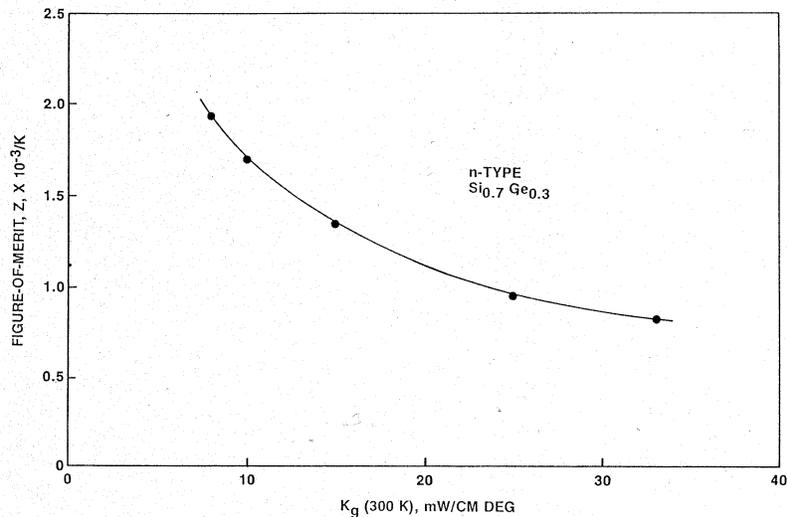

FIGURE 6. Average Thermoelectric Figure of Merit From 773 to 1273 K as a Function of the Lattice Thermal Conductivity at 300 K (ITM Final Report 1989).

IMPROVEMENT OF THE ELECTRICAL PROPERTIES

GaP Additions - Carrier Concentration Enhancement

Through about 1987, most studies focused on thermal conductivity reductions and little attention was given to the possibility of optimizing the electrical properties of n-type $Si_{80}Ge_{20}$ by increasing the carrier concentration. But since the work done in the 1960's at RCA (Rosi 1968) and in the Soviet Union (Erofeev 1966), it has been known that, unlike boron used for p-type materials, phosphorus (P) could only produce room temperature carrier concentrations up to 2.2×10^{20} cm^{-3} in n-type $Si_{80}Ge_{20}$, due to its limited solubility. Only recently, under the ITM program at GE, have new results on SiGe/GaP sparked renewed interest in high carrier concentrations in n-type materials (ITM Final Report 1989). Although the ITM studies were originally intended to characterize the influence of GaP additions on the thermal conductivity, as discussed in the preceding sections, contradictory results seemed to show that the GaP additions did alter the transport properties but not for the reasons originally expected.

Indeed, regardless of the theoretical suggestion of thermal conductivity reduction by small particulates, it retrospectively seems that the possibility of having stable GaP particles in a Si+Ge environment was quite limited. Since 1968, the work of Glazov (1968) on doping Si and Ge using III and V elements had shown there was no pseudo-binary equilibrium between Si or Ge and the III-V compounds investigated, as the ratio of the solid solubilities of the III and V elements was not retained upon incorporation into Si or Ge. Glazov also found that the solubility values depended on the stability of the corresponding III-V compounds.

The ITM work on heavily doped SiGe/GaP showed: 1) the sample composition was lower in Ga and Ge after hot-pressing and subsequent heat treatments; and 2) higher carrier concentrations could be obtained, up to 2.8×10^{20} cm^{-3}. Although a different interpretation was given at the time, these ITM samples were the first ones to exhibit carrier concentrations substantially higher than for standard SiGe material.

The first encouraging results on improvement of Z came in 1987 when JPL reported Z values 30% higher than standard SiGe could be achieved with proper GaP doping and high temperature heat treatments in air (Vandersande 1987). Shortly thereafter, TTC reported confirmation of these results using $Si_{80}Ge_{20}$ material doped with 2 mole% GaP (Vandersande 1988a). The improvement in Z due to heat treatments was widely reported in dramatic plots such as shown in Figure 7, which is due to Draper (1987).
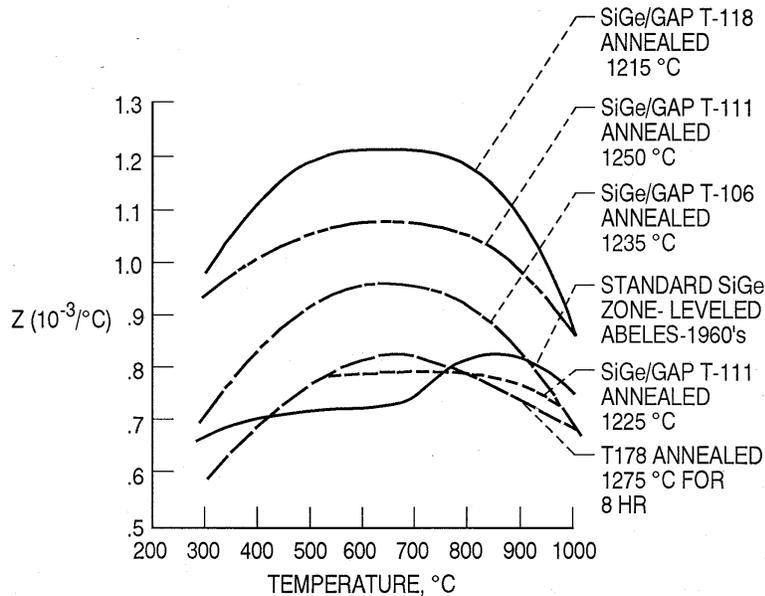

FIGURE 7. Figure of Merit of Annealed n-type SiGe/GaP as a Function of Annealing Temperature, after (Draper 1987).

The improvement in Z was attributed to a lower electrical resistivity brought about by higher carrier concentrations, while the Seebeck coefficient and the thermal conductivity barely changed. A preliminary model for the transport properties of n-type SiGe due to Vining (1988) supported the initial experimental findings and suggested increases in Z of 40% to 50% beyond these improved samples might be possible by increasing the doping level alone. This model predicted an improvement would result from an increase in power factor and reductions in the ambipolar and lattice contributions to the thermal conductivity. Moreover, a somewhat refined version of this model (Vining 1991c) indicates the experimental results on improved SiGe/GaP, shown in Figure 8, are entirely consistent with previous results on zone leveled materials, except that the SiGe/GaP has a higher carrier concentration. Calculations performed by Slack, using a somewhat distinct approach, reach generally similar conclusions (Slack 1991).
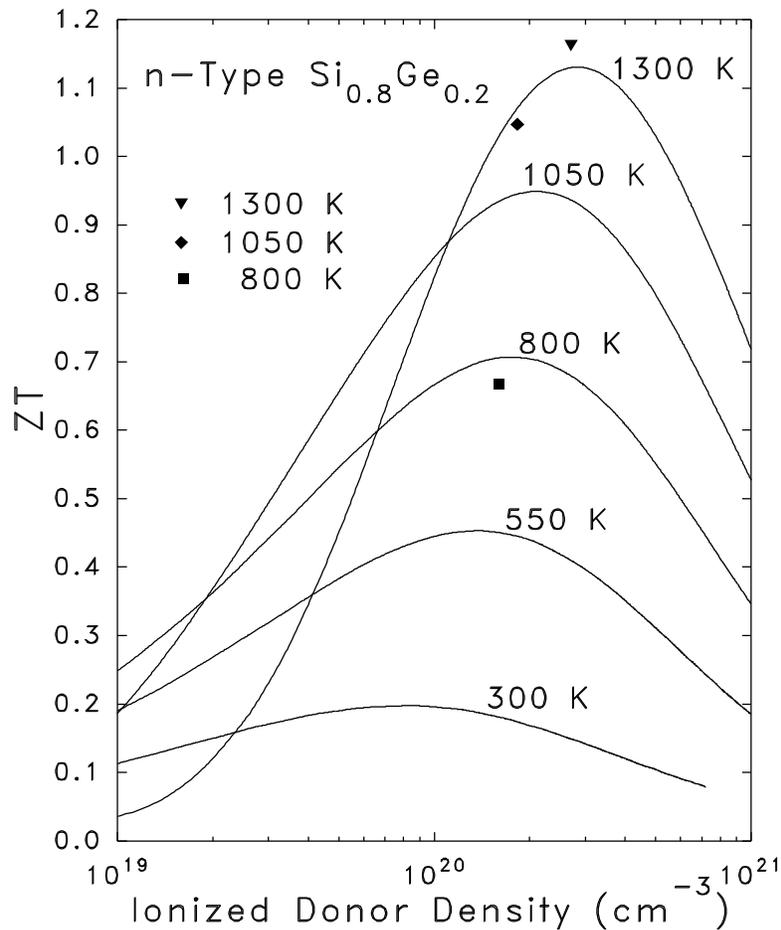
FIGURE 8. Dimensionless Figure of Merit of n-type SiGe Calculated as Described in (Vining 1991c). Solid Points Represent Experimental Results on T373, a Sample of SiGe/GaP.

However, because of the complexities of the manufacturing process for hot-pressed SiGe/GaP, it was difficult to control the amount of dopants introduced, the size of the grains and more generally the homogeneity of the samples. As previously pointed out, every processing variable affects the thermoelectric properties, obscuring the true relationships between transport properties and microstructure composition of these heavily-doped samples. Indeed, the first improved samples with integrated average Z values (between 873 and 1273 K) close to 1.0×10^{-3} K^{-1} were very difficult to reproduce. But comforted by the few experimental results and the theoretical predictions, an extensive effort was initiated at TTC, GE and JPL to obtain and study high Z SiGe/GaP samples (Vandersande 1988b). Development plans in 1988 called for determining the Ga+P amounts necessary for the improvement, understanding the nature of Ga+P doping in terms of dopant solid solubility changes and determining the role of the microstructure of the samples.

Experimental programs at GE-VF, TTC and JPL on hot-pressed SiGe/GaP concentrated on varying systematically the Ga/P ratios and the total Ga+P concentrations introduced in the samples using additions of SiP and GaP (Nakahara 1990). Microstructure analysis of the improved SiGe/GaP samples had shown the formation of Si-rich and Ge-rich SiGe areas within the samples, with substantial changes in Ga and P contents. One major finding was that the resulting Ga/P ratio in the SiGe matrix was always lower than 1 (Fleurial 1989a). Due to the lack of success in reproducing the Z improvements and the poor understanding of the mechanism(s) involved, a research effort directed towards the synthesis of high quality, homogeneous SiGe alloys was started at JPL, together with an

intensive theoretical approach for directing the experiments, using models based on physical chemistry (Borshchevsky 1989) and solid state physics (Vining 1989). Studies of the effect of processing methods on homogeneity in Si-Ge-GaP materials have also been performed at the University of Virginia (Kilmer 1991).

