

## Progress in Doping Ruthenium Silicide (Ru<sub>2</sub>Si<sub>3</sub>)

C.B. Vining and C.E. Allevato  
 Jet Propulsion Laboratory/California Institute of Technology  
 Pasadena, California 91109

### ABSTRACT

Ruthenium silicide (Ru<sub>2</sub>Si<sub>3</sub>) is currently under development as a promising thermoelectric material suitable for space power applications. Key to realizing the potentially high figure of merit values of this material is the development of appropriate doping techniques. In this study, manganese and iridium have been identified as useful p- and n-type dopants, respectively. Resistivity values have been reduced by more than 3 orders of magnitude. Anomalous Hall effect results, however, complicate interpretation of some of the results and further effort is required to achieve optimum doping levels.

### INTRODUCTION

Important progress has been made in the development of improved silicon-germanium (SiGe) thermoelectric materials for space power applications. The efficiency of SiGe-based devices, however, are expected to remain in the single digits due to theoretical limitations on the figure of merit of SiGe alloys.<sup>1</sup> New thermoelectric materials have the potential for much higher figure of merit values and efficiencies double or triple current state of the art levels are

entirely possible.<sup>2</sup>

As part of a general effort to develop new, more efficient thermoelectric materials, ruthenium silicide (Ru<sub>2</sub>Si<sub>3</sub>) has recently been under investigation both experimentally<sup>3,4,5</sup> and theoretically.<sup>6,7</sup> Undoped single crystals of Ru<sub>2</sub>Si<sub>3</sub> have been grown<sup>5</sup> for the first time and analysis suggests that figure of merit values much higher than state of the art SiGe are possible.<sup>7</sup> p-type Ru<sub>2</sub>Si<sub>3</sub> appears to have the potential for a factor of 3 improvement and n-type Ru<sub>2</sub>Si<sub>3</sub> may be 50% better than standard SiGe.

In order to achieve these figure of merit improvements, dopants must be identified for both n- and p-type Ru<sub>2</sub>Si<sub>3</sub>. In addition to being electrically active and sufficiently soluble to achieve optimum doping levels (expected to be on the order of 10<sup>26</sup> m<sup>-3</sup>), these dopants must not poison the carrier mobility. The predictions of high figure of merit assume the carrier mobility is reduced by doping similar to the reduction of mobility in doped silicon-germanium alloys. While this assumption is reasonable, actual data are not yet available. The purpose of the present study, then, is to identify candidate dopants and to determine their effect on the electrical properties of Ru<sub>2</sub>Si<sub>3</sub>.

																			H
Li	Be											+/-	B	C	N	O	F	Ne	
Na	Mg											+	Al	<b>Si</b>	P	S	Cl	Ar	
K	Ca	Sc	+ Ti	+ V	+ Cr	+✓ Mn	Fe	- Co	- Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	+ Mo	(Tc)	<b>Ru</b>	✓ Rh	✓ Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	+ Ta	+ W	+ Re	Os	✓ Ir	✓ Pt	Au	Hg	Tl	Pb	Bi	Po	At	Ra		

Figure 1. Candidate dopants examined experimentally are shown in bold with either (+) or (-) to indicate the sign of the room temperature Hall coefficient. A check mark indicates a substantial change was observed in the electrical resistivity.

## EXPERIMENTAL DETAILS

Thirty nine samples of high quality  $\text{Ru}_2\text{Si}_3$  have been grown from stoichiometric melts in boron nitride crucibles using a Bridgman-like technique described elsewhere.<sup>5</sup> Sixteen different dopants, shown in Figure 1, have been examined experimentally. Optical metallography indicates that all samples contain trace quantities of an impurity (< 1%), identified as a boron-rich phase by energy dispersive X-ray analysis. The impurities appear within grains as thin, plate-like inclusions 1-2  $\mu\text{m}$  thick and 15-20  $\mu\text{m}$  in lateral extent and are oriented along principle crystallographic planes. Grain sizes range from a few mm up, and in several cases essentially the entire sample was a single crystal.

