High Thermoelectric Figure of Merit of FeSb_{2-x} Thin Films via Defect Engineering for Low-Temperature Cooling Applications

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Received: 14 April 2021 / Accepted: 14 September 2021 / Published online: 21 October 2021
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Abstract

In general, both the thermal and electrical conductivity of metal/metalloid/semimetal materials decrease with increasing temperature; that is, these two parameters are in lockstep. Defect engineering has recently been proven to have tremendous potential for improving the thermoelectric performance of topological materials with two-dimensional layered structures. We have explored the effect of Sb point-defect engineering on the thermoelectric performance of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films at low temperatures. Thin-film surface and grain-boundary phonon scattering contribute to the overall decrease in the thermal conductivity (κ) compared with single crystals. The current results indicate that FeSb_{1.8} shows the lowest κ value, the main reason being that its nanostructure scatters more phonons over a wider wavelength range. In addition, the presence of Sb point defects enables an enhancement of the Seebeck coefficient (S) to $357 \mu\text{V/K}$ at 45 K for FeSb_{1.8} thin films, coupled with an imperceptible decrease in the corresponding electrical conductivity (σ). Despite these results, the power factor (PF) is much lower than that of single crystals. The optimal peak thermoelectric figure of merit (ZT) of ~ 0.071 at 55 K is one order of magnitude higher than the ZT_{max} of low-temperature FeSb₂ single crystals. These characteristics indicate that FeSb₂ thin films are promising materials for use in low-temperature thermoelectric devices.

Keywords Defect engineering · semiconductor · thermoelectrics · iron-based binary · magnetron sputtering

Introduction

The present shortage of fossil-fuel energy and increasing environmental pollution have become increasingly prominent issues. To date, the most effective way to alleviate this state has been the diversified and efficient multilevel utilization of energy. Thermoelectric materials (TMs), a kind of solid energy material that can realize direct mutual conversion between heat and electrical energy, have been developed rapidly in recent years and used in energy harvesting, waste heat power generation, refrigeration, and other fields.^{1–4} The dimensionless thermoelectric figure of merit (ZT)

$$ZT = \frac{S^2 T}{\rho \kappa} = \frac{S^2 T}{\rho(\kappa_c + \kappa_l)} \quad (1)$$

is usually considered to measure the thermoelectric conversion efficiency,^{5,6} where S is the Seebeck coefficient of the material, T is absolute temperature, κ is the total thermal conductivity, including the carrier (κ_c) and lattice contributions (κ_l), ρ is the electrical resistivity equal to the reciprocal of the electrical conductivity (σ), and S^2/ρ is known as the power factor (PF). Among these parameter, the three core factors ρ , S , and κ exhibit strong mutual dependence, so it is practical to optimize ZT only by the coordinated control of each, particularly for metal/metalloid/semimetal materials.^{7–11}

Recently, Kondo topological FeSb₂ has been widely reported due to its colossal Seebeck coefficient ($-45 \times 10^{-3} \text{ V/K}$).^{12,13} However, the high thermal conductivity ($\sim 500 \text{ W/m-K}$) and electrical resistivity ($\sim 10 \times 10^{-3} \Omega \text{ m}$) of bulk FeSb₂ limit its thermoelectric application.¹² As is well known, being a metal or semimetal, it is impossible to simultaneously obtain both low thermal conductivity and low electrical resistivity based on Ohm's law.¹⁰ However, in

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fact, FeSb₂ possesses a narrow bandgap (0.1 eV to 0.3 eV) because of the hybridization between the local *f*- or *d*-band and conduction band,¹⁴ as well as strong electron–electron correlations at the Fermi level.¹⁵ Topological semiconductors with these two physical characteristics have long been expected to become candidates for use in low-temperature thermoelectric applications.^{16,17} In recent years, the κ value of FeSb₂ has been greatly suppressed by introducing nanostructure,^{18–21} nanoinclusions,^{22,23} and dopants such as Co/Cr,²⁴ Te,¹⁷ Sn,²⁵ Mn,²⁶ Ni,²⁷ and Cu.²⁸ However, the resulting improvements of ZT in these reports have been unsatisfactory due to the decrease in S ; the reported thermoelectric properties of FeSb₂ are collated in Table II. Besides, Wang et al. revealed deformation-induced lattice imperfections in FeSb₂, and Sanchela et al. introduced Sb-site deficiencies in FeSb₂, both of which play an important role in improving phonon scattering.^{29,30} Unfortunately, the reduced σ value limited the enhancement of ZT . Meanwhile, Du et al. identified in theory that Sb vacancy defects could induce monoclinic distortion and generate in-gap states with Fe 3*d* orbital character, which will cause additional phonon scattering and substantially reduce the thermal conductivity.³¹

Low-dimensional TMs have developed into an eye-catching new research direction because the phonon scattering processes at surfaces and grain boundaries significantly reduce their thermal conductivity.^{32,33} Related reports have indicated that the PF of FeSb₂ thin films can be expected to be substantially improved compared with that of bulk FeSb₂.^{34–37} Based on defect engineering, in this work we obtain FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films by magnetron sputtering, and the comprehensive influence of Sb vacancies with phonon scattering on the thermoelectric properties was investigated.