Zone-leveling (ZL) and liquid phase epitaxy (LPE) were developed at JPL in order to grow bulk large grain, homogeneous ingots and single crystalline layers of doped SiGe. Also, experiments to diffuse P and/or As dopants into ZL SiGe materials were set up. The ZL method developed in the mid-60s at RCA (Dismukes 1965), produced ingots doped either by P, As or B only which, because of furnace limitations, were generally of a higher Ge content (typically $Si_{70}Ge_{30}$). The technique was redeveloped at JPL to produce $Si_{80}Ge_{20}$ doped with several elements simultaneously (Borshchevsky 1990a). Microprobe analysis of the grown ingots with various III and V dopant combinations demonstrated that good quality materials with a uniform Si/Ge ratio and dopant(s) content throughout the samples could be obtained. The addition of III and V elements together in the form of III-V compounds (such as BP or GaP) led to a very different result from the original equiatomic ratio of 1:1. This result clearly manifested the strong dissociation of III-V compounds such as GaP in the Si-Ge melt. Unfortunately, the processing temperature of the zone-leveling process is too close to the $Si_{80}Ge_{20}$ melting point to achieve high dopant concentrations, except for B, and the introduced amounts remained well below the optimum values (Borshchevsky 1990b).

Zone-leveled materials produced at JPL, together with original ingots manufactured by RCA, were used for diffusion experiments (Fleurial 1989b,c). Diffusion of P, As and P+As were conducted on ZL $Si_{70}Ge_{30}$, $Si_{80}Ge_{20}$ and $Si_{85}Ge_{15}$ samples doped with either P or As. Higher carrier concentrations were obtained by combining P and As as dopants. These higher values were reached exclusively in samples displaying localized inhomogeneities in SiGe composition together with second-phase inclusions similar in composition to compounds of P and As with Si and Ge. P-only diffusion did not succeed in increasing the carrier concentration of P-doped samples, demonstrating that the maximum P solid solubility had already been obtained in these samples. As-only doping was found to achieve carrier concentrations substantially higher than P-only doping, a result in contradiction with previous RCA work (Rosi 1968). This difference was accounted for by the high operating temperatures of the ZL process, incorporating the dopants into a Si-Ge melt, compared to the solid state diffusion process.

Actually, the JPL results correlated with work on heavily-doped Si (Fleurial 1990a) where As solid solubility and carrier concentrations are higher than for P. The large gap in carrier concentration between the P and the As diffusion experiments had been explained (Nobili 1982) by the difference in formation of dopant defects and complexes: 1) a precipitation mechanism for P, with the carrier concentration saturating at values independent of the total doping concentration; and 2) a clustering model for As, with the carrier concentration continuing to increase with the total doping concentration up to the solid solubility limit. This illustrated the fact that the actual carrier concentration obtained from a dopant is always lower than the dopant concentration, due to the polytropy of the impurities (Fistul 1967).

However, not only did P doping yield better carrier mobility values than As doping for similar carrier concentrations, but the difference in maximum carrier concentrations tended to decrease as the Si/Ge ratio increased from 70/30 to 85/15. Thus, As doping eventually proved unattractive, but this study was instrumental illuminating several points: 1) P-only doping did not yield carrier concentrations higher than already achieved on standard SiGe; 2) Ga+P was not the only combination to enhance carrier concentration; 3) carrier concentration enhancement is linked to impurity-rich second-phase inclusions and localized Si/Ge inhomogeneities; 4) doping heavily n-type SiGe materials was a complex problem and modeling of the doping mechanisms was required.
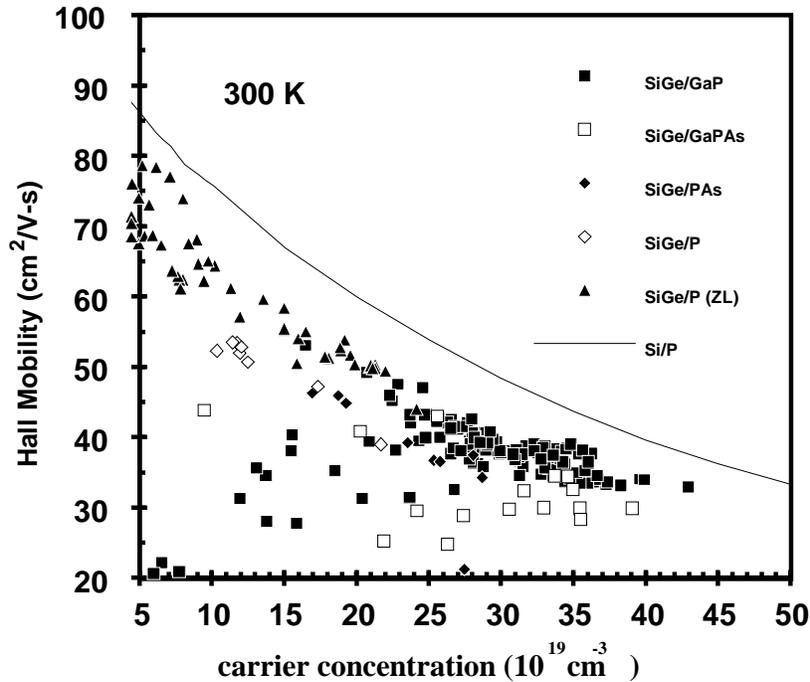
FIGURE 9. Room Temperature Hall Mobility of n-type SiGe Materials as a Function of Carrier Concentration, Redrawn From (Fleurial 1991b).

To further evaluate the potential of multi-doping for enhancing carrier concentrations, similar experiments were conducted at JPL on hot-pressed SiGe/P and SiGe/GaP materials obtained from TTC. Using 3 at% P and 1 at% Ga additions in $Si_{80}Ge_{20}$, high carrier concentration values above 3.5×10^{20} cm^{-3} have now been obtained repeatedly. Figures 9 and 10 display compilations of room temperature Hall mobility and electrical resistivity versus carrier concentration for n-type hot-pressed $Si_{80}Ge_{20}$ doped with P, P+As, Ga+P and Ga+P+As. For comparison, values obtained for ZL P-doped $Si_{80}Ge_{20}$ (Rosi 1968) and polycrystalline P-doped Si (Fleurial 1991b) samples are also reported.

These Figures demonstrate the large carrier concentration increases achieved by multidoping, from 2.2×10^{20} cm^{-3} for SiGe/P to 3.9×10^{20} cm^{-3} for SiGe/GaPAs and up to 4.3×10^{20} cm^{-3} for SiGe/GaP. Although, combining P and As did enhance the carrier concentration value by 25%, lower mobilities resulted in higher electrical resistivities. By comparing the mobility of zone-leveled SiGe/P material with the best values of the hot-pressed SiGe/GaP material, it seems clear that the mobility decrease is due only to the increase in carrier concentration, not to a poorer quality of the samples. Comparison with P-doped Si material tends to confirm this finding, showing that the top mobility curve of $Si_{80}Ge_{20}$ is shifted only due to the alloying effect, the shift becoming smaller for the highest carrier concentration. Thus, this top mobility curve representing the best electrical properties for a given carrier concentration, significantly extended the range of carrier concentrations accessible for Z optimization studies.
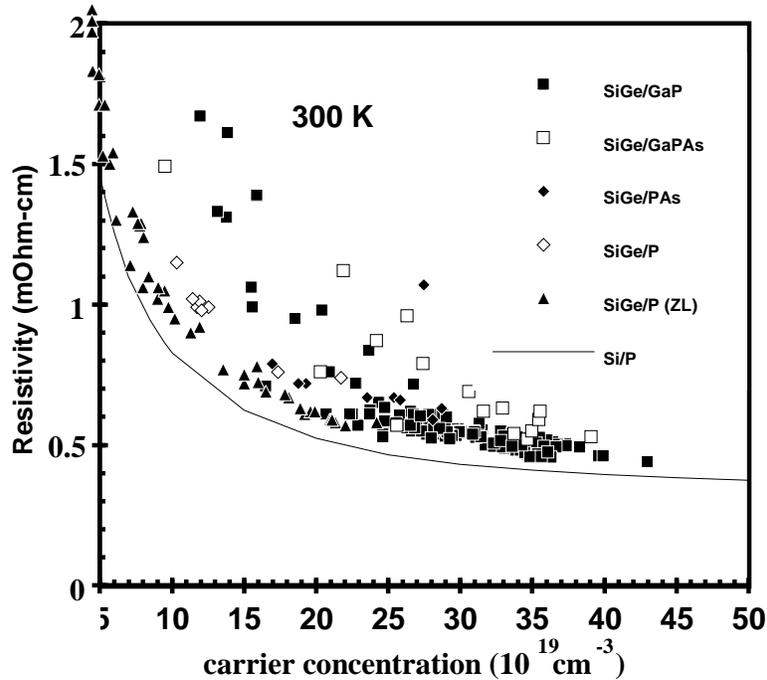
FIGURE 10. Room Temperature Electrical Resistivity of n-type SiGe Materials as a Function of Carrier Concentration, Redrawn From (Fleurial 1991b).

GaP Additions - Understanding the Mechanisms

During the course of these doping studies to produce heavily doped SiGe materials, it was found absolutely necessary to develop a thermodynamic model of the Si+Ge+Metal interaction at different temperatures. In other words, to calculate the relevant ternary and quaternary phase diagrams and predict the dopant(s) concentration(s) in Si-Ge alloys when multi-doping. Computation of these phase diagrams using a thermodynamic equilibrium model permitted calculation of liquidus temperatures and solvent solid solubility curves required for the growth and doping conditions of Si-Ge alloys from solution in metallic solvents such as Al, Ga, In, Sn, Pb, P, Sb and Bi (Fleurial 1990c). These results were then extended to quaternary solutions of Si-Ge with combinations of solvents such as Ga-In and Ga-P, supposing no thermodynamic interaction between the metallic solvents. Figure 11, redrawn from (Fleurial 1990c), shows the Ga solid solubility curves as a function of temperature for several Si-Ge alloys compositions. Similar results were obtained for several other systems of interest.

