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EXTRAPOLATED THERMOELECTRIC FIGURE OF MERIT OF RUTHENIUM SILICIDE

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Abstract

Recently, single crystals have been grown of a promising new thermoelectric material, ruthenium silicide (Ru_2Si_3). ***Although high figure of merit values have not actually been achieved as yet,*** the intrinsic properties of Ru_2Si_3 appear to be very favorable for thermoelectric applications. In this paper, the properties of undoped ruthenium silicide are extrapolated to heavily doped materials in order to provide some estimate of the thermoelectric figure of merit which ***might*** be achieved with optimal doping. In order to estimate the effect of doping several ***unverified assumptions*** have been made. First, is assumed that the carrier mobility of ruthenium silicide scales with doping level in the same way as the carrier mobility of silicon, decreasing substantially at the higher doping levels. It is assumed that the lattice component of the thermal conductivity does not vary doping level. All other effects of doping are accounted for using a simple, non-degenerate two band model for the transport properties. It is predicted that p-type ruthenium silicide may have a figure of merit more that 3 times the value of p-type silicon-germanium (SiGe) and that n-type ruthenium silicide may have a figure of merit 50% greater than n-type SiGe. While these estimates are subject to dangerously large uncertainties, they nevertheless are encouraging and provide some means for assessing the progress of experimental studies.

INTRODUCTION

Silicon-germanium (SiGe) thermoelectric energy conversion devices have provided reliable power for important space missions such as the Voyagers, Galileo and Ulysses, and will be used in the upcoming CRAF/Cassini missions. Important improvements in SiGe technology are currently being developed under the MOD-RTG, SP-100 and related technology programs. While substantial improvements are expected under these programs, the conversion efficiency will still remain relatively low because the theoretical limitations of SiGe thermoelectric materials are being approached (Slack and Hussain, 1991). For really substantial improvements in the efficiency of thermoelectric systems, a new class of thermoelectric materials must be developed.

In a recent survey directed at the properties of silicon-based compounds a number of materials were identified which may exhibit promising thermoelectric properties (Vining, 1990). Among these materials, Ru_2Si_3 has been confirmed to be a semiconductor both experimentally (Vining, 1990) and theoretically (Pecheur and Toussaint, 1991). The intrinsic properties of polycrystalline (Ohta, Vining and Allevato, 1991) and single crystal Ru_2Si_3 (Vining and Allevato, 1991) have been found to be quite promising for thermoelectric applications.

Although high figure of merit values have not actually been achieved as yet, sufficient data on intrinsic (i.e. undoped) Ru_2Si_3 is now available to begin to make extrapolations as to what the figure of merit of doped materials might be. In order to make these ***extrapolations*** a number of ***unverified assumptions*** must be made about the effect of doping on Ru_2Si_3.

This paper discusses the extrapolations to high doping levels and examines the thermoelectric figure of merit values which may result. In spite of the large uncertainties in such extrapolations, emphasized in the preceding paragraph, such estimates provide important guidance for the experimental program by bracketing the range of possible experimental results.

BASIC MODEL FOR THERMOELECTRICS

A standard two-band model, similar to an electrical model developed for n-type SiGe (Vining, 1991), is used to describe the electrical properties of Ru_2Si_3. Here, a much simplified model is employed since much less is known about Ru_2Si_3 than is known about SiGe. First, the carrier concentration at any temperature is determined by the following set of equations:

$$n_i = 2.5 \times 10^{19}\ (m_+ m_-)^{0.75} \left(\frac{T}{300}\right)^{3/2} e^{-E_g/k_B T}\ \mathrm{cm}^{-3} \tag{1}$$

$$n_\pm = \frac{1}{2}\sqrt{\Delta n^2 + 4 n_i{}^2} \pm \frac{1}{2}\Delta n, \tag{2}$$

where n_i, n_+, and n_-, are the intrinsic, hole and electron carrier concentrations, Δn is the net dopant density (positive for acceptors and negative for donors), $m_\pm$ are the carrier masses, in units of the free electron mass and E_g is the energy gap. If the mobilities of the holes (μ_+) and electrons (μ_-) are known, the electrical conductivity, Seebeck coefficient, Hall coefficient and the electronic contribution to the thermal conductivity may be calculated from:

