Thermoelectric Material



Thermoelectric Properties and Transport Mechanism of Pure and Bi-Doped SiNWs-Mg₂Si

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Through the use of nano-Si wires as additive, a significant improvement in the thermoelectric (TE) properties of Mg₂Si is achieved. SiNWs-Mg₂Si materials are prepared by a wet etching method followed by field activated pressure assisted synthesis (FAPAS). The results show that the presence of SiNWs successfully decouples the relationship between the electrical resistivity and the Seebeck coefficient of Mg₂Si. The effect of doping with Bi is also investigated. The results show that the addition of Bi changed the scattering mechanism, and a zT value of 0.47 is determined at 800 K for Mg₂Si_{0.99}Bi_{0.01}-0.005SiNWs. The presence of MgO as an impurity and its effect on zT are discussed.

1. Introduction

It is estimated that about 90% of the power generated in the world is by engines using combustion of fossil fuel with efficiencies of <40%. Consequently, about 10¹³ Watts are produced as waste heat to the environment.^[1] Thermoelectric (TE) functional materials can be utilized to directly convert waste heat energy into electric energy.^[2,3] The success of the TE materials in the utilization of waste heat is determined by the dimensionless figure of merit *zT*, which is defined as $zT = (a^2 \sigma T)/\kappa$, where *a*, σ , κ , and *T* are, respectively, the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature. Efforts to increase the *zT*values focus, obviously, on increasing *a* and σ and decreasing κ . Investigations aimed at increasing *zT* for several classes of TE materials have been made. These include silicides,^[4–7] half-Heuslers,^[8,9] and tellurides (e.g., those of Bi,^[10–12] Pb,^[13,14] and Ge^[15,16]). Of the silicides, that of magnesium, Mg₂Si, and its solid

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solutions have received a great deal of attention as TE materials for energy conversion in the mid-to-high temperature range. This is, in part, due to their low cost, non-toxicity, lightweight, and the abundance of their constituent elements.^[5]

As indicated above, increasing the figure of merit requires increasing both the Seebeck coefficient, *a*, and the electrical conductivity, σ . However, for materials with band-like transport, there is an inverse relationship between *a* and σ ,^[17] and thus there is need to devise methods to decouple these parameters. Using silver nanowires (AgNWs) in bulk conducting polymers, Liu

et al.^[18] reported such a decoupling, showing an increase in σ without a noticeable decrease in *a*. This observation is consistent with previous reports showing that the use of low-dimensional structures, such as superlattices and nanowires, could lead to higher *zT* values.^[19] Such a benefit can also be the result of a significant reduction in the thermal conductivity, another factor in increasing *zT*, as has been reported by Hochbaum et al.^[20] and Boukai et al.^[4] through the use of silicon nanowires (SiNWs), and by Hasegawa et al.^[21] for Bi and Si wires.

Recently, Yi et al.^[6] investigated the TE properties of Mg₂Si in which silicon nano-dots were introduced and found a significant reduction in its thermal conductivity. It was also shown that a zT value of 0.6 could be achieved at room temperature in rough SiNWs of \approx 50 nm diameter.^[20] The achieved zT value is 60 times that of bulk silicon. Thus, it seems reasonable to expect that the addition of SiNWs to bulk Mg₂Si, to form micro-nano composites, would lead to enhancement of the figure of merit. In this paper we report results of an investigation on the effect of incorporating SiNWs on the TE properties of pure and Bi-doped Mg₂Si.

2. Experimental Section

To prepare SiNWs, we started with n-type silicon wafers with <100> crystalline orientation and a resistivity, ρ , of 0.01–0.001 Ω cm. Each wafer was etched for 2.5–3.0 h in a bath containing a mixture of 0.035 mol L⁻¹ AgNO₃ and 20 wt.% HF. Then the wafer was placed in a solution of 60 wt.% nitric acid (HNO₃) and held there for 30 min so that the resulting silver wires, as by-product of wet etching, could be removed from the surface. Then the wafer was washed in an ethanol bath for 5 min under the action of an ultrasonic agitation. During this step, the SiNWs fell off the silicon wafer. The collected SiNWs were then dried under vacuum.