Building on the results achieved in Si-Ge growth using ternary systems, experiments were conducted at JPL involving more than one metallic solvent. SiGe thin films were grown by liquid phase epitaxy (LPE) out of Ga+In, In+P and Ga+In+P melts (Fleurial 1991c, Borshchevsky 1991). Attempts to grow Si-Ge material out of Ga+P melts proved unsuccessful, although high Ga/P(l) were used (values like 9 or 16), because of the difficulty in dissolving the GaP additions into the excess Ga, even at temperatures higher than 1373 K. Instead, as the solid solubility of In is much lower than Ga in $Si_{80}Ge_{20}$ and the liquidus temperatures for the two Si-Ge-Ga and Si-Ge-In ternary systems are very close in the range of interest, and as the melting point of InP (1343 K) could be reached by the LPE furnace, additions of InP were made into the excess Ga solvent.
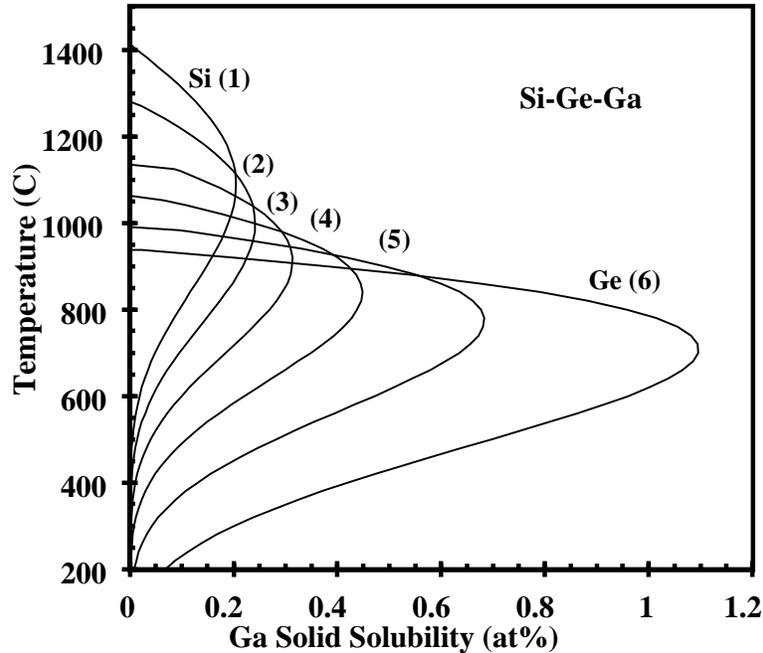
FIGURE 11. Calculated Ga Solid Solubility Curves as a Function of Temperature for Various Si-Ge Alloy Compositions in at%: (1) Si, (2) 80% Si, (3) 60% Si, (4) 40% Si, (5) 20% Si, (6) Ge.

Dopant solid solubilities in $Si_{80}Ge_{20}$ layers grown out of melts consisting of only column III solvents were very close to the values determined from the thermodynamic calculations based on the limiting binary systems, neglecting any additional multicomponent interaction. These results were predictable as no association in the melt exists between these elements. However, in the case of III-V combinations, the existence of compounds such as InP and GaP should bring some kind of association in the melt between these elements. This additional multicomponent interaction in the liquid phase was expected to modify dopant solid solubility behavior depending on the strength of this association (Glazov 1968). Neglecting a multicomponent interaction translated to systematically higher calculated liquidus temperatures than the observed by differential thermal analysis (DTA). A correction could be made to the model, but because of insufficient data a satisfactory recalculation of the quaternary phase diagram could not be carried out.

Microprobe analysis of the (III+V)-doped Si-Ge layers showed substantial differences between the experimental and calculated findings. The experimental Ga and P solid solubilities were more than fivefold higher than the values calculated neglecting multicomponent interactions. Such substantial enhancements indicate the Ga-P interaction could not be neglected. Additional experiments to grow bulk single crystals of SiGe by the traveling solvent method at JPL confirmed such changes of Ga and P solid solubilities (Fleurial 1991c, Borshchevsky 1993). These results also demonstrated that Ga additions to P-doped SiGe could significantly enhance the P solid solubility and thus increase their carrier concentrations.

The absence of similar effects when using only In+P melts shows that the In-P interaction is much weaker. This was expected because the strength of the III-V interaction, or ion pairing, is somewhat related to the melting point and stability of the corresponding III-V compound. Similar reasoning could be applied to the other III-V couples such as B-P, Al-P or Ga-Sb.

The schematic in Figure 12 has been presented numerous times during programmatic presentations although it was never published (Fleurial 1990b). It displays an enlarged portion of a section of the

Si-Ge-Ga-P phase diagram, illustrating how the increase in carrier concentration is obtained when double-doping by enhancing the P solid solubility and reducing the polytropy of P for certain Ga/P ratios.
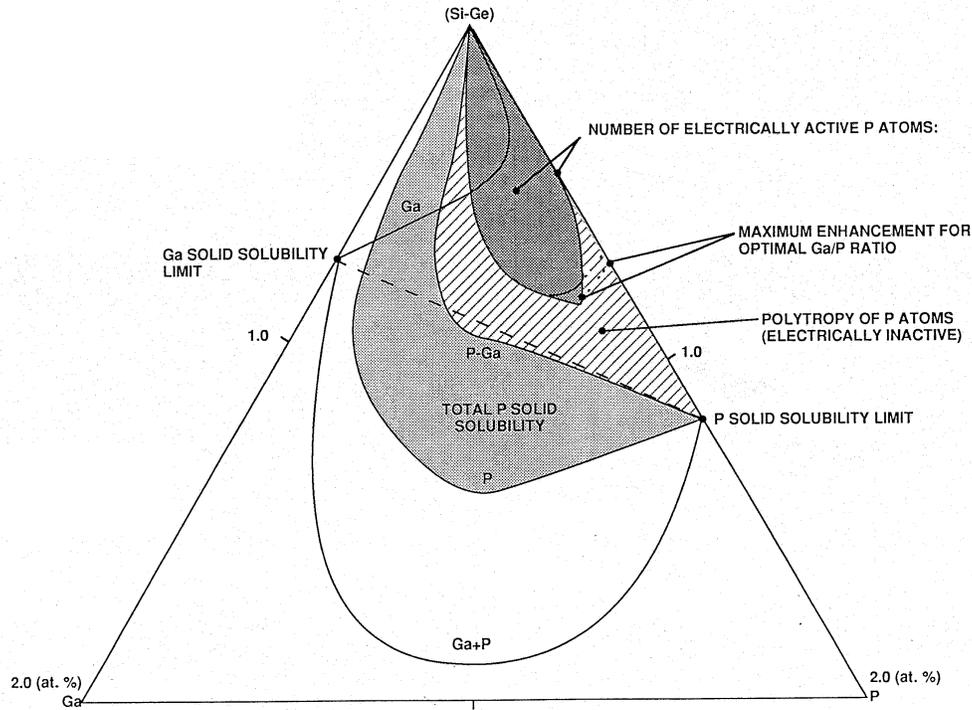

FIGURE 12. The (SiGe)-Rich Region of the (Si-Ge)-Ga-P Pseudoternary Phase Diagram Indicating the Region of Enhanced Carrier Concentrations (Fleurial 1990b).

The substantial changes in P solid solubility in Si-Ge alloys observed when Ga is added, demonstrated without any ambiguity that significant carrier concentration increases could be achieved for n-type hot-pressed $Si_{80}Ge_{20}$ thermoelectric materials. However, this also meant that understanding and controlling the doping mechanisms in these materials is a complex process, illustrated by the difficulty in reproducing high thermoelectric figures of merit.

Comparing the microprobe analysis of heavily-doped zone-leveled and hot-pressed materials, it was concluded that the high carrier concentrations reached in these samples were due to the formation of a complex multi-phase structure. The micrograph shown in Figure 13 is characteristic of this structure in hot-pressed SiGe/GaP materials (Fleurial 1991a). Si-rich and Ge-rich SiGe areas are mostly present, with inclusions rich in SiO_x, SiP_y (darkest spots) and other rich in Ge, GaP (brightest spots). Also, the Ge-rich SiGe areas have a much higher dopant concentration than the Si-rich SiGe areas, acting as reservoirs of dopants during subsequent temperature cycles. Although the mechanisms of carrier concentration enhancement were similar for diffused zone-leveled samples and diffused or annealed hot-pressed samples, the much smaller grain size of the latter enabled the development of a much larger number of dopant-rich phases. Thus, the capacity for dopant absorption of hot-pressed materials was far larger, accounting for the substantially higher carrier concentrations.
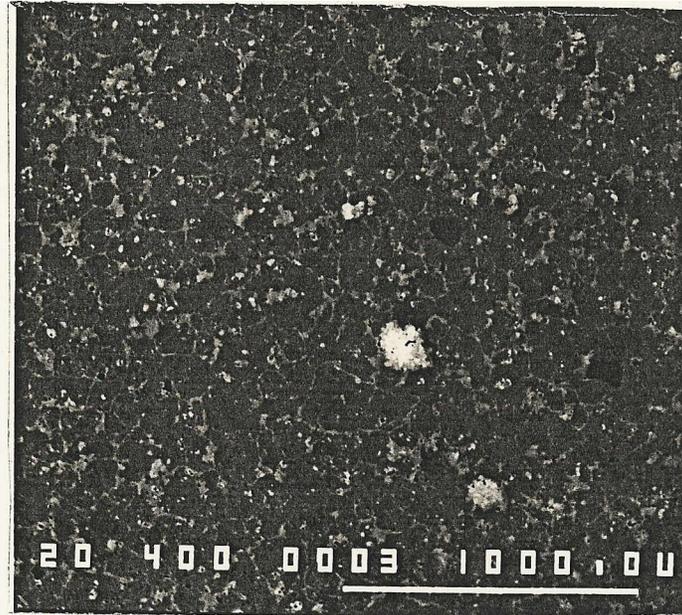
FIGURE 13. Micrograph of T-428, Hot-Pressed SiGe/GaP, After Various Heat Treatments (40x).

While at room temperature SiGe/GaP can exhibit carrier concentration values as much as twice the values for SiGe/P, high temperature Hall effect measurements conducted at JPL indicate this gap narrows rapidly above 1073 K, with no more than a 15 to 20% difference remaining at 1273 K. Similar effects had been observed before on pure Si doped with both III and V elements. An interpretation of these results expressed at JPL was that: 1) room temperature carrier concentration values are higher because of ion pairing between the Ga and P atoms in the form of electrically active Ga-P_n complexes, preventing the P from forming electrically inactive SiP_4 complexes and SiP precipitates; and 2) for temperatures higher than 1073 K, an increasing fraction of the Ga-P_n complexes redissolve into electrically inactive Ga-P pairs and SiP precipitates, reverting to standard SiGe/P electrical behavior. This reversible process would account for the very low resistivity values obtained on improved SiGe/GaP materials, due to high carrier concentration and good mobility values, the Ga dopant not acting as a carrier compensator.

