Thermoelectric Properties of Size-Controlled Si and Metal Silicides Nanocomposites

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Abstract. This paper describes our recent achievements of enhancement of the thermoelectric (TE) figure of merit $ZT$ in nanocomposites of Si and silicides of various metals (V, Ni, Ti, and Co). We proposed a method of melt spinning followed by spark plasma sintering for synthesis of the nanocomposites. Effect of the size of the structure on the TE properties of the nanocomposites is discussed.

1. Introduction

The efficiency of thermoelectric (TE) devices is determined by the temperature gradient across the devices as well as the properties of TE materials called dimensionless figure of merit $ZT = S^2T\rho^{-1}\kappa^{-1}$ where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $\rho$ is the electrical resistivity, and $\kappa$ is the total thermal conductivity ($\kappa = \kappa_{\text{lat}} + \kappa_{\text{el}}$, where $\kappa_{\text{lat}}$ and $\kappa_{\text{el}}$ are the lattice and electronic contributions, respectively) [1]. Well-known TE materials such as Bi$_2$Te$_3$ [2] and PbTe [3] exhibit the $ZT$ over unity, while the practical use of these materials is still limited as they consist of highly toxic and rare elements. Si-based TE materials provide desirable merits for the commercial utilization and mass production. Si exhibits good electrical properties (high $S^2\rho^{-1}$), but high $\kappa_{\text{lat}}$, resulting in a low $ZT$ (~0.02 in maximum at room temperature) [4]. Nanostructuring has emerged as promising approach to decrease $\kappa_{\text{lat}}$ and thus to enhance $ZT$ of Si-based TE materials. The enhanced $ZT$ of Si has been demonstrated in various nanostructures such as nanowires [5].

Recently, it has been revealed that nanocomposite structure reduces $\kappa_{\text{lat}}$ without significant influences on the electronic properties. To create such structure, we have proposed a method combining melt spinning (MS) and spark plasma sintering (SPS) [6]. In the MS procedure, mixtures of Si and various metals (V [7], Ni [8], and so on) with an appropriate ratio are melted and rapidly cooled, then ribbon-state nanocomposites composed of Si and metal silicides are obtained. To create bulk samples from the ribbons, the ribbons are sintered by SPS with keeping the nanostructures. Here, we review the recent results on the microstructure characterization as well as the TE properties of such nanocomposites.

2. Experimental Procedures

The Si-VSi$_2$ and Si-NiSi$_2$ nanocomposites with the chemical compositions of (Si$_{100}$P$_3$)$_{97}$V$_3$ and (Si$_{100}$P$_3$)$_{98}$Ni$_2$ were synthesized from chunks of Si (11N), P (6N), and chunks of V (4N) or Ni (3N), where P acts as an electron dopant. The mixtures were placed into boron nitride nozzles and melted via
induction heating in a flowing Ar atmosphere, and the molten alloys were rapidly solidified on a Cu roller. The rotation speed of the Cu roller with 30 cm diameter was set to be 2000, 4000, and 6000 rpm. The melt-spun ribbons obtained at each rotation speed were noted as MS (2000), MS (4000), and MS (6000). In order to synthesize the bulk samples from the MS ribbons, the SPS was carried out at 1473 K for 3 min for (Si100P3)97V3 and 1273 K for 4 min for (Si100P3)98Ni2. The sintered bulk samples prepared from the MS ribbons with each rotation speed are denoted as MS (2000)-SPS, MS (4000)-SPS, and MS (6000)-SPS.

The phase state and microstructure of the MS ribbons and the MS-SPS bulk samples were characterized by powder x-ray diffraction analysis (XRD; Ultima IV, Rigaku Co, Cu Kα) and scanning electron microscopy (FE-SEM, JSM-6500F, JEOL) at room temperature. The TE properties of the MS-SPS samples for (Si100P3)97V3 and (Si100P3)98Ni2 were measured from 300-1073 K. S and ρ were measured simultaneously using a commercial apparatus (ZEM-3, Ulvac). κ was evaluated from the relationship \( \kappa = \alpha C_p d \), where \( \alpha \), \( C_p \), and \( d \) are the thermal diffusivity, heat capacity, and density, respectively. \( \alpha \) was measured using a laser flash apparatus (LFA-457, Netzsch). \( C_p \) was evaluated from those of pure Si and metal silicides based on the Kopp-Neumann rule. \( d \) was calculated from the weight and dimensions of the bulk samples. The Hall carrier concentration (\( n_H \)) and Hall mobility (\( \mu_H \)) were measured using a Hall measurement system (Resitest8300, Toyo) at room temperature by the van der Pauw geometry in vacuum under applied magnetic field of 0.5 T.

3. Results and Discussion

As shown in Fig. 1, the powder XRD patterns of all samples exhibit very sharp peaks of Si as the main phase. In the (Si100P3)97V3 system (Fig. 1 (a)), small peaks of VSi2 [9] can be seen in both of the MS and MS-SPS samples. On the other hand, since NiSi2 has very similar XRD patterns to Si [9] as they have the small lattice mismatch, only peaks for Si can be seen in the (Si100P3)98Ni2 system (Fig. 1(b)). The XRD patterns of the MS and MS-SPS samples are very similar to each other, meaning that the phase states do not change during SPS.

