Synthesis and thermal transport of eco-friendly Fe-Si-Ge alloys with eutectic/eutectoid microstructure

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HIGHLIGHTS

- Eutectic/Eutectoid processing strategy to produce novel hierarchical microstructure.
- Thermal conductivity of FeSi2/Si semiconducting nanocomposite can be reduced with a few at% Ge.
- Local Ge incorporation into Si1-xGex nanoinclusions can be controlled via processing.
- Ge incorporation can reduce the η/Si1-xGex thermal boundary conductance by 91%.
- Local composition can supersede length scales, and may enhance thermal stability.

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ABSTRACT

The β-FeSi2/Si semiconducting nanocomposite is a promising thermoelectric system with eco-friendly materials. We show that small quantities of Ge can enhance the thermoelectric properties and widen the design space, if Ge content and spatial disposition can be controlled. We investigated the use of solidification combined with solid-state transformations to reduce the thermal conductivity via hierarchical modification of microstructure. Solidification of Fe28Si68Ge4 alloys leads to eutectic lamellar microstructure comprised of hyperstoichiometric α-FeSi2+h phase and diamond cubic Si1-xGex. The eutectic length scales can be varied over two orders of magnitude depending on solidification rate. Subsequent aging of the eutectic produces eutectoid decomposition, α-FeSi2 → β-FeSi2 + Si1-xGex, where the additional diamond cubic product is interleaved with the eutectic lamellae. By controlling both the frequency of β-FeSi2/diamond cubic heterogeneous interfaces, as well as the degree of Ge segregation into the eutectoid micro constituent, the thermal conductivity of the composite was varied from 22.8 W m⁻¹ K⁻¹ down to 8.3 W m⁻¹ K⁻¹. We analyze the thermal conductivity in terms of a series thermal resistance model, including thermal boundary conductances at the heterointerfaces, and show that the thermal boundary conductance is reduced by at least an order of magnitude when the diamond cubic micro constituent is enriched from 0 to 30 at% Ge. Avenues for additional microstructural improvements towards thermoelectric applications are discussed.

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1. Introduction

Current means of energy production are highly inefficient and the majority of the energy produced is released into the environment as waste heat [1]. Recapturing even a trivial percentage of this waste heat would equate to a significant amount of energy annually. Thermoelectrics are solid state materials capable of converting a thermal gradient into an electrical current. A material’s thermoelectric efficiency is quantified by a dimensionless figure of merit, $zT = S^2\sigma T/k$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $S^2\sigma$ is the power factor, $k$ is the thermal conductivity, and $T$ is the temperature. Optimizing these parameters is nontrivial, as they are intricately interconnected. While modern thermoelectric materials have advanced $zT$ in recent decades by exploiting complex crystal structures, nanojunctions, and small grain sizes [2], current materials remain costly and inefficient, and thermoelectrics are still largely used only in niche applications.

This paper will investigate a potential approach to improve the thermoelectric properties of the $\beta$-FeSi$_2$ system. This is motivated by the inexpensive, abundant, and non-toxic constituents providing the potential for an economical, and eco-friendly, thermoelectric materials system for harvesting waste heat, $\beta$-FeSi$_2$ is one of the few semiconducting transition metal silicides ($E_{gap} \approx 0.78$ eV) [3], with a complex Cmca crystal structure that contributes to a naturally high Seebeck coefficient and low thermal conductivity [4]. It is oxidation resistant to 900 K and has a high operational temperature that makes it ideal for hot environments. However, the thermoelectric performance is limited by the poor electrical conductivity [5]. Together these properties contribute to only a modest $zT$, with the highest reported value being $zT = 0.4$ at 700 K for Co-doped $\beta$-FeSi$_2$ [6]. In the binary Fe-Si system, the metallic $\alpha$-FeSi$_{2.5}$ (a ≈ 0.3) phase is stable at high temperatures, but decomposes through a eutectoid isotherm at 937 C to stoichiometric $\beta$-FeSi$_2$ and diamond cubic (DC) Si [7].

Zhao et al. [8] suggested that hierarchical control and optimization across multiple length scales could significantly improve $zT$. Here we will show that the Fe-Si-Ge ternary system provides opportunities for creating hierarchical structures by exploiting a strategy combining both liquid and solid state processing. Eutectic solidification leads to lamellar microstructure, L → $\alpha$-FeSi$_{2.5}$ + Si$_{1-x}$Ge$_x$. Subsequent eutectoid decomposition, $\alpha$-FeSi$_{2.5}$ → $\beta$-FeSi$_2$ + Si$_{1-y}$Ge$_y$, results in a second level of structural inhomogeneity, interleaved within the eutectic lamellae. Length scales of the eutectic microconstituents are controlled by the solidification rate, while length scales of the eutectoid are dictated by the aging temperature and time. Inherently, there is a third structural length scale, which is the grain size, or more accurately, the pearlitic colony size. Just as importantly, the segregation of the overall Ge into the different microconstituents plays a major role in determining thermal conductivity, and likely the electrical conductivity of the system as well.