In addition to the thirty nine samples grown from stoichiometric melts, one sample has been grown from a silicon-rich melt. Use of a silicon-rich melt allowed lowering the temperature of the crystal growth by 200 K and boron contamination in this sample was below detectable limits.

A van der Pauw geometry was employed for the Hall effect and electrical resistivity measurements on each sample.<sup>8</sup> In spite of the large grain sizes achieved, many samples were sufficiently cracked to raise concerns about the reliability of the electrical property measurements. For all of the results reported here, crack-free portions at least a few mm in extent were selected for electrical measurements in order to minimize these concerns. The geometry employed for the Hall effect measurements is shown in Figure 2.

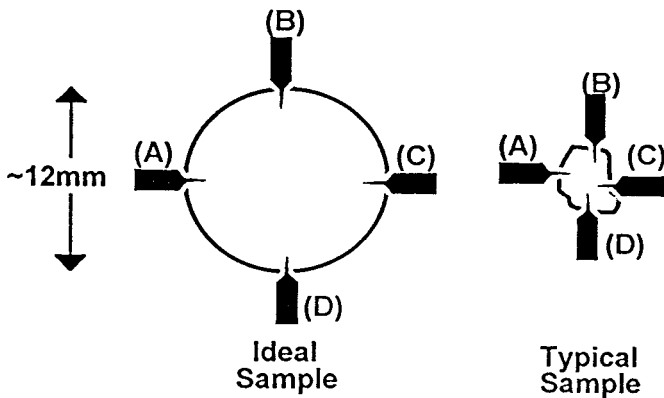


Figure 2. Ideal and typical sample geometry for electrical resistivity and Hall effect measurements

The unusual nature of some of the Hall effect results reported below warrant a somewhat more extended discussion of the measurement technique. The Hall effect apparatus is in regular use characterizing a variety of materials and has been verified to yield results on standard materials, such as doped silicon, within a few percent of literature values. Resistivity results are typically precise to within  $\pm 0.5\%$  and Hall coefficient results are typically precise to within  $\pm 5\%$ . Errors larger than these limits are occasionally observed due to loss of electrical contact with the sample or actual sample breakage during the measurement. In these cases the measurement has simply been repeated.

Samples with resistivity and Hall coefficient values covering the entire range reported in this study have been accurately determined on other materials using the same apparatus. The hardware and software have been carefully examined and tested for possible sources of systematic errors and none have been identified which could significantly affect the results reported here.

Even though the Hall effect apparatus employed appears reliable, two key assumptions for use of the van der Pauw method are in some doubt in the present case. First, the van der Pauw method assumes the sample is homogeneous. In the present case, however, plate-like inclusions of unknown electrical properties have been observed. Second, the van der Pauw method assumes the sample is isotropic, while the orthorhombic crystal structure of  $\text{Ru}_2\text{Si}_3$  assures that its properties cannot be entirely isotropic.

## RESULTS AND DISCUSSION

Figure 3 shows typical high temperature electrical resistivity and Hall effect results for a sample of  $\text{Ru}_2\text{Si}_3$  doped with Ti. These results, however, are typical of most of the  $\text{Ru}_2\text{Si}_3$  samples measured, with some variations when the dopants have strongly affected resistivity results. From room temperature up to 500 K the resistivity is large,  $\sim 0.03 \Omega\text{-m}$ , and nearly temperature independent, as expected for a lightly doped extrinsic semiconductor. Above 500 K the resistivity drops nearly exponentially with temperature, with a slope typical of the intrinsic regime of a semiconductor with a band gap of about 1 eV. The electrical resistivity, therefore, is quite typical of a lightly doped semiconductor.

The Hall coefficient ( $R_H$ ), however, behaves in a most unusual way. The Hall coefficient which can be determined using probes A and C as the voltage probes (see Figure 2) and probes B and D as the current probes. Data determined with this geometry are indicated by the label AC-BD in Figure 3. Alternatively, the Hall coefficient may also be determined by reversing the roles of the current and voltage probes, as indicated by the label BD-AC in Figure 3.