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Figure 1. a) Surface morphology of etched Si wafer; (b) synthesized silicon nano-wires; (c) XRD patterns of prepared samples; solid diamond (\blacklozenge) denotes the MgO impurity phase; (d) Fracture surface morphology of Mg₂Si-0.005SiNWs; (e) and (f) high resolution TEM images of Mg₂Si-0.005SiNWs. The inset in (a) shows a magnified view of the surface; the inset in (e) shows an enlarged view of a SiNWs; the inset in (d) shows fracture surface macro-morphology of Mg₂Si-0.005SiNWs; the inset in (f) shows the fast Fourier transform pattern of the Mg₂Si-0.005SiNWs composite.

To prepare samples of Mg₂Si-*x*SiNWs (x = 0.0, 0.003, 0.005, 0.01) and Mg₂Si_{1-*y*}Bi_{*y*}-*x*SiNWs (y = 0.01, 0.015, 0.02), we started with powders of magnesium (\leq 75 μ m, 99.99% pure), silicon (\leq 75 μ m, 99.99% pure), and bismuth (\leq 75 μ m, 99.99% pure), plus the prepared SiNWs, as described above. All powders (Mg, Si, and Bi) were obtained from Aladdin, Shanghai, China.

The magnesium and silicon powders were mixed in an Mg:Si ratio of 2.05:1 to synthesize undoped Mg₂Si-*x*SiNWs. They were ball-milled together for 30 min in a polytetrafluoroethylene (PTFE) jar to obtain a homogeneous mixture using a QM-3B high-speed vibratory mill. For preparation of the bismuth doped samples, powders of silicon with different contents of bismuth were ball-milled for 8 h at 15-min intervals. The crystallite size of the milled powder, as determined by XRD, was less than 100 nm. Then magnesium and the SiNWs were added to the jar with a molar ratio of Mg: Si_{1-y}Bi_y: *x*SiNWs of 2.05:1:*x*. The mixture was then ball-milled for 30 min to obtain Mg₂Si_{1-y}Bi_y-*x*SiNWs. Mg was added with an excess of 2.5% over its stoichiometric amount to compensate for loss due to evaporation and oxidation during the process.

About 2 g of each mixture were loaded into a graphite die having an internal diameter of 20 mm for reaction and consolidation, as described in previous papers.^[22–24] All materials were handled under an argon gas atmosphere inside a glove-box. The mixed powder inside the die was rapidly heated to 908 K in the FAPAS system, described adequately in previous investigations.^[22–24] Heating was done by the application of a direct current of 300–1000 A and a dwell time of 3 min. A pressure of 60 MPa was applied during this time. Then the temperature was increased to 1023 K and held there for 15 min. After that, the power was turned off and the sample was allowed to cool naturally. During the entire reaction and sintering process, a vacuum level of less than 18 Pa was maintained. The density of the annealed samples was measured at more than 99% of the theoretical value. Finally, the samples were cut into appropriate sizes and polished for observations and measurement.

Phase composition and microstructure of the prepared samples were determined by X-ray diffraction (XRD, KEVEX, SIGMA, TD-300XRD, Cu target), scanning electron microscopy (SEM, Zeiss 1550 VP), and TEM (JEOL2100F). The Seebeck coefficient was measured using a light-pipe method with tungsten–niobium thermocouples under high vacuum.^[25] Hall coefficient and resistivity measurements were made by the four-probe Van der Pauw method with a 0.8T magnetic field under high-vacuum conditions.^[26] The thermal conductivity was calculated by the relationship $\kappa = \rho DC_p$, where ρ is the sample density (calculated by the Archimedes method), D is the thermal diffusion coefficient (measured on a NetzschLFA-457 laser thermal conductivity instrument), and C_p is the Dulong–Petit heat capacity value reported by Schiltz and Riffel.^[27]

3. Results and Discussion

3.1. Microstructural Characterization

The morphology of an etched surface of the Si wafer is shown in **Figure 1a**. The figure shows closely interconnected pores which are arrayed in a perpendicular direction to the surface. An enlarged view of the surface features is shown in the inset in Figure 1a. In this figure, uniform and vertically aligned SiNWs can be discerned. The vertical orientation of the SiNWs is believed to be the consequence of gravity effect during etching. Furthermore, the observed bunching of the silicon wires is likely