Experimental Procedures

Magnetron sputtering was used to prepare polycrystalline FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films.³⁷ Initially, the sputtering target was prepared by hot-press sintering in Ar atmosphere. Fe powder (99.99%) and Sb powder (99.99%) were weighed according to the stoichiometric ratio, and the well-mixed powders were filled into a graphite mold and placed in the hot pressing furnace. The hot-pressing parameters were set at a temperature of 400°C, pressure of 30 MPa, and heat holding time of 60 min. After grinding and polishing, a target with diameter of 60 mm and height of 3.2 mm was obtained. In the direct-current magnetron sputtering process, Ar (purity 99.99%) was used as sputtering gas. The sputtering conditions were silicon substrate temperature of 350°C, target–substrate spacing of 10 cm, sputtering pressure of 0.6 Pa, constant flow of 8 standard cubic centimeters per minute (SCCM), sputtering power of 10 W, and growth time

of 3 h. The same procedure was then repeated for weighing, sintering, and sputtering the samples.

Just as in our previous work,³⁸ the phase composition of the thin films was determined by x-ray diffraction (XRD) analysis. The crystal morphology and structural properties of the thin films were characterized by field-emission scanning electron microscopy (FESEM), selected-area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM). The chemical and elemental composition were analyzed by energy-dispersive x-ray spectroscopy (EDS) and high-resolution x-ray photoelectron spectroscopy (HRXPS). In a Quantum Design physical property measurement system (PPMS), the low-temperature in-plane S and ρ of the films were measured using the thermal transport option (TTO) in the range from 5 K to 320 K. The Hall resistivity (ρ_H) was measured using the alternating-current (AC) transport option (ACT), and the Hall coefficient (R_H) was calculated as

$$R_H = \rho_H / B, \quad (2)$$

where B is the scanning magnetic field. The κ value was measured using the three-omega (3ω) method^{39,40} as shown in Fig. 8a.

Results and Discussion

Structure and Composition

Figure 1a shows the XRD patterns of the four FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films. A weak peak (marked with an asterisk) located at 28.8° indicates the presence of minute amounts of Sb in the FeSb₂ film, which may be due to the slightly low Sb vapor pressure at 350°C. It is easily observed that the FeSb₂ films grew preferentially with (101) crystal orientation, and the diffraction peaks at 31.4° and 66.6° match well with the standard probability density function (PDF) card (no. 34-1184), indicating that the films have marcasite orthorhombic system. The FeSb_{2-x} films were

Fig. 1 (a) XRD patterns of FeSb₂, FeSb_{1.9}, FeSb_{1.8}, and FeSb_{1.7} thin films. (b) Typical cross-sectional SEM image of FeSb_{1.8} thin film.

polycrystalline specimens, as verified by Fig. 5a. Although the excellent orientation in (101) and (202) crystal directions creates the illusion that the films are single crystals according to the XRD patterns. With the increase of the Sb vacancies, the peaks along (101) and (202) crystal orientation shift to small angles. The Bragg equation states that⁴¹

$$2d \sin \theta = \lambda, \quad (3)$$

where the wavelength λ is constant during diffraction. The Bragg angle (θ) moves toward smaller angle when the lattice plane spacing (d) becomes wider. This change in the lattice structure can be attributed to lattice internal strain and lattice distortion induced by Sb vacancies. At the same time, the weakening of the peak intensity and the increase of the full-width at half-maximum (FWHM) with more Sb vacancies indicates a degradation of the crystallinity. Figure 1b shows a typical cross-sectional SEM image of the FeSb_{1.8} thin film, clearly showing that the typical thickness of a single-layer film is about 700 nm.

There is internal lattice strain in the FeSb_{2-x} films due to the mismatch of the crystal lattice and thermal expansion coefficient between the film and substrate, as well as the interaction between film-adjacent grains and grain boundaries. Furthermore, considering the strain effect caused by crystal defects and deformation, we calculated the average crystalline size and lattice strains used the uniform deformation model (UDM) in the Williamson–Hall (W–H) plot method, as shown in Fig. 2;⁴² that is,

$$\beta \cos \theta = 4\epsilon \sin \theta + K\lambda/D, \quad (4)$$

where K (0.94), λ (80.15406 nm), D , θ , and ϵ are the shape factor, wavelength of the x-ray source, average crystalline size, peak position in radians, and lattice strain, respectively. Also, β is the FWHM (the broadening of the XRD peaks) in radians, including the combined effect of crystallite size and microstrain. The slopes and y intercepts of the fitting lines in Fig. 2a–d give the values of ϵ and $K\lambda/D$, from which the lattice strain and average crystalline size can be obtained. Both the ϵ and D values of the FeSb_{2-x} films (Table I) initially increase then decrease with increasing Sb vacancies. Also, ϵ reaches a maximum value, while in contrast, D reaches a minimum value at FeSb_{1.8}, indicating the worst crystalline quality for this sample (Table II).