For any well behaved material, the difference between these two configurations is used as a check of the internal consistency of the measurement technique since the two sets of data are expected to be identical. In the case of  $\text{Ru}_2\text{Si}_3$ , however, the two sets of data are qualitatively different and do not even agree in sign over most of the temperature range.  $R_H$  for a lightly doped semiconductor should be large and nearly temperature independent in the extrinsic region, which judging from the resistivity should extend up to about 500 K. Neither set of Hall data behave in this way. Instead, the Hall coefficient is small near room temperature increases rapidly in magnitude until about 500 K and the two sets of data do not even have the same sign.

Above about 800 K, both sets of Hall coefficient data are positive and decrease rapidly with increasing temperature. While this rapid decrease is as expected for an intrinsic semiconductor, the two sets of data still are quite different in magnitude.

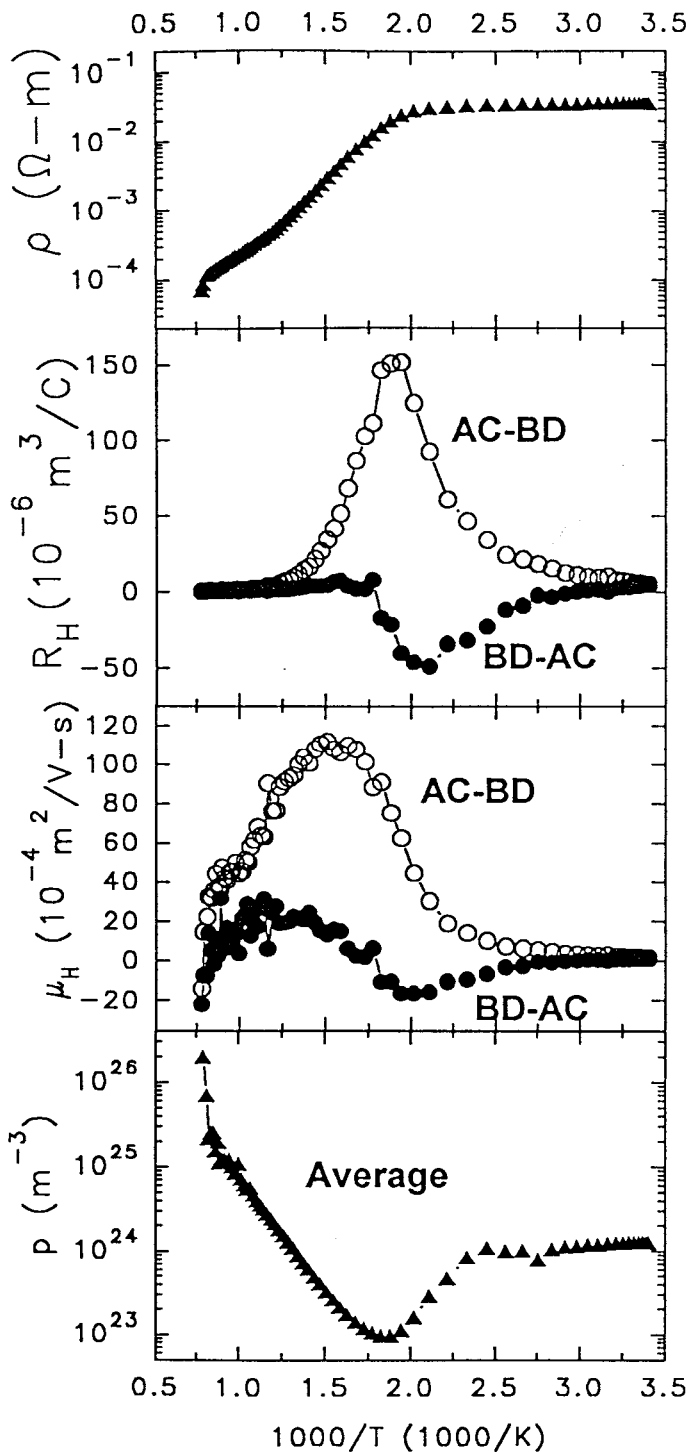


Figure 3. Electrical resistivity, Hall Coefficient, Hall mobility and apparent hole concentration for  $\text{Ru}_2\text{Si}_3$ . Data shown are for a sample doped with Ti, but are typical of all samples prepared to date.