Figure 2. Temperature dependence of the: (a) Seebeck coefficient, α ; (b) electrical resistivity, ρ ; and (c) power factor *PF* of Mg₂Si-*x*SiNWs (x = 0.0, 0.003, 0.005, 0.01): inset in (a): schematic diagram of the energy filtering effect^[28,29] (grain boundary potential E_b; bottom of conduction band E_c; top of valence band E_v).

the result of electrostatic attraction. The morphology of typical Si wires is shown in Figure 1b. The wires had a relatively smooth surface and a diameter of about 100 nm. Figure 1c shows the XRD patterns of all sample compositions. The figure show $2\theta = 43^{\circ}$, which is attributed to MgO. This peak becomes less evident as the amount of Bi in the sample is increased. The microstructure of a fracture surface of a sintered sample of Mg₂Si-0.005SiNWs is shown in Figure 1d. The image reveals a lamellar polycrystalline structure, in which the interlamellar distance is less than 300 nm (shown in inset). It shows no discernable porosity or inclusions, indicating that the synthesis of highly dense products was achieved. The figure also shows a single SiNW embedded in the matrix, an observation providing evidence that silicon nano-wires survived the consolidation process. A TEM image of the Mg₂Si-0.005SiNWs composites is shown in Figure 1e. The figure shows dispersed SiNWs in the matrix (marked in square), each nano-wire having a diameter of about 100 nm (magnified image in inset). Figure 1f shows the interface between SiNW and the Mg₂Si matrix, indicating that bonding between the wire and the matrix was achieved. The fast Fourier transform (shown as an inset in Figure 1f) shows a pattern representing the cubic Mg₂Si crystal structure of the matrix. The inset figure also shows darker spots which are of the nano-silicon phase.

3.2. Effect of SiNWs on the TE Properties of Mg₂Si

The temperature dependence of the Seebeck coefficient and the resistivity of Mg₂Si-xSiNWs (x = 0.0, 0.003, 0.005, 0.01) over the range of 300–775 K is shown in Figures 2a and 2b, respectively. The figures show an increase in both parameters as a result of the addition of SiNWs to Mg2Si. The increase in the Seebeck coefficient is likely due to the introduction of interfaces between the SiNWs and the Mg₂Si matrix, which improve the coefficient by filtering out the lower energy carriers. The energy filtering effect (shown schematically^[28,29] in the inset of **Figure 2**a) allows the higher energy carriers to across the barrier, resulting in an increase in the density of states near the Fermi level, and thus an enhancement of the Seebeck coefficient. Theoretical calculations on the increase in the Seebeck coefficient by an energy filtering effect have been reported.^[30-32] And similar observations have been reported in the literature.^[33–35] The electrical resistivity, ρ , is determined by the number of charge carriers, n, and by their mobility, μ , with $1/\rho = ne\mu$. That is, a high carrier concentration (seen in Figure 3a) gives rise to a low resistivity as expected.^[6] Heremans et al.^[34,35] reported that the energy filtering effect

the carrier mobility in bulk nanostructured PbTe-based materials. In the present work, the addition of SiNWs to Mg₂Si







Figure 3. Temperature dependence of the: (a) carrier density, n_{Hi} (b) carrier mobility, μ_{H} of Mg₂Si-xSiNWs (x = 0.0, 0.005).

appears to have decoupled the relationship of the Seebeck coefficient and mobility successfully, as well as the resistivity. Consequently, the power factor for samples with x = 0.005 has been significantly increased, by a factor of more than 3 at lower temperatures (400 K) and a factor of more than 2 at higher temperatures (725 K), as seen in Figure 2c.

From the results plotted in Figure 2a-c, it can be seen that samples with x = 0.005 (i.e., Mg₂Si-0.005SiNWs) have the best values for the Seebeck coefficient, resistivity, and power factor. Consequently, this composition became the focus of further study. A decrease in resistivity is typically attributed to an increase of both carrier concentration and carrier mobility. In this work, the introduction of SiNWs was found to lead to a small increase in the carrier concentration before thermal excitation commences at about 550 K, as shown in Figure 3a. The increase in carrier mobility is mainly due to the role of SiNWs as a one-dimensional high-speed channel for carriers. A similar phenomenon was observed in bulk materials with nano-rods, in which the latter provide charge carrier transport pathways.^[36] The main carrier scattering mechanism can be predicted theoretically from the dependence of the mobility on temperature. In Figure 3b it is seen that the mobility decreases with increasing Tas $\widetilde{T^{-3/2}}(\mu \sim T^{-p})$, which indicates that acoustic phonon scattering dominates the carrier transport in this sample, as for non-degenerate semiconductors.^[37,38] Comparing the trends of the lines in Figure 3b, it can be concluded that the addition of SiNWs does not change the carrier scattering mechanism of Mg₂Si.