GaP Additions - Reproducing Improvements in Z

Because high carrier concentrations had only been obtained in hot-pressed materials, crystal growth techniques were largely dropped at JPL. Efforts then focused on the conditions necessary to reproducibly achieve a high Z. In 1990, a JPL/TTC program performed systematic high temperature annealing of supersaturated (Ga+P)-doped SiGe materials at various temperatures and for different amounts of time (Fleurial 1991a,e and Scoville 1991a,b). These experiments indicated the formation of a multi-phase structure with Si-rich and Ge-rich Si-Ge regions was responsible for substantial increases in carrier concentrations, sometimes close to a factor of two at room temperature compared to standard P-doped SiGe materials. Optimization of the electrical properties of n-type materials throughout the extended temperature range was started, guided by the JPL theoretical work described in the preceding section.

Results reported on both large cylindrical samples and thin disks showed that substantial variations in microstructure and composition brought by the different annealing temperatures and times led to significant differences in electrical properties. It was particularly demonstrated how the changes in Ga and P concentrations correlated with annealing condition and electrical properties.
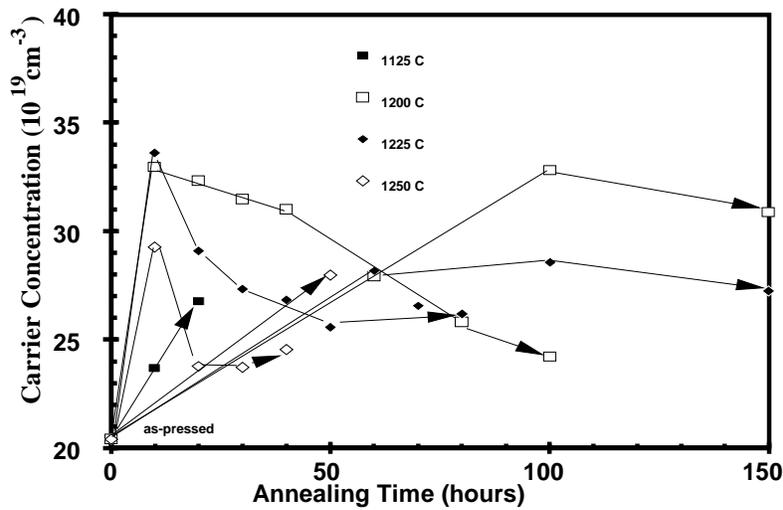
FIGURE 14. Changes in Room Temperature Carrier Concentrations of SiGe/GaP Samples
With Annealing Time and Temperature, Redrawn From (Fleurial 1991b).

Figures 14 and 15, show changes in carrier concentration with annealing time and changes in mobility with carrier concentration for various annealing temperatures. The initial increases in carrier concentration (Figure 14, after the first anneal) appear typical of the dopant redistribution occurring in SiGe/GaP. Actually, the mobility values also increase dramatically after the first anneal (Figure 15), sometimes translating into electrical resistivity reductions of 60% over the entire temperature range (298-1273 K). Subsequent anneals generally lower the carrier concentration, but at a slow rate, with corresponding changes in mobility.
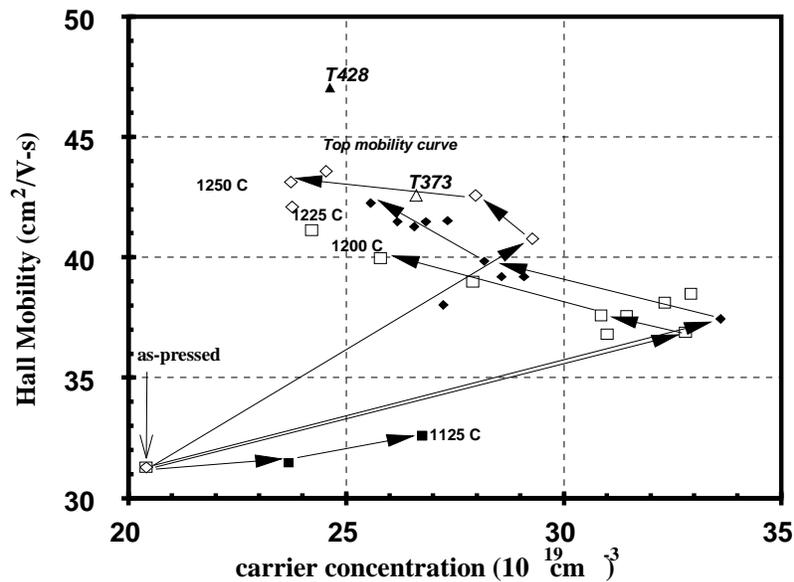

FIGURE 15. Room Temperature Hall Mobility Versus Carrier Concentration for SiGe/GaP. Curves Show Changes in Electrical Properties for Various Annealing Temperatures With Successive Heat-Treatments, Redrawn From (Fleurial 1991b).
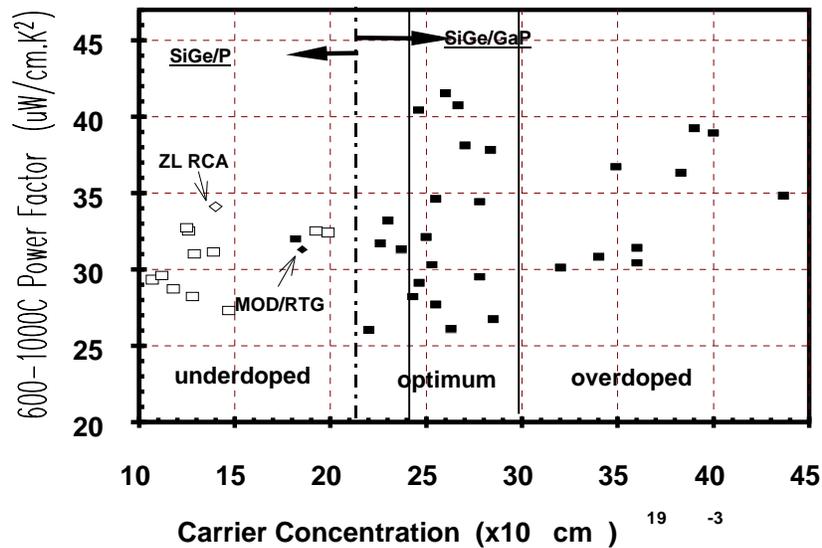
FIGURE 16. Integrated Average Power Factor (873-1273 K) of n-type Hot-Pressed $Si_{80}Ge_{20}$ Versus Room Temperature Carrier Concentration, Redrawn From (Fleurial 1991b).

Figure 14 also displays several curves for a same annealing temperature, but for different annealing times. These curves have shown that the loss of dopants due exposure to high temperatures depends on sample geometry (surface to volume ratio), an effect attributed to formation of a coherent Ga_2O_3 layer on the outer surface of the overdoped samples inhibiting carrier concentration loss and grain growth.

The power factor (S^2/ρ) of hot-pressed SiGe/P and SiGe/GaP is presented on Figure 16, where the integrated average of the power factor over the 873 - 1273 K temperature range is plotted as a function of room temperature carrier concentration. The only available RCA data on P-doped ZL $Si_{80}Ge_{20}$ (Rosi 1968) and the current standard SiGe materials are also shown for comparison.

The dotted line in Figure 16 represents the maximum power factor curve as calculated using the model described in (Vining 1991b). Note that the calculation reproduces the relatively steep increase in power factor observed experimentally between 1 and $3x10^{20}$ cm^{-3}. Both the calculation and the experimental results qualitatively indicate the power factor changes little for carrier concentrations above $n=3x10^{20}$ cm^{-3}, which is reasonable agreement considering the uncertainties and extrapolations involved.

It was also clear that the P-doped only SiGe was underdoped, and that all samples showing low mobility values on Figure 9 were situated well below the maximum power factor curve of Figure 16, stressing the value of measuring the room temperature mobility for monitoring the improvement. The systematic preparation at TTC of hot-pressed samples with P:Ga atomic ratios ranging from 6:1 to 1:1 with a total P concentration varied between 2 and 3 at.% resulted in the determination of optimum conditions for achieving best electrical properties of n-type SiGe/GaP material. The experimentally found optimal room temperature electrical properties consist in a) Hall mobility ranging from 45 to 40 $cm^2.V^{-1}.s^{-1}$; b) carrier concentration between 2.5 and $3.0x10^{20}$ cm^{-3}; c) electrical resistivity between 0.55 and $0.52x10^{-3}$ Ω-cm. To obtain these properties, the P:Ga ratio must be close to 3:1 with a Ga concentration on the order of 0.75 at.%. The minimal grain size necessary to achieve these high mobility values has been found to be about 20 to 30 μm.
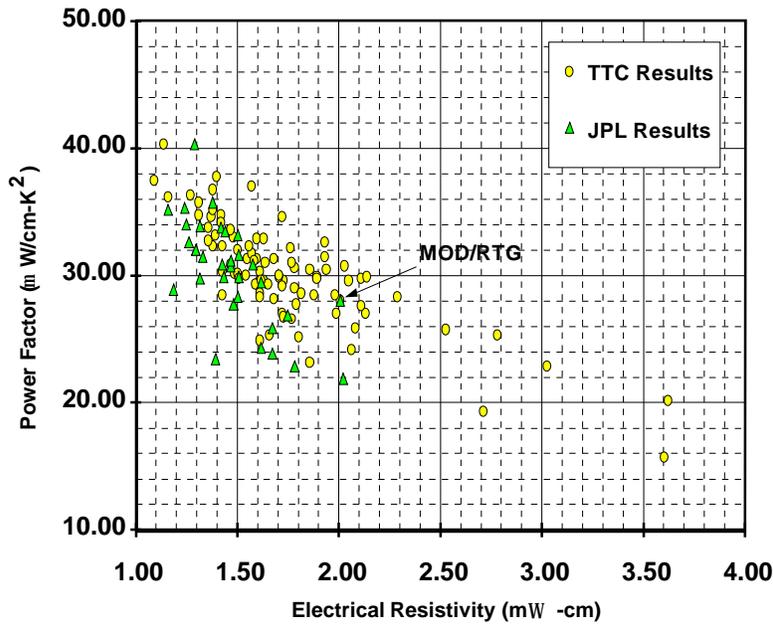
FIGURE 17: 600-1000 C Integrated Average Power Factor of recent n-Type SiGe/GaP Samples Versus Integrated Average Electrical Resistivity, Redrawn From (Fleurial 1993a).
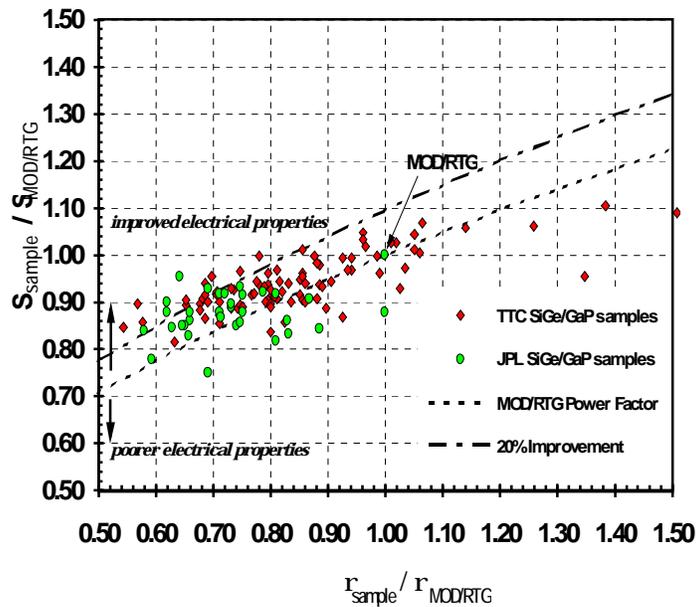

FIGURE 18: 600-1000 C Integrated Average Properties Normalized to MOD/RTG Values: Power Factor of Recent n-Type SiGe/GaP Samples Versus Electrical Resistivity, Redrawn From (Fleurial 1993a).

