Proceedings of the IX International Conference on Thermoelectrics (USA)
(JPL Document # D-7749), p. 249 (1990).

SILICIDES AS PROMISING THERMOELECTRIC MATERIALS

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ABSTRACT

In conventional thermoelectric materials (Bi_2Te_3, PbTe, SiGe), the conduction and valence bands are derived from s and p orbitals. But most thermocouple wire materials (chromel, alumel, WRe, PtRh) involve alloys with partially filled d-bands, resulting in Seebeck values much larger than for metals with filled or empty d-bands (such as Cu or Na, respectively). Semiconductors for which the valence and/or conduction band are dominated by d-band character may be able to combine the high Seebeck values typical of transition metal alloys, with the ability to achieve optimum doping levels typical of conventional thermoelectric materials. Certain metal-silicon compounds appear to have this desirable combination of properties. In this paper, compounds of silicon with elements from groups 1 through 8, including the d-band elements, are reviewed for their potential as high figure of merit (ZT) thermoelectric materials. A number of materials are identified which appear to have the potential for ZT values much greater than ZT ≈ 1 typical of current state of the art materials.

I. INTRODUCTION

The theory of thermoelectricity indicates thermoelectric energy conversion systems can, in principle, approach the maximum efficiency permitted by thermodynamics (ie the Carnot efficiency), which is about 55% for current radioisotope thermoelectric generator (RTG) heat sources and heat rejection systems. But even after 30 years of space experience with this technology, efficiencies remain relatively low, 6-7% for RTG's (Skrabek, 1990; Schock 1990) using silicon-germanium (SiGe) alloys developed in the 1960's (Dismukes, 1964) The room for growth is therefore quite large, almost an order of magnitude in efficiency.

The efficiency of current thermoelectric devices can be dramatically enhanced by the development of advanced thermoelectric materials. The optimum efficiency of a thermoelectric device is

$$\eta_{opt} = \left[\frac{\sqrt{ZT+1} - 1}{\sqrt{ZT+1} + 1} \right] \frac{T_h - T_c}{T_h},$$

which is exact in the limit of small $T_h - T_c$ and approaches the Carnot limit as $ZT \Rightarrow \infty$. Here, ZT is the usual dimensionless figure of merit

$$ZT = \sigma S^2 T/\lambda,$$

where σ is the electrical conductivity, S is the Seebeck coefficie and λ is the thermal conductivity.

A variety of theoretical methods are available for calculatin the thermoelectric properties of semiconductors which can estimate optimized ZT of a given material, provided experimental estimates various material parameters are available. Any <u>particular</u> materia then, does have a maximum ZT, as determined by the parameters for material. But theory predicts that <u>some</u> materials should have ZT values much higher than have been achieved to date.

As an example, consider a material for which the effects of minority electrical carriers and heat conduction by the lattice ma neglected. In this case the figure of merit becomes

$$ZT = S^2/\mathcal{L},$$

where $\mathcal{L}$ is the Lorenz number. But, the Seebeck coefficient can b increased without limit (in this case) by simply lowering the carr concentration. Seebeck values of 1000 μV/K or larger are often attained poor electrical conductors, which yields ZT = 68! And y = 1 has never been exceeded by much, and certainly ZT=2 or more h not been reached.

Since theory places no upper limit on ZT, the question arise where are they? Indeed, so long as ZT values of the best known thermoelectric materials remains near ZT ≅ 1, a serious question arises as to whether some as-yet unstated physical law actually <u>prevents</u> much higher values. The development of a material with much higher figure of merit, say ZT = 3 or more, would go a long toward settling this concern.

Much smaller improvements, however, would still be of immens technological value. The cost of safe manufacture and deployment nuclear power supplies remains very high, so improvements in the conversion efficiency (without sacrificing lifetime, reliability versatility) result in large savings. Moreover, for many space applications there is no practical alternative to the use of nucl energy as the primary power source. Multi-year planetary explora spacecraft such as the Voyager's and the recently launched Galile would not be possible without the radioisotope heat sources on bo Long term lunar exploration also generally requires nuclear heat sources to provide power during the two week lunar night. And, a power demands grow, radioisotope thermoelectric generators (RTG's nuclear reactors, such as the current SP-100 development program (Mondt, 1989), will increasingly need to be lighter and cheaper.

Thus, the experimental and theoretical search for improved thermoelectric materials serves not only to enhance the performan proven thermoelectric technology, possibly by a large margin, but the same time may significantly advance the fundamental understan of electrical and thermal transport in solids.

This paper examines the possibility of attaining much higher conversion efficiencies using silicides as thermoelectric materi Section II discusses the properties desired in a thermoelectric material. Section III reviews the properties of silicides as th pertain to thermoelectric applications and section IV summarizes results of this survey.

PROPERTIES FOR A THERMOELECTRIC MATERIAL

eristics to be considered in the search for n
ic materials include those needed: 1) to achi
o use the materials in applications. When es
criteria, care must be taken to avoid excludi
using excessively narrow selection criteria.
teria must be sufficiently definite to limit
number of candidate materials.
inciples for achieving a high figure of merit
Ioffe (Ioffe, 1957) for a standard band-type
r:

h value of A' = $m_*^{3/2}\mu/\lambda_\ell$ where m_* is the carrie
s, μ is the mobility in cm^2/V-s and λ_ℓ is the
rmal conductivity in mW/cm-K,
d gap, E_g, greater than about $4k_BT$, and
able to the extrinsic regime.

ff in properties represented by the factor A'
gle band model for semiconductors. Actually,
a number of additional factors, but A' captur
eatures required. Moreover, the parameters e
d with a minimum of experimental information
e useful as a screening tool, at least for co
emiconductors.
may be improved by increasing the effective
the mobility and/or reducing the lattice ther
y. The large band gap requirement (2) stems
the thermal excitation of minority carriers
coefficient and increases the thermal conduc
irement stems from the need to be able to exp
optimum doping levels.
inciples for using a material in a device dep
ific application. However, some general crit

mical, structural and thermal stability,
ility to form sound electrical and thermal con
ufacturable in suitable quality and quantity.

ten some trade off between these two types of
igh enough, even very substantial applications
come with sufficient effort. On the other ha
low ZT may be useful if the material is cheap

pace power applications, state of the art SiGe
among the best known and are excellently suite
ns. For n-type SiGe at 1000 K, using paramete
odel for the figure of merit (Vining, 1990) (
= 2.6 and $ZT_{max} \cong 1$. The success of SiGe for
ns can be best summarized by noting that the
s have been operating flawlessly for over 12

this technology. This combination of reliability and performance will be difficult to replace.

III. PROPERTIES OF METAL SILICIDES

In this section each of the metal-silicon systems from the first ten columns of the periodic table will be reviewed. In many cases sufficient transport data are available to estimate A' for the silicides and these data are summarized in Table 1. The number of possible doping and alloying combinations, however is very large. This, combined with the technical difficulties of preparing and characterizing high quality samples of refractory materials, has meant that little or no data are available for a great many promising materials.

Each of the silicides of the metals from groups 1 through 8 will be examined in turn.

Table 1: Thermoelectric parameters of silicides at 300 K

Material Name	Melting Point K	Type	m_* m_e	μ cm^2/V-s	k_ℓ mW/cm-K	A'	ZT_{max}	E_g eV	Ref.
(Si,Ge)	1550	n	1.4	68	44	2.6	1.0	0.7	a, b
(Si,Ge)	1550	p	1^*	40	44	0.9	0.7	0.7	a
Mg_2Si	1300	n	1^*	-	-	14.	0.8	0.7	c, d
$BaSi_2$	1450	p			16		0.2	0.48	e, f
$CrSi_2$	1763	p	5	9.2	68	1.5	-	0.35	g, h, i
$MnSi_{1.73}$	1550	p	1^*	40	29	1.4	0.7	0.67	j, k, l, m
$ReSi_2$	2250	p	1^*	105	55	1.9	-	0.12	n, o
$FeSi_2$	1255	p	4	4	40	0.8	0.2	0.9	p
$FeSi_2$	1255	n	1^*	2	40	0.05	0.4	0.9	q
Ru_2Si_3	1970	p	7.5	7.3	12	12.6	-	0.9	This Study
Ru_2Si_3	1970	n	3.9	0.54	12	0.35	-	0.9	This Study