The Hall mobility mimics much of the behavior of the Hall coefficient, as it must since the Hall mobility is calculated from the electrical resistivity and Hall coefficient by

$$\mu_H = R_H/\rho.$$

The carrier concentration is calculated from the Hall coefficient in the usual manner from

$$n, p = 1/e|R_H|,$$

where  $n$  or  $p$  is used to indicate whether the Hall coefficient is negative ( $n$ , electron density) or positive ( $p$ , hole density). The average of Hall coefficients (AC-BD and BD-AC) has been used to calculate the apparent hole concentration shown in Figure 3.

The Hall coefficient behaves unusually over the entire temperature range, but the behavior below 500 K appears particularly unusual. This is illustrated in Figure 4, which summarizes the apparent Hall mobility as a function of the apparent carrier concentration at 300 K and again at 400 K for doped and undoped samples with p-type average Hall coefficients. The 400 K data represent the same samples as the 300 K data points, but each sample was heated to 1300 K between the two measurements. The Hall coefficient used for this plot is the average of the two independent measurements, AC-BD and BD-AC.

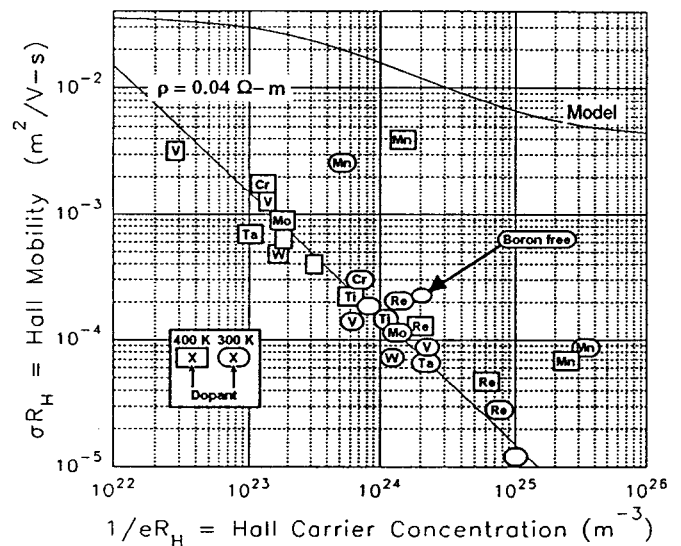


Figure 4. Hall mobility as a function of Hall carrier concentration for p-type  $\text{Ru}_2\text{Si}_3$ . The line indicates a dopant-independent resistivity of  $0.04 \text{ }\Omega\text{-m}$  and the curve indicates room temperature mobilities expected based on analysis of high temperature data.<sup>7</sup> The arrow indicates the sample prepared free of boron contamination.

With the exception of the two Mn doped samples, all of the results shown in Figure 4 are close to the line of constant resistivity and far below the low temperature mobility values previously estimated by extrapolation.<sup>7</sup> Thus, the Hall coefficient varies by almost 3 orders of magnitude while the resistivity varies by only about a factor of 3 for most of these samples. Note that the mobility of the sample prepared free of boron-rich inclusions is slightly higher, but qualitatively similar to the main population of samples. This result suggests that the correlation shown is probably not a consequence of boron contamination, which is reasonable since the contamination was present in such low quantities in any case. Mn doped samples, however, fall well above this line, indicating significantly lower resistivity values than the other samples. Thus, as indicated by the check mark in