Eutectoid decomposition of the binary Fe-Si system ($\alpha$-FeSi$_{2.5}$ → $\beta$-FeSi$_2$ + Si) has already been explored as a way to enhance thermoelectric performance. Kinetics of the eutectoid decomposition have been established via time-temperature-transformation (TTT) diagrams for undoped and lightly doped systems [9] [10] [11], and it has been shown that increased volume fraction of Si [12] and finer eutectoid length scales [13] [14] [15] appreciably improve thermoelectric performance. Our previous work [15] showed that nanostructuring of the eutectoid DC microconstituent was achieved by annealing at large undercooling, thereby increasing the $\beta$/Si interface density. This effectively reduces thermal conductivity of the nanocomposite, although the effects of two-phase decomposition on the power factor are still unknown. A new strategy that could significantly improve the performance of these materials is to create ternary Fe-Si-Ge alloys. Alloying Fe-Si with Ge provides an additional degree of freedom to enhance thermoelectric properties. Ge alloying can reduce thermal conductivity via both alloy scattering of phonons [16] and, as will be shown in this work, through modification of the thermal boundary conductance of the hetero-interfaces [17] [18] [19] [20] [21]. Ge additions to the DC phase will also reduce the bandgap [22], thereby reducing band offsets with the $\beta$ phase. Mohebali et al. showed that spark plasma sintering P-doped SiGe with Co-doped $\beta$-FeSi$_2$ yields a sharp increase in power factor and $k$. When compared to the control sample, the Ge additions increased $zT$ by nearly 2× with a final value of 0.54 [23]. However, in their work, the nature of the resulting microstructure and its connection to the thermoelectric properties was not reported.

This paper discusses the hierarchical microstructures produced through process control of eutectic and eutectoid transformations and their effect on thermal conductivity. Different from the sintering approach of Mohebali et al. [23], we explore the effects of casting ternary Fe-Si-Ge alloys. In particular, we examine the microconstituent length scales and compositions resulting from arc melting, which produces relatively low solidification rates, and melt-spinnning, which produces much higher solidification rates. We will show that the disposition of the Ge in the eutectic and eutectoid microconstituents is strongly affected by the casting conditions. Thermal conductivity was measured for the various samples and the interface thermal boundary conductance was determined as a function of Ge content in the eutectoid microconstituent, Si$_{1-y}$Ge$_y$. We show that carefully controlling solidification rate and eutectoid decomposition of the ternary alloy leads to microstructural and compositional control over the thermal conductivity. In particular, we show that the Ge content in the diamond cubic phase can greatly reduce the $\beta$/DC thermal boundary conductance.

2. Materials and methods

Bulk samples were prepared via arc-melting from a charge composed of Fe (99.999%), Si (99.999%+), and Ge (99.999%) in a thoroughly evacuated chamber backfilled with ~500 Torr argon atmosphere. The arc was initially struck on a Ti getter to minimize oxygen contamination. A ~50 g charge was melted consecutively via a high-current arc on different sides to ensure homogeneity. The melt was then allowed to cool slowly (cooling rate of order 10$^2$ C/ sec) to room temperature on a water chilled Cu crucible. In order to evaluate the effects of cooling rate on microstructure, half of this boule was sectioned off for melt-spinning. Remelting was performed in the same chamber under the same initial conditions, but where the Cu crucible was fitted with a 2 mm diameter boron nitride aperture leading to a rotating copper plate. Capillary forces contain the melt in place, sealing the aperture and effectively dividing the chamber in two. Argon gas was backfilled into the upper chamber until a pressure differential of about 380 Torr was reached, forcing the melt through the aperture onto the Cu plate, rotating at 1200 rpm, and the solidified ribbon was thrown into a collection arm. Bulk compositional analysis was performed on the slow-cool sample by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). Roughly 40 mg of the slow-cool sample was digested in a 3:2 solution of HNO$_3$ and HF, and was analyzed three times in order to determine error. The bulk composition was found to be Fe$_{29}$Si$_{66}$Ge$_{4}$. The Ge content was not explicitly varied here, although this is of interest for future work. Here, our emphasis is on controlling and determining how Ge partitions throughout the microstructure as a function of process variations.

Samples were subjected to isothermal aging to foster eutectoid
decomposition. Each sample was encapsulated in a fused quartz ampoule that was evacuated to 5 mTorr and backfilled with Ar. This was cycled three times, with the second to last including a slight heating of the quartz tube, in order to remove any residual water vapor. The final Ar backfill was to a pressure of ~180 Torr. The ampoules were aged in a tube furnace and then quenched to room temperature in water. The ribs were fragile and required careful mounting in conducting epoxy and polishing for microstructural characterization.