The large carrier concentration increases obtained by heavily doping hot-pressed SiGe samples with several dopants such as Ga, P and As have been instrumental in the improvement of the power factor. By doubling the range of room temperature carrier concentrations attained with P-only doping (Figure 16), optimization of the electrical properties was made possible. Simultaneous doping with adequate concentrations of Ga and P resulted in up to 30% increase in power factor over n-

MOD/RTG materials (Figure 17). This is mostly due to a sharp decrease in the electrical resistivity over the 300-1000 C temperature range (up to 45%) combined to a much smaller decrease in the Seebeck coefficient (up to 15%), as seen in Figure 18.

The decrease of mobility with carrier concentration for these heavily doped SiGe/GaP samples was not affected by the additions of Ga, a potential acceptor impurity (Fleurial 1991b). This is attributed this to the nature of the Ga-P interaction resulting in the creation of Ga-P_n complexes, thus preventing Ga to act as a compensator and to degrade the mobility. Recent results on heavily P-only doped samples prepared by mechanical alloying and subsequent hot-pressing have confirmed this theoretical explanation (Han 1992). The authors reported carrier concentration as high as 3.0×10^{20} cm^{-3}; but no difference in Hall mobility values with our SiGe/GaP samples with similar doping levels. This demonstrated that point defect scattering is solely responsible for the lower mobility values obtained in optimized heavily doped SiGe/GaP compared to P-doped Si.

In Figures 17 and 18, it is clear that low electrical resistivity values systematically resulted in high power factor values. Also, the magnitude of the reproducible improvement is now about 20%, as larger values can be obtained but are hard to duplicate with the current processing conditions. Such improvement have been recently confirmed on mechanically alloyed SiGe samples, using similar P and Ga doping concentrations and with 20-50 μm grain size (Cook 1992). Indeed, the successive high temperature heat treatments tend to eventually degrade the electrical properties, but they are still necessary to ensure sufficient grain growth and dopant redistribution in the samples. To remedy these difficulties, change to the current hot-pressing parameters are investigated to obtain substantial grain growth in situ. This can be achieved through longer pressing time and/or higher pressing temperature. Preliminary results indicate that the loss of dopant in vacuum remained at reasonable levels, and that these new experimental conditions are successful at reproducing good quality samples with improved electrical properties (Fleurial 1993b).
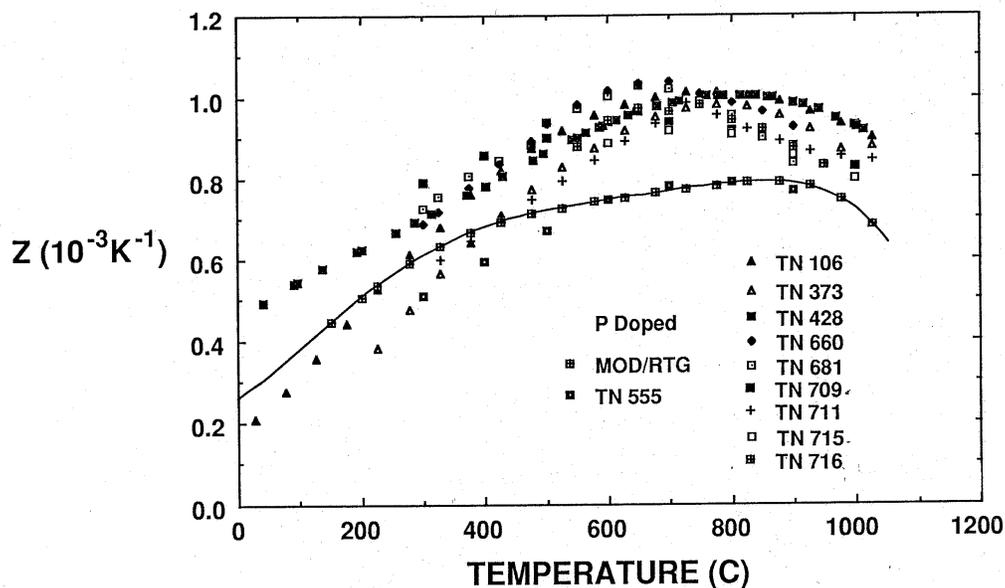

FIGURE 19. Figure of Merit Results for n-type SiGe/GaP Compared to Samples Doped With Phosphorus Only, Labeled MOD/RTG and TN 555.

Figure 19 displays Z versus temperature for the improved SiGe/GaP samples obtained over the past year, including previous results first obtained in 1987 (samples TN 106 and TN 373). Comparison with current standard materials (represented by the labels MOD-RTG and TN 555) show that

improvements of about 30% in 873-1273 K integrated average Z have been obtained: from 0.78×10^{-3} K^{-1} up to 1.0×10^{-3} K^{-1}. This substantial increase in Z represents the maximum improvement to be reached by optimization of the electrical properties alone (Fleurial 1991b). To reach the goal of 1.1×10^{-3} K^{-1} set by the SP-100 program for n-type SiGe, thermal conductivity reductions by introduction of inert scattering centers, similar to the program described above for p-type SiGe, are to be applied.

The carrier concentration enhancement mechanisms appear to be understood, the optimum electrical properties and the maximum Z values have been identified. The desired microstructure and composition have been determined. Current efforts at TTC, GE and JPL have developed a reliable SiGe/GaP manufacturing procedure for reproducibly obtaining average Z values of 0.9×10^{-3} K^{-1} in the 300-1000°C tempoerature range, a 15% improvement over baseline MOD/RTG materials. Work is in its final stages, but it seems probable that Z values of $0.95-1.0 \times 10^{-3}$ K^{-1} will also be reproducibly demonstrated in the near future.

SiGe/GaP Solubility and Precipitation Effects

Preliminary studies of the long term effects of GaP in SiGe have been performed at Ames (Tschetter 1990), JPL (Vandersande 1989), and Cardiff (Rowe 1990, Rowe 1991, Min 1991). The Ames study reproduced Raag's results on dopant precipitation (Raag 1978) in SiGe and extended these studies to n-type SiGe/GaP as prepared by GE-VF. As shown in Figure 20, the time and temperature dependencies are significantly altered in SiGe/GaP, presumably due to some combination of solubility and kinetic coefficient variations. Indeed while acknowledging a non-standard behavior, it has been found by several authors that SiGe/GaP MOD/RTG material was inferior to standard P-doped SiGe in the high temperature range (Fu 1992).
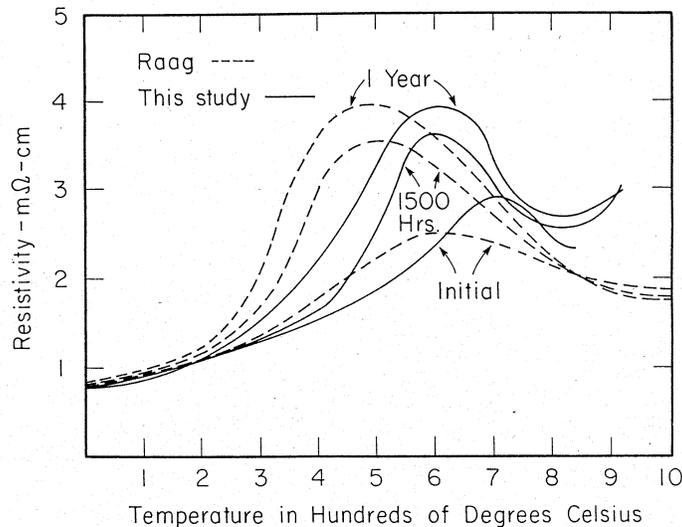

FIGURE 20. Electrical Resistivity of n-type SiGe (Dashed Line) and SiGe/GaP (Solid Line) as a Function of Temperature and Time (Tschetter 1990).

However, baseline MOD/RTG materials do not present any substantial improvement in Z over standard samples due their unoptimized atomic concentration of Ga and P dopants (2% of each). A more realistic test needed to be done using high power factor improved SiGe/GaP samples, which have a much different microstructure and composition (high P/Ga ratio). It was expected that the same mechanisms that resulted in increased P solid solubility and P electrical activity would also improve the dopant precipitation data, provided that optimal P:Ga ratio be met. Figure 21 (a), 21 (b), 21 (c) and 21 (d) display the results of long term resistivity measurements done in isothermal

furnaces at respective temperatures of 450ºC, 600ºC, 800ºC and 1000ºC. The changes of resistivity over time for improved SiGe/GaP samples and standard SiGe/P samples demonstrate after more than 1850 hours of continuous operation that the SiGe/GaP samples retained their much lower electrical resistivity (except at 600 C where values are very close together). Moreover, at 450 C and 1000 C the rates of resistivity increase are substantially larger for standard SiGe/P samples. At 600 C and 800 C these rates are almost identical. These results confirmed that the substantial improvements in power factor over the entire temperature range were retained, especially for the most heavily-doped samples (Fleurial 1993a).