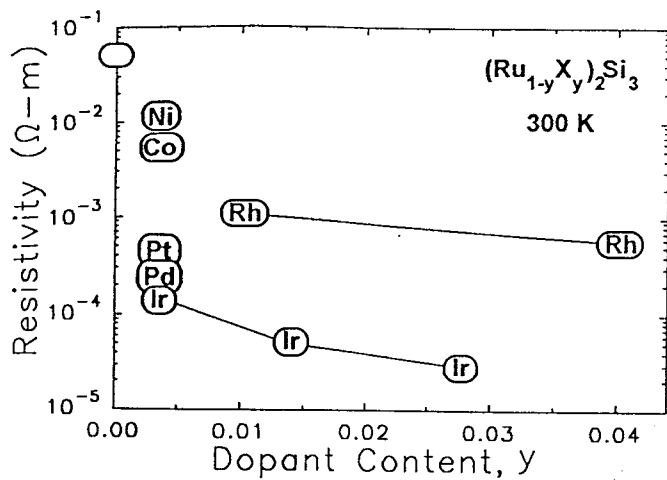


Figure 5. Electrical resistivity of  $\text{Ru}_2\text{Si}_3$  with n-type dopants compared to the resistivity of an undoped sample.

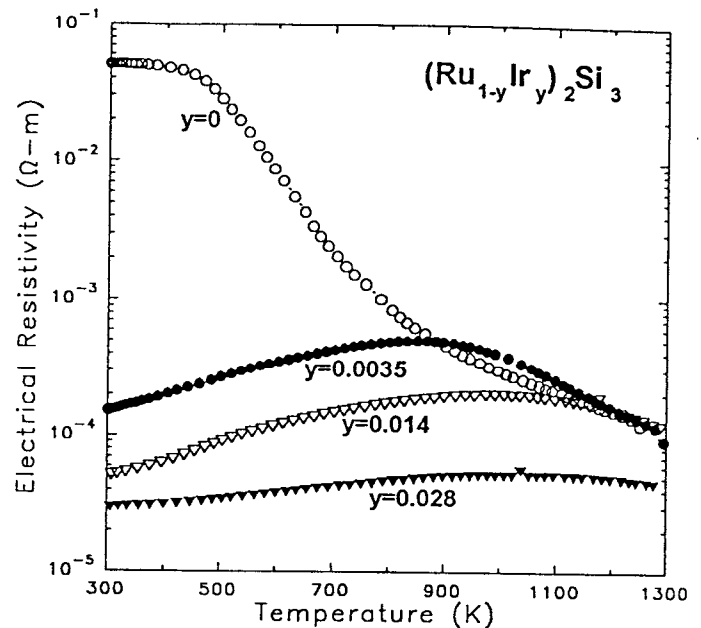


Figure 6. The temperature dependence of the electrical resistivity of  $\text{Ru}_2\text{Si}_3$  for four different Ir doping levels.

Figure 1, Mn is the only effective p-type dopant identified to date.

The anomalous behavior of the Hall coefficient in Figures 3 and 4 strongly suggests the usual interpretation of Hall effect results is not valid in the present case. The correct interpretation of these data is not yet clear, but it seems very unlikely that the carrier concentration could actually change by three orders of magnitude with so little effect on the electrical resistivity. Nevertheless, Mn doped samples clearly behave differently from the rest and future development of p-type  $\text{Ru}_2\text{Si}_3$  will focus on Mn doping.

Figure 5 shows the electrical resistivity as a function of nominal dopant content for dopants which resulted in an n-type Hall coefficient. Ir was found to be the most effective n-type dopant, decreasing the resistivity by 3 orders of magnitude, more than any other dopant examined. The temperature dependence of the electrical resistivity indicates that at the highest Ir content examined to date ( $y=0.028$ ),  $\text{Ru}_2\text{Si}_3$  remains extrinsic to up to 1300 K. This is important because suppressing minority carrier contributions to the Seebeck and thermal conductivity is critical for achieving high thermoelectric figure of merit values.

## CONCLUSIONS

Mn has been identified as a useful dopant for preparing p-type  $\text{Ru}_2\text{Si}_3$  and Ir has been identified as a useful dopant for preparing n-type  $\text{Ru}_2\text{Si}_3$ . This result was the primary goal of the current investigation and represents important progress toward developing a high figure of merit material. Anomalous Hall effect results, however, raise concerns about how to properly characterize the electrical properties of these materials. Anisotropy of the transport properties may play a role, but no consistent interpretation of the available Hall data has yet been developed. Future efforts will attempt to resolve these uncertainties and prepare optimally doped, high figure of merit  $\text{Ru}_2\text{Si}_3$ .

## ACKNOWLEDGMENTS

The work described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

## REFERENCES

1. G.A. Slack and M.A. Hussain, *J. Appl. Phys.* 70, 2694 (1991).
2. C.B. Vining in *25th Intersociety Energy Conversion and Engineering Conference*, Vol. 2, (American Institute of Engineers, New York) 387 (1990).
3. C.B. Vining, J.A. McCormack, A. Zoltan, and L.D. Zoltan in *8th Symposium on Space Nuclear Power Systems*, edited by M.S. El-Genk and M.D. Hoover (American Institute of Physics, New York) 458 (1991).
4. T. Ohta, C.B. Vining, and C.E. Allevato in *26th Intersociety Energy Conversion and Engineering Conference*, Vol. 3, (American Institute of Engineers, New York) 196 (1991).
5. C.B. Vining and C.E. Allevato in *Xth International Conference on Thermoelectrics*, Cardiff, Wales, (1992) edited by D.M. Rowe, to be published.
6. P. Pecheur and G. Toussaint, *Phys. Lett.* A160, 193 (1991).
7. C.B. Vining in *9th Symposium on Space Nuclear Power Systems, AIP Conference Proceedings 246*, edited by M.S. El-Genk and M.D. Hoover (American Institute of Physics, New York) 338 (1992).
8. J. McCormack and J.-P. Fleurial in *Modern Perspectives on Thermoelectrics and Related Materials*, edited by D.D. Allred, C.B. Vining and G.A. Slack, (Materials Research Society, Pittsburgh, Pennsylvania) 135 (1991).

IECEC-92  
San Diego, CA  
August 3-7, 1992



# Proceedings of the 27th Intersociety Energy Conversion Engineering Conference

P-259 • Volume 3

## Conversion Technologies Electrochemical Conversions

Conversion Technologies: AMTEC  
Heat Engines and Advanced Cycles  
Terrestrial Batteries  
Terrestrial Electric Propulsion  
Heat Pumps  
Fuel Cells for Terrestrial Applications  
Magnetohydrodynamics  
Terrestrial Thermionics  
Thermoelectrics  
Thermionic Converters

Permission to photocopy for internal or personal use, or the internal or personal use of specific clients, is granted by SAE for libraries and other users registered with the Copyright Clearance Center (CCC), provided that the base fee of \$5.00 per article is paid directly to CCC, 27 Congress St., Salem, MA 01970. Special requests should be addressed to the SAE Publications Group. 1-56091-264-2/92\$5.00

No part of this publication may be reproduced in any form, in an electronic retrieval system or otherwise, without the prior written permission of the publisher.

ISBN 1-56091-264-2 Paperbound (SAE)  
SAE/P-92/259  
Library of Congress Catalog Card Number: 92-80985  
Copyright 1992 Society of Automotive Engineers, Inc.

IEEE Catalog Number: 92CH3164-1  
ISBN 0-7803-0693-7 Casebound (IEEE)  
0-7803-0694-5 Microfiche (IEEE)

Positions and opinions advanced in these papers are those of the authors' and not necessarily those of SAE. The authors are solely responsible for the content of the paper. For permission to publish this paper in full or in part, contact the SAE Publications Group.



All SAE papers, standards, and selected books are abstracted and indexed in the SAE Global Mobility Database