Prior to scanning electron microscopy (SEM), all samples were polished to mirror finish with 0.05 μm diamond spray. Over the course of polishing ~1-2 mm of material was removed from the bulk samples and ~10-20 μm for the ribbons. SEM was performed in a FEI Quanta 650 operated at 10 KV, primarily in backscatter detection mode (BSE) for enhanced compositional contrast. Select samples were further examined using electron backscatter diffraction (EBSD) to obtain β + Si colony size and crystallographic orientation. To remove surface deformation prior to EBSD scans, these samples were finished with a vibratory polish with 0.05 μm colloidal silica. EDS was used for areal chemical analysis of microconstituents from high resolution compositional maps. Chemical composition of a single phase was determined by areal sampling and averaging; these measurements were then averaged with measurements from the same phase in different areas of the sample. This provides a much broader dataset than would be achieved by point analysis, and is more indicative of the actual composition. SEM images were also used to determine the length scales of microconstituents and the interface density by the method of linear intercepts. Representative micrographs from each sample were typically analyzed with 45 lines, so that the size and spacing for each microconstituent was averaged over multiple measurements. Lengthscale analysis was performed in ImageJ.

Powder X-ray diffraction (XRD) samples were prepared via grinding with a mortar and pestle. The powder from several ribbons weighs less than a milligram, so procuring large amounts of powder is infeasible. The powder from several ribbons was collected on one side of a clean strip of double sided tape and was carefully fixed to a quartz zero diffraction plate. XRD data was obtained from a PANalytical X’Pert Pro MPD for phase identification and Rietveld refinement. High-resolution data was obtained by scanning from 15 - 80° 20 for 10 h to ensure a broad spectrum with high signal to noise ratio. Rietveld refinement is a technique that utilizes the least squares method to fit a theoretical XRD spectrum to a measured one.

Transmission Kikuchi diffraction (TKD) [24] was used to determine the composition and orientation of microconstituent phases, but at lengthscales much finer than possible through SEM-EDS. A sufficiently large aged ribbon was fixed onto a Cu specimen mount with a 2 mm aperture, and ion milled (Gatan, Precision Ion Polishing System) for ~3 h with guns at 10° (top) and 5° (bottom). After a hole pierced the sample, the angles were reduced to 5° and 2° respectively, and the sample was milled for another hour. The stage was cooled with liquid nitrogen to suppress beam-induced phase transformations.

Thermal conductivity was measured via time domain thermoreflectance (TDTR) [25] [26] [27] at room temperature. TDTR is an optical pump-probe measurement technique that utilizes a train of ultra-fast laser pulses to induce a modulated heating event and measure the temperature dependent change in reflectance of the sample surface between pulses. The heat capacity of the two-phase material was determined by a weighted sum of β-FeSi2 [28] and Si [29] according to their volume fractions. The heat capacities of Si and Ge are nearly equivalent, so the Si value was used for thermal conductivity calculations for all Si1-xGe x. The small spot size and shallow penetration depth of the incident beam make it an ideal technique for thermal conductivity measurements of challenging samples, such as epoxy mounted ribbons, where the beam can be positioned to avoid fractures in the slow-cool sample, which would otherwise bias the measured thermal conductivity.

3. Results and discussion

We will refer to samples produced from direct arc melting as “slow-cool” and those produced from melt-spinning as “rapid-cool”. The mean cooling rate of the melt-spun material is estimated as 106 °C/s, vs. 101 °C/s from the arc melt.

As-cast, the slow-cool sample exhibits eutectic microstructure with an α-FeSi2-δ matrix containing DC SiGe lamellae (Fig. 1a). Close examination of the lamellae show that copious amounts of α-FeSi are entrained within them (Fig. 1b). Fractures are present throughout the sample, but the interlamellar regions are typically free of cracks. Fracture is likely caused by large thermal gradient stresses generated during cooling of the boule. The relatively slow cooling rate promoted growth of coarse eutectic microstructures: DC lamellae with thicknesses of 44 ± 11 μm and interlamellar spacing of 131 ± 44 μm, based on linear intercept analysis. This results in an effective density of DC/α-FeSi2-δ interfaces of 0.01 interfaces/μm. The low interface density, presence of metallic α-FeSi, and cracks are deleterious to the thermoelectric properties.

