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# A PROMISING NEW THERMOELECTRIC MATERIAL: RUTHENIUM SILICIDE

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## ABSTRACT

Experimental and theoretical efforts directed toward increasing thermoelectric figure of merit values ($ZT=\sigma S^2T/\lambda$, where $\sigma$=electrical conductivity, S=Seebeck coefficient and $\lambda$=thermal conductivity) by a factor of two or three have been encouraging in several respects. An accurate and detailed theoretical model developed for n-type silicon-germanium (SiGe) indicates that ZT values several times higher than currently available are expected under certain conditions. These new, high ZT materials are expected to be significantly different from SiGe, but not unreasonably so. Several promising candidate materials have been identified which may meet the conditions required by theory. One such candidate, ruthenium silicide, currently under development at the Jet Propulsion Laboratory, has been estimated to have the potential to exhibit figure of merit values four times higher than conventional SiGe materials. Recent results are summarized.

## INTRODUCTION

The principal advantages of thermoelectric energy conversion for space power applications are high reliability and long operation lifetime. For many applications, these qualities alone are sufficient to make thermoelectrics the technology of choice. The high cost and mass of available heat sources, however, are strongly leveraged by the efficiency of the conversion system and this drives the search for more efficient systems.

It is often assumed, however, that the only options for major improvements in efficiency must involve technologies other than thermoelectrics. After all, recent quantitative improvements in thermoelectrics, such as 20-30% higher ZT values for SiGe (Vandersande et al. 1987), while technologically very significant, do not qualitatively alter the relatively low efficiency of thermoelectrics.

Still, there are several fundamental reasons to believe the search for much higher ZT values may eventually succeed. Thermodynamic principals are no more restrictive on the thermoelectric process than any other energy conversion cycle. Beyond the omnipresent Carnot limit, thermodynamics places no further constraints on the efficiency of thermoelectrics. Yet the best materials exhibit ZT values not much more than 1, which limits the efficiency possible with to around 17% of the Carnot efficiency. This, using the very best available materials and only over a narrow range of temperatures around the peak ZT values for those materials.

## THEORETICAL CONSIDERATIONS

So, why are thermoelectrics so inefficient? If the problem is not in the thermodynamics, where is it? One possible answer might lay in the physics of thermoelectric materials. And although many theoretical studies of thermoelectric properties have concluded that there was at most a very large limit on ZT (Wood, 1988), until recently these models had not been applied to SiGe.

Today, a theoretical model is available for n-type SiGe (Vining 1990a, 1991) which quantitatively describes all of the thermoelectric properties of these materials using conventional theoretical expressions appropriate for semiconductors. These results remove any concern that the current theoretical

understanding thermoelectric materials be somehow inadequate to describe real, practical materials such as SiGe. The calculations are in fact neither exotic nor especially difficult, but merely tedious.

The n-type SiGe model has also been extended in order to examine the effect of variations of the fundamental parameters on ZT (Vining, 1990c). Using this method, the properties of a hypothetical material, differing from the available SiGe alloys in some specific way, may be examined. Physically reasonable variations of several of the fundamental parameters of these models readily yield ZT values several times higher than currently available. One such hypothetical material results from replacing the germanium atoms with some other atom of the same size and charge, but with a different mass. Such atoms do exist, of course, and are called isotopes of germanium, although the range of masses actually available is somewhat limited.

