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Silicon Germanium

Cronin B. Vining
Jet Propulsion Laboratory/
California Institute of Technology

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I. ABSTRACT

This chapter summarizes the preparation techniques and materials properties required for practical applications of silicon germanium alloys. The relationship between the phase diagram and choice of preparation technique is discussed and two proven methods, zone leveling and hot pressing, are described. Key physical properties such as thermal expansion and mechanical strength are summarized and trends in thermoelectric properties as functions of composition, doping level and temperature are illustrated. Representative thermoelectric property data are presented in tabular form and the critical degradation mechanisms of sublimation and dopant precipitation are discussed. Finally, the agreement between modern theory and proven experimental results is presented.

II. INTRODUCTION

Silicon germanium alloys (SiGe) were first used in space in the SNAP-10A nuclear reactor and have been the exclusive choice for radioisotope thermoelectric generators (RTGs) launched by the USA since 1976 (¹). Primary considerations for space power applications are reliability and high operating temperatures to take advantage of the T^4 dependence of radiator heat rejection rates. In addition to having attractive thermoelectric and physical properties, SiGe devices can operate at temperatures up to about 1300 K without significant degradation. A number of reviews of the properties of SiGe alloys are available^{2,3,4,5,6} and the principles of generator design and fabrication are discussed elsewhere in this Handbook. This chapter will therefore emphasize aspects of SiGe required for practical applications.

III. PREPARATION

Although silicon and germanium are completely miscible in both the liquid and solid state, the large separation between the liquidus and the solidus complicate the preparation of homogeneous solids. Figure 1 illustrates solidification of $\text{Si}_{0.8}\text{Ge}_{0.2}$ (C_S) from a liquid with composition $\text{Si}_{0.545}\text{Ge}_{0.455}$ (C_L). Upon cooling, the first solid deposited is enriched in Si compared to the melt and cast ingots typically exhibit severe alloy segregation. Preparation of homogeneous solids requires either some method to maintain the composition of the melt during solidification or some process to homogenize the solid phase. A variety of methods employing either strategy are available and two successful variants are described in the following sections.

Regardless of preparation method, however, the number of important processing parameters is rather large. While the effect of each parameter will not be discussed in detail here, it should be emphasized that variations in many parameters will significantly affect the properties of the resulting material. Accurate process control is therefore critical to preparing a reproducible product. Porosity, density, thermopower and resistivity measurements are relatively simple to perform and provide a great deal of quality control information. Porosity provides a sensitive measure of densification and density is a reliable indicator of composition. Doping level may be monitored by measuring the thermopower at room temperature and resistivity provides a sensitive measure of overall sample quality.

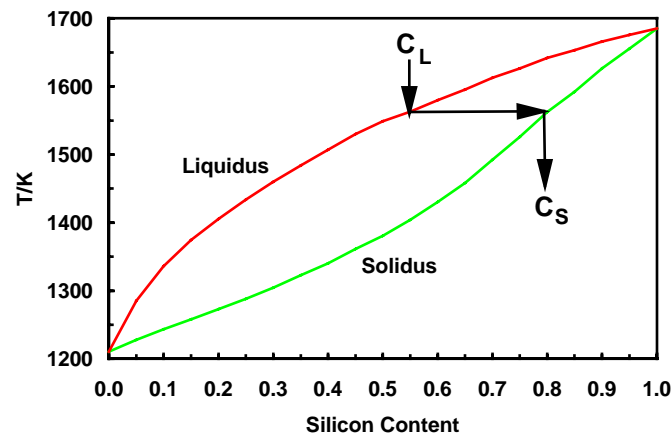


FIGURE 1. Si-Ge phase diagram indicating solidification of $\text{Si}_{0.8}\text{Ge}_{0.2}$.⁷

A. ZONE LEVELING

The zone leveling method was used to prepare SiGe for the first space application of SiGe thermoelements in the SNAP-10A nuclear reactor.¹ The procedure is illustrated schematically in Fig. 2. A charge bar is prepared by any convenient method (e.g. casting, powder metallurgy) with the desired final composition (C_S). A zone bar is similarly prepared with a composition (C_L) chosen to have a freezing point at the same temperature as the melting point of the charge bar, as indicated in Fig. 1. The zone bar is then heated to the melting point of the charge bar and the resulting liquid zone caused to traverse the length of the charge bar. As the liquid zone moves to the right, the charge bar is consumed at the leading edge of the liquid zone and a homogeneous ingot of SiGe freezes out of the trailing edge. To prevent constitutional supercooling, growth rates typically cannot exceed about 0.5-1 mm/hour.