The 50 μm thick, melt-spin ribbons, although brittle, do not exhibit cracking. Formation of the ε phase was suppressed, only appearing in low amounts on the ribbon surface. The melt-spin sample increased the solidification rate four orders of magnitude vis-à-vis the slow-cooled sample. As can be seen in Fig. 1 c, the faster rate significantly reduced the eutectic lengthscale: the average lamella thickness was 129 ± 60 nm with an interlamellar spacing of 1.5 ± 0.5 μm. As a result, the DC/ε interface density increased fifty-fold, to 0.54 interfaces/μm. Both the rapid-cool and slow-cool samples were analyzed with EBSD and it was determined that the SiGe lamellae grow along the (001) habit plane of tetragonal α-FeSi2-δ; however, we have not identified any specific in-plane orientation relation between the DC and ε phases.

Subsequent isothermal aging caused eutectoid decomposition of the ε phase into pearlitic colonies of β + Si. This decomposition appears to proceed similarly to that observed in the Fe-Si binary system, resulting in eutectoid lamellae having similar dimensions and morphologies for similar aging conditions. The eutectoid Si initially forms as lamellae, but then evolves into nanowires with continued heat treatment. The slow-cool (Fig. 2a) and the rapid-cool (Fig. 2b) samples were aged at 567 °C for 120 h (slow-cool + 567 °C/120 h) and 56 h (rapid-cool + 567 °C/56 h) respectively, to fully decomposed the ε phase into pearlitic β + Si. This results in a local interface density of ~11.0 DC/DC interfaces/μm for each sample. At these aging temperatures the eutectoid lamellae do not significantly coarsen or evolve.

For the slow-cool sample, the coarse eutectic structures do not constrain pearlitic colony size, and they only provide a negligible area for heterogeneous nucleation sites; hence a longer time is required to obtain complete transformation. While the average colony diameter was not measured for the slow-cooled sample, we assume that the value is similar to a binary (Fe-Si) sample aged at 567 °C for 56 h (slow-cool + 567 °C/56 h), with an average diameter of 16.0 ± 15.3 μm [15]. However, the melt-spun samples have significantly higher nucleation rate for pearlitic colonies, where the fine eutectoid lamellae provide facile and abundant nucleation sites. When aging is initiated below the eutectoid isotherm in this sample, Si locally diffuses to epitaxially grow on the eutectic lamellae, which leaves Si-depleted regions adjacent to the eutectic lamellae. These regions have a higher chemical driving force for β nucleation, which initiates cooperative lamellar growth [30]. As a result, the
eutectoid transformation reaches near complete decomposition at 567 °C for 56 h, without requiring a Cu accelerant [31]. The mean pearlitic colony size is only 800 ± 490 nm, due to both the higher nucleation density and steric restrictions on growth due to the fine eutectic lamellae. EBSD maps and the resultant colony diameter distributions can be found in the Supplementary Information.

An additional melt-spun ribbon was aged at 900 °C for 9 days (rapid-cool + 900 °C/216 h) to produce a coarsened, spheroidized microstructure (Fig. 2c) with the microconstituents ostensibly at their equilibrium compositions. For temperatures above ~700 °C [15] the eutectoid interlamellar spacing exceeds the eutectic interlamellar spacing; hence the Si and Ge atoms released by eutectoid decomposition diffuse directly into the pre-existing eutectic lamellae. Simultaneously, the lamellae also break up into quasi-equiaxed particles. The DC particles have average 1.0 ± 0.9 μm diameter and are spaced 2.4 ± 1.7 μm apart.

The disposition of Ge through the hierarchical eutectic/eutectoid decomposition process is of great interest as the interplay between phases and their composition is important for thermal and electronic transport. When the solidification front velocity is comparable to solute diffusion, as it is for rapid solidification, solute uptake into the solid can exceed equilibrium concentrations [32] [33]. Melt-spinning not only reduces eutectic length scales, but also changes the composition of the microconstituents, as shown in Table 1. EDS-SEM shows that the composition of the as-cast slow-

![Image](image_url)
cool α phase was on average Fe24.6Si77.4Ge1.0. The Ge content of the rapid-cool ribbon nearly doubled to Fe24.8Si77.2Ge1.0. Aging the ribbon above 1000 °C (which is above the eutectoid isotherm) caused the α composition to evolve to ∼1.6 at% Ge; the combined results suggest that the solid solubility limit of Ge in the α-phase is 1.6 at% near 1000 °C. The composition of the α phase is important because the amount of Ge present governs the Ge content of the eutectoid DC lamellae after decomposition. Chemical analysis of the β phase (only) was performed by transmission EDS on the rapid-cool + 567 °C/56 h sample, this technique produces finer resolution composition maps than are otherwise possible with standard SEM-EDS. Fig. 3 illustrates the disposition of Ge after the eutectoid decomposition. The majority of the Ge entrained in the α phase was ejected along with Si into the eutectoid nanowires, leaving the composition of the β phase as Fe34.7Si64.4Ge0.6. EDS was performed on the β phase of the rapid-cool + 900 °C/216 h sample, and composition was determined to be Fe34.7Si64.4Ge0.6. Both of these values agree with other measurements of Ge solid solubility in β [34].

