Thermoelectric properties of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$

Yuji Ohishi^{a*}, Afiqa Mohamad^a, Yoshinobu Miyazaki^{a,b}, Hiroaki Muta^a, Ken Kurosaki^a, and Shinsuke Yamanaka^{a,c}

^a Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka, 565-0871, Japan

^b Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

^c Research Institute of Nuclear Engineering, University of Fukui, 1-2-4 Kanawa-cho, Tsuruga, Fukui, 914-0055, Japan

Abstract

The thermoelectric properties of Mo-substituted CrSi_2 were studied. Dense polycrystalline samples of Mo-substituted hexagonal C40 phase $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$) were fabricated by arc melting followed by spark plasma sintering. Mo substitution substantially increases the carrier concentration. The lattice thermal conductivity of CrSi_2 at room temperature was reduced from 9.0 to 4.5 $\text{W m}^{-1} \text{K}^{-1}$ by Mo substitution due to enhanced phonon–impurity scattering. The thermoelectric figure of merit, ZT , increases with increasing Mo content because of the reduced lattice thermal conductivity. The maximum ZT value obtained in the present study was 0.23 at 800 K, which was observed for the sample with $x = 0.30$. This value is significantly greater than that of undoped CrSi_2 ($ZT = 0.13$).

Semiconductor, Intermetallic compounds, Thermal conductivity, Electrical properties

*E-mail address: ohishi@see.eng.osaka-u.ac.jp

1. Introduction

The efficiency of thermoelectric (TE) conversion depends on the dimensionless figure-of-merit, ZT , of the material components, which is defined by $ZT = (S^2 \sigma / \kappa) T$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity (i.e., the sum of the electrical thermal conductivity, κ_{ele} , and the lattice thermal conductivity, κ_{lat}), and T is the absolute temperature [1]. Transition metal semiconducting silicides are potential candidates for TE materials, because they are environment-friendly, stable at high temperatures, and inexpensive [1]. To date the disilicide of chromium (CrSi_2) has attracted attention as a promising TE material because of its semiconducting nature [2, 3] and thermal oxidative stability in air up to 1000 K [4].

CrSi_2 has a hexagonal C40 crystal structure with a space group of $P6_222$ [5, 6]. Stoichiometric CrSi_2 is a degenerate p-type semiconductor [2] with an indirect band gap of 0.35 eV [7]. A previous study on single-crystal and polycrystalline CrSi_2 has shown that CrSi_2 has a moderately high Seebeck coefficient of about $100 \mu\text{V}\cdot\text{K}^{-1}$ and an electrical conductivity of $\sim 1 \times 10^5 \Omega^{-1}\cdot\text{m}^{-1}$ at room temperature [2]. However, its high thermal conductivity ($10 \text{ W}\cdot\text{mK}^{-1}$ at room temperature [6]) keeps the ZT value of CrSi_2 relatively low compared to that of currently available TE materials such as PbTe- and Bi_2Te_3 -based alloys.

The thermal conductivity of CrSi_2 is dominated by phonon contribution [8]. Thus, a promising approach for improving TE performance is to reduce the lattice thermal conductivity by impurity doping, because impurities scatter phonons and block phonon transport. Several groups have attempted to enhance TE performance of CrSi_2 by substitution of the Si site with Al [8] or the Cr site with Mn [3] or V [9, 10]. To the best of our knowledge there has been no report of substitution of the Cr site with Mo, which is a Cr congener. Based on the CrSi_2 – MoSi_2

pseudo-binary phase diagram, the solubility limit of MoSi_2 in CrSi_2 is 20–30% [11]. Because the phonon–impurity scattering rate increases as a function of the difference in mass between the substituted atoms and the matrix [12], Mo substitution is expected to reduce the lattice thermal conductivity of CrSi_2 . The objectives of this paper are to fabricate Mo-substituted $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ and to study the effect of Mo substitution on the TE properties of CrSi_2 .

2. Experimental

Alloys with nominal compositions of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$, and 0.35) were prepared by arc melting a mixture of Cr, Mo, and Si in an Ar atmosphere. The purity of the starting materials was 99.9% for Cr, 99.95% for Mo, and 11N for Si. Subsequently, the ingots were ball-milled for 2 h using tungsten carbide media. The resulting powders were sintered by spark plasma sintering (SPS) at 1473 K for 5 min at a pressure of 100 MPa under Ar flow (Dr Sinter SPS-515A, Sumitomo Coal Mining Co., Ltd.). The sintered bodies were then heat-treated for 12 h at 1273 K under vacuum.