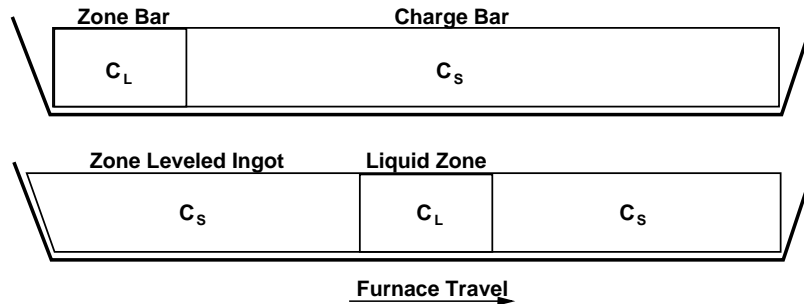


FIGURE 2. Schematic of the zone leveling procedure showing the initial arrangement of the materials (above) and the situation during zoning (below).²

Phosphorus is the preferred for n-type materials and boron is the only p-type dopant sufficiently soluble for thermoelectric applications. Either of these dopants may be added to the charge and zone bars. When preparing n-type materials it is desirable to control the vapor pressure of phosphorus over the liquid zone to achieve the high doping levels desired for optimum figure of merit. With proper choice of conditions zone leveling can prepare high quality polycrystalline materials with transport properties indistinguishable from single crystals. The primary disadvantage of this technique is the long time required to prepare samples.

B. HOT PRESSING

Today, powder metallurgical methods are generally preferred for production of significant quantities of SiGe primarily because large, good quality samples can be prepared from powders in a single day. Also, relatively large variations of preparation conditions can be tolerated while still producing satisfactory thermoelectric properties.⁸ Hot pressed SiGe has been used in RTGs aboard the LES 8, LES 9, Voyager I, Voyager II, Galileo and Ulysses spacecraft. The following preparation procedure is representative of, although not identical to, the procedure used to prepare SiGe for RTGs.

Typically, a 4-to-1 atomic ratio of silicon and germanium is induction melted in fused silica crucibles under vacuum. For p-type materials 0.08 weight % boron is placed in the crucible before heating and for n-type materials 0.55 weight % phosphorus is added directly to the melt to minimize losses due to vaporization. The melt is cast into a water cooled copper mold and mechanically pulverized to -80 mesh powder. A planetary ball mill may be used to further reduce the median particle diameter to 2-10 μm , which improves both the homogeneity and strength of the final compact. The powders are placed in TZM dies and molds lightly coated with graphite to reduce friction during compact ejection. Pressure sintering is performed under 180 MPa of pressure, applied after reaching 1513 K. Pressure is released after 30 minutes when the

compact is ejected from the die and allowed to cool. SiGe compacts 5.08 cm diameter and 2.54 cm thick have been routinely prepared in this manner and larger sizes have occasionally been produced.

IV. PROPERTIES

A wide variety of physical, thermal and thermoelectric properties are required for the design of reliable thermoelectric devices. The most essential properties are summarized in the following sections.

A. PHYSICAL

Thermal expansion and mechanical strength considerations are critical to the design of thermoelectric devices and some of the more important properties for SiGe are summarized in Table 1. The greatest stresses often arise when the device cools following the final high temperature fabrication processes. Differential thermal expansion at the joints between dissimilar materials results in stresses that can easily exceed the maximum stress of the thermoelectric material. As is typical of ceramic materials, SiGe is 3-4 times stronger in compression than in tension. It is therefore preferred that the materials in contact with SiGe have a somewhat larger thermal expansion, so that they contract more than SiGe on cooling and keep the SiGe in compression rather than under tension. It is interesting to note that p-type SiGe can typically withstand greater stress than n-type SiGe.