Local chemical analysis of individual DC eutectoid lamella by EDS is nontrivial, owing to their small length scales and the enveloping β matrix, which invariably contributes a Si signal that confounds the measurement. Instead, we performed Rietveld refinement of high resolution XRD data to calculate the distinct lattice parameters from the eutectoid and eutectic microconstituents. Since the Si1₋ₓGeₓ lattice parameter is composition dependent [35], DC composition can be readily extracted from this data. A representative XRD spectrum for the aged samples can be found in the Supplementary Information. Rietveld refinement of these spectra shows that the specimens aged at 567 °C entrain a significant fraction of the total Ge present within the eutectoid lamellae, increasing from 6 at% Ge in the slow-cool + 567 °C/120 h sample to about 18 at% for the rapid-cool + 567 °C/56 h sample. The reduced Ge content in the eutectoid DC in the slow-cool + 567 °C/120 h sample is consistent with the lower Ge content in the as-cast α phase of this specimen. As seen in Fig. 4, melt-spinning is effective at increasing the Ge content in both the eutectic and eutectoid lamellae. These values are significant. It has been shown that as little as 10% Ge in Si that reduces the thermal conductivity by an order of magnitude via alloy scattering of phonons [17] [36] [18]. At the same time, the bandgap is reduced by about 100 meV [37], and more closely aligns with the 0.78 bandgap of β [3]. The DC phase in the rapid-cool + 900 °C/216 h sample had a composition of Si71Ge29, which is close to the equilibrium composition seen in the as-cast slow-cool sample. In order to convert DC lattice parameter to Ge concentration, the DC microconstituent with at% Ge of 6, 18 and 31 respectively. The data for the binary Fe-Si samples obtained earlier are also shown. Fig. 5a depicts the four samples plotted according to their thermal conductivity vs. the β/DC heterointerface density in the eutectoid structure only. Discussion of how the interface density is obtained and the role of the eutectoid lamellae can be found later. The samples aged at 567 °C, which are circled in the figure, have similar length scales for the Si1₋ₓGeₓ eutectoid nanowires in the β matrix, irrespective of the different Si1₋ₓGeₓ eutectoid lamellae arising from the casting conditions. Despite the similar length scales, the thermal conductivity of the eutectoid microstructure decreases by almost 2×, associated with the increasing at% Ge in the DC phase. The phonon scattering efficiency of Ge-rich DC inclusions is further demonstrated by examining the rapid-cool + 900 °C/216 h sample: despite having an order of magnitude lower density of heterointerfaces, the thermal conductivity is approximately the same as the rapid-cool + 567 °C/56 h sample, 8.9 ± 0.6 and 8.3 ± 0.7 W m⁻¹ K⁻¹, respectively. This reduction cannot be fully attributed to enhanced alloy scattering.

Table 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Slow-Cool</th>
<th>Rapid-Cool</th>
</tr>
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<tbody>
<tr>
<td>Fe24.6Si77.4Ge1.0</td>
<td>Fe24.8Si77.2Ge1.0</td>
<td></td>
</tr>
<tr>
<td>Fe24.5Si77.3Ge1.1</td>
<td>Fe23.9Si77.2Ge2.0</td>
<td></td>
</tr>
<tr>
<td>Si1Ge27</td>
<td>Si1Ge27</td>
<td></td>
</tr>
<tr>
<td>Si0.6Ge0.4</td>
<td>Si0.6Ge0.4</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Transmission EDS composition map illustrating large amounts of Ge segregation into eutectoid nanowires. The overlay in the center shows the transmission micrograph of the same area.

Fig. 4. Diagram depicting the lattice parameters and composition of DC phases determined by Rietveld refinement.
We consider two general methods that can be employed to account for the effects of interfacial phonon scattering on the thermal conductivity. The first is rooted in the Callaway model for thermal conductivity [39], which is a modified Debye model [40] [41] that specifically considers how phonon transport depends on the size of a structure, such as the diameter of free-standing SiGe nanowires relative to the phonon mean free path (MFP), along with the MFP of other phonon scattering events. When the phonon bulk MFP is longer than nanowire diameter, low frequency phonons are additionally scattered by the boundary and become a significant factor in thermal conductivity of SiGe nanowires [42] [17]. This lowers the SiGe nanowire thermal conductivity below the alloy limit [38]. We also note this approach has been well studied for polycrystalline/nano-grained materials [43] [44] [18] [45], and has demonstrated reasonable agreement in describing reductions in thermal conductivity due to grain boundaries in a chemically homogeneous material [46] [47].