Four SEM surface images of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films are shown in Fig. 3a–d. There are rectangular grains with high crystallinity in FeSb₂, FeSb_{1.9}, and FeSb_{1.8}. The grain sizes of the FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) films are in the range of 100 nm to 300 nm, 200 nm to 400 nm, 50 nm to 280 nm, and 50 nm to 500 nm, respectively. The average grain size of FeSb₂ is slightly smaller because

Table I ϵ and D values calculated from XRD data by W–H method

Film	ϵ	D (nm)
FeSb ₂	0.0003036	207
FeSb _{1.9}	0.00203	261
FeSb _{1.8}	0.00521	130
FeSb _{1.7}	0.00118	161

Fig. 2 W–H method plots using the UDM model for (a) FeSb₂, (b) FeSb_{1.9}, (c) FeSb_{1.8}, and (d) FeSb_{1.7} thin films.

Table II Thermoelectric properties of FeSb₂

Material	$S_{\max}$ ($\mu\text{V/K}$)	S^2/ρ ($\text{mW/K}^2\text{m}$)	κ (W/m-K)	ZT	Ref
FeSb ₂ single crystal	-45,000 at 10 K	230 at 12 K	500 at 15 K	0.005 at 12 K	12
FeSb _{2-x} As _x ($x = 0.01, 0.03$)	-7000 at 15 K, $x = 0.01$	8 at 20 K $x = 0.01$	130 at 20 K	0.0012 at 20 K	13
FeSb _{2-x} Te _x ($x = 0.001, 0.003, 0.01, 0.065, \text{ and } 0.16$)	-900 at 30 K	8 at 30 K	52 at 40 K $x = 0.001$	0.013 at 110 K, $x = 0.16$	17
FeSb ₂ polycrystalline bulk (chemical synthesis and spark plasma sintering (SPS))	39 at 450 K	0.68 at 400 K	10 at 210 K 7.2 at 300 K	0.04 at 500 K 0.02 at 300 K	18
FeSb ₂ polycrystalline bulk (elements reaction and hot pressing)	-181 at 25 K		9.5 at 50 K		19
FeSb ₂ nanostructured polycrystalline (solvo-thermal approach and SPS)	-102 at 30 K	0.03 at 60 K 0.05 at 300 K	2.5 at 300 K	~ 0.0018 at 60 K 0.006 at 300 K	19
FeSb ₂ nanocomposite (solvochemical approach and SPS)	-64 at 35 K				20
FeSb ₂ nanostructured polycrystalline (hot pressing)	-352 at 20 K	0.088 at 50 K	0.1 at 20 K 0.34 at 50 K	0.013 at 50 K	21
FeSb _{2.06-x} %In ($x = 0, 0.5, 1, \text{ and } 3$)	-350 at 40 K $x = 0$		$\kappa_L \sim 4.5$ at 50 K $x = 0.5$		22
FeSb ₂ Ag _m ($m = 0, 0.028, 0.11, 0.22, \text{ and } 0.33$)	-105 at 50 K $m = 0$	0.1 at 50 K $m = 0.11$	0.24 at 50 K $m = 0.028$	0.02 at 50 K, $m = 0.11$	23
Fe(Sb _{1-x} Te _x) ₂ ($x = 0.005, 0.01, 0.05, \text{ and } 0.1$)	-150 at 100 K $x = 0.1$	3.5 at 100 K $x = 0.1$	5 at 20 K, $x = 0.1$ 7 at 100 K, $x = 0.1$	0.05 at 100 K, $x = 0.1$	24
(Fe _{1-x} Cr _x)Sb ₂ ($x = 0.1, 0.2, \text{ and } 0.5$)	-8 at 10 K $x = 0.5$		10 at 20 K, $x = 0.5$ 27 at 25 K, $x = 0.2$ 42 at 50 K, $x = 0.1$	0.004 at 10 K, 0.23 at 300 K, $x = 0.2$ 0.38 at 300 K, $x = 0.1$	24
(Fe _{1-x} Co _x)Sb ₂ ($x = 0.05 \text{ and } 0.2$)	-10 at 10 K $x = 0.05$		8 at 20 K, $x = 0.2$ 40 at 20 K, $x = 0.05$	0.02 at 300 K, $x = 0.2$ 0.03 at 300 K, $x = 0.05$	24
FeSb _{2-x} Sn _x ($x = 0, 0.01, 0.02, 0.03, 0.06, 0.09, 0.12, \text{ and } 0.15$)	-30 at 50 K $x = 0.01$	0.08 at 25 K $x = 0$	2 at 25 K $x = 0$	0.001 at 25 K $x = 0$	25
FeSb ₂ Cu _y ($y = 0.0225, 0.045, \text{ and } 0.09$)	-93 at 60 K $y = 0.0225$	0.164 at 60 K $y = 0.0225$	0.39 at 60 K $y = 0.045$	0.027 at 70 K $y = 0.045$	28
FeSb ₂ polycrystalline bulk (levitation melting and hot deformation)	-225 at 60 K	2.025 at 60 K	4 at 60 K	0.021 at 65 K	29
FeSb _{2-x} ($x = 0, 0.1, \text{ and } 0.2$) bulk (solid-state reaction)	-420 at 20 K $x = 0.1$ -300 at 20 K $x = 0.2$	0.0155 at 30 K $x = 0.1$ 0.011 at 30 K $x = 0.2$	2.4 at 50 K $x = 0.1$ 0.5 at 65 K $x = 0.2$	0.0003 at 25 K $x = 0.1$ 0.0011 at 30 K $x = 0.2$	30
FeSb ₂ film (pulsed laser deposition)	-80 at 35 K 22 at 300 K	0.019 at 35 K 0.011 at 300 K			34
FeSb ₂ film (epitaxial growth on MgO substrate)	-160 at 20 K	1.2 at 50 K			35
FeSb ₂ film (magnetron sputtering)	-160 at 50 K	0.512 at 50 K			37

