Thermoelectric Properties of Silicides

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1. ABSTRACT

For the most commonly used 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) consist of alloys with partially filled d-bands, because Seebeck values are much larger for d-band alloys than for metals with filled or empty d-bands (such as Cu or Na, respectively). Certain silicide semiconductors which exhibit d-band character in the valence and/or conduction band may be able to combine the Seebeck enhancement effect characteristic of transition metal alloys, with the ability to achieve optimum doping levels typical of conventional thermoelectric materials. In this chapter, the thermoelectric properties of compounds of silicon combined with elements from groups 1 through 8, including the d-band elements, are reviewed. 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.

2. INTRODUCTION

Even after more than 30 years of experience with thermoelectric technology, efficiencies remain relatively low, seldom exceeding 1/8 of the limiting Carnot efficiency. The difficulty is that available materials have limited performance, as characterized by the usual dimensionless figure of merit

$$ZT = \frac{\sigma S^2 T}{\lambda}$$

where σ is the electrical conductivity, S is the Seebeck coefficient and λ is the thermal conductivity. Each of the most commonly used thermoelectric materials, such as Bi_2Te_3, PbTe, and SiGe, have a maximum ZT ~ 1. Since there is no fundamental upper limit on ZT the room for growth must nevertheless be considered quite large, amounting to almost an order of magnitude in efficiency.

In order to achieve significantly higher efficiencies, new materials are needed. Probably these new materials will differ from the conventional thermoelectric materials in some fundamental way. Fortunately, candidate materials are not difficult to identify, because in some ways the most commonly used thermoelectric materials represent an extremely narrow class of materials: all are composed exclusively of elements from the right-hand portion of the periodic table and all are dominated by s- and p-bonding. One promising class of materials is the transition metal silicides, where the d-electrons qualitatively alter the bonding and transport properties compared to simple s-, p-bonded materials. A few silicides, such as $FeSi_2$ and the higher manganese silicides ($MnSi_{\sim 1.75}$) are discussed in more detail in dedicated chapters elsewhere in this handbook. But for many promising materials, insufficient data are available to reliably estimate thermoelectric performance.

This chapter examines the occurrence and properties of silicide semiconductors with an emphasis on the possibility of attaining high thermoelectric conversion efficiencies. Section 3 discusses the general criteria used to evaluate the available literature on a candidate thermoelectric material. Section 4 reviews the properties of silicides as they pertain to thermoelectric applications and section 5 summarizes the results of this survey.

3.   EVALUATION CRITERIA

Before considering specific materials, this section provides a brief summary of the characteristics which suggest potential for a high figure of merit material. Characteristics to be considered include those needed: 1) to achieve a high figure of merit and 2) to use in applications. When establishing such search criteria, care must be taken to avoid excluding promising materials due to excessively narrow selection criteria. At the same time the criteria must be sufficiently definite to limit the search to a tractable number of candidate materials.

The principles for achieving a high figure of merit have been discussed by Ioffe[1] for a standard band-type semiconductor:

1) high value of $A' = (T/300) (m^*/m_e)^{3/2} \mu/\lambda_{ph}$ where m^* is the carrier effective mass, μ is the mobility in cm^2/V-sec and λ_{ph} is the lattice thermal conductivity in mW/cm-K (for simplicity, the units for A' will be omitted throughout this chapter);

2) band gap, E_g, greater than about $4k_B T$; and

3) dopable to the extrinsic regime.

The trade off in properties represented by the factor A' comes from a simple, single band model for semiconductors. ZT actually depends on a large number of additional factors, but A' captures the essential features. Moreover, the parameters entering A' may be estimated with a minimum of experimental information and can therefore be useful as a screening tool, at least for conventional band-type semiconductors.

So, ZT may be improved by increasing the effective mass, increasing the mobility and or reducing the lattice thermal conductivity. The large energy gap requirement stems from the need to suppress the thermal excitation of minority carriers, which quenches the Seebeck coefficient and increases the thermal conductivity. The doping requirement stems from the need to achieve the optimum doping level: overdoping results in a small Seebeck coefficient, while underdoping results in excessively large resistivity values.

The considerations for practical utilization of a material can depend strongly on the anticipated application. However, some general criteria include:

4) chemical, structural and thermal stability;

5) ability to form sound electrical and thermal connections; and

6) manufacturable in suitable quality and quantity.

There is often some trade off between these two types of requirements. If ZT is high enough, even very substantial applications difficulties may be overcome with heroic device development efforts. On the other hand, even a relatively low ZT may be useful if the material is sufficiently inexpensive and easy to use.