However, the application of this phonon-interface scattering rate approach towards predicting heterogeneous composites, including those that contain internal interfaces that separate heterogeneous materials, or even different phases of the same material, is questionable. This, in part, is due to the finite temperature drop that can exist across an interface or interfacial region that separates two different materials. This temperature drop, which is quantitatively related to the TBC across the interface [48], is driven by the differing phonon energies, group velocities, and dispersions in the different materials, along with localized defects and impurities [49] [50].

Thus, a conceptually simpler model to account for additional phonon thermal resistances due to the presence of internal interfaces directly considers this boundary as an additional resistance [50]. Here, we will use this TBC-based thermal conductivity approach to analyze the phonon thermal transport in our samples; thus, in this context, we examine how TBC varies with Ge content in the alloy system, yielding insight into the role of interface composition on TBC. This alloy composition effect on TBC has only been observed previously interfaces in metallic alloys [51]. In metallic systems, thermal transport is dominated by electrons; thus, electron effects (such as electron-phonon coupling in interfacial regions) may not be easily dismissed [52] [53] [54] [55]. Therefore, our present analysis on alloy composition on non-metal/nanowire interfaces offers more direct unique insight into the role of alloy composition on phonon-dominated TBC.

Assuming that scattering events in the bulk of each phase and at the interfaces are independent, our systems can be modeled as a thermal circuit with series resistances (via Matthiessen’s rule), given by

\[
\frac{1}{\kappa_T} = \frac{f_\beta}{\kappa_\beta} + \frac{f_{\text{DC}}}{\kappa_{\text{DC}}} + \frac{1}{\lambda_{\beta,\beta}h_{k,\beta,\beta}} + \frac{1}{\lambda_{\beta,\text{DC}}h_{k,\beta,\text{DC}}}
\]

where the \( f_\beta \) and \( \kappa_\beta \) are the volume fractions and thermal conductivities for the \( \beta \) and DC (Si\(_{1-x}\)Ge\(_x\)) phases, respectively. The \( \lambda_{\beta,\beta} \) and \( \lambda_{\beta,\text{DC}} \) are the mean distances between interfaces (the reciprocal interface density), and the \( h_{k,\beta,\beta} \) and \( h_{k,\beta,\text{DC}} \) are the thermal boundary conductances. Two interface types are considered: \( \beta/\beta \) grain boundaries and \( \beta/\text{DC} \) heterointerfaces.

The phase volume fractions \( f_\beta \) were obtained from Rietveld analysis of the XRD data. The thermal conductivity of the \( \beta \)-FeSi\(_2\) phase is taken as 19.7 ± 4 W/m-K; this value was determined in our previous work [15], although the result is modified here to account for the geometric effects described later. The thermal conductivities of Si\(_{1-x}\)Ge\(_x\) alloys as a function of Ge content were taken from Ref. [38]. Fig. 5 b shows the thermal conductivities measured by TDTR at room temperature, and compares these with the bulk thermal conductivities only (i.e., the sum of the first two terms on the right side of Eq. (1)). Clearly, the bulk resistances alone, even with alloy scattering, cannot account for the observed reductions in thermal conductivity. This again indicates the importance of considering the TBC at the \( \beta/\text{FeSi}_2/\beta/\text{Si}_{1-x}\)Ge\(_x\) interfaces, as we discussed above.

Our previous work determined the TBC for the \( \beta \)-FeSi\(_2\)/Si interface after eutectoid decomposition in the binary Fe-Si system, using a similar analysis [15]. In that work, we did not take into account the possible differences between interface density measured using linear intercepts from a 2D micrograph and the actual interface density in 3D. As a first-order approximation, a simple geometric model is used here to compare the length of interface per area from micrographs and the 3D surface area per
volume, at constant volume fraction of β and DC phases. The aspect ratios of planar lamellae were varied such that the geometry evolved from sheet to lath to wires. A 2D to 3D correction factor was determined from the model that estimates the interface density is a factor of 2 larger for idealized nanowires vs. planar lamellae. A similar model was made for equiaxed particles approximated by spheres in 3D vs. projected circles in 2D.

Table 2 summarizes relevant data and calculation results for the samples of interest. The following assumptions were made in order to determine how thermal boundary conductance of the β/DC interface depends on Ge content from eqn. (1). For all the samples, the grain size, manifested in the $a_{β/γ}$ term of eqn. (1), was ignored. In most of the samples this is justified by the relatively large grain size, such that grain boundary scattering contributes negligibly to the measured thermal conductivity. However, for the rapid-cool + 567°C/56 h sample, ignoring the 800 nm grain size implies there will be some grain boundary scattering contributions to $k$ that will not be accounted for. In all samples, the eutectic lamellae are also ignored. In the samples with coarse lamellae, the TDTR probe was positioned between the lamellae and only measured the eutectoid structure anyway, so the resistance analysis must also account for the lamellae. However, the fine scale lamellae (cf. Fig. 1c) are included in the TDTR measurement. Their exclusion from the analysis of eqn. (1) via both interfacial and bulk effects, is justified by (1) their small interface density and thus small contribution to TBC and (2) via both interfacial and bulk effects, is justifiable by (1) their small interface density and thus small contribution to TBC and (2) the relatively small variation of the bulk thermal conductivity of $\beta$-SiGe alloys in the range $x = 0.23–0.81$ [38].