TABLE 1. Typical physical properties of hot pressed silicon-germanium.

	T (K)	Units	p-type Si _{0.8} Ge _{0.2}	n-type Si _{0.8} Ge _{0.2}
Density	300	gm/cm ³	2.99	2.99
Thermal Expansion	300	10 ⁻⁶ /K	3.98	4.20
	600	10 ⁻⁶ /K	4.26	4.43
	900	10 ⁻⁶ /K	4.55	4.66
	1200	10 ⁻⁶ /K	4.84	4.89
	1400	10 ⁻⁶ /K	5.03	5.05
Porosity			1%	1%
Dopant			Boron	Phosphorus
Nominal Composition		atomic %	0.23	0.59
Compressive Strength^a				
Maximum Stress	300	MPa (±20%)	653	473
Maximum Strain	300	% (±25%)	0.42	0.37
Modulus	300	GPa (±7%)	154	129
Tensile Strength^b				
Maximum Stress	300	MPa (±20%)	201	129
	875	MPa (±20%)	292	143
	1375	MPa (±20%)	310	182*
Maximum Strain	300	% (±25%)	0.15	0.11
	875	% (±25%)	0.20	0.10
	1375	% (±25%)	0.49	>0.69*
Modulus	300	GPa (±7%)	137	145
	875	GPa (±7%)	151	165
	1375	GPa (±7%)	103	114*

Test Methods: a - cylinders, b - 4 point flexure,

*Two of three samples tested did not fail due to high ductility at 1375 K.

B. THERMOELECTRIC

This section provides an overview of some of the more important effects of composition, temperature, doping level and dopant type on the thermoelectric properties of SiGe. Figure 3 illustrates the composition dependence of ZT for silicon-rich alloys. The addition of germanium to silicon increases ZT to technically useful values, primarily due to increased scattering of phonons associated with the random distribution of Si and Ge atoms in the alloy. Except very near pure silicon, ZT is seen to be relatively insensitive to composition, and for this reason sintered materials can yield good performance even when homogenization is incomplete.

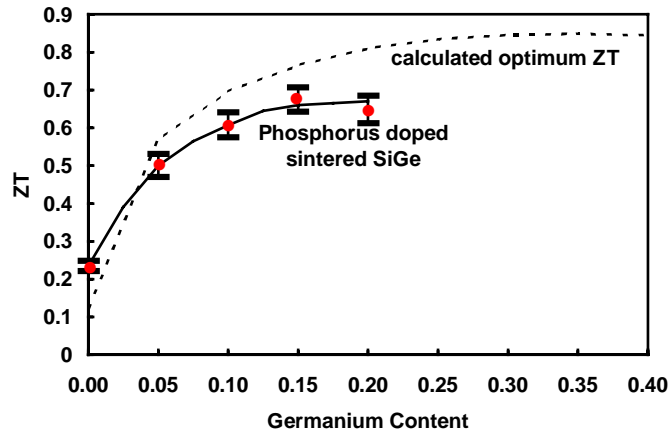


FIGURE 3. Dimensionless figure of merit averaged from 575 to 1275 K. The points are experimental results on sintered n-type Si-Ge with 2 atomic percent phosphorus⁹ and the dashed line is the theoretical maximum ZT calculated using the model described in reference .¹⁰

Figure 4 illustrates the temperature dependence of the thermoelectric properties for boron doped, zone leveled $\text{Si}_{0.7}\text{Ge}_{0.3}$ with several different doping levels. At these doping levels, the electrical resistivity and Seebeck coefficient generally increase with increasing temperature, which is more characteristic of metals than semiconductors. Up to about 1000 K, the thermal resistivity also increases with temperature, a behavior typical of electrical insulators. As temperatures are further increased, the Seebeck coefficient, electrical resistivity and thermal resistivity will all decrease with increasing temperature due to the thermal excitation of charge carriers. Another effect, associated with the solubility and diffusion characteristics of the dopants, will be discussed below.