![Figure 1](image.png)

**Figure 1.** Powder XRD patterns of (Si100P3)97V3 and (Si100P3)98Ni2 synthesized by MS and MS followed by SPS.

In Fig. 2, the presence of two phases can be observed clearly, where white dots and dark area correspond to the metal silicide precipitates and Si matrix, respectively. In both the (Si100P3)97V3 and (Si100P3)98Ni2 systems, the nanocomposites containing a few dozen nm size precipitates were obtained in the MS ribbons, while the size increased to several µm size after SPS. The VSi2 or NiSi2 precipitates exist throughout the Si matrix and their size decreases with increasing the Cu roller speed. The estimated average sizes of the VSi2 precipitates are 5 ± 2 µm, 2 ± 2 µm, and 0.5 ± 0.5 µm for MS (2000)-SPS, MS (4000)-SPS, and MS (6000)-SPS, respectively. On the other hand, the estimated average sizes of the NiSi2 precipitates are 8 ± 2 µm and 1 ± 0.5 µm for the MS (2000)-SPS and MS (4000)-SPS, respectively.
Figure 2. SEM images of (Si100P3)97V3. (a) MS (2000), (b) MS (2000)-SPS, (c) MS (6000), and (d) MS (6000)-SPS. SEM images of (Si100P3)98Ni2. (e) MS (2000), (f) MS (2000)-SPS, (g) MS (4000), and (h) MS (4000)-SPS.

As can be seen in Fig. 3, there are no clear trends between \( \mu_H \) and size of the precipitates and matrix grains, while as the size of the precipitates and matrix grains decrease, the \( \kappa_{\text{lat}} \) decreases. As the results, the ratio of \( \mu_H/\kappa_{\text{lat}} \) which is the most important parameter to determine the \( ZT \) increases with decreasing the size of both precipitates and Si matrix grains (Figs. 3(e) and 3(f)).

Figure 3. Effects of size of the silicide precipitates (VSi2 and NiSi2) and Si matrix grains on room-temperature values of the Hall mobility \( \mu_H \), lattice thermal conductivity \( \kappa_{\text{lat}} \), and \( \mu_H/\kappa_{\text{lat}} \) of MS-SPS bulk samples of (Si100P3)97V3 and (Si100P3)98Ni2: (a) \( \mu_H \) vs. size of the metal silicide precipitates, (b) \( \mu_H \) vs. size of the Si matrix grains, (c) \( \kappa_{\text{lat}} \) vs. size of the metal silicide precipitates, (d) \( \kappa_{\text{lat}} \) vs. size of the Si matrix grains, (e) \( \mu_H/\kappa_{\text{lat}} \) vs. size of the metal silicide precipitates, and (f) \( \mu_H/\kappa_{\text{lat}} \) vs. size of the Si matrix grains.

Temperature dependences of \( S \), \( \rho \), \( \kappa_{\text{lat}} \), and \( ZT \) of the MS-SPS bulk samples of (Si100P3)97V3 [7] and (Si100P3)98Ni2 [8] are shown in Fig. 4. In these figures, the data for the samples with the same chemical compositions but synthesized by a traditional arc melting are shown for comparison. These samples are denoted as ARC. In both (Si100P3)97V3 and (Si100P3)98Ni2, the \( S \) values of the MS-SPS samples are almost the same with that of ARC. On the other hand, the \( \rho \) values of the MS-SPS (Si100P3)97V3 samples are slightly higher but those of the MS-SPS (Si100P3)97Ni2 samples are clearly lower than those of the ARC samples. In the (Si100P3)97V3 system, small size of the microstructure leads to increase in the carrier-grain boundary scattering, while in the (Si100P3)97Ni2 system, the NiSi2 precipitates would have little influences on the carrier-grain boundary scattering due to the small lattice mismatch between Si and NiSi2. As shown in Fig. 4 (c), the \( \kappa_{\text{lat}} \) of all MS-SPS samples are significantly lower than those of the
ARC samples, where the metal silicide precipitates scatter heat carrying phonons effectively. In both systems, the MS-SPS samples show higher $ZT$ values than those of ARC samples. The best $ZT$ value is 0.23 at 1073 K obtained for the $(\text{Si}_{100}\text{P}_{3})_{98}\text{Ni}_{2}$ MS (2000)-SPS sample.

Figure 4. Temperature dependences of (a) Seebeck coefficient $S$, (b) electrical resistivity $\rho$, (c) lattice thermal conductivity $\kappa_{\text{lat}}$, and (d) dimensionless figure of merit $ZT$ of MS-SPS bulk samples of $(\text{Si}_{100\text{P}_{3}})_{97}\text{V}_{3}$ [7] and $(\text{Si}_{100\text{P}_{3}})_{88}\text{Ni}_{2}$ [8]. Each TE property was repeatly measured a few times at each measurement temperature; the deviations for $S$, $\rho$, and $\alpha$ were estimated to be 2%, 3%, and 3%, respectively, resulting in approximately 10% deviation for $ZT$.

4. Conclusion
The Si-VSi$_2$ and Si-NiSi$_2$ nanocomposites with the chemical compositions of $(\text{Si}_{100}\text{P}_{3})_{97}\text{Ni}_{3}$ and $(\text{Si}_{100\text{P}_{3}})_{88}\text{Ni}_{2}$ were successfully synthesized by MS followed by SPS (MS-SPS method), where VSi$_2$ and NiSi$_2$ disperse homogeneously throughout Si matrix. The size of the metal silicide precipitates and Si matrix grains is much smaller than those of the ingot samples prepared by a conventional arc melting method and decreases with increasing the rotation speed of the Cu roller in the MS process. The MS-SPS samples exhibit significantly reduced $\kappa_{\text{lat}}$ with keeping high $\mu_{\text{H}}$. In both $(\text{Si}_{100\text{P}_{3}})_{97}\text{Ni}_{3}$ and $(\text{Si}_{100\text{P}_{3}})_{88}\text{Ni}_{2}$, the MS-SPS samples show higher $ZT$ values than those of the ingot samples. The MS-SPS method has a great advantageous for suppressing $\kappa_{\text{lat}}$ with keeping high $\mu_{\text{H}}$, resulting in the enhancement of $ZT$.

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