For space power applications, state of the art SiGe alloys have ZT values among the best known[2] and are excellently suited for high temperature applications. Since transition metal are

relatively refractory materials, SiGe alloys are a reasonable baseline for comparison purposes. For SiGe, using parameters taken from recent theoretical models (see Table 1), we find $A' = 2.6$ and $ZT_{max} = 1$ for n-type SiGe[3] and $A'=1.2$ and $ZT_{max} = 0.7$ for p-type SiGe.[4]

This example serves to highlight the fact that the relationship between A' and ZT_{max} is only qualitative, even for an extensively studied material such as SiGe. There is considerable error for most of the entries in Table 1 and because they were extracted from a wide variety of sources, considerable caution must be exercised in any comparisons. Still, large values of A' do generally correlate with high ZT values, so these values can be of some use as a qualitative guide.

4. PROPERTIES OF METAL SILICIDES

In this section each of the metal-silicon systems from the first ten groups of the periodic table will be reviewed. Useful reviews are available on the preparation,[5,6] thermodynamics,[7] electrical properties[8] and thermoelectric properties[9] of transition metal silicides. 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 very promising materials.

With the exception of the alkali and alkaline earth silicides, semiconducting behavior is observed in only the more silicon-rich silicides. This is a straightforward result of the usual requirement that all bands must be either completely filled or completely empty for a material to exhibit semiconducting behavior. The alkali and alkaline earth elements have only one or two valence electrons and it is relatively easy to use all of the valence electrons in bonds, regardless of the proportion of metal to silicon atoms. Transition metals have many more valence electrons and if the silicon content is too low, there will almost certainly be metal-metal bonds, resulting in metallic conduction behavior. All known metal-rich transition metal silicides are metallic. Many

of the more silicon-rich compounds, however, do exhibit semiconducting behavior and each of the metal silicides from groups 1 through 8 will be examined in the following sections.

4.1. 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 band gaps near 0.5 - 1 eV,[10] but little else is known about them. Notable are Mg_2Si, Ca_2Si, Sr_2Si and their germanide and even stannide analogs. Based on the known semiconducting properties of these materials,[11] Nicolaou has predicted ZT = 3 and larger for certain solid solutions.[12] Recently, ZT = 0.8 has been reported for $Mg_2(Si,Sn)$ solid solutions.[13] Marchuk et al[13] reports μ/λ_{ph} values for $Mg_2(Si,Sn)$ which, using $m^*/m_e = 1$ yields the extraordinary value of A' = 14. Results of Noda et al[14, 15] also indicate large values for A' and ZT as large as 1.68 for $Mg_2Si_{0.6}Ge_{0.4}$. The large values of A' and the band gap (0.7 eV), combined with the ability to alloy these materials, are all excellent indications that even higher ZT values will be achieved with further development.

$BaSi_2$, with $E_g \cong 0.48$ eV, has been reported to have $S^2\sigma = 1.0$ $\mu W/K^2$-cm for a sample with S = + 600 $\mu V/K$.[11] Assuming acoustic phonon scattering and a constant mobility, an optimum power factor of $S^2\sigma \cong 11$ $\mu W/K^2$-cm is estimated. Combined with $\lambda_{ph} = 16$ mW/cm-K[16] yields ZT=0.2 at 300 K. With optimized doping and alloying, this material may also be of interest. For all the alkali and alkaline earth compounds, however, considerable handling difficulties can be anticipated due to chemical reactivity. Also, many systems exhibit low melting point eutectic compositions.

4.2. RARE EARTH SILICIDES

All of the rare earth elements (Sc, Y, La-Lu) form metallic silicides, with the possible exception of α-$LaSi_2$ which may be described as small band gap (0.19 eV)[11] n-type semiconductor. The binary rare earth-silicon compounds, therefore, appear to be of little interest for thermoelectric applications.

4.3. GROUP IVB AND VB SILICIDES

The group IVB (Ti, Zr, and Hf) and VB (V, Nb, and Ta) elements all form metallic disilicides. Nevertheless, $Nb_xTa_{1-x}Si_yGe_{2-y}$ alloys have been investigated and a sample of NbSiGe was reported to have ZT=0.5 (17) or ZT=1.5 (18) at 1300 K. The ZT=1.5 value is particularly suspicious, however, since the quoted electrical resistivity and thermal conductivity values violate the Wiedemann-Franz law. It is worth pointing out here that the crystal structure of $TiSi_2$ (19) is the proto-type for a large family materials[20] known as Nowotny chimney-ladder compounds. The unit cell in this family can be very large, consisting of a chimney-ladder of subcells, each of which is similar to the $TiSi_2$ unit cell. The metal atoms occupy nearly regular sites, similar to the β-Sn structure type, while the silicon (or other group IV) atoms occupy sites which vary slightly from subcell to subcell.