$$\sigma = en_+\mu_+ + en_-\mu_-, \text{ and} \tag{3}$$

$$S = \frac{k_B}{e}\left[en_+\mu_+ (2 + \eta) - en_-\mu_- (2 - \eta + E_g/2k_BT) \right]/\sigma, \tag{4}$$

$$R_H = \frac{3\pi}{8}\left[en_+\mu_+{}^2 - en_-\mu_-{}^2 \right]/\sigma^2, \text{ and} \tag{4}$$

$$\lambda_{el} = \left(\frac{k_B}{e}\right)^2 \sigma T \left[2 + \frac{en_+\mu_+\ en_-\mu_-}{\sigma^2} (4 + E_g/k_BT)^2 \right] \quad . \tag{5}$$

Here, η is the reduced chemical potential and is given by:

$$\eta = \operatorname{asinh}\left(\frac{\Delta n}{2n_i}\right) + E_g/2k_BT + \frac{3}{4}\ln\left(\frac{m_+}{m_-}\right). \tag{7}$$

COMPARISON TO INTRINSIC Ru_2Si_3

Figures 1 through 3 show the Hall coefficient, Hall mobility and Seebeck coefficient for two samples cut from a single crystal of Ru_2Si_3 compared to analysis presented previously (see Vining and Allevato, 1991). The dashed lines have been calculated using equations 1 through 6, with the following values for the unknown parameters:

$$E_g = 1.08 \text{ eV}, \tag{8}$$

$$m_+ = m_- = 2.93, \tag{9}$$

$$\mu_+ = 10900/T \text{ cm}^2/\text{V-s, and} \tag{10}$$

$$\mu_- = 72.2 \text{ cm}^2/\text{V-s}. \tag{11}$$

The agreement between the simple model and experiment is seen to be quite good in the intrinsic region between about 500 K and about 1240 K. Above 1240 K, both samples appear to undergo a phase transformation, an effect reported previously for Ru_2Si_3 (Poutcharovsky et al., 1975 and Susz et al., 1980).

EXTRAPOLATION TO HEAVILY DOPED Ru_2Si_3

In order to extend this model to heavily doped materials some assumptions must be made because ***data are not yet available on high quality heavily doped samples.*** The equations presented above are expected to provide a reasonable description of the effect of doping, with two major exceptions. First, the model neglects any influence doping will have on the lattice thermal conductivity. Generally the lattice thermal conductivity decreases substantially with increasing doping level. In SiGe alloys, for example, doping decreases the lattice thermal conductivity by about 33%, which is very beneficial to the figure of merit. For this study, the beneficial effects of doping on the lattice thermal conductivity are neglected.

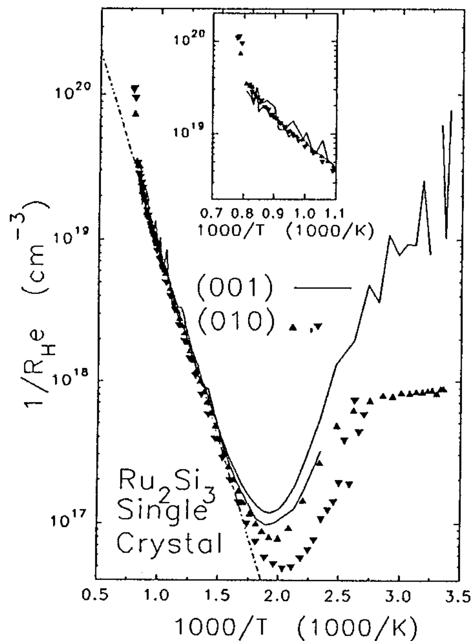

FIGURE 1: Inverse Hall coefficient in carrier concentration units for single crystal Ru_2Si_3. The solid lines and symbols represent two samples cut from the same single crystal ingot.