[a] Dismukes, 1964.
[b] Vining, 1990.
[c] Nicolaou, 1976.
[d] Marchuk, 1989.
[e] Samsonov, 1980.
[f] Spitzer, 1970.
[g] Shinoda, 1964.
[h] Nikitin, 1961.
[i] Nishida, 1972.
[j] Bienert, 1966.
[k] Bienert, 1968.
[l] Vedernikov, 1988.
[m] Korshunov, 1964.
[n] Neshpor, 1960.
[o] Neshpor, 1966.
[p] Birkholz, 1989.
[q] Hesse, 1969.
* Ad hoc estimate.

ALKALI AND ALKALINE EARTH SILICIDES

Many of the alkali and alkaline earth silicides and germanides are known to be semiconductors. Several of the alkali mono-silicides and mono-germanides (NaSi, NaGe, KGe), are semiconductors with b gaps near 0.5 - 1 eV (Tegze, 1989), but little else is known abo them. Notable are Mg_2Si, Ca_2Si, Sr_2Si and their germanide and e\ stannide analogs. Based on the known semiconducting properties these materials (Samsonov, 1980), Nicolaou has predicted ZT ≅ 3 larger (Nicolaou, 1976) for certain solid solutions. Recently, 0.8 has been reported for Mg_2Si-Mg_2Sn solid solutions (Marchuk, Although no estimate is available for the effective mass in thes materials, Marchuk reports μ/λ_ℓ values which, using $m_*/m_e = 1$, yi the extraordinary value of A' = 14. The large values of A' and band gap (0.7 eV), combined with the ability to alloy these mate are all excellent indications that even higher ZT values will be achieved with further development.

$BaSi_2$, with with $E_g \cong 0.48$ eV (Samsonov, 1980), has been re to have $S^2\sigma \cong 1.0\ \mu W/K^2$-cm for a sample with S = +600 μV/K. Ass acoustic phonon scattering and a constant mobility, an optimum factor of $S^2\sigma \cong 11\ \mu W/K^2$-cm is estimated for S = 172 μV/K. Comb with k_ℓ = 16 mW/cm-K (Spitzer, 1970) yields ZT = 0.2 at 300 K. optimized doping and alloying, this material may also be of int For all the alkali and alkaline earth compounds, however, consi handling difficulties can be anticipated due to chemical reacti and low melting point eutectic compositions.

RARE EARTH SILICIDES

All of the rare earth elements (Sc, Y, La-Lu) form metalli silicides, with the possible exception of α-$LaSi_2$ which may be described as a small band gap, 0.19 eV (Samsonov, 1980), n-type semiconductor. The binary rare earth-silicon compounds, theref are of little interest for thermoelectric applications.

GROUP IVB AND VB SILICIDES

The group IVB (Ti, Zr, and Hf) and VB (V, Nb, and Ta) elem all form metallic disilicides. It is worth pointing out, howe the crystal structure of $TiSi_2$ (Jeitschko, 1977) is the proto-t a large family of materials (Nowotny, 1970) known as Nowotny chimney-ladder (Pearson, 1970) compounds. The unit cell in thi consists of a chimney-ladder of sub cells, each of which is its similar to the $TiSi_2$ unit cell. The metal atoms occupy nearly sites, similar to the β-Sn structure type, while the silicon a occupy sites which vary slightly from subcell to subcell.

An interesting characteristic of the Nowotny chimney-ladd compounds is the "magic" number of 14 valence electrons per me (VEC = 14), a remarkably predictive rule for the occurrence of gap in these materials (Nowotny, 1970). 14 valence electrons enough to fill the 4 s-p type bonding states of the β-Sn struc type, plus 10 more to fill all of the d-states for each metal. rule, $TiSi_2$ with only VEC = 12, has the Fermi level deep in th d-states and the material is a metal, as is observed.

Cr, Mo, AND W SILICIDES

The group VIB elements (Cr, Mo, and W) finally have enough valence electrons to provide the "magic" number of VEC = 14 for the disilicides. Although not strictly a member of the Nowotny chimney-ladder structure type, $CrSi_2$ is a semiconductor, consistent with the "magic" number of VEC = 14, and has a reasonably large A' value of 1.5, which compares well to the value for SiGe (see Table 1). While the value of A' may be further increased by lowering λ_ℓ through alloying (Nikitin, 1961; Neshpor, 1965), $CrSi_2$ is intrinsic at high temperatures due to the small band gap, 0.35 eV (Nishida, 1972), and is therefore of little interest for high temperature thermoelectric applications.

α-$MoSi_2$ and WSi_2 are p-type semi-metals with relatively low carrier concentrations (4.0 and 7.5 x 10^{21} cm^{-3}, respectively) and high mobilities (59 and 67 cm^2/V-s, respectively) (Neshpor, 1960). In this case it seems the "magic" number of VEC = 14 was not sufficient to actually create a band-gap, but instead resulted in a reduced density of states at the Fermi level and a small number of carriers. Any of the compounds $CrSi_2$, $MoSi_2$ and WSi_2 might be made into useful thermoelectrics, if only they exhibited larger band gaps.

Mn AND Re SILICIDES

MnSi (Samsonov, 1980; Mayer, 1960; Nikitin, 1958; Spitzer, 1970) as well as the higher manganese silicides (Samsonov, 1980; Neshpor, 1960; Mayer, 1960; Nikitin, 1958; Neshpor, 1960; Bienert, 1968; Bienert, 1966; Vedernikov, 1988; Korshunov, 1964) are of some interest as thermoelectrics. While the monosilicide probably has too small a band gap to be useful at high temperatures, the higher silicides have ZT values up to 0.8-0.9 (Bienert, 1966; Vedernikov, 1988; Korshunov, 1964). Using m_*/m_e=1 for holes, we estimate A' = 1.4, which again compares well to SiGe.

Early work was uncertain as to the precise composition of the material. It is now known that the higher manganese silicides actually form with with a variety of compositions such as $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, $Mn_{27}Si_{47}$ (Zwilling, 1974) and probably others, each of which is a Nowotny chimney-ladder compound with VEC near 14. Al substitutions result in the ternary compound $MnAl_{0.75}Si_{1.25}$ which exhibits opposite signs for the Hall and Seebeck coefficients, explained by an unusual band structure (Fedorov, 1989). Clearly, much remains to be done in this system and even higher ZT values can be expected with proper development.

$ReSi_2$, like $CrSi_2$, has a favorable A' = 1.9 (again assuming m_*/m_e=1), but has too small a band gap (0.12 eV) to be useful (see Table 1).

Fe, Ru, AND Os SILICIDES

β-$FeSi_2$ is a useful, inexpensive thermoel
currently under development for use in automo
and as a source of small amounts of emergency
Birkholz has reviewed the properties of β-FeS
which are summarized in Table 1. The ease of
compensate in some applications for the relat
very low value of A' = 0.05 n-type β-$FeSi_2$ is
fairly substantial ZT = 0.4 by analysis of bo
1969) and optical properties (Birkholz, 1970)
conduction mechanism is by small polaron hopp
parameter A' may still be of some predictive
readily compared to conventional band-type co
values.

The compounds Ru_2Si_3, Os_2Si_3 and Os_2Ge_3 a
chimney-ladder compounds, with structures sim
(Poutcharovsky, 1974; Poutcharovsky, 1975), a
number of 14 valence electrons per metal. Ru
are semiconductors, as expected, with reporte
0.34 eV (Susz, 1980), and 2.3 eV (Schellenber

In order to estimate A' for these materi
resistivity, Hall effect, Seebeck coefficient
(using thermal diffusivity data and the Debye
capacity) measurements have been performed in
arc-melted sample of Ru_2Si_3. These results a
where the solid lines for the Hall and Seebec
analysis using a standard, non-degenerate 2-
temperature independent effective masses and
results of the analysis, summarized in Table
for p-type materials and A' = 0.35 for n-typ

Since studies on single crystals, alloy
yet to be performed, such a large value of A'
arc-melted samples suggests very high ZT val
in this system. Even the value A' = 0.35 de
parameters should not be discouraging so ear
these materials.

Finally, in the Os-Si system, one more
reported: $OsSi_2$, isostructural with β-$FeSi_2$,
(Schellenberg, 1988). The greater mass of Os
$OsSi_2$ will have a much lower thermal conduct
Measurements on high quality samples of OsSi
effective mass, mobility and thermal conduct
useful.

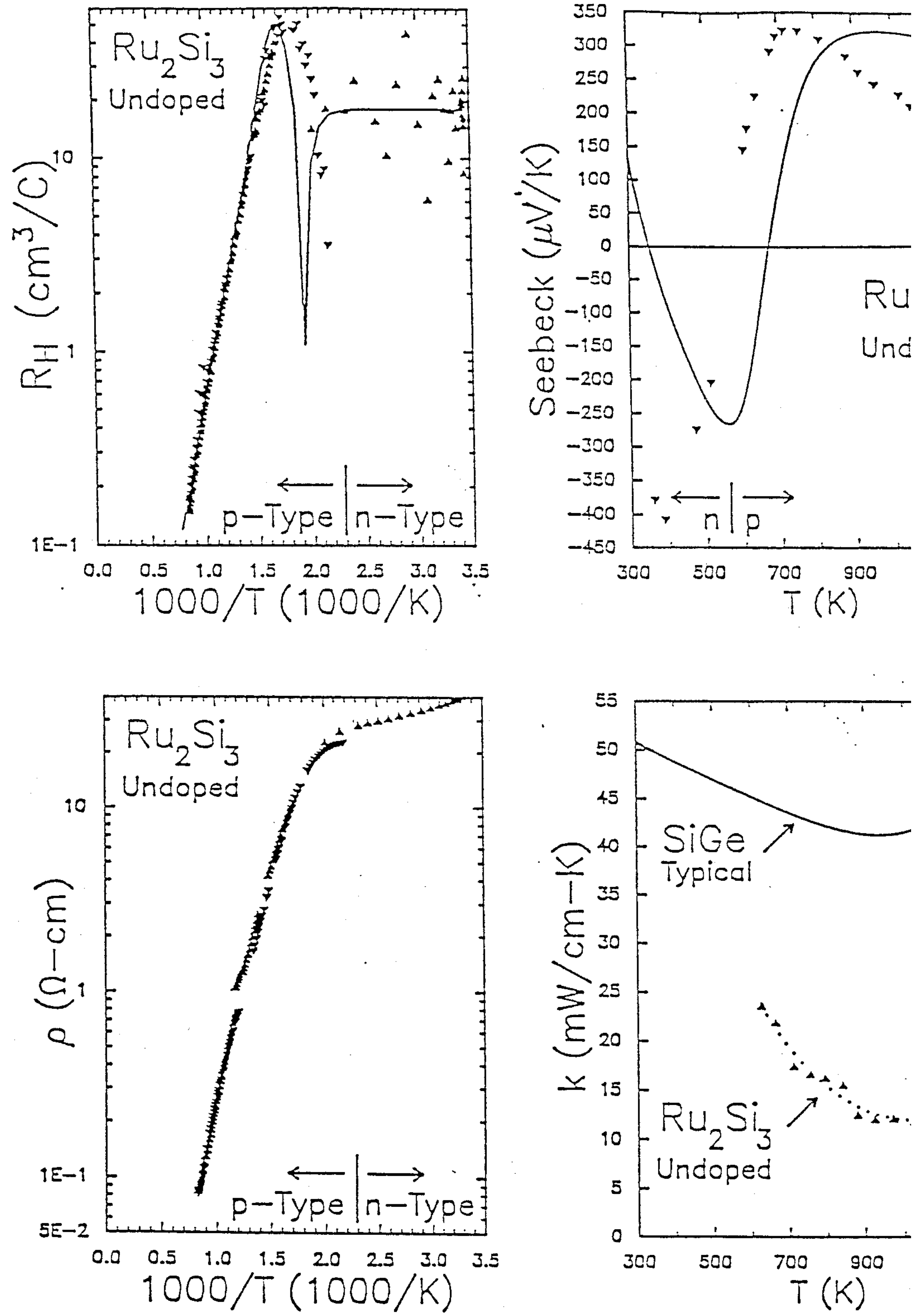

Fig. 1. Hall coefficient, Seebeck coefficient, electrical re
and thermal conductivity for Ru_2Si_3. Solid lines re
two-band model for the Hall and Seebeck coefficients

Co, Rh, AND Ir SILICIDES

The cobalt silicides, CoSi and $CoSi_2$, have too large a concentration (Neshpor, 1960) to be useful as thermoelectri Rh_3Si_4, Rh_4Si_5 and their Ir analogs have been reported (Eng 1968; Engström and Persson, 1968; Engström, 1970). Rh_4Si_5 are Nowotny chimney-ladder compounds with the "magic" numbe valence electrons per metal atom, and may therefore be sem with interesting thermoelectric properties. Neither the R Ir-Si phase diagrams are available, however, and no transp been reported on any of these materials.

Ni, Pd, AND Pt SILICIDES

All of the Ni group silicides are metallic and of lit thermoelectrics. It is worth noting, however, that alloys and Pt are important thermocouple materials due to their r large Seebeck coefficient values, a result of the d-band c the electronic structure of these metals.

SUMMARY

Many silicide semiconductors have been identified, se which are of considerable interest as thermoelectric mater values nearly as large as in SiGe have already been achiev $Mg_2(Si,Sn)$ alloys and $MnSi_{1.7}$. Certainly higher ZT values achieved with optimum alloying and doping in oriented sing The high mobilities, large effective masses and low therma conductivity values of $MoSi_2$, WSi_2, $CrSi_2$ and $ReSi_2$ make t interesting also, if only they had a substantial band gap doping levels could be optimized.

A number of Ru, Os, Rh and Ir silicides are known or semiconductors with sufficiently large band gaps, althoug is known about them to estimate their figure of merit val the most interesting compounds in this group may be the N chimney-ladder compounds Ru_2Si_3, Os_2Si_3, Rh_4Si_5 and Ir_4Si_5, the "magic" number of 14 valence electrons per transition element. These compounds are structurally related to MnS more refractory and, because of the heavier elements invo expected to have lower thermal conductivity values. Thes observations, combined with the estimate A' = 12.6 for p- reported here, indicate the value of further development thermoelectric materials.

Many silicides with the potential for large ZT value have not been closely examined, if at all. In a few impo (Rh-Si and Ir-Si) even the phase diagrams remain incomple development of detailed theoretical models for this class semiconductor, combined with experimental results on high samples of a few representative systems such as Ru_2Si_3, a evaluate the potential of this class of materials to exhibit high ZT.

ACKNOWLEDGEMENTS

The author would like to thank Dr. R. N. Shelton for providing access to arc-melting facilities and for useful discussions. 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.

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