The long term dopant precipitation test has now been running for more than 5600 hours without any significant departure from the results obtained at 1850 hours (Fleurial 1993b).
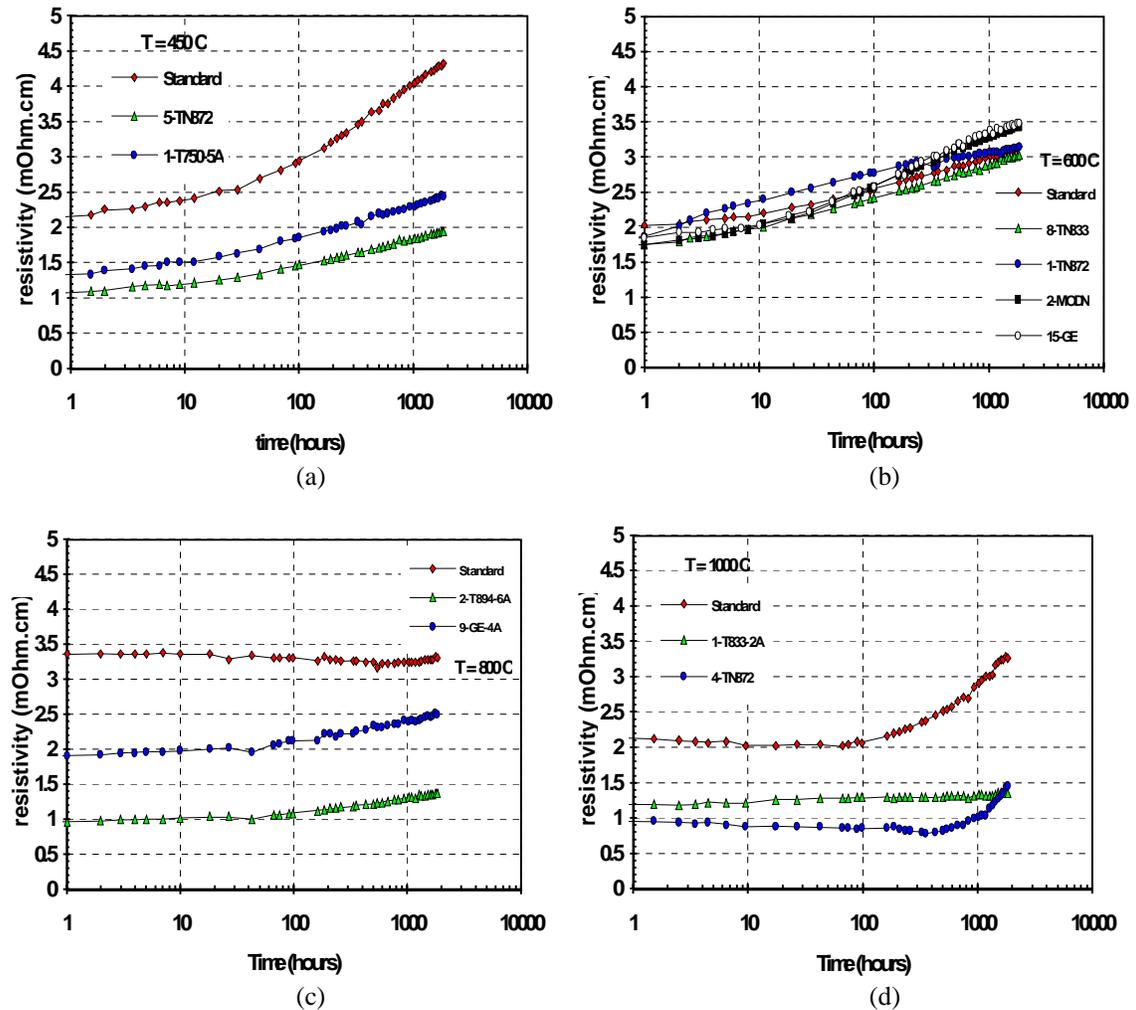
FIGURE 21: Dopant Precipitation Study of Improved n-Type SiGe/GaP Samples Compared to Standard P-Doped Only SiGe Samples: Data After 1850 hours at Temperatures of 450 C (a), 600 C (b), 800 C (c) and 1000 C (d), Redrawn from (Fleurial 1993a).

SUMMARY AND OPEN QUESTIONS

The variety of preparation methods, characterization techniques and theoretical tools applied to SiGe over the past 15 years testifies to the vitality of current thermoelectric materials development

activities. The "fine grain" ideas for lowering thermal conductivity have evolved into a quite different approach of inert particulate additions. The idea of adding GaP has evolved tremendously, to the point that today improvements are attributed not to thermal conductivity reductions, as originally supposed, but to electrical property enhancements.

Yet in spite of the changes, both approaches appear nearly ready for practical applications and are entering the final development stages. The inert particulate approach for lowering thermal conductivity still requires some attention to the electrical properties. And both the particulate and carrier concentration enhancement approaches still require long term studies and device manufacturing processing development on improved materials.

But have those early ideas really been exhausted? The fine grain idea in fact remains something of an open question. The correlation between reduced mobility and reduced thermal conductivity reported for fine grain SiGe in (Vining 1991a) is at this point largely empirical. It is still possible that this correlation results from entirely different mechanisms acting independently on the phonons and on the carriers (such as described by Slack 1991), but are coincidentally similar in magnitude. After all, the grain boundary phonon scattering mechanism described by Rowe is probably not the mechanism responsible for the observed thermal conductivity reductions, as evidenced by the unexpected temperature dependence shown in Figure 2. Some clever trick may yet be found to avoid degradation of electrical properties in fine grain SiGe and realize the predicted improvements in Z.

And what was wrong with those early results on SiGe/GaP, which indicated such large gains in Z due to thermal conductivity reductions? Even extensive efforts have not reproduced the early material properties, which may simply be erroneous. The usual problems of performing all the important measurements on precisely the same material, changes in sample properties between (and during!) measurements and propagation of experimental errors may be to blame.

The bicouple results, however, seemed very persuasive to many in the field. But this test actually could at most conclude that the "SiGe/GaP" *devices* were better than the "fine grain SiGe"*devices*. Relatively less could be said about the absolute Z values of the materials, for a variety of reasons. Contributing factors include: 1) the unique bicouple device geometry employed; 2) the significant device-to-device variability observed in the "fine grain SiGe" devices; 3) uncertainties about internal resistances (both electrical and thermal); 4) non-optimal device geometries; and 5) test instrumentation difficulties. Given the experience of recent years it seems unlikely that the "SiGe/GaP" used in the bicouples was better than standard SiGe, although it may have been better than the particular "fine grain SiGe" materials actually used in that test for comparison.

Still, the efforts to understand fine grain SiGe and SiGe/GaP have been useful. Because of the need for higher carrier concentrations to achieve optimum electrical properties, the fine grain approach has been dropped because of accelerated dopant precipitation effects even during the course of high temperature thermoelectric properties measurements. Additions of GaP are now exclusively used for enhancing the carrier concentration of n-type materials by double doping mechanisms. Systematic experimental and theoretical studies on n-type and p-type materials have resulted in determining the range of microstructure, composition, doping level and electrical properties necessary to achieve improved Z values. Optimization of the hot-pressing process to approach these optimal parameters with a minimal amount of heat treatments is in its final stages. Currently reproducible average Z values in the 300-1000°C temperature range are 0.9×10^{-3} K^{-1} for n-type SiGe/GaP and 0.59×10^{-3} K^{-1} for n-type SiGe/B, a substantial combined 18% increase over the performance of baseline MOD/RTG materials. Addition of ultra fine BN particles to lower the lattice thermal conductivity could possibly bring another 15% improvement.

While many workers have made significant contributions, the efforts of Rowe and Raag deserve special note. Both made contributions in the 1970's, during a period of extremely limited resources

for thermoelectric materials work, and most of the work today can be traced fairly directly to those early studies. Some future contribution may yet allow major improvements in SiGe, beyond the levels described here, but the standard of comparison has been raised significantly and any such new concept must certainly go well beyond the efforts described in this overview.

Acknowledgments

References

Amano, T., B. J. Beaudry, K. Gschneidner, Jr., R. Hartman, C. B. Vining, and C. A. Alexander (1987) "High-Temperature Heat Contents, Thermal Diffusivities, Densities, and Thermal Conductivities of N-Type SiGe(GaP), P-Type SiGe(GaP), and P-Type SiGe Alloys," *J. Appl. Phys.*, 62(3): 819-823.

Bajgar, C., R. Masters, N. Scoville, and J. Vandersande (1991) "Thermoelectric Properties of Hot Pressed P-Type SiGe Alloys," in *Proc. of 8th Symposium on Space Nuclear Power Systems*, CONF-910116, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 440-445.

Beaty, J. S., J. L. Rolfe, and J. W. Vandersande (1990) "Properties of 100 Å P-Type Atomclusters and Thermoelectric Material," in *Proc. of 25th Intersoc. Energy Conv. Eng. Conf.*, P. A. Nelson, W. W. Schertz, and R. H. Till, eds., American Institute of Chemical Engineers, New York, NY, 2: 379-381.

Beaty, J. S., J. L. Rolfe, and J. W. Vandersande (1991a) "Thermoelectric Properties of Hot-Pressed Fine Particulate Powder SiGe Alloys," in *Proc. of 8th Symposium on Space Nuclear Power Systems*, CONF-910116, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 446-450.

Beaty, J. S., J. L. Rolfe, and J. W. Vandersande (1991b) "Thermoelectric Properties of Hot-Pressed Ultra-Fine Particulate SiGe Powder Alloys with Inert Additions," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 105-110.

Bhandari, C. M. and D. M. Rowe (1978) "Fine Grained Silicon Germanium Alloys as Superior Thermoelectric Materials," in *2nd International Conf. on Thermoelectric Energy Conversion*, IEEE Cat. No. 78CH 1313-S Reg 5, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 32-35.

Bhandari, C. M. and D. M. Rowe (1980) "Silicon-Germanium Alloys as High-Temperature Thermoelectric Materials," *Contemp. Phys.*, 21(3): 219-242.

Borshchevsky, A., and J. P. Fleurial (1989) "Computation of Ternary Phase Diagrams for LPE Single Crystal Growth of SiGe Alloys," in *Eighth International Conf. on Thermoelectric Energy Conversion*, ISBN 2-905267-15-1, H. Scherrer and S. Scherrer, eds., Institut National Polytechnique de Lorraine, Nancy, France: 87-90.

Borshchevsky, A., J. P. Fleurial, J. W. Vandersande, and C. Wood (1990a) "Preliminary Results on Zone-Leveling of Multidoped SiGe Thermoelectric Alloys," in *Proc. of 7th Symposium on Space Nuclear Power Systems*, CONF-900109, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 229-233.