uncombined Sb may segregate to grain boundaries and further limit the coarsening and local epitaxial growth of individual grains during the film growth. From the quantitative EDS analysis in Fig. 3e–h, we infer the stoichiometry of Fe and Sb to be 1/2, 1/1.9, 1/1.8, and 1/1.7, respectively. Therefore, the formation of FeSb₂, FeSb_{1.9}, FeSb_{1.8}, and FeSb_{1.7} is further confirmed.

We selected ten points for EDS detection analysis in four SEM images, respectively. We only detected element Sb but no Fe in several areas in FeSb₂. Conversely, we obtained both Fe and Sb concurrently in any area of FeSb_{1.9}, FeSb_{1.8},

and FeSb_{1.7} based on multiple dots. Figure 4 shows the typical area selected from FeSb₂ with a corresponding blue circle in Fig. 3a. This further proves the presence of uncombined Sb in FeSb₂ and is the same as the XRD patterns in Fig. 1a.

The SAED pattern taken from the FeSb₂ film is shown in Fig. 5a. The diffraction pattern is composed of a series of concentric rings with different radii, indicating its polycrystalline nature. In the HRTEM images in Fig. 5b–e, the (101) crystal plane spacing of the FeSb_{2-x} ($x = 0, 0.1, 0.2, \text{ and } 0.3$) thin films increases from 0.25 nm to 0.38 nm sequentially,

Fig. 3 SEM surface images, EDS spectra, and composition ratio of (a, e) FeSb_2 , (b, f) $\text{FeSb}_{1.9}$, (c, g) $\text{FeSb}_{1.8}$, and (d, h) $\text{FeSb}_{1.7}$ thin films

Fig. 4 EDS spectrum of selected area taken from the blue circle in Fig. 3a.

Fig. 5 (a) SAED pattern of FeSb_2 film, and HRTEM images of (b) FeSb_2 , (c) $\text{FeSb}_{1.9}$, (d) $\text{FeSb}_{1.8}$, and (e) $\text{FeSb}_{1.7}$ thin films.

Fig. 6 HRXPS spectra of (a) Fe 2p of FeSb_2 thin film, and (b) Sb 3d of FeSb_2 , $\text{FeSb}_{1.9}$, $\text{FeSb}_{1.8}$, and $\text{FeSb}_{1.7}$ thin films

which is the reason why the XRD diffraction peaks move to small angles.

Figure 6 presents the Fe and Sb HRXPS spectra for studying the chemical state of the elements. The valence state analysis was corrected based on the binding energy of C 1s (284.6 eV). Figure 6a shows the HRXPS spectrum of Fe 2p of FeSb_2 thin film. There are two characteristic peaks at 710.7 eV and 724.3 eV, corresponding to the orbital binding energies of $\text{Fe} 2p_{3/2}$ and $\text{Fe} 2p_{1/2}$, respectively. They are located between the values for Fe^{2+} (710.4 eV and 724.0 eV) and Fe^{3+} (711.4 eV and 725.0 eV),⁴³ indicating coexistence of Fe^{2+} and Fe^{3+} . Figure 6b shows the HRXPS spectra of Sb 3d, where the signals at 528.1 eV, 528.0 eV, 528.0 eV, and 528.0 eV, and

527.9 eV correspond to Sb 3d_{5/2} binding energies of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3), respectively. Likewise, the signals at 537.5 eV, 537.4 eV, 537.4 eV and 537.3 eV correspond to the Sb 3d_{3/2} binding energies of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3), respectively. The spin–orbit splitting energies of characteristic peaks are all within the range of 9.4 ± 0.1 eV. With increasing Sb vacancies, the intensities of the characteristic peaks decrease and the peaks shift in the direction of lower binding energy. However, the offsets are all less than 0.2 eV, indicating that the chemical bonding mode of Fe–Sb does not change considering the measurement error.