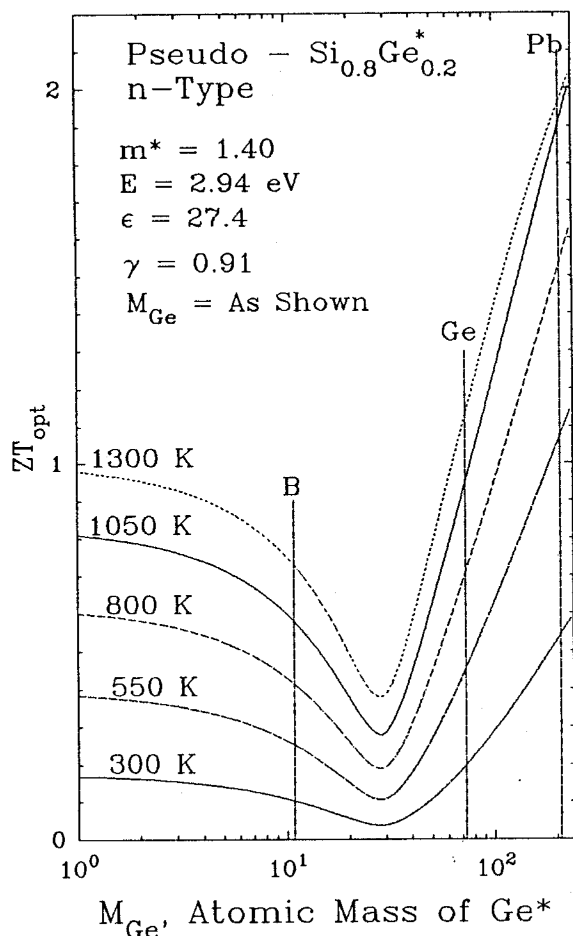


FIGURE 1.: $ZT_{opt}$ Versus the Mass of Pseudo-Germanium, Indicated by Ge*. Vertical Lines Indicate the Actual Masses of Boron (B), Germanium (Ge) and Lead (Pb).

Figure 1 shows the figure of merit of this silicon-"pseudo-germanium" alloy as a function of the mass of the "pseudo-germanium" atoms and temperature. The vertical lines indicate the actual masses of boron, silicon and lead. The figure shows that if an isotope of germanium were available with a mass as great as the mass of a lead atom, the ZT of this material would be roughly twice as large as the ZT of ordinary SiGe.

An actual alloy of silicon and lead would also be expected to have a large ZT value, although the values would be somewhat different than shown in Figure 1 because lead has a different size than the pseudo-germanium used in this calculation. Unfortunately, this difference in size means that lead is not soluble in silicon to any significant extent and silicon-lead alloys are not possible.

This, and other examples discussed in Vining 1990c, lead to the conclusion that the relatively low ZT values available today are not due to limits imposed by the physics of thermoelectricity, but merely due to the chemistry of the available materials. One approach, then, is to find a material governed by the same physics as SiGe alloys, but has sufficiently different chemistry that the fundamental parameters allow optimization for large ZT.

## SILICIDES AS THERMOELECTRIC MATERIALS

A survey of the binary compounds of silicon has yielded a number of compounds with great promise for use as high temperature thermoelectric materials (Vining 1990b), but very little detailed information is available on the high temperature thermoelectric properties of these materials. Data on high quality, thoroughly characterized samples are essentially non-existent. $Ru_2Si_3$, $Os_2Si_3$, $OsSi_2$, $Rh_4Si_5$, and $Ir_4Si_5$ for example, are known to be high melting point semiconductors and from consideration of their crystal structure and related compounds are expected to have low thermal conductivity values. These properties, coupled with the potential for a large number of doping and alloying combinations, make them particularly attractive as candidate thermoelectric materials.

For each of the conventional thermoelectric materials systems, such as SiGe, PbTe, and $Bi_2Te_3$, the electrical power factor ($\sigma S^2$) can be optimized by adjusting the doping level and the thermal conductivity, $\lambda$, can be minimized by adjusting the major components of the alloy. All of the commonly used thermoelectric materials were developed by optimizing the doping and alloying.

The charge carriers in each of the conventional semiconductors are derived from s- and p-bands because the elements involved come from the right-hand portion of the periodic table. Thermocouple wires such as chromel, alumel, W-Re, Pt-Rh, etc., however, are generally made from elements from the middle of the periodic table, where the charge carriers originate in the d-bands. The major advantage of the d-bands is that they generally provide much larger Seebeck voltages than are found in simpler metals like aluminum (although still generally smaller than can be achieved in semiconductors). Since a principle component of these new silicon-based compounds is a transition-metal from the middle of the periodic table, they too may exhibit larger Seebeck voltages than conventional thermoelectrics due to the presence of d-bands.

These silicon-based compounds, therefore, may be able to combine the doping and alloying approach so successful in developing the current generation of thermoelectrics, with the Seebeck enhancement effect utilized in conventional thermocouple wire materials.

## EXPERIMENTAL DETAILS

In order to investigate the potential of this class of materials, $Ru_2Si_3$ was chosen for experimental development. Eleven samples of $Ru_2Si_3$ were prepared by arc-melting on a water cooled copper hearth under argon, using zirconium as an oxygen getter. Each sample, weighing about 5 g, was melted, turned over and remelted several times. Weight loss during the melting represented less than 0.4% of the silicon content of each sample. Densities were determined using an immersion technique and were within a few percent of the expected X-ray densities. Two samples of stoichiometric $Ru_2Si_3$, four samples with successively increasing silicon content, and one sample each with a few percent boron, aluminum, manganese, cobalt and rhodium were prepared. X-ray diffraction measurements were performed on an automated Seimens diffractometer. Seebeck, Hall effect and thermal diffusivity measurements were performed on selected samples from 300 K to 1300 K.

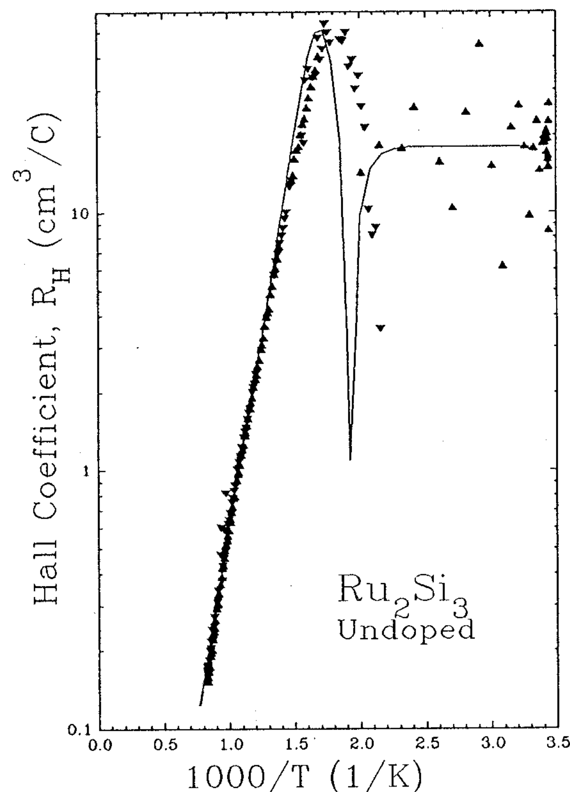

FIGURE 2. Hall Coefficient for Undoped $Ru_2Si_3$ as a function of Temperature. Solid Line Represents a Two-Band Model.

## RESULTS

The arc-melted samples are hard, and brittle and were easily pulverized to powder form for the X-ray measurements. Most samples exhibited some degree of faceting on the upper surface (which cooled last) and showed cracks visible to the eye. All samples exhibited the $Ru_2Si_3$ crystal structure as the major phase. The four samples with excess silicon exhibited successively more intense silicon X-ray lines and no observable shift (to within ±0.01 Å), consistent with at most a very narrow homogeneity range for the compound $Ru_2Si_3$. The cobalt-doped sample showed a trace of $CoSi_2$ and the boron doped sample showed a trace of $RuB_2$, while the two undoped samples and the samples doped with aluminum, manganese and rhodium showed no trace of second phase.

Figure 2 shows the Hall coefficient for an undoped sample $Ru_2Si_3$ from room temperature to 1200 K. The second undoped sample and the silicon-rich samples show qualitatively similar behavior. The Hall coefficient is n-type and roughly constant below 430 K. Above 430 K the Hall coefficient is p-type, peaks around 500 K and decreases exponentially with further increase in temperature. From the high

temperature slope of this line the band gap is estimated at about 0.9 eV.

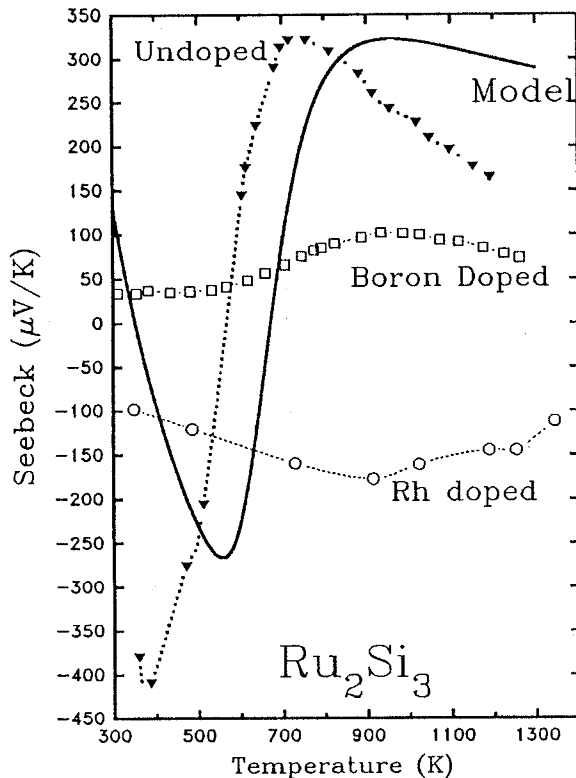


FIGURE 3. The Seebeck Coefficient for Three Samples of $Ru_2Si_3$. Solid Line Represents a Two-Band Model for the Undoped Sample.

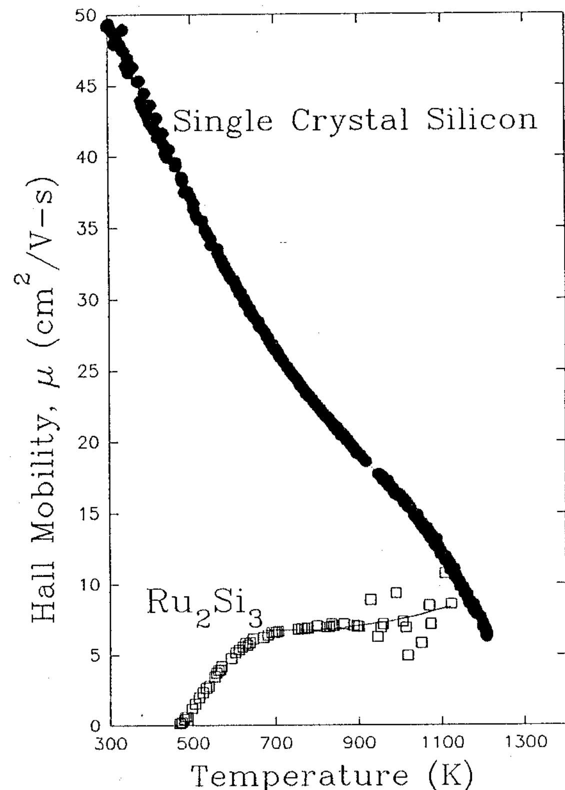


FIGURE 4. Hall Mobility as a function of Temperature for Undoped $Ru_2Si_3$ and Single Crystal Silicon.

Figure 3 shows the Seebeck coefficient for the undoped sample of Figure 2, as well as the boron doped sample and the rhodium doped sample, which were p-type and n-type, respectively, as expected. The absolute values of the Seebeck for the boron and rhodium doped sample peak at around 100 μV/K and -200 μV/K, respectively, which is in approximately the right range for thermoelectric applications. The aluminum and manganese doped samples were also expected to be p-type, but in fact were n-type. While the cobalt doped sample was expected to be n-type, and in fact was p-type.

The solid lines in Figures 2 and 3 represent a simple two-band model for the undoped sample, which is seen to account for the change in sign of these coefficients from negative to positive with increasing temperature. This kind of behavior is not at all unusual in lightly doped semiconductors. The simplest interpretation of this behavior is that this sample contains a small number of n-type dopants, estimated at about $4 \times 10^{17}$ $cm^{-3}$, which dominate the behavior at lower temperatures. But, at higher temperatures where both electrons and holes are thermally excited in large numbers, p-type behavior dominates due to the higher mobility of the thermally excited holes.

Figure 4 shows the Hall mobility of the undoped $Ru_2Si_3$ sample and a sample of single crystal p-type silicon for comparison purposes. The Hall mobility of the $Ru_2Si_3$ sample goes through zero at around 430 K, due to the change in sign of the Hall coefficient as shown in Figure 2 above. This, again, is an artifact of the competition between the n-type dopants dominating the behavior at low temperatures and the higher mobility of the holes which dominates at higher temperatures. A sample of $Ru_2Si_3$ lightly doped with p-type dopants, say $4 \times 10^{17}$ $cm^{-3}$ boron, will show the simpler behavior exhibited by the single crystal silicon. The major point here is that by 1100-1200 K, $Ru_2Si_3$ has a mobility very similar to p-type silicon, which is already greater than the mobility of p-type SiGe.

Figure 5 shows the thermal conductivity of three samples of $Ru_2Si_3$ and a curve typical of SiGe. The undoped sample of $Ru_2Si_3$ has a shape similar to the shape of the SiGe curve, first decreasing and finally increasing with increasing temperature, but is several times lower. The thermal conductivities of the doped samples of $Ru_2Si_3$ increase with increasing temperature, which is typical of metallic behavior and indicates the effectiveness of boron and rhodium as dopants.

From the data on undoped $Ru_2Si_3$ shown in Figures 2-4, the effective masses of the electrons and holes can be estimated, as well as the electron and hole mobilities. These values are summarized in Table 1. Also shown in Table 1 are typical values for the thermal conductivity and the parameter $(m_{eff})^{3/2}\mu/\lambda$, which is thought to be some measure of the figure of merit which might be expected for optimized samples. The larger effective masses of $Ru_2Si_3$ compared to SiGe is typical of d-band materials and can be seen to compensate for the lower mobilities.

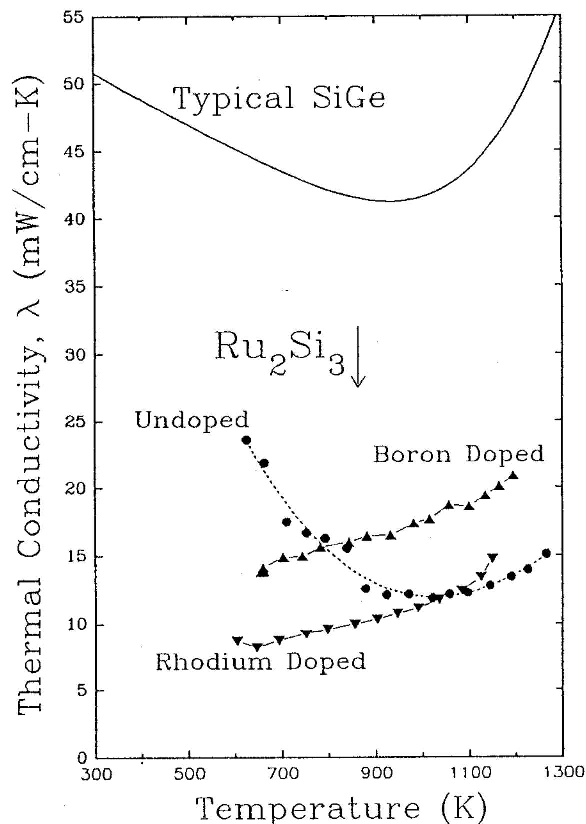


FIGURE 5. Thermal Conductivity of Three Samples of $Ru_2Si_3$ and a Curve Typical of SiGe.

## DISCUSSION

$Ru_2Si_3$ has an orthorhombic structure, so the properties are expected to be different in each of the three distinct crystallographic directions. Since these arc-melted samples are polycrystalline, the measured properties represent some crystallographic average compared to the properties of a single crystal. This, and the cracks resulting from differential thermal expansion of the individual crystallites, cast uncertainty on the analysis of the present data.

Table 1. Comparison of the Thermoelectric Parameters of SiGe and $Ru_2Si_3$ at 300 K.

| | Type | $m_{eff}$ | $\mu$ | $\lambda$ | $m_{eff}^{3/2}\mu/\lambda$ |
|---|---|---|---|---|---|
| SiGe | p | 1.0 | 40 | 44 | 0.91 |
| $Ru_2Si_3$ | p | 7.5 | 7.3 | 12 | 12.6 |
| SiGe | n | 1.4 | 68 | 44 | 2.6 |
| $Ru_2Si_3$ | n | 3.9 | 0.54 | 12 | 0.35 |

The simplicity of the arc-melting technique, however, allows preparation of clean samples from which rough estimates can be made relatively easily. Estimates made on such samples must be considered preliminary and oriented samples will be required to confirm these results and complete the doping and composition studies for optimum ZT values.

Still, the properties of $Ru_2Si_3$ are quite promising. The temperature dependence of the thermal conductivity of the undoped sample is close to 1/T below 1000 K, which is typical of phonon-phonon scattering. This suggests the already low thermal conductivity values may be reduced even further by alloying.

The large effective mass values, estimated from the Hall and Seebeck coefficient data shown in Figures

2 and 3 and summarized in Table 1, strongly support the conjecture that the d-bands of the transition metal element (ruthenium) work to enhance the Seebeck coefficient.

The least attractive properties at this point are the mobility values, particularly for the n-type materials. But the mobilities of semiconductors often improve dramatically with improved preparation technique and the p-type mobilities (Figure 4) are already competitive with p-type silicon, at least at high temperatures. Also, the values in Table 1 have been estimated from an undoped sample and the predictive value of $(m_{eff})^{3/2}\mu/\lambda$ for the thermoelectric figure of merit depends on the reliability of the much-simplified analysis. Indeed, the n-type rhodium-doped samples actually exhibits ZT values of about 0.25 between 900 and 1300 K, which is already better than might have been expected based on the $(m_{eff})^{3/2}\mu/\lambda$ value shown in Table 1 for n-type $Ru_2Si_3$.

## CONCLUSIONS

The preliminary results on $Ru_2Si_3$ support the theoretical suggestion that substantial improvements in ZT values may be possible with these materials. Just as importantly, $Ru_2Si_3$ is a member of a family of closely related compounds which provides much greater latitude for modifying the basic material for high ZT than is possible with simpler materials like SiGe alloys. Even at this early stage in development, the low thermal conductivity values and large effective mass values are very attractive. While the n-type mobility value is currently rather low, there is some reason to believe this is an artifact of the arc-melting preparation technique. Efforts to grow high quality crystals from the melt are now underway at the Jet Propulsion Laboratory in order to improve the mobility values and complete the doping and alloying studies needed to optimize the thermoelectric figure of merit.

## Acknowledgments

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