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Thermoelectric properties of Rh-doped Ru_2Si_3 prepared by floating zone melting method

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Abstract

Precipitation-free samples of Rh-doped Ru_2Si_3 were prepared by the floating zone (FZ) method. The temperature dependences of the electrical resistivities and the Seebeck coefficients of Rh-doped Ru_2Si_3 (Rh content = 0, 4, 6 mol%) were measured. The electrical resistivities of both 4% and 6% Rh-doped Ru_2Si_3 were smaller than those of undoped Ru_2Si_3 prepared by the FZ method and 4% Rh-doped one prepared by other methods. The maximum value of the Seebeck coefficients for all samples was −175 μV/K at 673 K for 4% Rh-doped Ru_2Si_3. The dimensionless thermoelectric figure of merit reached 0.8 for 4% Rh-doped Ru_2Si_3 at 1073 K, which was about 50% larger than that of optimized n-type SiGe. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

To solve global environmental problems and energy problems, the solid-state direct energy conversion has been regarded to have a great possibility. Although the most commonly used thermoelectric materials, such as Bi_2Te_3, PbTe and SiGe, have high figure of merit ZT, the values of ZT of these materials were not over about unity and, thus, their efficiencies remain relatively low. The optimum efficiency of a thermoelectric device is expressed by

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

where T_h is the temperature at heat source and T_c is at heat sink. The dimensionless thermoelectric figure of merit ZT is given as

$$ZT = \alpha^2 T/\rho\lambda, \quad (2)$$

where ρ is the electrical resistivity, α is the Seebeck coefficient, T is the absolute temperature and λ is the thermal conductivity. In order to achieve significantly higher efficiencies (high ZT), new materials are needed. Some transition metal silicides such as $FeSi_2$ and $MnSi_{1.75}$ have been thought to be high-ZT thermoelectric materials since d-electrons have the possibility to alter the bonding condition and transport properties compared to simple s- or p-electrons. Noble metals with 5d-electrons such as Ru, Rh and Pd are produced as some of the most abundant fission products in irradiated nuclear fuels.

Ruthenium sesquisilicide (Ru_2Si_3) is an isostructural Nowotny chimney-ladder compound with valence electrons per metal atom (VEC) = 14 [1]. An interesting characteristic of the Nowotny chimney-ladder compounds is the magic number of 14 VEC, a remarkably predictive rule for the occurrence of a band gap in these materials [2]. Fourteen valence electrons are enough to fill the 4s–p-type bonding states of this structure. A model for the thermoelectric properties of doped Ru_2Si_3 has been developed based on the high-temperature data on electrical resistivity, Hall effect, Seebeck coefficient and thermal conductivity in the intrinsic region of Ru_2Si_3 [3]. From this model, ZT max for p-type Ru_2Si_3

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has been predicted to be three times larger than p-type SiGe, and that for n-type Ru_2Si_3 was predicted to be by 50% larger than n-type SiGe [4]. Although various preparation methods and many dopants have been investigated experimentally in order to obtain a much higher figure of merit for Ru_2Si_3, the expected values of thermoelectricity have not been attained [5,6], due to precipitations in single crystals produced from the reaction with the crucible used in Bridgman-like preparation methods or to the interruption in the current paths at grain boundaries in polycrystal samples. In our preceding study [7], the undoped Ru_2Si_3 prepared by the floating zone melting (FZ) method showed higher electrical conductivity than that of the single crystalline sample prepared by the Bridgman (BM) method.

In this study, the effects of Rh-doping were studied on samples prepared by the FZ method to improve the electrical property of Ru_2Si_3. The dimensionless thermoelectric figure of merit of Rh-doped Ru_2Si_3 was also calculated and compared with that of well-known SiGe.