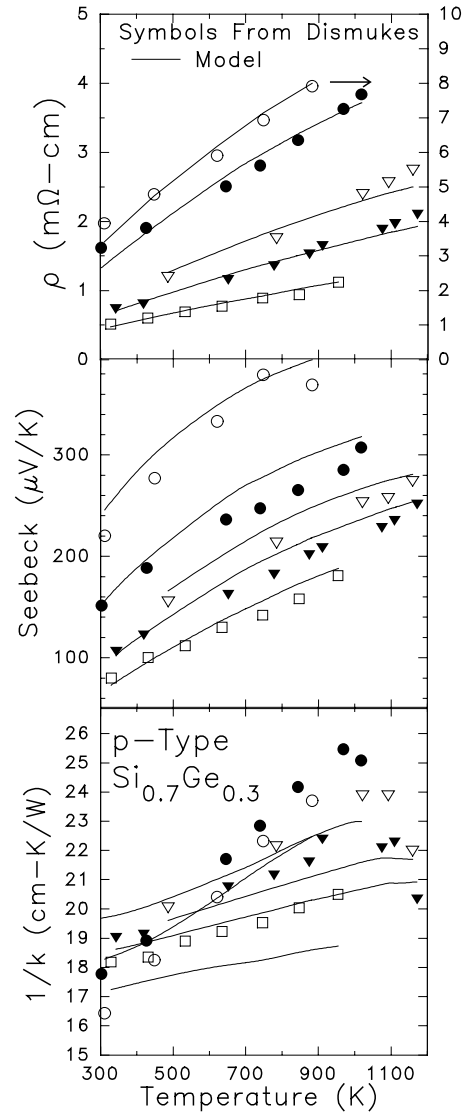


FIGURE 4. Resistivity, Seebeck and thermal conductivity for p-type $\text{Si}_{0.7}\text{Ge}_{0.3}$. The points are experimental results¹¹ and the lines are calculated.¹²

Note that while the individual properties vary strongly with doping level, as illustrated in Fig. 4, the figure of merit is relatively insensitive to doping level in the vicinity of the optimum doping level, as illustrated in Fig. 5 for zone leveled n-type $\text{Si}_{0.7}\text{Ge}_{0.3}$. The precise value of the optimum doping level varies somewhat with composition and temperature, but is usually in the range of

$1\text{-}3 \times 10^{20} \text{ cm}^{-3}$ for n-type SiGe and $2\text{-}4 \times 10^{20} \text{ cm}^{-3}$ for p-type SiGe (not shown).

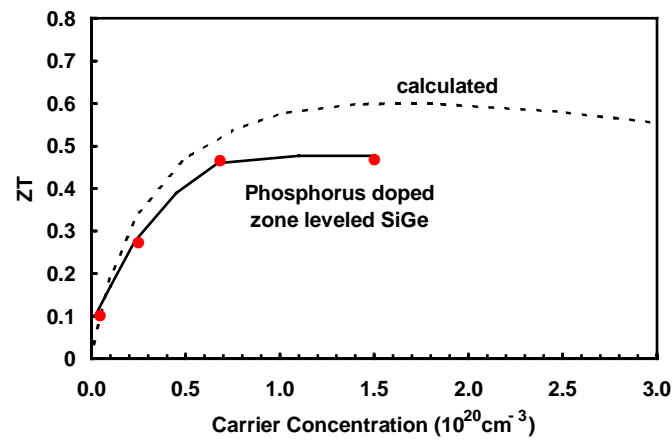


FIGURE 5. Dimensionless figure of merit (averaged from 300 to 1000 K) for zone leveled n-type $\text{Si}_{0.7}\text{Ge}_{0.3}$ (ref. 11) and the dashed line is calculated using the model described in reference 10.

Achieving precisely optimum ZT values can be rather difficult and it should be emphasized that almost any variation in processing will affect the individual thermoelectric properties. But often reproducibility is more important than the absolute maximum ZT and satisfactory results can generally be achieved using preparation and process monitoring methods such as outlined above. Tables 2 and 3 summarize typical thermoelectric properties for p-type and n-type sintered SiGe.