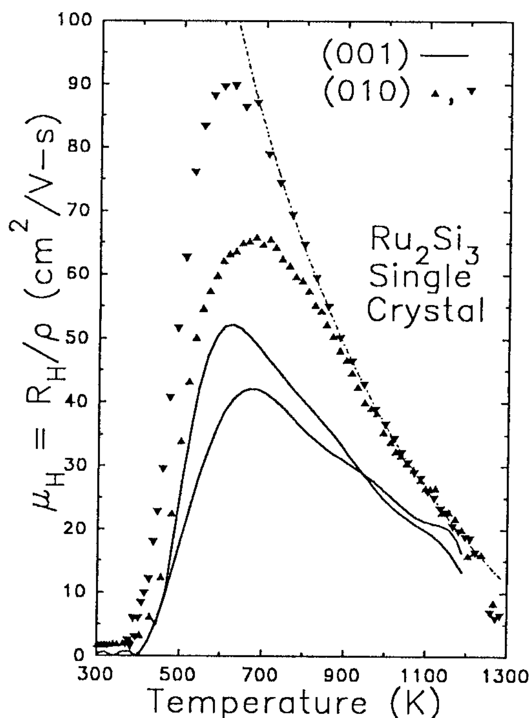

FIGURE 2: Hall mobility for single crystal Ru_2Si_3. The solid lines the symbols represent two samples cut from the same single crystal ingot. The dashed line is calculated using the model.

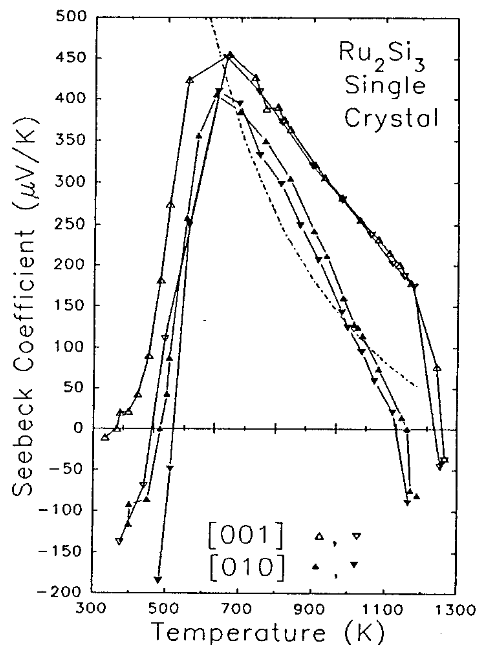

FIGURE 3: Seebeck coefficient for single crystal Ru_2Si_3. The solid lines are guides for the eye. The dashed line was calculated using the model.

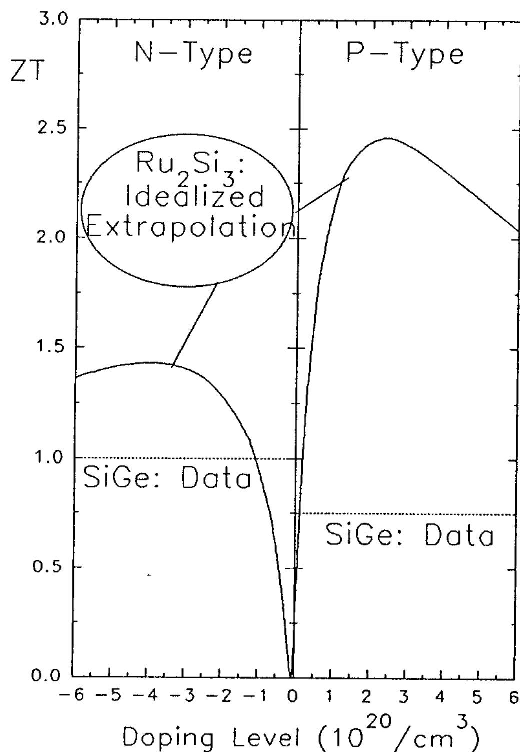

FIGURE 4: Extrapolated dimensionless figure of merit for heavily doped Ru_2Si_3, assuming high mobility values can be achieved. Dashed lines indicate approximate state of the art for SiGe.

The carrier mobilities should decrease substantially with increasing doping level, but insufficient data are available to estimate the size of this effect in Ru_2Si_3. Ample data are available on other semiconductors and in silicon, for example, the degradation of the mobility with doping level can be reasonably approximated by expressions of the form:

$$\mu = \mu_{min} + (\mu_{max} - \mu_{min})/(1 + (n/n_o)^{\alpha}) , \tag{12}$$

where the constants are determined empirically, as discussed in (Slack, 1991).