2. Experimental

2.1. Sample preparation

Alloys of Rh-doped (0%, 4.0% and 6.0%) Ru_2Si_3 were first made by arc melting cold-pressed powder mixtures of 99.9% pure ruthenium powder, 99.9% pure rhodium powder and 99.999% pure silicon powder under purified argon with Ti getter. Then a polycrystalline rod sample, prepared by the arc melting method, was recrystallized by using the FZ method in a purified argon gas flow for preventing the oxidation of Ru_2Si_3. The apparatus for the FZ method has two infrared heating furnaces of the double ellipsoidal type with two 1.5 kW halogen lamps as the heat source. Samples were shaped into cylindrical rods of about 1.5–2.5 mm in diameter and about 10–20 mm in length. Weight loss during recrystallization was measured and found in all cases to be less than 1%. Annealing at 1200 K up to 12 h was done in evacuated quartz tubes lined with molybdenum foil. X-ray diffraction analysis indicated the presence of a single phase for each sample. The lattice parameters of the samples are shown in Table 1. The Rh contents before and after FZ melting were measured by inductively coupled plasma spectrometry and found not to have changed as shown in Table 2.

2.2. Measurements of thermoelectric properties

The Seebeck coefficient and electrical resistivity were measured simultaneously at each temperature. The electrical resistivity was measured by d.c. 4-wire technique using the Pt wires of each thermocouple as current leads. The current was applied by a regulated d.c. power supply and the voltage and current were measured with digital voltmeters. The Seebeck coefficients were calculated from the least squares regressions of the thermoelectromotive forces as a function of the temperature difference. The Hall effects were measured at room temperature.

Table 1
Lattice parameters of Rh-doped Ru_2Si_3 at room temperature

	a (nm)	*b* (nm)	*c* (nm)
Undoped Ru_2Si_3	1.1063(8)	0.8947(8)	0.5532(8)
4%Rh-doped Ru_2Si_3	1.1109(8)	0.8952(8)	0.5545(8)
6%Rh-doped Ru_2Si_3	1.1063(8)	0.8941(8)	0.5532(8)

Table 2
Rh contents in the samples before and after FZ melting

	Nominal value (mol%)	Before FZ melting (mol%)	After FZ melting (mol%)
04%Rh-doped Ru_2Si_3	4.0	4.1 ± 0.1	4.1 ± 0.1
6%Rh-doped Ru_2Si_3	6.0	6.0 ± 0.1	5.9 ± 0.1

3. Results and discussion

The temperature dependences of electrical resistivities ρ and the Seebeck coefficients α are shown in Figs. 1 and 2, respectively. The electrical resistivity values of Rh-doped Ru_2Si_3 obtained in this study are shown in comparison with those of the undoped arc melted one [4], the undoped one prepared by the Bridgman method [8], the Rh-4% doped arc melted one [7], and the Rh-4% doped one prepared by the Bridgman method [5]. At room temperature the electrical resistivity of undoped FZ sample extremely decreased by about two orders of magnitude compared to those of a typical arc sample [4] and one order of magnitude compared to that of undoped Ru_2Si_3 by the Bridgman method [8]. By doping with Rh, the resistivities of Ru_2Si_3 were reduced by about one order of magnitude in the extrinsic region and the more the Rh doping, the smaller the electrical resistivity became. The difference in the electrical resistivity between doped and undoped Ru_2Si_3 decreased in the intrinsic region above 1000 K.

The Seebeck coefficients of undoped Ru_2Si_3 exhibited n-type semiconducting behavior below about 800 K and changed to p-type semiconducting behavior above 800 K. The Seebeck coefficients of 4% and 6% Rh-doped Ru_2Si_3 prepared by FZ method were negative and reached a minimum around 700 K. The values of 4% and 6% Rh-doped samples made by FZ method in this study were not so different from those prepared by arc melting [7].