The densities of the samples were calculated from the measured weight and dimensions. Powder X-ray diffraction (XRD) patterns were obtained at room temperature after SPS to identify the crystal structure using Cu $K\alpha$ radiation with a Rigaku X-ray diffractometer, Ultima IV. The lattice constants of the $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ samples were evaluated from the XRD patterns using an extrapolation method. Charge carrier concentrations and mobilities were determined by Hall measurements with a ResiTest 8340 system (Toyo Co.) under a magnetic field of 0.5 T in van der Pauw geometry. Electrical conductivity and the Seebeck coefficient were measured using commercial equipment (ZEM-3, Ulvac Inc.). A four-point current-switching technique was employed for measuring electrical conductivity. A static DC method was used for the Seebeck coefficient measurement. Thermal conductivity was calculated from the heat capacity, thermal diffusivity, and density. Thermal diffusivity was measured by a laser flash technique

using an LFA 457 apparatus (Netzsch). The heat capacity of CrSi_2 was taken from the FactSage FactPS thermodynamic database [13].

3. Results and discussions

The powder XRD patterns of the $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ samples obtained at room temperature are shown in Figure 1 together with literature data for the hexagonal C40 phase of CrSi_2 and the orthorhombic C11_b phase of MoSi_2 [5, 14]. The reflection peak positions of the samples agree well with those of the C40 phase of CrSi_2 except for the sample with $x = 0.35$. The impurity peaks are assigned to the C11_b phase of MoSi_2 . The measured densities and the lattice parameters of each sample evaluated from the reflection peak positions and theoretical densities are summarized in Table 1. The bulk densities of the samples exceed 97% of the theoretical density (T.D.). The variation in lattice parameters with composition is shown in Figure 2. The lattice parameters a and c of pure CrSi_2 agree well with literature values [6]. Parameters a and c of samples with $x = 0.00$ – 0.30 increase linearly with Mo content in accordance with Vegard's law. On the other hand, the lattice parameters of the alloy with $x = 0.35$ are almost identical with those of $x = 0.30$, suggesting a deviation from Vegard's law. This deviation is due to segregation of the C11_b phase. The XRD patterns and lattice parameters of the samples indicate that the solubility limit of Mo in $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ is in the range of $0.30 < x < 0.35$. This limit is consistent with the CrSi_2 – MoSi_2 pseudo binary phase diagram reported by Wei [11].

Figure 3 presents the composition dependence of the carrier concentrations and mobilities of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ at room temperature. Unfortunately, we could not obtain data from the sample with $x = 0.05$ because of breakage of the sample. Conduction was confirmed to be p-type for all samples by Hall Effect measurements. The carrier concentration was determined to be $7.7 \times 10^{20} \text{ cm}^{-3}$ for CrSi_2 , which is close to literature values [2, 9]. No change in carrier concentration is

expected upon substitution of an element from the same group; however, the carrier concentration increases significantly with Mo substitution.

The temperature-dependences of the electrical conductivity and Seebeck coefficient of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ are shown in Figures 4 (a) and (b), respectively. The electrical conductivity increases with increasing Mo content, because of the increase in carrier concentration. The electrical conductivity decreases with increasing temperature below 700–900 K, as is typically observed for a degenerate semiconductor. The increase in electrical conductivity above 700–900 K suggests an increase of carrier concentration at elevated temperature. The Seebeck coefficient of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ decreases with increasing Mo content due to the increase in carrier concentration. The linear increase of the Seebeck coefficient below 700 K is related to the high carrier concentration of the samples, and the decrease at higher temperatures is attributed to the increase of the carrier concentration at elevated temperature. This increase of the carrier concentration may be caused by thermal excitation of carriers or formation of defects that act as acceptors.

To check that degenerate limit holds for all the samples, we calculated the reduced fermi energy dependence of the Seebeck coefficient. For a single-band model, S is expressed by [15]:

$$S = \pm \frac{k_B}{q} \left\{ \frac{(s+5/2)F_{s+3/2}(\varepsilon_F)}{(s+3/2)F_{s+1/2}(\varepsilon_F)} - \varepsilon_F \right\} \quad (1)$$

where $F_n(\varepsilon_F)$ is the n th order Fermi integral and ε_F is the reduced Fermi level, which are given by

$$F_n(\varepsilon_F) = \int_0^\infty \frac{\varepsilon^n}{1 + \exp(\varepsilon - \varepsilon_F)} d\varepsilon \quad (2)$$

$$\varepsilon_F = \frac{E_f}{k_B T} \quad (3)$$

The parameter s is -0.5 for scattering by ionized impurities and 1.5 for scattering by acoustic phonons. Figure 6 shows the reduced Fermi level dependence of the Seebeck coefficient at 300 K calculated using eq. (1). This figure shows that the reduced Fermi level is as large as $e_F \approx 2.5$ at 300 K even for the sample with the highest Seebeck coefficient, indicating that all the samples in this study are degenerate semiconductors.