An interesting characteristic of the Nowotny chimney-ladder compounds is the "magic" number of 14 valence electrons per metal atom (VEC = 14), a remarkable predictive rule for the occurrence of a band gap in these materials.[20] The rule was thought to originate from the observation that 14 valence electrons are enough to fill the 4 s-p type bonding states of the β-Sn structure type, plus 10 more to fill all of the d-states for each metal. Recent calculations, however, suggest that the gap is found within the d states, contrary to the filled d-band interpretation.[21] The rule itself remains useful, even if the causal relationship is unclear, because chimney-ladder compounds with VEC=14 are typically semiconductors while others, such as $TiSi_2$ with only VEC = 12, are found to be good conductors.

4.4. Cr, Mo, AND W SILICIDES

Although not a member of the Nowotny chimney-ladder structure type, $CrSi_2$ is a large effective mass[22] semiconductor, consistent with the "magic" number of VEC = 14, and has a reasonably large A' value of 2.5 for p-type material, which compares well to the value for SiGe (see Table 1). While the value of A' can be further increased by lowering λ through alloying,[23,24]

$CrSi_2$ is intrinsic at high temperatures due to the small band gap (0.35 eV)[25,26] and 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-sec, respectively).[27] 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. All three of the compounds $CrSi_2$, $MoSi_2$ and WSi_2 might be made into useful thermoelectrics, if only they exhibited a larger band gap.

4.5. Mn AND Re SILICIDES

MnSi[11, 16, 2830] and the higher manganese silicides[11,2729,3137] 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 (32, 36, 37). 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 a variety of compositions such as $Mn_{11}Si_{19}$, $Mn_{15}Si_{26}$, $Mn_{27}Si_{47}$ (38) 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.[39] 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 a small band gap (0.12 eV), and therefore cannot be expected to have a large ZT (see Table 1). Still, the number of alloying possibilities, such as $Re_{1-x}Mo_xSi_2$ or the closely related $Cr_{1-x}V_xSi_2$ (40), is rather large and some of these materials may be sufficiently inexpensive to be of some interest.

4.6. Fe, Ru, AND Os SILICIDES

β-FeSi$_2$ is a useful, inexpensive thermoelectric material, currently under development for use in automobiles[41] and as a source of small amounts of emergency power.[42] Birkholz has reviewed the properties of β-FeSi$_2$ (43), which are summarized in Table 1. The relative ease of preparation and low cost compensate in some applications for the relatively low ZT values. The very low value of A' = 0.05 for n-type β-FeSi$_2$ is reconciled with the fairly substantial ZT = 0.4 by analysis of both transport[44] and optical properties[45] which indicate the conduction mechanism is by small polaron hopping. In this case, the parameter A' may still be of some use but cannot be readily compared to A' values for more conventional materials with band-type conduction. There has also been some interest, mostly in Japan, in β-FeSi$_2$ prepared by a novel RF-plasma technique.[46]

The compounds Ru$_2$Si$_3$, Os$_2$Si$_3$ and Os$_2$Ge$_3$ are isostructural, VEC=14, Nowotny chimney-ladder compounds,[47] with structures similar to Ru$_2$Ge$_3$ and Ru$_2$Sn$_3$ (48). Ru$_2$Si$_3$, Ru$_2$Ge$_3$, and Os$_2$Si$_3$ are semiconductors, as expected, with reported band gaps of 1.08 eV,[49] 0.34 eV,[50] and 2.3 eV[51] respectively, although electronic structure calculations for Ru$_2$Si$_3$ suggest the band gap is within the d-states, rather than above,[21] as discussed above.

A model for the thermoelectric properties of doped Ru$_2$Si$_3$ have been developed based on high temperature measurements of electrical resistivity, Hall effect, Seebeck coefficient and thermal conductivity in the intrinsic region.[52] Based on this model, ZT$_{max}$ for p-type Ru$_2$Si$_3$ has been predicted to be up to 3 times larger than p-type SiGe and n-type Ru$_2$Si$_3$ is predicted to be 50% better than n-type SiGe. To date, large ZT values have not yet been realized for Ru$_2$Si$_3$ due to doping difficulties, in spite of efforts to identify suitable dopants.[53, 54]

Finally, in the Os-Si system, one more semiconductor has been reported: OsSi$_2$, isostructural with β-FeSi$_2$ and has been reported have a band gap of 1.8 eV[55] or 2.3 eV.[51] The much greater mass of Os compared to Fe, suggests OsSi$_2$ will have a much lower thermal conductivity than FeSi$_2$. Measurements on high quality samples of OsSi$_2$ to estimate the effective mass, mobility and thermal conductivity values would be very interesting.