Borshchevsky, A., J. P. Fleurial, and J. W. Vandersande (1990b) "Experimental Approaches for Improving SiGe Thermoelectric Efficiency at JPL," in *Proc. of 25th Intersoc. Energy Conv. Eng. Conf.*, P. A. Nelson, W. W. Schertz, and R. H. Till, eds., American Institute of Chemical Engineers, New York, NY, 2: 397-401.

Borshchevsky, A. and J. P. Fleurial (1991) "Growth of SiGe from Metallic Solutions," in *10th International Conf. on Thermoelectrics*, D. M. Rowe, ed., Babrow Press, Cardiff Wales, UK: 19-26.

Borshchevsky, A. and J. P. Fleurial (1993) "Growth of Heavily-Doped SiGe from Metallic Solutions," *J. Crystal Growth*, 128: 331-337.

Cahill, D. G., H. E. Fischer, T. Klitsner, E. T. Swartz, and R. O. Pohl (1989) "Thermal Conductivity of Thin-Films - Measurements and Understanding," *J. Vac. Sci. Technol.*, A7: 1259.

Cahill, D. G. and R. O. Pohl (1991) "Is There a Lower Limit to the Thermal Conductivity of Solids?," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 27-38.

Cockfield, R. D. and P. D. Gorsuch (1984) "The Bicouple - An Alternative Approach for Thermoelectrics," in *Proc. of 19th Intersoc. Energy Conv. Eng. Conf.*, W. Dodson, ed., American Nuclear Society, New York, NY: 2229-2234.

Cody, G. D., B. Abeles, J. P. Dismukes, and F. D. Rosi (1990) in "Research and Development of the Silicon-Germanium Thermoelectric Power Generator: The Long Term Payoff of Basic Research," *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA:. 182-205.

Cook, B. A., B. J. Beaudry, J. J. Harringa, and W. J. Barnett (1989) "The Preparation of SiGe Thermoelectric Materials by Mechanical Alloying," in *Proc. of 24th Intersoc. Energy Conv. Eng. Conf.*, W. D. Jackson, ed., Institute of Electrical and Electronics Engineers, New York, NY, 2: 693-700.

Cook, B. A., B. J. Beaudry, J. J. Harringa, and W. J. Barnett (1991) "Thermoelectric Properties of Mechanically Alloyed P-Type $Si_{80}Ge_{20}$ Alloys," in *Proc. of 8th Symposium on Space Nuclear Power Systems*, CONF-910116, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 431-439.

Cook, B.A., J. L. Harringa, B. J. Beaudry, and S. H. Han (1992) "Relationship between Thermoelectric Properties and the P/Ga Ratio in Mechanically Alloyed N-Type Si-20 at.% Ge Alloys," in *Proc. of XI International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 28-32.

Cook, B. A., J. H. Harringa, and B. J. Beaudry (1993) "A Solid State Approach to the Production of Kilogram Quantities of $Si_{80}Ge_{20}$ Thermoelectric Alloys," in *Proc. of 10th Symposium on Space Nuclear Power Systems*, *AIP Conf. Proc. 271*, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 777-783.

Dismukes, J. P. and L. Ekstrom (1965) "Homogeneous Solidification of Ge-Si Alloys," *Transactions of the Metallurgical Society of AIME,* 233: 672-680.

Draper, S. L. (1987) "The Effect of High Temperature Annealing on the Microsctructure and Thermoelectric Properties of GaP doped SiGe," NASA Technical Memorandum 100164.

Duncan, W. and A. J. Barlow (1985) "Thermoelectric Alloy Composition," *European Patent 0185499*, 25 June 1986.

Duncan, W. (1989) "Properties of SiGe," in *Eighth International Conf. on Thermoelectric Energy Conversion*, ISBN 2-905267-15-1, H. Scherrer and S. Scherrer, eds., Institut National Polytechnique de Lorraine, Nancy, France: 96-97.

Elsner, N. B., and J. H. Norman (1990) "SiGe Alloys with Sn and Pb Additons," in *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA: 227.

Eck, M. (1984) Unpublished Results, Fairchild Space and Electronics Company, Germantown, MD.

Erofeev, R. S., E. K. Iordanishvilii, and A. V. Petrov (1966) "Thermal Conductivity of Doped Si-Ge Solid Solutions," *Sov. Phys.-Sol. St.*, 7: 2470-2476.

Fistul', V. I. (1967) *Heavily Doped Semiconductors*, Plenum Press, New York, NY: 252-266 and 273-280.

Fleurial, J. P. (1989a) "Thermodynamical Model for SiGe," Unpublished Results, *5th SiGe Integration Meeting*, Thermoelectron Technology Corporation, Waltham, MA.

Fleurial J.P. (1989b) "Double Doping of SiGe," Unpublished Results, *5th SiGe Integration Meeting*, Thermoelectron Technology Corporation, Waltham, MA.

Fleurial, J. P., C. B. Vining, and A. Borshchevsky (1989c) "Multiple Doping of Silicon-Germanium Alloys for Thermoelectric Applications," in *Proc. of 24th Intersoc. Energy Conv. Eng. Conf.*, W. D. Jackson, ed., Institute of Electrical and Electronics Engineers, New York, NY, 2: 701-705.

Fleurial, J. P. and A. Borshchevsky (1990a) "Mechanisms of Carrier Concentration Enhancement in Multidoped SiGe," in *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA: 206-221.

Fleurial, J. P. (1990b) "Dopants Behavior in n-Type SiGe," Unpublished Results, *6th SiGe Integration Meeting*, GE Valley Forge, PA.

Fleurial, J. P., and A. Borschevsky (1990c) "Si-Ge-Metal Ternary Phase-Diagram Calculations," *J. Electrochem. Soc.*, 137(9): 2928-2937.

Fleurial, J. P., A. Borshchevsky, and J. W. Vandersande (1991a) "Improved N-Type SiGe/GaP Thermoelectric Materials," in *Proc. of 8th Symposium on Space Nuclear Power Systems*, CONF-910116, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 451-457.

Fleurial, J. P., A. Borshchevsky, and J. W. Vandersande (1991b) "Optimization of the Thermoelectric Properties of Hot-pressed n-type SiGe Materials by Multiple Doping and Microstructure Control," in *10th International Conf. on Thermoelectrics*, D. M. Rowe, ed., Babrow Press, Cardiff Wales, UK: 156-162.

Fleurial, J. P., A. Borshchevsky, and D. Irvine (1991c) "LPE Growth of Doped SiGe Layers Using Multicomponent Phase Diagrams Calculations," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 123-134.

Fleurial, J. P. (1991d) Unpublished Results, Jet Propulsion Laboratory, Pasadena, CA.

Fleurial, J. P., A. Borshchevsky, and J. W. Vandersande (1991e) "Effect of Microstructure and Composition on the Improvement of N-Type SiGe/GaP Material," in *Proc. of 26th Intersoc. Energy Conv. Eng. Conf.*, D. L. Black, ed., American Nuclear Society, La Grange Park, IL, 3: 202-207.

Fleurial, J. P., J. W. Vandersande, N. Scoville, C. Bajgar, and J. Beaty (1993a) "Progress in the Optimization of N-Type and P-Type SiGe Thermoelectric Materials," in *Proc. of 10th Symposium on Space Nuclear Power Systems*, *AIP Conf. Proc. 271*, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 451-457.

Fleurial, J. P. (1993b) Unpublished Results, Jet Propulsion Laboratory, Pasadena, CA.

Fu, L. W., D. M. Rowe, and G. Min (1992) "Long Term Electrical Power Factor Stability of High Temperature Annealed SiGe/GaP Thermoelectric Alloys," in *XI International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 83-86.

Glazov, V. M. and V. S. Zemskov (1968) *Physico-chemical Principles of Semiconductor Doping*, IPST, Jerusalem, Isreal.

Gogishvili, O., Sh., I. P. Lavrinenko, S. P. Lalykin, T. M. Melashvili, and I. D. Rogovoy (1990) "Highly Homogeneous Silicon-Germanium Thermoelectric Alloys Produced by Using Mechano-Chemical Synthesis," in *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA: 271-277.

Goldsmid, H. J. and A. W. Penn (1968) "Boundary Scattering of Phonons in Solid Solutions," *Phys. Lett.*, 27A(8): 523-524.

Gunther (1982) "Solitons and Their Role in the Degradation of Doped Silicon-Germanium Alloys," in *IV International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 104-114.

Han, S.H., Cook, B.A. and Gschneidner, K.A. (1992) "Effect of Doping Process on Phosphorous Solubility in $Si_{80}Ge_{20}$," in *XI International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 57-61.

Harringa, J. L., B. A. Cook, and B. J. Beaudry (1992) "Effects of Vial Shape on the Rate of Mechanical Alloying in $Si_{80}Ge_{20}$," *J. Mater. Sci.*, 27(3): 801-804.

Henderson, C. M., E. R. Beaver, Jr. (1966) *U.S. Patent 3,285,017*.

Improved Thermoelectric Materials, Development of (1989) Final Technical Progress Report for the period from 28 September 1984 through 17 April 1989, US-DOE Contract Number DE-AC01-84NE-32123.

JPL/TTC SP-100 Technical Workshop (1991) August.

Kilmer, R. J., W. A. Jesser, and F. D. Rosi (1991) "Effect of Melt-Growth Processing Methods on Si-Ge-GaP Homogeneity," *Appl. Phys. Lett.*, 58(22): 2529-2531.

Klemens, P. G. (1991) "Thermal Conductivity of N-Type Si-Ge," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 87-94.

Loughin, S., D. X. Centurioni, A. G. Robison, J. J. Maley, and J. P. Fleurial (1993) "High-Boron P-Type Silicon Germanium Thermoelectric Material Prepared by the Vacuum Casting and Hot Pressing Method," in *Proc. of 10th Symposium on Space Nuclear Power Systems*, *AIP Conf. Proc. 271*, M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 747-752.

McLane, G., C. Wood, J. Vandersande, V. Raag, and L. Danielson (1986) in *Proc. of VI International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 311-321.

Meddins, H. R. and J. E. Parrott (1976) "The Thermal and Thermoelectric Properties of Sintered Germanium-Silicon Alloys," *J. Phys. C: Solid State Phys.*, 9: 1263-1276.

Miller, S. A. (1983) in *Amorphous Metallic Alloys*, F. E. Luborsky, ed., Butterworth, London, UK.

Min, G., and D. M. Rowe (1991) "The Effect of High-Temperature Heat-Treatment on the Electrical-Power Factor and Morphology of Silicon Germanium-Gallium Phosphide Alloys," *J. Appl. Phys.*, 70: 3843-3847.

Modular Radioisotope Thermoelectric Generator (RTG) Program (1983-1991) US-DOE contract number DE-AC01-83NE-32112.