Figure 6 (a) gives the temperature-dependence of the thermal conductivities observed in this study. It is obvious from this figure that the thermal conductivities of the samples decrease significantly with increasing Mo content. The thermal conductivity, κ , is the sum of the lattice thermal conductivity, κ_{lat} , and the electrical thermal conductivity, κ_{el} . The value of κ_{el} was calculated using the Wiedemann–Franz–Lorenz relationship, $\kappa_{el} = L \cdot \sigma \cdot T$, where L is the Lorenz number ($2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$). The lattice thermal conductivity, κ_{lat} , is obtained by subtracting κ_{el} from the observed total thermal conductivity κ . Figure 6 (b) shows the temperature-dependence of the calculated values of κ_{lat} and κ_{el} . Although the lattice contribution is predominant, the electrical contribution increases with increasing Mo content, because of the decrease in lattice thermal conductivity and the increase in electrical conductivity.

The temperature-dependence of ZT is shown in Figure 7. Mo substitution significantly enhances the ZT of CrSi_2 , especially in the temperature range of 700–1000 K. The ZT values increase with increasing Mo content and reach a maximum value of 0.23 at $x = 0.30$, which is the solubility limit of Mo in CrSi_2 . This value is 78% higher than that of CrSi_2 ($ZT = 0.13$). Although Mo substitution improves the ZT substantially, the maximum ZT value is still much less than that of currently available thermoelectric materials ($ZT \approx 1$).

To achieve higher ZT values further reduction of the lattice thermal conductivity is necessary. Figure 8 presents the composition dependence of κ_{lat} , which shows that κ_{lat} decreases with increasing Mo content. This decrease is attributed to the enhanced phonon-impurity scattering produced by the substitution of Mo. While the gradients of the κ_{lat} curves are steep in

the range of $x \leq 0.15$, they become shallow when $x > 0.15$. To gain insight into the possibility of the further reducing κ_{lat} the lower limit of the lattice thermal conductivity, κ_L , was calculated using Cahill's model [16]. Based on this model, κ_L is given by

$$\kappa_L = \left(\frac{\pi}{6}\right)^{1/3} k_B V^{-2/3} \sum_i \left[v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \right] \quad (1)$$

where k_B is the Boltzmann constant, V is the volume of the primitive cell, v is the phonon group velocity, and θ is the Debye temperature. The subscripted notation i represents the phonon branch; there are one longitudinal (L) and two degenerate transverse (T) phonon branches. The Debye temperature is expressed by

$$\theta_i = \frac{\hbar \cdot v_i}{k_B} \left(\frac{6\pi^2}{V} \right)^{1/3}. \quad (2)$$

The parameters needed for the calculation are v_i and V . We determined values for these parameters from the literature: $8696 \text{ m}\cdot\text{s}^{-1}$ for v_L and $5644 \text{ m}\cdot\text{s}^{-1}$ for v_T [17]. The value of V was calculated from the lattice parameters [6] and found to be $108 \text{ \AA}^3$. The calculated value of κ_L for CrSi_2 at 300 K is $0.44 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is significantly smaller than the minimum value of $4.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ obtained for the sample with $x = 0.30$. This result suggests that further reduction of the lattice thermal conductivity is possible through additional phonon scattering.

4. Conclusions

We have fabricated dense polycrystalline samples of Mo-substituted hexagonal C40 phase $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0-0.30$). The lattice thermal conductivity of these materials decreases from 9.0 to $4.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ with increasing Mo content at room temperature due to enhanced phonon-impurity scattering. The carrier concentration increases with increasing Mo content reaching $2.9 \times 10^{21} \text{ cm}^{-3}$ for the sample with $x = 0.30$. This increase in carrier concentration may

originate from a change in band structure upon Mo substitution. The ZT values at 800 K increase upon Mo substitution from 0.13 at $x = 0$ to 0.23 at $x = 0.30$. Because the lower limit of the lattice thermal conductivity of CrSi_2 is $0.44 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, further reduction of lattice thermal conductivity is possible by additional phonon scattering.