μ_{max} represents the intrinsic mobility and can be estimated for holes and electrons in Ru_2Si_3 from Equations (9) and (10). μ_{min} represents the mobility at very high doping levels and is estimated here by simply scaling μ_{min}/μ_{max} to the same ratios observed in silicon. α and n_o are taken to be the same values as in silicon.

Thus, at 1200 K we arrive at the following estimates for the mobilities of doped Ru_2Si_3:

$$\mu_+ = 10.2 + \frac{90.8 - 10.2}{1 + \left(\frac{n}{5 \times 10^{17}\ cm^{-3}}\right)^{0.82}}\ cm^2/V\text{-}s, \tag{13}$$

and

$$\mu_- = 4.5 + \frac{72.2 - 4.5}{1 + \left(\frac{n}{1.3 \times 10^{17}\ cm^{-3}}\right)^{0.91}}\ cm^2/V\text{-}s. \tag{14}$$

It should be emphasized that these estimates for the mobilities at high doping levels are little more than speculation and there are no supporting data whatever. Nevertheless, using these equations and an estimate for the lattice thermal conductivity of 0.01 W/cm-K at 1200 K taken from (Vining and Allevato, 1991), all of the important thermoelectric properties can be calculated at any doping level. Figure 4 shows the thermoelectric figure of merit for heavily doped Ru_2Si_3 calculated using these assumptions.

CONCLUSIONS AND CAUTIONS

The extrapolations presented here indicate Ru_2Si_3 *may* eventually have figure of merit values 50% larger than n-type SiGe and 3 times larger than p-type SiGe. Experimental results to date are much lower than these values and too low to be of any practical value. In order to achieve these high figure of merit values, high quality, heavily doped samples of Ru_2Si_3 with high mobility values must be prepared. Several very serious obstacles must be overcome to achieve this.

First, dopants must be identified which create carrier densities in excess of 10^{20} cm^{-3}. Second, the mobility must not degrade too rapidly with increased doping. An experimental program is currently underway at JPL to identify suitable dopants and while these two criteria have not yet been simultaneously satisfied, the doping experiments are still in the very early stages and some encouraging results have been obtained.

These extrapolations are useful even with the rather limited range of validity because they help to guide the experimental program by constraining the results. If mobilities on the order of 5 to 10 cm^2/V-s and carrier concentrations on the order of 10^{20} cm^{-3}s cannot be attained, for example, then some other experimental approach might be required.

Acknowledgments

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References

Ohta, T., C. B. Vining, and C.E. Allevato (1991) "Characteristics of a Promising New Thermoelectric Material: Ruthenium Silicide," in *Proc. of the 26th Intersociety Energy Conversion Engineering Conference*, American

Institute of Chemical Engineers, New York, pp. 196-201.

Pecheur, P. and G. Toussaint (1991) "Electronic Structure of Ru_2Si_3," *Mat. Res. Soc. Symp. Proc.* Vol. 234, edited by D. Allred, C. Vining and G. Slack, to be published.

Poutcharovsky, D.J., K. Yvon, and E. Parthé (1975) "Diffusionless Phase Transformations of Ru_2Si_3, Ru_2Ge_3 and Ru_2Sn_3: I. Crystal Structure Investigations," *J. Less Common Metals,* **40**, pp. 139-144.

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

Susz, C.P., J. Muller, K. Yvon, and E. Parthé (1980) "Diffusionless Phase Transformations of Ru_2Si_3, Ru_2Ge_3 and Ru_2Sn_3: I. Crystal Structure Investigations," *J. Less Common Metals,* **71**, pp. P1-P8.

Vining, C. B. (1990) "Silicides as Promising Thermoelectric Materials," in *Proc. of the IXth International Conference on Thermoelectrics (USA)*, C. B. Vining ed., 19-21 March, 1990, Jet Propulsion Laboratory internal document D-7749, pp. 249-259.

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

Vining, C.B. and C.E. Allevato (1991) "Intrinsic Thermoelectric Properties of Single Crystal Ru_2Si_3," in *Proc. of the Xth International Conference on Thermoelectrics*, D.M. Rowe ed., to be published.