Nakahara, J. F. and M. J. Platek (1990) "Development of N-Type SiGe/GaP Alloys for the SP-100 Program," in *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA: 222-226.

Nobili, D., A. Armigliato, M. Finetti, and S. Solmi (1982) "Precipitation as the Phenomenon Responsible for the Electrically Inactive Phosphorus in Silicon," *J. Appl. Phys.*, 53: 1484-1491.

Owusu-Sekyere, K., W. A. Jesser, and F. D. Rosi (1989) "Characterization of SiGe and SiGe-GaP Thermoelements," *Materials Science and Engineering*, 3(3): 231-240.

Parrott, J. E. (1969) "The Thermal Conductivity of Sintered Semiconductor Alloys," *J. Phys. C: Solid State Phys.*, 2: 147-151.

Pearsall, T. P. (1989) "Silicon-Germanium Alloys and Heterostructures - Optical and Electronic Properties," *Critical Reviews in Solid State and Materials Sciences*, 15(6): 551-600.

Pisharody, R. K. and L. P. Garvey (1978) "Modified Silicon-Germanium Alloys with Improved Performance," in *Proc. of 13th Intersoc. Energy Conv. Eng. Conf.*, American Institute of Chemical Engineers, New York, NY: 1963-1968.

Raag, V. (1978) "Comprehensive Thermoelectric Properties of N- and P-Type 78% Si-22% Ge alloy," in *2nd International Conf. on Thermoelectric Energy Conversion*, IEEE Cat. No. 78CH 1313-S Reg 5, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 5-10.

Raag, V. (1984) "Thermoelectric Properties of SiGe Alloys," in *Third Working Group Meeting on Thermoelectrics*, Jet Propulsion Laboratory internal document number JPL D-1335, Pasadena, CA: 353-367.

Rosi, F. D. (1968) "Thermoelectricity and Thermoelectric Power Generation," *Solid-State Electronics*, 11: 833-868.

Rosi, F. D. (1991) "The Research and Development of Silicon-Germanium Thermoelectrics for Power Generation," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 3-26.

Rowe, D. M. (1974) "Theoretical Optimization of the Thermoelectric Figure of Merit of Heavily Doped Hot-Pressed Germanium-Silicon Alloys," *J. Phys. D: Appl. Phys.*, 7: 1843-1846.

Rowe, D. M., V. S. Shukla, and N. Savvides (1981a) "Phonon Scattering at Grain Boundaries in Heavily Doped Fine-Grained Silicon-Germanium Alloys," *Nature*, 290: 765-766.

Rowe, D. M. and V. S. Shukla (1981b) "The Effect of Phonon-Grain Boundary Scattering on the Lattice Thermal Conductivity and Thermoelectric Conversion Efficiency of Heavily Doped Fine-Grained, Hot-Pressed Silicon Germanium Alloy," *J. Appl. Phys.*, 52(12): 7421-7426.

Rowe, D. M. (1987) "Recent Advanced in Silicon Germanium Alloy Technology and an Assessment of the Problems of Building the Modules for a Radioisotope Thermoelectric Generator," *Journal of Power Sources*, 19: 247-259.

Rowe, D. M. (1989) "United States Activities in Space," in *Eighth International Conf. on Thermoelectric Energy Conversion*, ISBN 2-905267-15-1, H. Scherrer and S. Scherrer, eds., Institut National Polytechnique de Lorraine, Nancy, France: 96-97.

Rowe, D. M., and G. Min (1990) "High-Temperature Heat-Treatment of Silicon-Germanium-Gallium Phosphide Alloys," *J. Phys. D: Appl. Phys.*, 23: 258-261.

Rowe, D. M., G. Min, and S. G. K. Williams (1991) "Silicon Germanium-Gallium Phosphide Research at ELSYM, Cardiff," in *10th International Conf. on Thermoelectrics*, D. M. Rowe, ed., Babrow Press, Cardiff Wales, UK: 181-185.

Savvides, N. and H. J. Goldsmid (1973) "The Effect of Boundary Scattering on the High-Temperature Thermal Conductivity of Silicon," *J. Phys. C: Solid State Phys.*, 6: 1701-1708.

Schock, A. (1983) "Revised MITG Design, Fabrication Proceedure, and Performance Predicitons," in *Proc. of 13th Intersoc. Energy Conv. Eng. Conf.*, American Institute of Chemical Engineers, New York, NY: 1093-1101.

Scoville, A. N., C. Bajgar, J. W. Vandersande, and J. P. Fleurial (1991a) "High Carrier Concentration Improved N-Type SiGe/GaP Alloys," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 117-122.

Scoville, A. N., C. Bajgar, J. W. Vandersande, and J. P. Fleurial (1991b) "High Figure of Merit N-Type SiGe/GaP Alloys," in *Proc. of 26th Intersoc. Energy Conv. Eng. Conf.*, D. L. Black, ed., American Nuclear Society, La Grange Park, IL, 3: 224-229.

"Silicon Germanium (SiGe) Radioisotope Thermoelectric Generator (RTG) Program for Space Missions" (1984) Fifty-Sixth Technical Progress Report, US-DOE contract number DE-AC01-79ET-32043.

Sittig, M. (1970) *Thermoelectric Materials*, ISBN: 8155-0313-X, Noyes Data Corporation, Park Ridge, NJ: 189-191.

Slack, G. A. (1979) "The Thermal Conductivity of Nonmetallic Crystal," *Solid State Physics*, 34: 1-71.

Slack, G. A. and M. A. Hussain (1991) "The Maximum Possible Conversion Efficiency of Silicon-Germanium Thermoelectric Generators," *J. Appl. Phys.*, 70: 2694-2718.

Taylor, R. E. and H. Groot (1980) "Thermophysical Properties of Silicon Germanium/Gallium Phosphide," Unpublished Results, Thermophysical Properties Research Laboratory report #TPRL 221, Purdue University, West Lafayette, IN.

Tschetter, M. J., and B. J. Beaudry (1990) "Effect of GaP on the Resistivity Versus Time at Elevated Temperatures of N-Type $Si_{80}Ge_{20}$ Alloys," in *Proc. of 25th Intersoc. Energy Conv. Eng. Conf.*, P. A. Nelson, W. W. Schertz, and R. H. Till, eds., American Institute of Chemical Engineers, New York, NY, 2: 382-386.

Vandersande, J. W., C. Wood, and S. L. Draper (1987) "Effect of High Temperature Annealing on the Thermoelectric Properties of GaP Doped SiGe," in *Novel Refractory Semicondutors*, *Mat. Res. Soc. Symp. Proc. 97*, D. Emin, T. L. Aselage, and C. Wood, eds., Materials Research Society, Pittsburgh, PA: 347-352.

Vandersande, J. W., C. Wood, S. L. Draper, V. Raag, M. Alexander, and R. Masters (1988a) in *Trans. of 5th Symp. Space Nuclear Power,* M. S. El-Genk and M. D. Hoover, eds., American Institute of Physics, New York, NY: 1: 629-632.

Vandersande, J. W. and C. Wood (1988b) Unpublished Results, *CSTI High Capacity Power Project Review*, Lewis Research Center, Cleveland, OH..

Vandersande, J. W. (1989) Unpublished Results, Jet Propulsion Laboratory, Pasadena, CA.

Vandersande, J. W., J. McCormack, A. Zoltan, and J. Farmer (1990a) "Effect of Neutron Irradiation on the Thermoelectric Properties of SiGe Alloys," in *Proc. of 25th Intersoc. Energy Conv. Eng. Conf.*, P. A. Nelson, W. W. Schertz, and R. H. Till, eds., American Institute of Chemical Engineers, New York, NY, 2: 392-396.

Vandersande, J. W., J. McCormack, A. Zoltan, and J. Farmer (1990b) "Neutron Irradiation of SiGe Alloys," in *Proc. of IX International Conf. on Thermoelectrics (USA)*, C. B. Vining, ed., Jet Propulsion Laboratory internal document number D-7749, Pasadena, CA: 228-233.

Vandersande, J. W. and J. P. Fleurial (1991) Unpublished Results, *GE-JPL Technical Meeting on Thermoelectric Material Development*, GE AstroSpace, Valley Forge, PA.

Vandersande, J. W. and J. P. Fleurial (1992a) Unpublished Results, *MOD-RTG Materials Development Meeting*, GE Astrospace, Valley Forge, PA.

Vandersande, J. W., J. P. Fleurial, J. S. Beaty, and J. L. Rolfe (1992b) in *Proc. of XI International Conf. on Thermoelectrics*, K. R. Rao, ed., The University of Texas at Arlington, Arlington, TX: 21-23

Vining, C. B. (1988) Unpublished Results, Jet Propulsion Laboratory, Pasadena, CA.

Vining, C. B. (1989) "Electrical and Thermal Model," Unpublished Results, *5th SiGe Integration Meeting*, Thermoelectron Technology Corporation, Waltham, MA.

Vining, C. B. (1990) "High Figure of Merit Thermoelectrics: Theoretical Considerations," in *Proc. of 25th Intersoc. Energy Conv. Eng. Conf.*, P. A. Nelson, W. W. Schertz, and R. H. Till, eds., American Institute of Chemical Engineers, New York, NY, 2: 387-391.

Vining, C. B., W. Laskow, J. O. Hanson, R. R. Van der Beck, and P. D. Gorsuch (1991a) "Thermoelectric Properties of Pressure-Sintered $Si_{0.8}Ge_{0.2}$ Thermoelectric Alloys," *J. Appl. Phys.*, 69: 4333-4340.

Vining, C. B. (1991b) "A Model for the High Temperature Transport Properties of Heavily Doped P-Type Silicon-Germanium Alloys," in *Modern Perspectives on Thermoelectrics and Related Materials*, *Mat. Res. Soc. Symp. Proc. 234*, D. D. Allred, C. B. Vining, and G. A. Slack, eds., Materials Research Society, Pittsburgh, PA: 95-104.

Vining, C. B. (1991c) "A Model for the High Temperature Transport Properties of Heavily Doped P-Type Silicon-Germanium Alloys," *J. Appl. Phys.*, 69,: 331-341.

White, D. W. (1990) "Phonon Scattering and Thermal Conductivity in Semiconductors with Thermoelectric Applications," PhD Thesis, University of Connecticut, Storrs, CN.

White, D. P. and P. G. Klemens (1992) "Thermal Conductivity of Thermoelectric $Si_{0.8}Ge_{0.2}$ Alloys," *J. Appl. Phys.*, 71: 4258-4293.

Wood, C. (1988) "Materials for Thermoelectric Energy Conversion," *Reports on Progress in Physics*, 51: 459-539.