The temperature dependence of the total thermal conductivity of Mg₂Si-*x*SiNWs is shown in **Figure 4**. The figure shows a small decrease in the total thermal conductivity as a result of the addition of SiNWs over the entire temperature range. Besides the lower thermal conductivity of the SiNWs themselves, the interface scattering of phonons with different wavelengths by both nanointerface and defects also contributes to the decrease. The lattice thermal conductivity from the total, that is, $\kappa_L = \kappa - \kappa_e$. We calculated the electronic thermal conductivity, $\kappa_e = L_0 T/\rho$, where L_0 , *T*, and ρ are the Lorenz number, the absolute temperature, and the resistivity, respectively. The room temperature L_0 value is about $2.2 \times 10^{-8} W\Omega K^{-2}$.^[39] As shown in the inset of Figure 4, the relationship between lattice thermal conductivity and temperature is of the form $\kappa_L \sim T^{-1}$, indicating that phonon scattering remains the main scattering mechanism of phonon transport.^[40]

The dependence on temperature of the calculated zT values of Mg₂Si and Mg₂Si-*x*SiNWs samples is shown in **Figure 5**. It is clearly evident that a very significant improvement in zT is obtained as a result of the addition of SiNWs. When the content of SiNWs is 0.005, an improvement by a factor of more than 4 at 625 K is seen. However, notwithstanding this improvement, the zT values for the Mg₂Si-*x*SiNWs samples are too low for practical considerations. Our focus then turned toward doping of these samples.

3.3. Complex Effect of the Addition of SiNWs and Bi on $\mathsf{Mg}_2\mathsf{Si}$

It has been reported that the combination of a nanocomposite structure along with the doping by a heavy atom, such as Bi, can



Figure 4. Temperature dependence of the total thermal conductivity of Mg_2Si -xSiNWs (x = 0.0, 0.003, 0.005, 0.01). (The inset shows the lattice thermal conductivity of SiNWs- Mg_2Si).







Figure 5. Temperature dependence of zT of Mg₂Si-xSiNWs (x = 0.0, 0.003, 0.005, 0.01).

provide a large number of carriers to optimize the TE properties of Mg₂Si.^[6,41,42] To understand the effect of SiNW on the transport properties of heavily doped Mg₂Si, we prepared samples with additions of Bi. **Figure 6** shows the thermoelectric properties of the Mg₂Si_{1-y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$) samples. As can be seen from Figures 5 and 6a, the heavy doping effect is the main part of optimizing the figure of merit values. Also seen from Figure 6a is that the 0.01 Bi doped nanocomposite has the best performance with a figure of merit of about 0.47 at 800 K. This value is lower than that for Mg₂Si_{1%Bi} with nano-silicon particles reported previously for the same temperature,^[6] and is primarily due to a lower Seebeck coefficient (Figure 6c) and a higher total thermal conductivity (Figure 6d). These differences are attributed mainly to the different processing methods utilized.

The resistivity of all Bi-doped Mg₂Si-0.005SiNWs samples slightly increased with increasing temperature over the entire range, Figure 6b. The figure shows that samples with nano-silicon wires have lower resistivities than those of samples with nano-silicon particles^[6] at lower temperatures (300–550 K), and



Figure 6. Temperature dependent of: (a) *zT* value of Mg₂Si_{1-y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$) and the 2.5 mol% Si doped Mg₂Si_{1%Bi} literature data.^[6] (b) Electrical resistivity ρ of Mg₂Si_{1y}Bi_y-0.005SiNWs ($\gamma = 0.01, 0.015, 0.02$) and the 2.5 mol% Si doped Mg₂Si_{1%Bi} literature data.^[6] (c) Seebeck coefficient, α and (d) total thermal conductivity κ of Mg₂Si_{1y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$) and the 2.5 mol% Si doped Mg₂Si_{1%Bi} literature data.^[6] (c) Seebeck coefficient, α and (d) total thermal conductivity κ of Mg₂Si_{1y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$) and the 2.5 mol% Si doped Mg₂Si_{1%Bi} literature data.^[6] The inset (I) and (II) show the temperature dependence of electrical resistivity ρ and the power factor PF of Mg₂Si_{1-y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$), respectively. The inset in (d) shows the temperature dependence of lattice thermal conductivity κ_L Mg₂Si_{1-y}Bi_y-0.005SiNWs ($\gamma = 0.0, 0.01, 0.015, 0.02$).