For the rapid-cool + 900°C/216 h ternary alloy, the sample has two distinct particle sizes, so all measurements are an average of the two. With these simplifications, the last column of Table 2 summarizes the resultant $h_b$'s, which are plotted vs. Ge content in Fig. 6. The largest error in this calculation comes from the uncertainty of the interface density and in the measured thermal conductivities.

By using Matthiesen’s rule, the β/Si interface was calculated to have a TBC of 571 ± 51 MW m−2 K−1. Compared to the TBC of other semiconductor/semiconductor interfaces, this value is close to the upper limit of measured TBC’s in the phonon-dominated regime [49]. However, the Ge content of the DC phase has a significant effect on the TBC at this heterointerface, as seen in Fig. 6. It is interesting to consider the rapid-cool + 900°C sample. The extended high-temperature anneal coarsened and spheroidized the DC phase, producing Si69Ge31 particles with diameters ranging from 1–10 μm. As such, the application of Matthiesen's Rule, Eq. (1), seems particularly reasonable. For example, the TBC across the β/Sl69Ge31 yields a TBC of 49 ± 10 MW m−2 K−1, an order of magnitude lower than that across the β/Si interface. Even with the potential uncertainties in the interface density, the presence of 31% Ge in the DC phase appears to significantly reduce the thermal boundary conductance of the β/DC heterointerface.

It should be recognized that a series resistance model wherein bulk thermal conductivities and a single-valued thermal boundary conductance are taken as independent is clearly an oversimplification. Future work should compare these predictions with diffuse-mismatch modeling, and with re-interpretation of the data in terms of the Callaway-Debye picture. This more rigorous modeling approach is beyond the scope of this current work. However, our experimental results, and the simple series resistance model, do point to a clear and important role of the Ge content in both bulk alloy scattering, and in enhancing length scale effects associated with the heterophase structure.

These results herein suggest that minimum thermal conductivity in the β-FeSi2/DC composite requires a nanostructured DC phase with ~30 at% Ge to take full advantage of alloy scattering and TBC effects, as well as potential benefits of reduced bandgap in the DC phase. Eutectoid decomposition efficiently creates nanowires and large heterointerface densities, but Ge entrainment in eutectic lamellae impedes our ability to segregate Ge into the finer-scale eutectoid nanowires. It is not likely that we can bypass the eutectic by choice of ternary composition. However, a possible route would utilize even faster solidification rates. This would produce a true nanoscale eutectic with very high Ge content (at least 60 at %). Subsequent low temperature conversion would promote eutectoid decomposition, $γ → β$-Si, and if the eutectic interlamellar spacings can be retained on the nanoscale, the eutectoid Si would simply diffuse to the lamellae, but without significant coarsening. We are currently pursuing this processing path. On the other hand, it is interesting that the rapid-cool + 900°C/216 h sample (Fig. 2c), which is not strictly hierarchical, provides a relatively low thermal conductivity due to the high Ge content in the diamond cubic phase, and may have advantages in the thermoelectric power factor and may enhanced thermal stability at elevated temperatures. The latter still requires careful

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**Table 2** Summary of relevant data for and results of the Matthiesen’s rule calculations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solidification</th>
<th>Process</th>
<th>Interface</th>
<th>DC Composition</th>
<th>$f_b$</th>
<th>$f_{dc}$</th>
<th>3D (μm/int)</th>
<th>3D (nm)</th>
<th>$K_{Ge}$ (W/mK)</th>
<th>$K_T$ (W/mK)</th>
<th>3D (MW/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe28.4Si11.6</td>
<td>Slow-Cool</td>
<td>567°C/56h</td>
<td>Eutectoid/β</td>
<td>S100</td>
<td>0.825</td>
<td>0.175</td>
<td>22.66 ± 3.45</td>
<td>45.5</td>
<td>149.0</td>
<td>12.1 ± 1.0</td>
<td>571 ± 51</td>
</tr>
<tr>
<td>Fe28Si6Ge4</td>
<td>Slow-Cool</td>
<td>900°C/56h</td>
<td>Eutectoid/β</td>
<td>S100</td>
<td>0.828</td>
<td>0.172</td>
<td>0.44 ± 0.11</td>
<td>227.27</td>
<td>22.8 ± 5.0</td>
<td>10.1 ± 1.5</td>
<td>518 ± 48</td>
</tr>
<tr>
<td>Rapid-Cool</td>
<td>567°C/56h</td>
<td>Eutectoid/β</td>
<td>Eutectic/β</td>
<td>S100</td>
<td>0.862</td>
<td>0.138</td>
<td>23.70 ± 2.85</td>
<td>42.3</td>
<td>23.51</td>
<td>10.1 ± 1.5</td>
<td>518 ± 48</td>
</tr>
<tr>
<td></td>
<td>900°C/216h</td>
<td>SiGe/β</td>
<td>Eutectic/β</td>
<td>S100</td>
<td>0.678</td>
<td>0.232</td>
<td>0.01 ± 0.00</td>
<td>100000.0</td>
<td>14.85</td>
<td>8.3 ± 0.7</td>
<td>341 ± 49</td>
</tr>
</tbody>
</table>