Acknowledgments

This work was supported by the ALCA (Advanced Low Carbon Technology Research and Development Program) of the Japan Science and Technology Agency.

Reference

- [1] D. Rowe, ed., *Thermoelectrics Handbook: Macro to Nano*, CRC Press, Boca Raton, 2006.
- [2] I. Nishida, *J. Mater. Sci.* 7 (1972) 1119–1124.
- [3] I. Nishida, T. Sakata, *J. Phys. Chem. Solids* 39 (1978) 499–505.
- [4] J. Ma, Y. Gu, L. Shi, L. Chen, Z. Yang, Y. Oian, *J. Alloys Compd.* 376 (2004) 176–179.
- [5] JCPDS X-ray Powder Diffraction File No. 01-076-8541.
- [6] T. Dasgupta, J. Etourneau, B. Chevalier, S. F. Matar, A. M. Umarji, *J. Appl. Phys.* 103 (2008) 113516-1–6.
- [7] M. C. Bost, J. E. Mahan, *J. Appl. Phys.* 63 (1988) 839–844.
- [8] Z. J. Pan, L. T. Zhang, J. S. Wu, *Scripta Materialia* 56 (2007) 245–248.
- [9] Z. J. Pan, L. T. Zhang, J. S. Wu, *Scripta Materialia* 56 (2007) 257–260.
- [10] H. Hohl, A.P. Ramirez, T.T.M. Palstra, E. Bucher, *J. Alloys Compd.* 248 (1997) 70–76.
- [11] F.-G. Wei, Y. Kimura, Y. Mishima, *Mater. Trans.* 42 (2001) 1349–1355.
- [12] B. Abeles, *Phys. Rev.* 131 (1963) 1906–1911.
- [13] FactSage. www.factsage.com.
- [14] JCPDS X-ray Powder Diffraction File No. 01-072-6181.
- [15] D. Rowe, ed., *CRC Handbook of Thermoelectrics*, CRC Press, Boca Raton, 1995.
- [16] D. G. Cahill, S. K. Watson, and R. O. Pohl, *Phys. Rev. B* 46 (1992) 6131–6140.
- [17] M. Nakamura, *Met. Mater. Trans. A* 25, (1994) 331–340.

Figure captions

Figure 1. Powder X-ray diffraction patterns of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$, and 0.35) together with literature data for the hexagonal C40 phase of CrSi_2 and the orthorhombic C11_b phase of MoSi_2 [5, 14].

Figure 2. (Color online) Composition dependence of the lattice parameters of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$, and 0.35).

Figure 3. (Color online) Composition dependence of the carrier mobility and carrier concentration of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$).

Figure 4. (Color online) Temperature dependence of (a) electrical conductivity and (b) Seebeck coefficient of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$).

Figure 5. (Color online) Seebeck coefficient as a function of the reduced Fermi level.

Figure 6. (Color online) (a) Temperature dependence of the thermal conductivity of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$). (b) Lattice and electrical thermal conductivity of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$) estimated by the Wiedemann–Franz–Lorenz relationship.

Figure 7. (Color online) Temperature dependence of ZT of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$).

Figure 8. (Color online) Composition dependence of the lattice thermal conductivity of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0\text{--}0.30$).

Table captions

Table 1. Sample characteristics of $\text{Cr}_{1-x}\text{Mo}_x\text{Si}_2$ ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30$, and 0.35).

Figure1

Figure2

Figure3

Figure4(a)

Figure4(b)

Figure 5

Figure6(a)

Figure6(b)

Figure 7

Figure8

Table 1.

Y. Ohishi et al.

Composition x	Bulk density (g cm ⁻³)	Phases	Lattice parameters		X-ray density (g cm ⁻³)	T.D. (%)
			a (Å)	c (Å)		
0	4.99	C40	4.437(5)	6.369(7)	5.01	99.6
0.05	5.03	C40	4.441(12)	6.375(3)	5.05	99.7
0.1	5.05	C40	4.458(11)	6.387(2)	5.09	99.0
0.15	5.09	C40	4.467(11)	6.392(2)	5.17	98.4
0.2	5.16	C40	4.482(8)	6.403(3)	5.24	98.5
0.25	5.17	C40	4.499(7)	6.420(3)	5.27	98.1
0.30	5.23	C40	4.519(14)	6.420(3)	5.34	97.9
0.35	5.20	C40, C11 _b	4.520(7)	6.420(3)	5.39	97.4