Electrical Transport Properties

Figure 7a shows S as a function of temperature. The Seebeck coefficient is negative at low temperature but becomes positive at 115 K. $|S|$ tends to increase with reducing Sb content at low temperature, which can be attributed to the negative S values of FeSb₂ at $T < 130$ K in contrast to the positive values of semimetal Sb single crystal.^{44,45} However, the fact that the $|S|$ of FeSb polycrystals approaches zero at low temperature prevents the Sb content in FeSb_{2-x} from being infinitely reduced.¹⁵ It can be observed that $|S| \sim 174.5 \mu\text{V/K}$ is obtained at 45 K for FeSb₂, and the maximum value of $|S|$ is $357 \mu\text{V/K}$ at 45 K for FeSb_{1.8}. At room temperature, both Sb and FeSb₂ have extremely similar positive values of S .⁴⁴ Therefore, the S values of all the samples barely vary as the Sb content decreases when the temperature is above 130 K.

The σ calculated from ρ of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) is shown in Fig. 7b (inset). σ is determined by the carrier concentration (n), Hall carrier mobility (μ_H), and

carrier charge (q).⁴⁶ Contrary to the tendency of S , σ tends to decrease step by step as the Sb content is reduced. We ascribe this to the decreased carrier concentration seen in Fig. 7d due to Sb defects in FeSb_{2-x} thin films. Related to its high carrier concentration ($5.4 \times 10^{21} \text{ cm}^{-3}$), the room-temperature σ value (1550 S/cm) of FeSb₂ thin film is two orders of magnitude higher than that of polycrystalline bulk FeSb₂,³⁰ and this comes from its excellent crystallinity and grain orientation.

The power factor (PF) in Fig. 7c reveals a trade-off between S and σ . Because of the increased S and slightly reduced σ , we observe a significant PF improvement below 100 K for FeSb_{2-x} ($x = 0.1, 0.2$, and 0.3) thin films compared with FeSb₂. A maximum PF of $\sim 4.5 \text{ mW/m}\cdot\text{K}^2$ at 50 K is achieved for FeSb_{1.8}, representing an improvement of about 275% over FeSb₂ thin film. The PF_{max} is two orders of magnitude higher than FeSb_{2-x} prepared by solid-state reaction, with $\text{PF}_{\text{max}} \sim 0.015 \text{ mW/m}\cdot\text{K}^2$.³⁰ Despite this, the improvement is extremely negligible in comparison with the PF of $\sim 230 \text{ mW/m}\cdot\text{K}^2$ reported for FeSb₂ single crystal.¹²

The n and μ_H values were obtained from R_H using the formulas

$$n = 1/|R_H|q, \quad (5)$$

$$\mu_H = |R_H|/\rho. \quad (6)$$

The variation of n and μ_H with the Sb vacancies at 55 K and 305 K is shown in Fig. 7d, revealing that n is extremely sensitive to tiny changes in the purity in terms of Sb vacancies. With the introduction of Sb vacancies, there is first a decrease in n then an increase, accompanied by an increase then decrease in μ_H . μ_H is defined as

$$\mu_H = q\tau/m^*, \quad (7)$$

where τ , and m^* are the carrier relaxation time and carrier effective mass, respectively.^{47,48} It can thus clearly be inferred that, when $x < 0.2$, the carrier scattering probability decreases, leading to the increase of μ_H . The growing n and violent lattice vibration lead to a reduction in μ_H with increasing temperature. n reaches a maximum of $5.46 \times 10^{21} \text{ cm}^{-3}$ for FeSb₂ at 305 K, and μ_H reaches a maximum of $12.92 \text{ cm}^2/\text{V}\cdot\text{s}$ for FeSb_{1.8} at 55 K.

One of the mechanisms of semiconductor transport stems from point defects.⁴⁹ Most point-defect engineering is dedicated to doping, vacancy, interstitial, and antisite defects.^{50–53} Significant enhancements have been achieved in the performance of TMs based on Bi₂Te₃,^{52,53} MnTe,⁵⁴ GeTe,^{55,56} SnTe,⁵⁷ Mg₃Sb₂,⁵⁸ MnSi_{1.74},⁵⁹ CuFeS₂,^{61,60} etc. via point-defect engineering. The charge imbalance produced by point defects (Sb vacancies in this study) changes the transport properties of the carriers. In another explanation, the lattice distortion induces the periodic potential field

Fig. 7 Temperature dependence of (a) S , (b) σ calculated from ρ (inset), and (c) PF of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films, and (d) variation of n and μ_H with Sb vacancies at 55 K and 305 K.

near it to deviate from normalization, causing scattering of carriers or phonons.⁵⁰

Thermal Transport Properties

Existing optimization strategies based on defect engineering mainly focus on regulation of electroacoustical structures.^{49,62,63} In thermoelectric solids, the core factors ρ , S , and κ that dominate the ZT values are external manifestations of defect-mediated carriers, phonons, and their mutual coupling.⁵³ Defect engineering regulates these factors through two basic strategies based on the weak correlation between electrical performance and lattice thermal conductivity. One is energy band engineering, which can improve the PF by adjusting the electronic band structure.^{49,62,64} The other is phonon engineering, as applied here, which can reduce κ_l by improving the phonon scattering.^{65,66}

A schematic showing the measurement of the thermal conductivity according to the 3ω method is illustrated in Fig. 8a. An Al metal bridge deposited on the FeSb_{2-x} thin film was used as a film heater and a temperature sensor for detection. An SiO_2 interlayer with thickness of about 10 nm to 20 nm was deposited by sputtering to ensure electrical insulation between the metal bridge and film. When inputting an AC signal power with a frequency of ω , Joule heating with a frequency of 2ω and the resulting oscillating resistance at 2ω were generated in the Al metal bridge, since the resistance of the Al metal material is directly proportional to temperature. The diffusion and penetration depth of the thermal wave into the thin film depend on the thermal conductivity (κ) of the film and the AC frequency. The AC voltage signal with a frequency of 3ω was extracted by phase-locked amplification, and the κ of the thin-film samples could then be derived according to the temperature fluctuation of the Al metal bridge. Firstly, the measurement accuracy was verified by measuring the κ of the Si substrate and sputtered SiO_2 film and comparing the results with previously reported values.⁶⁷ The κ value of SiO_2 and FeSb_{2-x} composite film was then measured by using the differential 3ω method. Next, the κ value of FeSb_{2-x} film was calculated using the thickness of each film layer and the known κ value of SiO_2 film according to their thermal resistance in series.

The κ_l , κ_c (inset), and κ values of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films are presented in Fig. 8b, c. The lattice contribution represents over 60% of the total thermal conductivity (Fig. 8b) according to the $\kappa - \kappa_c$ results (Fig. 8b), while a minority contribution of carriers was calculated on the basis of the Wiedemann–Franz law:

$$\kappa_c = L_0 \sigma T \quad (8)$$

(Fig. 8c, inset), where the Lorenz number $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$.⁶⁸ The κ shows a similar feature to that of

Fig. 8 (a) Schematic of κ measurement setup, and temperature dependence of (b) κ_l , (c) κ and κ_c (inset), and (d) ZT below 150 K and in the range of 5 K to 320 K (inset) of FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films.

polycrystalline bulk FeSb_2 .^{19,20} The variation of κ shows nonmonotonicity with added Sb vacancies, first increasing then decreasing, which is consistent with the reports of Zhu et al. and Sanchela et al.^{22,30} The maximum κ of FeSb_2 thin film is $3.88 \text{ W/m}\cdot\text{K}$, two orders of magnitude lower than the κ ($\sim 500 \text{ W/m}\cdot\text{K}$) of FeSb_2 single crystals prepared by a flux method.¹² This overall decrease in κ can be attributed with high likelihood to the thin films' surface and grain-boundary phonon scattering, and the enhanced grain-boundary Kapitza resistance.⁶⁹ Among the four different ratios, $\text{FeSb}_{1.8}$ shows the lowest κ_l , with nanostructure presumably being the main reason. The smallest average grain size, and more grain boundaries that scatter more phonons in a wider wavelength range, are the underlying causes. The variation of κ_l at low and high temperature is different widely. Phonon grain-boundary scattering is dominant at low temperatures for κ_l , while generally κ depends mainly on κ_l .⁷⁰ There are fewer phonon excitations in the crystal lattice when $T < 50 \text{ K}$, and the penetration rate of phonons with long wavelength and low frequency at grain boundaries surpasses the scattering rate, so κ_l increases with increasing T . At $T > 50 \text{ K}$, a large number of high-frequency phonons are excited, and the increase of the phonon amplitude leads to a shorter average free path, then κ_l decreases and causes the drop of κ .

The variation of ZT for the FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films below 150 K is shown in Fig. 8d. The peak of ZT increases from 0.016 for FeSb_2 to 0.071 for $\text{FeSb}_{1.8}$ at 55 K, providing an unambiguous indication of the

nanostructure effect. Although the PF is much lower than that of single crystal, the drastic reduction in κ contributes to the increase in ZT . The optimal peak ZT value is one order of magnitude larger than the $ZT \sim 0.005$ at 10 K reported for single-crystal samples.¹³ Compared with the ZT of ~ 0.05 at 100 K reported by Wang et al., the temperature at peak is lower.²⁴ The inset shows the variation of ZT at temperatures up to 320 K. ZT at 320 K reaches 0.43 for FeSb_{1.8} and is almost ten times higher than that at 55 K due to the reduction in κ at room temperature.

Conclusions

By utilizing point-defect engineering, FeSb_{2-x} ($x = 0, 0.1, 0.2$, and 0.3) thin films with high crystallinity and high-density grain distribution were prepared by magnetron sputtering. The thermoelectric properties were measured from 5 K to 320 K. The significant decrease of the thermal conductivity is the joint effect of enhanced grain boundaries, Kapitza thermal resistance, and phonon scattering mechanisms, viz. at the thin-film surfaces, grain boundaries, and Sb point defects. The change of the carrier transport properties caused by Sb vacancies is dramatically beneficial to promote the electrical performance. An improvement of $\sim 275\%$ in the power factor was obtained for FeSb_{1.8}, with a peak of 4.5 mW/m·K² at 50 K. The ZT value of FeSb_{1.8} was enhanced to 0.071 at 55 K, the highest low-temperature ZT value reported for this material to date. The strong phonon scattering and weak carrier scattering are the two reasons contributing to this improvement. Additionally, through the strategy of changing the magnetron sputtering temperature, time, and pressure or other factors, we can further explore and improve the ZT of FeSb_{2-x} thin films. Controlling the size, concentration, and distribution range of defects as specific methods could help with the preparation and to extend the application of TMs.

Acknowledgments This study is partially supported by the National Natural Science Foundation of China under grant nos. 21371049 and 51372070, Henan Province Natural Science Foundation Research Project Funding (162300410040), and the Key Scientific and Technological Research Project of Henan Province, China (202102310598), Gas-sensitive properties of SnSe hollow microspheres for Henan innovative science and technology team (CXTD2017111), and the Key Project of Education Department of Henan Province (no. 14B430010).

Conflict of Interest The authors declare that they have no conflicts of interest.

References

1. F. Frobenius, G. Gaiser, U. Rusche, and B. Weller, *J. Electron. Mater.* 45, 1433 (2016).
2. A. Tarancón, *Nat. Electron* 2, 270 (2019).
3. I. Petsagkourakis, K. Tybrandt, X. Crispin, I. Ohkubo, N. Satoh, and T. Mori, *Sci. Tech. Adv. Mater.* 19, 836 (2018).
4. N. Nandihalli, C.J. Liu, and T. Mori, *Nano Energy* 78, 105186 (2020).
5. Z.G. Chen, X. Shi, L.D. Zhao, and J. Zou, *Prog. Mater. Sci.* 97, 283 (2018).
6. W.D. Liu, Z.G. Chen, and J. Zou, *Adv. Energy Mater.* 8, 1800056 (2018).
7. C.J. Vineis, A. Shakouri, A. Majumdar, and M.G. Kanatzidis, *Adv. Mater.* 22, 3970 (2010).
8. J.R. Sootsman, D.Y. Chung, and M.G. Kanatzidis, *Angew. Chem. Int. Ed.* 48, 8616 (2009).
9. M.G. Kanatzidis, *Chem. Mater.* 22, 648 (2010).
10. J. Wang, X. Jia, D.S. Nkemeni, G. Li, and S. Zhou, *Sol. Energy Mater. Sol. Cells* 206, 110265 (2020).
11. C. Gayner, and K.K. Kar, *Prog. Mater. Sci.* 83, 330 (2016).
12. A. Bentien, S. Johnsen, G.K.H. Madsen, B.B. Iversen, and F. Steglich, *EPL* 80, 17008 (2007).
13. P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen, and F. Steglich, *Dalton Trans.* 39, 1012 (2010).
14. P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen, and F. Steglich, *J. Phys. Conf. Ser.* 150, 012049 (2009).
15. Y. Sun, E. Zhang, S. Johnsen, M. Sillassen, P. Sun, F. Steglich, J. Bøttige, and B.B. Iversen, *Thin Solid Films* 519, 5397 (2011).
16. S. Guo, T. Jia, and Y. Zhang, *J. Phys. Chem. C* 123, 18824 (2019).
17. P. Sun, M. Søndergaard, Y. Sun, S. Johnsen, B.B. Iversen, and F. Steglich, *Appl. Phys. Lett.* 98, 72105 (2011).
18. M. Saleemi, M.Y. Tafti, A. Jacquot, M. Jägle, M. Johnsson, and M.S. Toprak, *Inorg. Chem.* 55, 1831 (2016).
19. K. Wei, J. Martin, and G.S. Nolas, *Mater. Lett.* 122, 289 (2014).
20. A. Datta, and G.S. Nolas, *Eur. J. Inorg. Chem.* 1, 55 (2012).
21. H. Zhao, M. Pokharel, G. Zhu, S. Chen, K. Lukas, Q. Jie, C. Opeil, G. Chen, and Z. Ren, *Appl. Phys. Lett.* 99, 163101 (2011).
22. S. Zhu, W. Xie, D. Thompson, T. Holgate, M. Zhou, Y. Yan, and T.M. Tritt, *J. Mater. Res.* 26, 1894 (2011).
23. H. Zhao, M. Pokharel, S. Chen, B. Liao, K. Lukas, C. Opeil, G. Chen, and Z. Ren, *Nanotechnology* 23, 505402 (2012).
24. K. Wang, R. Hu, J. Warren, and C. Petrovic, *J. Appl. Phys.* 112, 013703 (2012).
25. A. Bentien, G.K.H. Madsen, S. Johnsen, and B.B. Iversen, *Phys. Rev. B* 74, 205105 (2006).
26. M.A. Kassem, Y. Tabata, T. Waki, and H. Nakamura, *J. Phys. Conf. Ser.* 868, 12019 (2017).
27. J. Janaki, A. Mani, A.T. Satya, T.G. Kumary, S. Kalavathi, and A. Bharathi, *Phys. Status Solidi B* 249, 1756 (2012).
28. M. Koirala, H. Zhao, M. Pokharel, S. Chen, T. Dahal, C. Opeil, G. Chen, and Z. Ren, *Appl. Phys. Lett.* 102, 213111 (2013).
29. Y. Wang, C. Fu, T. Zhu, L. Hu, G. Jiang, G. Zhao, D. Huo, and X. Zhao, *J. Appl. Phys.* 114, 184904 (2013).
30. A.V. Sanchela, A.D. Thakur, and C.V. Tomy, *J. Materiom.* 1, 205 (2015).
31. Q. Du, L. Wu, H. Cao, C.J. Kang, C. Nelson, G.L. Pascut, T. Besara, T. Siegrist, K. Haule, G. Kotliar, I. Zaliznyak, Y. Zhu, and C. Petrovic, *npj Quantum Mater.* 6, 13 (2021).
32. R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, *Nature* 413, 597 (2001).
33. M.S. Dresselhaus, G. Chen, M.Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J.P. Fleurial, and P. Gogna, *Adv. Mater.* 19, 1043 (2007).
34. Y. Sun, S. Canulescu, P. Sun, F. Steglich, N. Pryds, J. Schou, and B.B. Iversen, *Appl. Phys. A* 104, 883 (2011).
35. A.T. Duong, S.H. Rhim, Y. Shin, V.Q. Nguyen, and S. Cho, *Appl. Phys. Lett.* 106, 032106 (2015).
36. Y. Sun, S. Canulescu, P. Sun, F. Steglich, N. Pryds, J. Schoub, and B.B. Iversen, *Mater. Chem. Phys.* 129, 105 (2011).

37. Y. Sun, S. Johnsen, P. Eklund, M. Sillassen, J. Bøttiger, N. Oeschler, P. Sun, F. Steglich, and B.B. Iversen, *J. Appl. Phys.* 106, 033710 (2009).
38. J. Wang, X. Jia, S. Lou, G. Li, and S. Zhou, *ACS Omega* 5, 12409 (2020).
39. A. Moridi, L. Zhang, W. Liu, S. Duvall, A. Brawley, Z. Jiang, S. Yang, and C. Li, *Surf. Coat. Technol.* 334, 233 (2018).
40. W. Liu, and A.A. Balandin, *Appl. Phys. Lett.* 85, 5230 (2004).
41. N. Saowadee, K. Agersted, and J.R. Bowen, *J. Microsc.* 266, 200 (2017).
42. H. Kafashan, *J. Electron. Mater.* 48, 1294 (2019).
43. T. Yamashita, and P. Hayes, *Appl. Surf. Sci.* 254, 2441 (2008).
44. A. Boyer, D. Deschacht, and E. Groubert, *Thin Solid Films* 76, 119 (1981).
45. F. Volklein, *Thin Solid Films* 191, 1 (1990).
46. G.J. Snyder, and E.S. Toberer, *Nat. Mater.* 7, 101 (2008).
47. Q. Zeng, J. Shen, H. Zhang, J. Chen, B. Ding, X. Xi, E. Liu, W. Wang, and G. Wu, *J. Phys. Condens. Matter* 31, 425401 (2019).
48. A. Mekys, J. Storasta, A. Zindulis, A.P. Smilga, and S. Balakauskas, *Acta Phys. Pol. A* 114, 903 (2008).
49. Z. Li, C. Xiao, H. Zhu, and Y. Xie, *J. Am. Chem. Soc.* 138, 14810 (2016).
50. C. Zhao, Z. Li, T. Fan, C. Xiao, and Y. Xie, *Research* 2020, 1 (2020).
51. Y. Sun, W. Qiu, L. Zhao, H. He, L. Yang, L. Chen, H. Deng, X. Shi, and J. Tang, *Chem. Phys. Lett.* 755, 137770 (2020).
52. L. Hu, T. Zhu, X. Liu, and X. Zhao, *Adv. Funct. Mater.* 24, 5211 (2014).
53. Y. Liu, M. Zhou, and J. He, *Scr. Mater.* 111, 39 (2016).
54. W. Xie, S. Populoh, K. Gałazka, X. Xiao, L. Sagarna, Y. Liu, M. Trottman, J. He, and A. Weidenkaff, *J. Appl. Phys.* 115, 103707 (2014).
55. Z. Liu, W. Gao, W. Zhang, N. Sato, Q. Guo, and T. Mori, *Adv. Energy Mater.* 10, 2002588 (2020).
56. J. Shuai, Y. Sun, X. Tan, and T. Mori, *Small* 16, 1906921 (2020).
57. Y. Pei, L. