

CHARACTERISTICS OF A PROMISING NEW THERMOELECTRIC MATERIAL: RUTHENIUM SILICIDE

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ABSTRACT

Investigation on ruthenium silicide is under development as a experimental efforts directed toward high thermoelectric figure of merit values by a factor of two or more. This material has been identified as a candidate to high figure of merit depend on an accurate and detailed theoretical consideration. By preliminary study on arc-melted samples, it has been estimated that ruthenium silicide have the potential to obtain figure of merit values four times higher than conventional silicon-germanium material. In order to realize the high figure of merit values high quality crystal from the melt are needed. A Bridgman like method have been employed and has realized much better crystals than arc-melted ones. Recent results are still preliminary, however, further support that ruthenium silicide is a promising thermoelectric material.

INTRODUCTION

The thermoelectric figure of merit ($ZT = S^2T/\rho\lambda$, where S =Seebeck coefficient, ρ =electrical resistivity and λ =thermal conductivity) many times current state of the art values are entirely possible even within the range of microscopic parameters observed in real materials, which are concluded with a theoretical consideration for high figure of merit thermoelectrics[1]. This means that thermoelectric energy conversion devices are expected to reach efficiencies of 34% or more of the Carnot efficiency, even employing actual materials. Considering the high reliability and long life time as principal advantages of the solid state direct energy conversion, it would have a great impact on energy conversion technology, especially on space power technology such as SP100 project, to realize high efficiency thermoelectric devices.

This study is an attempt to actualize above mention of high efficiency thermoelectrics by investigating binary compounds of silicon, especially ruthenium silicide. For this purpose high quality crystals with single phase and well oriented large grains are re-

quired. Even early stage of investigation, many results support that ruthenium silicide is a promising thermoelectric material.

SILICIDES AS THERMOELECTRIC MATERIALS

Many theoretical studies of thermoelectric properties have concluded that was at most a very large limit on ZT [2], but these models had not been applied to silicon-germanium(SiGe) until recently. Today a self-consistent and theoretical model is available n-type SiGe alloys which quantitatively describes all of the thermoelectric properties of these materials using conventional expressions appropriate for semiconductors[3],[4]. The model calculations agree with data to 15% which are made in 21 samples with variation in carrier densities from 10^{18} to 3×10^{20} cm^{-3} and temperature from 300 to 1300K.

These results remove any concern that the current theoretical understanding thermoelectric material be somehow inadequate to describe real, practical materials such as SiGe.

This model has also been extended in order to examine the effect of variations of the microscopic parameters on ZT [1]. Using this method, even the range of microscopic parameters observed in real materials, 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 different mass.

Figure 1 shows ZT values of this silicon-"isotope of germanium" alloy as function of the mass of the "isotope of germanium" and temperature. The figure shows that if an isotope of germanium were available with mass as great as the mass of a lead atom, the ZT of this material would be twice as large as the ZT of ordinary SiGe.

An actual alloy of silicon and lead is not possible. Lead is not soluble in silicon because the lead atom is too big to fit in the crystal structure. If it were soluble, however, much higher ZT value would be expected.

This and other examples[1] lead to the

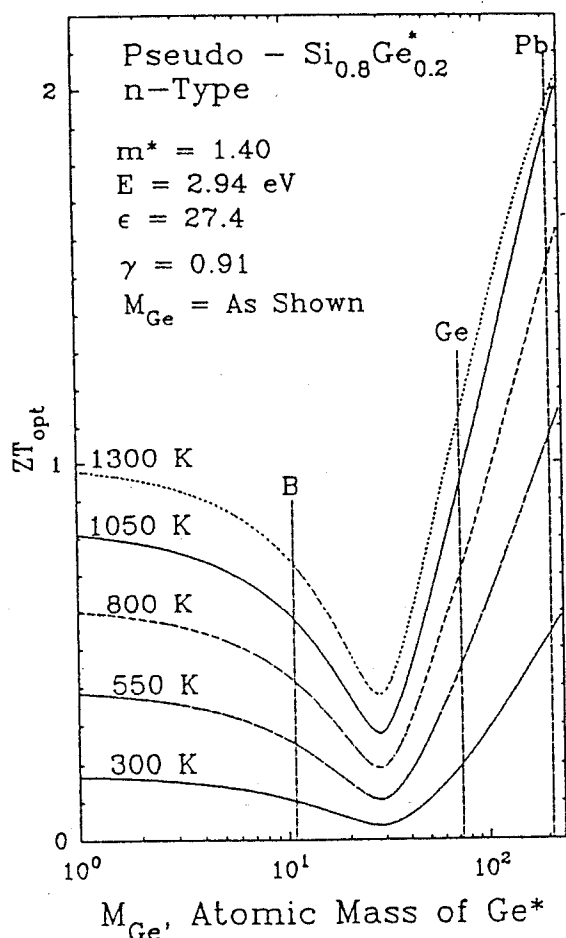


Figure 1. ZT_{opt} Versus the Mass of "Isotope of Germanium", Indicated by Ge^* . Vertical Lines indicate the Actual Masses of Boron(B), Germanium(Ge) and Lead(Pb).

conclusion that one approach for improving ZT values is to find material governed by the same physics as SiGe alloys, but with sufficiently different chemistry that the microscopic parameters allow optimization for large ZT.

One candidate material group which is suitable for this approach is the binary compound of silicon and a transition-metal[5]. Ru_2Si_3 , Os_2Si_3 , OsSi_2 , Rh_4Si_5 , and Ir_4Si for example, are known to be high melting point semiconductors and from consideration of this 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, are the same properties as each of the conventional thermoelectric materials systems, such as SiGe, PbTe and Bi_2Te_3 have. These properties also makes it possible to optimize ZT values by adjusting the doping level for electrical power factor (S^2/ρ) and by adjusting the major components of the alloys for minimization of the thermal conductivity (λ).

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 originated in the d-bands. The major advantage of the d-bands is that they generally provide much larger Seebeck voltage than found in simple metals like aluminum. 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 voltage than conventional thermoelectrics due to the presence of d-bands.

These silicon based compounds, therefore, may be able to combine the doping and alloying capability successful in the development of current generation of thermoelectrics, with the large Seebeck voltage used in conventional thermoelectric wire materials.

In order to investigate the potential of this class of materials, ruthenium sesquisilicides (Ru_2Si_3) was chosen for experimental development. Several arc-melted samples of Ru_2Si_3 were prepared. It has been confirmed that Ru_2Si_3 is the preferred semiconductor composition and that there are several candidate dopants. In particular boron and rhodium are useful p and n-type dopants, respectively.

The preliminary results on arc-melted Ru_2Si_3 support the theoretical suggestion that substantial improvements in ZT values may be possible with these materials[6]. Efforts to grow high quality Ru_2Si_3 crystals from the melt are necessary in order to improve the mobility values and complete the doping and alloying studies needed to optimize the thermoelectric figure of merit.

EXPERIMENTAL

In order to obtain high quality samples, a Bridgman like method using a two zone furnace was employed(Figure 2). Pyrolytic boron nitride and pyrolytic graphite were used as crucibles. The temperature gradient parallel to the crystal growth direction around the crucible was about 30K/cm, the cooling rates were 1K/hour to 2K/hour. Each sample, weighing about 7g, was melted in the crucible and was grown directionally. Typical dimensions of samples are 12 mm diameter and 20 mm high. Densities were determined using an immersion technique and were within 1 to 5 percent of the expected densities. Three stoichiometric samples were prepared with variation of crucibles and growing rates. Scanning Electron Microscopy-Electron Probe Micro Analyses(SEM-EPMA) were performed. Seebeck, Hall effect and thermal diffusivity measurements were performed on a selected sample from 300K to 1300K.

RESULTS

The Bridgman samples exhibited fewer cracks than the arc-melted samples visible to the eye. By optical microscopy the Bridgman

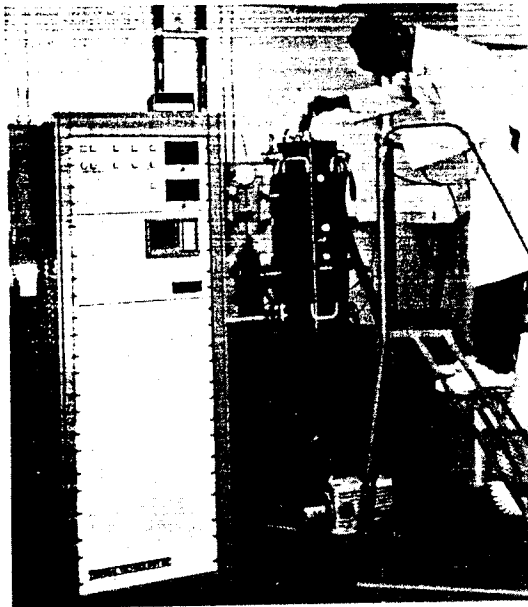


Figure 2. Two Zone Furnace for a Bridgman Like Method.

samples also exhibited fewer cracks and larger grains than the arc-melted samples. Two Bridgman samples exhibited multi-phase, phase of Ru_2Si_3 , phase of $RuSi$ and phase of silicon, and a Bridgman sample had a major phase of Ru_2Si_3 and a minor phase between the grain boundaries of the major Ru_2Si_3 phase.

Figure 3 shows a macro-structure across a diameter of the two phase ingot which appears to be only a few, large regions (up to 2-3mm each) of oriented Ru_2Si_3 . The thin darker regions are the minor phase with a eutectic-like micro-structure. Dominant grain size of this two phase sample was about 1 mm. Measurements on following thermoelectric properties were performed on the large regions of oriented Ru_2Si_3 such as Figure 3.



Figure 3. A Macro-Structure of Undoped Ru_2Si_3 .

Figure 4 shows the Hall coefficient for the undoped sample from room temperature to 1300K. The Hall coefficient is n-type and roughly constant below 550K. Above 550K it is p-type, peaks around 660K and decreases exponentially with increase in temperature.

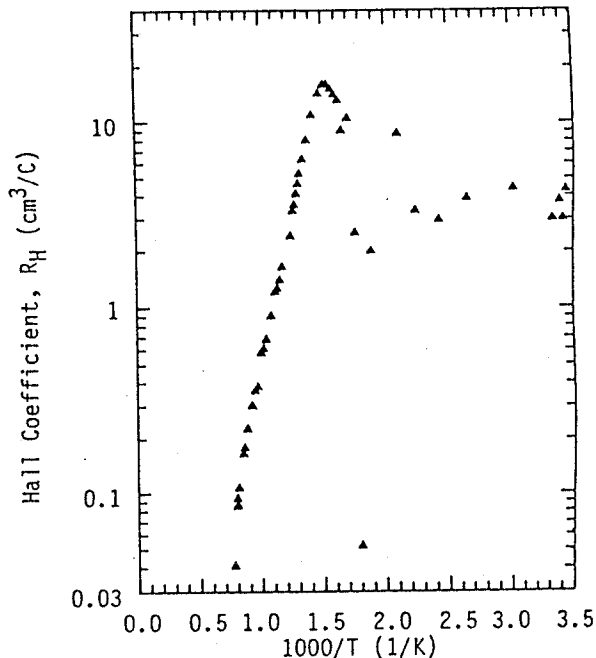


Figure 4. Hall Coefficient For Undoped Ru_2Si_3 .

Figure 5 shows the Seebeck coefficient for the undoped sample. The Seebeck coefficient also exhibits the change in sign from negative to positive with increasing temperature. The figure shows the n-p transition at around 550K, in good agreement with the Hall coefficient data in Figure 4.

The simple description of this behavior is that this sample contains a small number of n-type dopants, measured at about $2 \times 10^{18} cm^{-3}$, which dominated the behavior at lower temperatures. But, at higher temperatures where electrons thermally excited in large number from the valence to the conduction band, its electronic properties are dominated by the thermally excited holes because of its higher mobility than the electrons.

Figure 6 shows the resistivity of the undoped sample from room temperature to 1300K. The resistivity is roughly constant below 550K, n-type region. Above 550K, p-type region, the resistivity decreases exponentially with increase in temperature. From the slope of the lower and the higher temperature portion of p-type region, the band gap is estimated at about 1.19 eV and 0.72 eV, respectively.

Figure 7 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 550K, due to the change

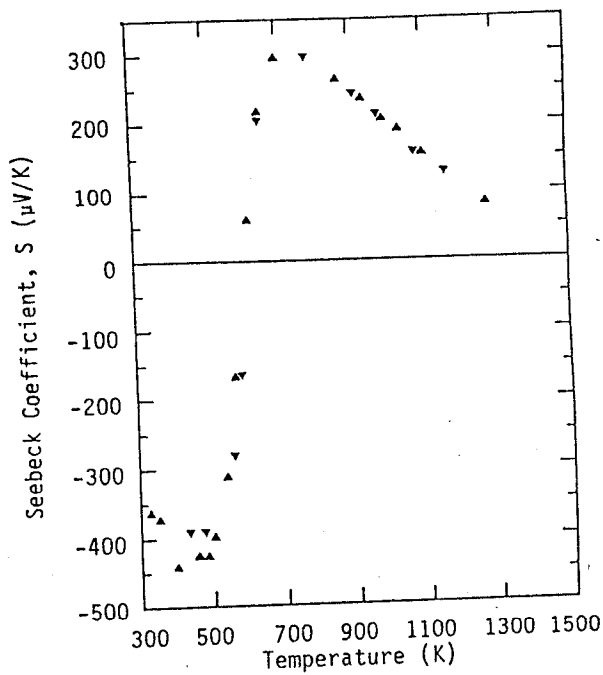


Figure 5. The Seebeck Coefficient for Undoped Ru_2Si_3 .

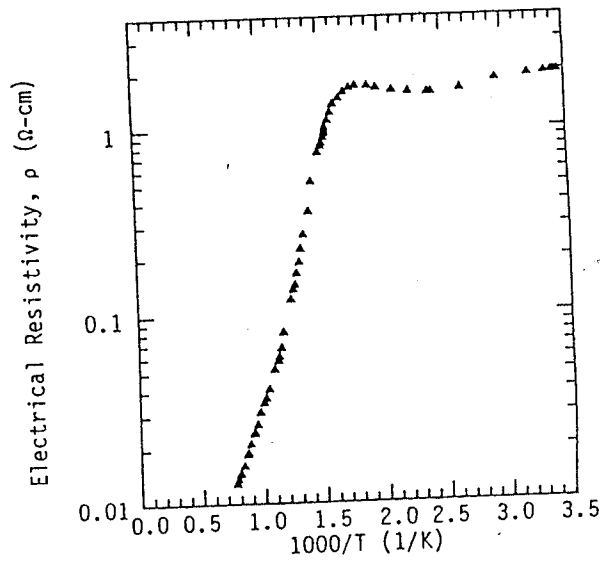


Figure 6. Electrical Resistivity for Undoped Ru_2Si_3 .

in sign of the Hall coefficient as shown in Figure 4. 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 temperature. The major point here is that by 800-1300K, Ru_2Si_3 has a mobility very similar to p-type silicon, which is already greater than the mobility of p-type SiGe.