Fig. 6. Thermal boundary conductance for the β/DC heterointerface, calculated from Matthiesen’s rule.
investigation in deliberately-doped samples.

4. Conclusions

Ge additions to the Fe-Si system provide significant flexibility for modifying the structure and properties of Fe-Si-based thermoelectrics. Hierarchical microstructure was produced by combining eutectic and eutectoid decomposition in Fe₅₂Si₆₇Ge₄ alloys, ultimately producing a nanocomposite structure of β-Fe₃Si₂ with embedded SiGe alloys of varying alloy composition. Rapid solidification of Fe-Si-Ge was shown to (1) reduce the length scales of eutectic lamella by two orders of magnitude, (2) eliminate the unwanted α-FeSi phase, and (3) increase the final Ge content in the nanoscale eutectoid nanowires.

The composition of DC nanoinclusions may be the most important aspect of this system for reducing overall thermal conductivities, and should also provide the greatest reduction in bandgaps and band offsets relative to the β-matrix. We analyzed the thermal conductivity of the composite structure in terms of the effects of a Ge-dependent thermal boundary conductance associated with the β-Fe₃Si₂/Si–Ge heterointerfaces. Up to 30 at% Ge was incorporated into the DC microconstituents using rapid eutectic solidification combined with eutectoid decomposition. As a result, the thermal conductivity of the system was reduced from 12.1 ± 1.0 MW m⁻¹ K⁻¹ to 8.9 ± 0.6 MW m⁻¹ K⁻¹, which shows results primarily from a significant reduction in thermal boundary conductance across the β-Fe₃Si₂/SiGe interface. While the β-Fe₃Si₂/Si interface exhibits a relatively high thermal boundary conductance of 571 ± 51 MW m⁻² K⁻¹, this value drops markedly with the inclusion of Ge into the diamond cubic. Values as low as 49 ± 10 MW m⁻² K⁻¹, 91% lower than that across the β-Fe₃Si₂/Si interfaces, were obtained in at the maximum Ge incorporation.

Noting that the overall Ge content is still only 4 at%, so that the high abundance and low toxicity of the primary Fe and Si components suggest that further pursuit of thermoelectric optimization through microstructure control in the dilute ternaries is warranted. This could be achieved by varying the overall Ge content, increasing the rate of solidification, or precise doping of microconstituents. Alternate methods, such as powder processing, could be ideal for producing fine, compositionally controlled Si₁₋ₓGeₓ nanoinclusions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.matchemphys.2017.12.038.

References

[8] D.D. Noonan, A.L. Effland, C.E. Knoebel, The composition of DC nanoinclusions may be the most important aspect of this system for reducing overall thermal conductivities, and should also provide the greatest reduction in bandgaps and band offsets relative to the β-matrix. We analyzed the thermal conductivity of the composite structure in terms of the effects of a Ge-dependent thermal boundary conductance associated with the β-Fe₃Si₂/Si–Ge heterointerfaces. Up to 30 at% Ge was incorporated into the DC microconstituents using rapid eutectic solidification combined with eutectoid decomposition. As a result, the thermal conductivity of the system was reduced from 12.1 ± 1.0 MW m⁻¹ K⁻¹ to 8.9 ± 0.6 MW m⁻¹ K⁻¹, which shows results primarily from a significant reduction in thermal boundary conductance across the β-Fe₃Si₂/SiGe interface. While the β-Fe₃Si₂/Si interface exhibits a relatively high thermal boundary conductance of 571 ± 51 MW m⁻² K⁻¹, this value drops markedly with the inclusion of Ge into the diamond cubic. Values as low as 49 ± 10 MW m⁻² K⁻¹, 91% lower than that across the β-Fe₃Si₂/Si interfaces, were obtained in at the maximum Ge incorporation.

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