TABLE 2. Typical thermoelectric properties for p-type silicon-germanium.

T (K)	Electrical Resistivity ($10^{-5} \Omega\text{-m}$)	Seebeck Coefficient ($\mu\text{V/K}$)	Thermal Conductivity (W/m-K)	Heat Capacity (J/gm-K)	ZT unitless
300	1.14	121			
400	1.32	144	4.80	0.647	0.131
500	1.51	161	4.70	0.649	0.184
600	1.71	176	4.57	0.658	0.237
700	1.93	189	4.41	0.672	0.295
800	2.16	203	4.25	0.687	0.359
900	2.41	216	4.12	0.703	0.423
1000	2.68	228	4.07	0.719	0.478
1100	2.96	237	4.14	0.736	0.505
1200	3.19	240	4.38	0.754	0.501
1300	3.26	233	4.84	0.772	0.446

TABLE 3. Typical thermoelectric properties for n-type silicon-germanium.

T (K)	Electrical Resistivity ($10^{-5} \Omega\text{-m}$)	Seebeck Coefficient ($\mu\text{V/K}$)	Thermal Conductivity (W/m-K)	Heat Capacity (J/gm-K)	ZT unitless
300	0.85	-108			
400	1.01	-136	4.45	0.647	0.165
500	1.17	-165	4.31	0.649	0.269
600	1.36	-190	4.19	0.658	0.380
700	1.61	-213	4.08	0.672	0.486
800	1.86	-233	3.99	0.687	0.583
900	2.06	-247	3.93	0.703	0.679
1000	2.11	-253	3.93	0.719	0.775
1100	1.97	-250	4.01	0.736	0.870
1200	1.78	-242	4.20	0.754	0.938
1300	1.91	-243	4.53	0.772	0.890

C. DEGRADATION MODES

SiGe thermocouples have accumulated over 250 million device hours in space applications without a single known thermoelectric failure. This remarkable success has been achieved by following conservative design principles and paying close attention to the possible failure mechanisms and degradation modes. This section describes some of the more important lifetime limiting degradation modes for SiGe alloys.

1. Sublimation

Sublimation is one of the primary degradation mechanisms for a high temperature SiGe thermoelectric device. SiGe sublimation degrades performance in at least two ways. First, SiGe deposits on the surroundings can result in either thermal or electrical shorts around the thermoelectric device. Second, continued sublimation can eventually erode the thermoelectric device to the point of electrical open circuit and/or mechanical failure. Figure 6 illustrates steady state loss rates for uncoated SiGe and for SiGe coated with Si_3N_4 which, combined with a knowledge of the exposed surface area and temperature profile of the device, allows estimates of erosion rates. SiGe devices for space applications have typically been coated with Si_3N_4 and wrapped with a quartz yarn.

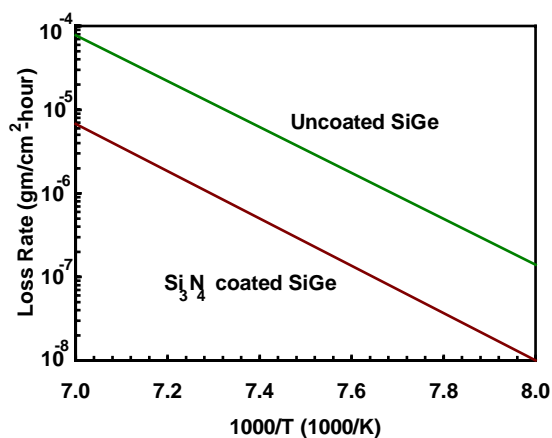


FIGURE 6. Material loss rates for $\text{Si}_{0.78}\text{Ge}_{0.22}$ with and without a 1200 nm coating of Si_3N_4 .¹³

2. Dopant Precipitation

SiGe thermoelectric materials are intentionally supersaturated with dopants in order to achieve the highest possible figure of merit. Therefore under most operating conditions (below about 1400 K) dopants will tend to precipitate from solid solution forming localized precipitates and decreasing the carrier concentration within the thermoelectric material. For practical purposes this effect is well described by the conventional Lifshitz-Slyozov model. Particles smaller than a critical radius (the size of which depends on temperature) tend to dissolve, which can actually result in a temporary increase in the carrier concentration with time until the smallest particles are consumed. Larger precipitates tend to grow in size, at a rate which is determined by the diffusion constant of the dopant.

For phosphorus doped SiGe, precipitation rates are most pronounced between about 600 and 900 K, as illustrated by the changes in the electrical resistivity shown in Fig. 7. It should be emphasized that Fig. 7 illustrates the time dependence of material held at a fixed temperature. Measurements performed as a function of temperature on any particular sample would appear very different. At lower temperatures the degree of supersaturation may be very large, but because diffusion is so slow that precipitation occurs at a negligible rate and the resistivity increases only slowly with time. At higher temperatures diffusion is very fast, but dopants are more soluble and again precipitation is relatively slow. Indeed, phosphorus diffusion is so fast at high temperatures that the peak typically observed in the resistivity of n-type SiGe at about 1000 K (see the 50 hour curve in Fig. 7) is due to precipitated phosphorus dissolving into the SiGe matrix and increasing the carrier concentration during the measurement. This effect is sometimes misinterpreted as the onset of excitation of minority carriers, which is a physically very distinct effect.

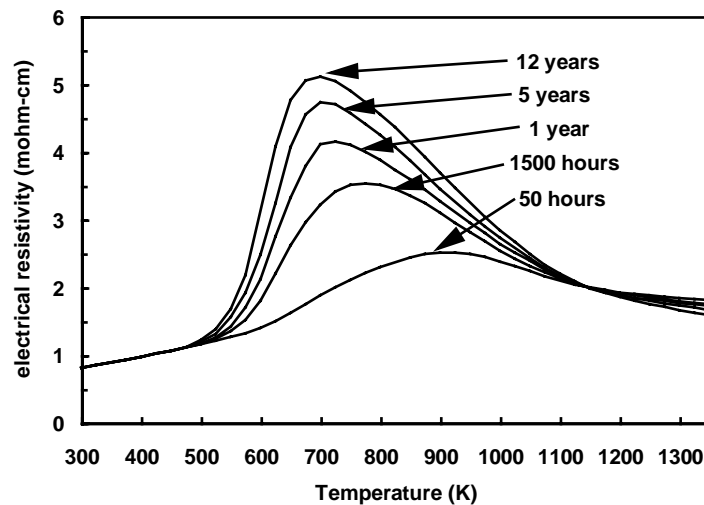


FIGURE 7. Estimated time dependence of the electrical resistivity of n-type $\text{Si}_{0.8}\text{Ge}_{0.2}$ for samples held isothermally at the indicated temperatures.¹⁴

Fortunately for practical applications, the effect of dopant precipitation on the Seebeck coefficient and thermal conductivity is smaller than the effect on the electrical resistivity, and the overall effect on ZT is smaller still due to compensatory changes in the individual properties. Also, the effects are less pronounced in boron doped materials because boron is both more soluble and has a lower diffusion rate compared to phosphorus.

V. THEORY

The theory of the thermoelectric properties of SiGe alloys is beyond the scope of this article, but may be described as a specialization of the general theory of semiconductors. Basically, the electrical and thermal properties of SiGe are considered to arise from electrons, holes and phonons simultaneously contained within the solid. Heat and electrical currents are attributed to the motion of these particles in response to applied forces, in the form of thermal or electrical gradients. Electrons and holes transport both electrical charge and heat through the solid, while phonons (which are nothing more than wave-like oscillations of the atoms about their equilibrium positions) transport only heat. Fig. 4 shows an example of the excellent agreement which has been achieved between this type of microscopic theory and experimental results.

VI. SUMMARY

Key aspects of SiGe preparation have been presented and typical materials properties critical to the design of practical thermoelectric devices have been summarized. While to date SiGe has been used almost exclusively for space applications, the mature basis of the technology and attractive physical and chemical properties summarized here make this material an attractive alternative for any application where reliable, long term performance in a demanding high temperature environment is required.

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