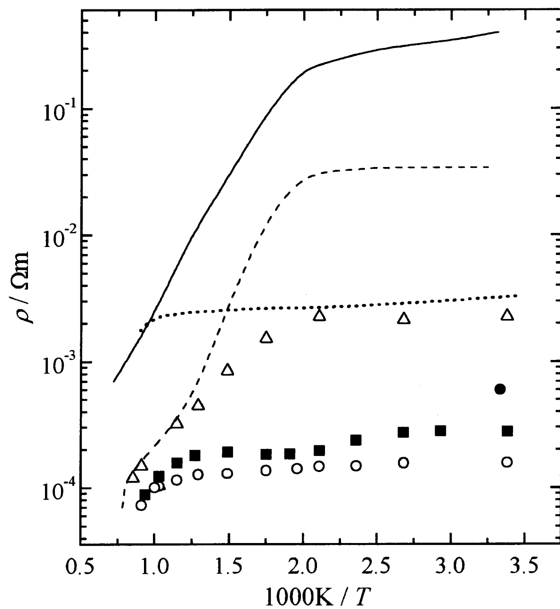

Fig. 1. Electrical resistivity of Ru_2Si_3: (△) undoped; (■) 4%Rh-doped; (○) 6%Rh-doped; (●) 4%Rh-doped Bridgman [5]; (———) undoped arc [4]; (- - - - - - - -) undoped Bridgman [8]; (· · · · · · · · ·) 4%Rh-doped arc [7].

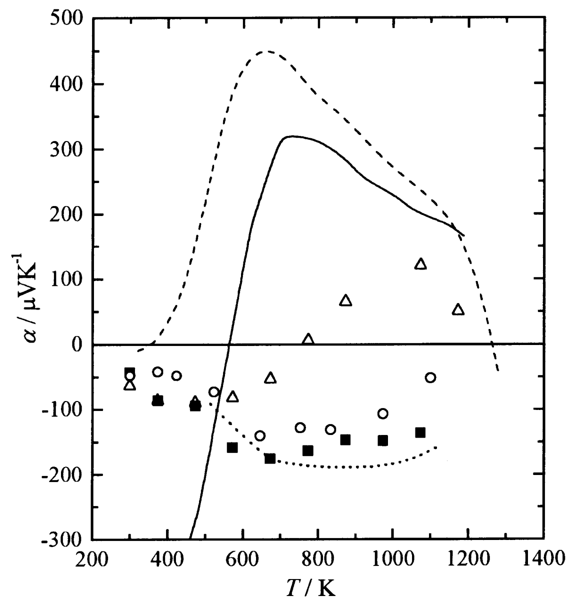

Fig. 2. Seebeck coefficient of Ru_2Si_3: (△) undoped; (■) 4%Rh-doped; (○) 6%Rh-doped; (———) undoped arc [4]; (- - - - - - - -) undoped Bridgman [8]; (· · · · · · · · ·) 4%Rh-doped arc [7].

The power factors α^2/ρ, calculated from the values in Figs. 1 and 2 are presented in Fig. 3. Although the power factors of undoped FZ-sample were not large, those of Rh-doped FZ samples were larger than those of optimized SiGe [9] above 800 K.

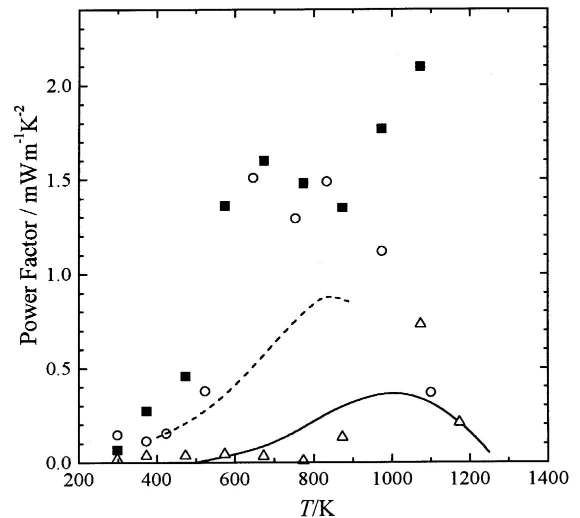

Fig. 3. Power factor (α^2/ρ) of Ru_2Si_3: (△) undoped; (■) 4%Rh-doped; (○) 6%Rh-doped; (———) undoped arc [4]; (- - - - - - - -) undoped sintered [12].

From the present results and thermal conductivity data [10], the dimensionless thermoelectric figures of merit ZT values were calculated using Eq. (2) and are shown in Fig. 4. The maximum ZT value of n-type Ru_2Si_3 seems to be about 50% larger rather than that of optimized p-type Si–Ge [9]. This large ZT value is due to very low electrical resistivity, relatively large Seebeck coefficient above 1000 K, and lower thermal conductivity than SiGe.

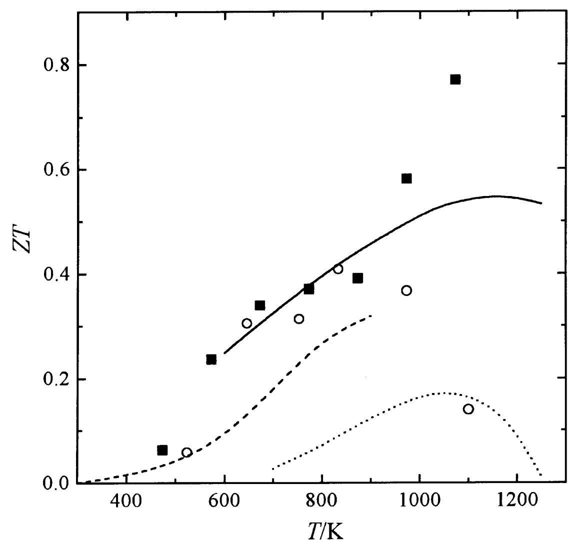

Fig. 4. Dimensionless figure of merit: (■) 4%Rh-doped; (○) 6%Rh-doped; (———) optimized n-type SiGe [9]; (- - - - - - - -) sintered undoped Ru_2Si_3 [12]; (· · · · · · · · ·) single crystal Ru_2Si_3 [8].

Table 3
Hall coefficient, carrier concentration and Hall mobility of Rh-doped Ru_2Si_3 samples at room temperature

	Hall coefficient (10^{-6} m^3 C^{-1})	Carrier concentration (10^{25} m^{-3})	Hall mobility (10^{-4} m^2 V^{-1} s^{-1})
4%Rh-doped Ru_2Si_3	2.9 ± 0.8	2.3 ± 0.7	10 ± 4
6%Rh-doped Ru_2Si_3	0.18 ± 0.05	3.5 ± 0.5	11 ± 3

The results of Hall coefficient, R_H, measurements at room temperature are given in Table 3. The carrier concentration n was calculated by usual manner of $n = 1/eR_H$ (e: electron charge) and Hall mobility μ was calculated from the electrical resistivity and the Hall coefficient with the relation $\mu = R_H/\rho$. According to theoretical investigations of Ru_2Si_3, the highest thermoelectric figure of merit would be achieved if we could realize the optimum doping concentrations (expected to be of the order of 10^{26} m^{-3}) and mobilities of the order of 5–10 $\times 10^{-4}$ m^2 V^{-1} s^{-1} simultaneously [11]. In this study the Hall mobility values of 4% and 6% Rh-doped samples were nearly equal to each other and were of the order of 10^{-3} m^2 V^{-1} s^{-1}, but the carrier densities were smaller than the optimum values. Suppressing minority carrier contributions to the Seebeck coefficient and thermal conductivity is critical for achieving high thermoelectric figure of merit. Since the solubility limit of Rh in Ru_2Si_3 is close to 6%, other dopants should be studied, such as Ir [5] which have a high solubility limit, enabling the extrinsic region in the electrical resistivity to be maintained at high temperatures.

4. Conclusion

The thermoelectric properties were measured in FZ-melted Rh-doped Ru_2Si_3. By using the FZ method, samples have large values of figure of merit. At 1073 K, the *ZT* of Ru_2Si_3 doped with 4% Rh was 0.77, about 50% larger than the *ZT* of optimized SiGe at the same temperature. The present result proved that the FZ method was useful to fabricate doped samples that lead to high efficient thermoelectric materials.

Acknowledgements

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