Figure 8 shows the thermal conductivity of the undoped Ru_2Si_3 sample and that of typical

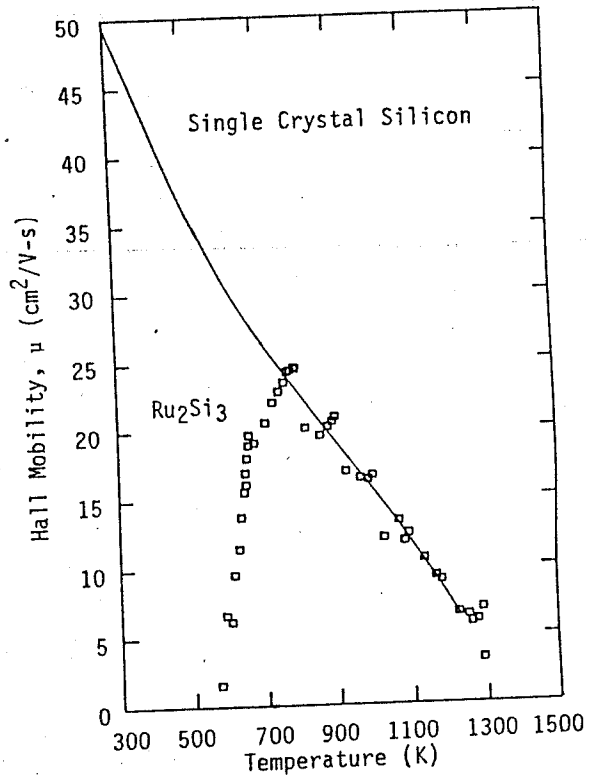


Figure 7. Hall Mobility for Undoped Ru_2Si_3 and a Curve of Single Crystal Silicon.

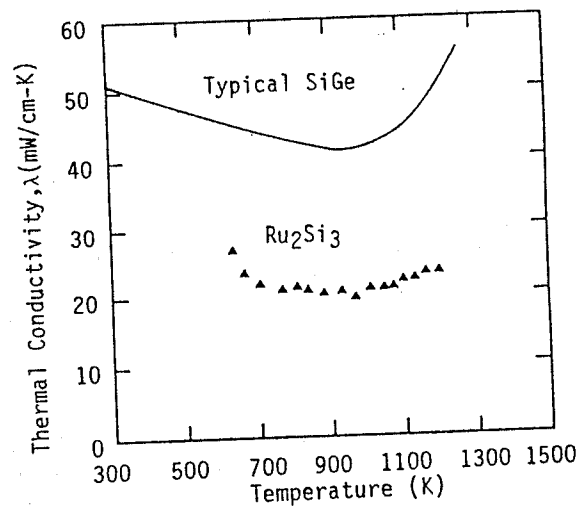


Figure 8. Thermal Conductivity for Undoped Ru_2Si_3 and a Curve Typical of SiGe.

SiGe. The undoped sample of Ru_2Si_3 has a shape similar to the shape of the SiGe curve, but is about two times lower.

From the data on undoped Ru_2Si_3 shown in Figure 4, 5 and 7, 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 $(m_{\text{eff}})^{3/2} \mu/\lambda$, which is thought to be some measure of the figure of merit which might be expected for optimized samples. The larger effective mass of Ru_2Si_3 compared to SiGe is typical of d-band materials. The larger mobilities of Ru_2Si_3 Bridgman samples compare to Ru_2Si_3 arc-melted ones is due to the fewer cracks and well oriented large grains.

DISCUSSION

Ru_2Si_3 is expected to have anisotropy due to its orthorhombic crystal structure. The Bridgman sample for thermoelectric measurements is oriented but has the second phase. This cast uncertainty on the analysis of the present data, but estimates can be made on this sample especially for the Hall effect and thermal diffusivity measurements better than those made on the arc-melted samples having many visible cracks, smaller and un-oriented grains[6]. Estimates made on this Bridgman sample must be considered still preliminary and single phase samples will be required to confirm these results and complete the doping and composition studies for optimizing ZT values.

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

	type	preparation	m_{eff}	μ	λ	$m_{\text{eff}}^{3/2} \mu/\lambda$
SiGe	p	Zone Level	1.0	40	44	0.91
Ru_2Si_3	p	Arc-Melting	7.5	7.3	12	13
Ru_2Si_3	p	Bridgman	4.5	37	20	18
SiGe	n	Zone Level	1.4	68	44	2.6
Ru_2Si_3	n	Arc-Melting	3.9	0.54	12	0.35
Ru_2Si_3	n	Bridgman	26	2.2	20	15

The properties of Ru_2Si_3 , especially p-type, are promising. The thermal conductivity, which is two times smaller than typical SiGe , is expected to exhibit similar values as those of the well oriented single phase samples. This is one of the major advantages of Ru_2Si_3 as a thermoelectric material, due to its complex structure and its large atomic mass.

The large effective mass values, estimated from the Hall and Seebeck coefficient data shown in Figures 4 and 5, reconfirmed the conjecture that the d-bands of the transition metal element (ruthenium) contribute to enhance the Seebeck coefficient in the same manner as arc-melted samples[6].

The mobility values for p-type materials are much more attractive than those estimated on the arc-melted samples[6]. The conservatively estimated mobility values for p-type Ru_2Si_3 materials at 300K are nearly the same as those for p-type SiGe materials. Even the measured p-type mobilities (Figure 7) are larger than p-type SiGe between 800K and 1300K.

The estimated n-type mobility at 300K are much smaller than n-type SiGe . This is because

the estimates made on the mobilities of the lightly doped materials such as the undoped Ru_2Si_3 sample at low temperature easily exhibit low values due to the tendency to be governed by both complex carrier sources and complex scattering mechanisms. Nevertheless, the factor of four increase in mobility of the Bridgman sample compared to the arc-melted sample, is quite promising.

CONCLUSIONS

The results on the Ru_2Si_3 Bridgman sample further support the theoretical suggestion that substantial improvements in ZT values may be possible with these materials as the same manner as the Ru_2Si_3 arc-melted samples. These results are still preliminary because the Bridgman sample has fewer cracks and larger, much more oriented grains than arc-melted sample, but has minor second phase. The low thermal conductivity values and large effective mass values are reconfirmed and attractive for thermoelectric materials. Especially p-type mobilities are much improved due to achieving better structure by Bridgman like method. While the n-type mobility values are estimated still low, there is some reasons to believe this is an artifact of the lightly doped materials. Efforts to grow high quality single phase crystals from the melt are necessary in order to confirm these results and complete the doping and alloying studies needed to optimize the thermoelectric figure of merit.

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REFERENCES

- [1]C.B.Vining,"High Figure of Merit Thermoelectrics: Theoretical Considerations," Proc. 25th Intersociety Energy Conversion Engineering Conference, P.A.Nelson,W.W.Scherntz and R.H.Till eds.,pp.387-391:1990.
- [2]C.Wood,"Material for Thermoelectric Energy Conversion," Reports on Progress in physics, Vol.51, pp.459-539:1988.
- [3]C.B.Vining,"A Model for the High Temperature Transport Properties of Heavily Doped n-type Silicon-Germanium Alloys, "Proc. Seventh Symposium on Space Nuclear Power Systems, M. S.El-Genk and M.D.Hoover eds., pp.224-228: 1990.
- [4]C.B.Vining,"A Model for the High Temperature Transport Properties of Heavily Doped n-type Silicon-Germanium Alloys,"J.Appl.Phys., Vol. 69,pp.331-341:1991.

- [5]C.B.Vining, "Silicides as Promising Thermoelectric Materials,"Proc.IXth International Conference on Thermoelectrics(USA), C.B. Vining ed.,pp.249-259:March,1990.
- [6]C.B.Vining, "A Promising New Thermoelectric Material: Ruthenium Silicide," Proc. Eighth Symposium on Space Nuclear Power Systems, M. El-Genk and M.Hoover eds.,pp.458-463:1991.

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- Post-deadline Papers
- Subject Index
- Author Index

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