Figure 7. Temperature dependence of the carrier mobility of $Mg_2Si_{1,y}Bi_{y}$ -0.005SiNWs (y = 0.0, 0.01, 0.015, 0.02).

about the same values at higher temperatures. The lower total thermal conductivity of the Si-particle samples^[6] is likely due to the high density of grain boundaries resulting from the use of MgH₂ as a starting material, which results in the formation of Mg₂Si with a grain size as fine as 100 nm.

The use of nanowires is expected to reduce the total thermal conductivity, but as seen in Figure 4, the reduction is not evident, a result that is likely due to the low content of the added nano-wires. Another likely contributor to the difference between the results of this work and those reported for samples containing Si-particles^[6] is the presence of MgO as an impurity. When MgH₂ is used as a starting material, there is no evidence for the presence of MgO in the synthesized Mg₂Si samples. This is in contrast to samples of this study which showed the presence of minor amounts of MgO, Figure 1c. The presence of MgO has a deleterious effect through its high thermal conductivity, $\approx 300 \,\mathrm{mW \, cm^{-1} \, K^{-1}}$.^[43] It has also been shown that the presence of MgO contributes to a reduction in the electrical conductivity of Mg₂Si due to a decrease in the Hall mobility.^[44] The presence of a few percentages of MgO has been shown to result in a 30% reduction in the zT value,^[44] implying that the best value in this study can be as high as ≈ 0.7 if no MgO was present.

While a clear advantage for the use of SiNWs as additions to Mg_2Si can be seen in this study, possible refinements in the synthesis and processing method are likely to lead to further optimization. For example, the use of MgH_2 as a starting material, and the employment of a one-step synthesis and consolidation process will lessen the disadvantages of external mixing, oxidization, and impurity contamination, and thus could positively impact the final properties of the TE material.

The nature of the scattering mechanisms of carriers can be deduced from a plot of $log(\mu)$ versus log(T), as shown in **Figure 7**. The carrier mobilities determined in this study decreased with increasing temperature, and for any given temperature, the mobility decreases with an increase in the Bi content. From the

relationship $\mu \sim T^{-p}$, Figure 7 shows that a *p*-value of 1 provides the best fit for our results. For degenerate semiconductors (such as heavily doped semiconductors), the acoustic phonon scattering is the main scattering mechanism with a relationship $\mu \sim T^{-1}$,^[45] which can explain the faster decrease of mobility at high temperatures. The experimental data in the literature^[6] match the fitting of $\mu_H \sim T^{3/2}$ and $\mu_H \sim T^{-3/2}$ at low and high temperature ranges, respectively, indicating scattering by grain boundaries and Si inclusions. Compared with silicon particles,^[6] nanowires as high-speed carrier channels can improve the mobility in the matrix, so the scattering is relatively weakened. With the addition of the heavy element, Bi, the performance of the matrix is greatly improved.

4. Conclusion

It was shown that a significant improvement in the power factor, *PF*, of Mg₂Si can be achieved by the addition of SiNWs. For x = 0.005, the power factor increased by more than a factor of 3 at lower temperatures (400 K) and more than a factor of 2 at higher temperatures (725 K) relative to that of intrinsic Mg₂Si. A more significant result of the incorporation of SiNWs, however, is the accomplishment of the decoupling of the Seebeck coefficient and the resistivity. The electrical properties and the Seebeck coefficient of the samples were significantly improved. The addition of 0.005 SiNWs reduced the total thermal conductivity of the samples by 8–10%, but it did not change the phonon scattering mechanism. When 0.01 Bi was added for samples containing 0.005 SiNWs, a *zT* value of 0.47 was obtained at 800 K.

Further optimization of the TE properties of Mg_2Si with Si nano-wires is likely through modification in the synthesis and processing method. The use of MgH_2 as a starting material and the employment of the one-step synthesis and consolidation process will likely lead to improvements in the TE property.

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Conflict of Interest

The authors declare no conflict of interest.

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