4.7. Co, Rh, AND Ir SILICIDES

The cobalt silicides, CoSi and $CoSi_2$, are inexpensive but have too large a carrier concentration[27] to be particularly useful as thermoelectrics. Two compounds of possible interest (Rh_3Si_4, Rh_4Si_5) have been reported in the Rh-Si system.[56] Although transport properties have not been reported for either rhodium compound, their Ir analogs (Ir_3Si_4 and Ir_4Si_5) have recently been found to be metallic.[57] Two further compounds in the Ir-Si system, Ir_3Si_5 and $IrSi_3$, appear to have no other isostructural compounds, but exhibit some semiconducting behavior and may be of some interest for thermoelectric applications.

4.8. Ni, Pd, AND Pt SILICIDES

All of the Ni group silicides are metallic and of little use as thermoelectrics. It is worth noting, however, that alloys based on Ni and Pt are important thermocouple materials due to their relatively large Seebeck coefficient values, a result of the d-band character of the electronic structure of these metals.

5. SUMMARY

Many silicide semiconductors have been identified and most of these are of at least some interest as thermoelectric materials. ZT values nearly as large as achieved in SiGe have already been achieved for $Mg_2(Si,Sn)$ alloys and $MnSi_{\sim1.75}$, and probably higher ZT values can be achieved with optimum alloying and doping in oriented single crystals. $CrSi_2$ and $ReSi_2$ probably could be turned into useful thermoelectric materials, except for their low band gap values.

Several Ru, Os and Ir silicides are semiconductors, but much too little is known about them to satisfactorily estimate their figure of merit values. Among the more interesting compounds in this group are the Nowotny chimney-ladder compounds Ru_2Si_3 and Os_2Si_3 which have the "magic" number of 14 valence electrons per transition metal element. These compounds are essentially isostructural with $MnSi_{\sim1.75}$, which is known to have reasonable ZT values, but are

more refractory and because of the heavier elements involved expected to have lower thermal

conductivity values.

The trends observed among the silicides may generally be expected to be followed by the

analogous germanides. Germanides will tend to have lower melting points, and smaller band gap

values, both of which restrict their use to temperatures somewhat less than the silicides. But, they

may also have both lower thermal conductivity values and larger mobility values, which could

prove useful. Even less is known about the germanides than is known about the silicides,

however, and considerable exploratory work will be required.

As this survey shows, many silicides with the potential for large ZT values have hardly been

examined. The development of detailed theoretical models for this kind of d-band semiconductor,

combined with experimental results on high quality samples of a few representative systems such

as Ru_2Si_3, are needed to evaluate the potential of this class of materials to exhibit high ZT values.

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TABLE 1. Representative thermoelectric parameters at 300 K and maximum ZT for selected materials.

Material Name	Melting Point, K	Type	m^*/m_e	μ cm²/V-sec	λ_{ph} mW/cm-K	A'	ZT_{max}	E_g eV	Ref.
(Si,Ge)	1550	n	1.4	68	44	2.6	1.0	0.7	2, 3
(Si,Ge)	1550	p	1.2	40	44	1.2	0.7	0.7	2, 4
$Mg_2(Si,Sn)$	1300	n	(1)			14	0.8	0.7	12, 13
$Mg_2(Si,Ge)$	1360	n	1.2	108	21	6.8	1.07	0.74	14, 15
$Mg_2(Si,Ge)$	1360	p	2.3	22	21	3.7	1.68	0.74	14, 15
$CrSi_2$	1763	p	5	15	68	2.5		0.35	23-26
$CrSi_2$	1763	n	20.2	0.15	68	0.2		0.35	23-22
$MnSi_{\sim1.75}$	1550	p	(1)	40	29	1.4	0.7	0.67	32,33,36,37
$ReSi_2$	2250	p	(1)	105	55	1.9		0.12	24, 27
$FeSi_2$	1255	p	4	4	40	0.8	0.2	0.9	43
$FeSi_2$	1255	n	(1)	2	40	0.05	0.4	0.9	44
Ru_2Si_3	1970	n	2.9	10	40	1.2		1.08	49, 52
Ru_2Si_3	1970	p	2.9	29	40	3.6		1.08	49, 52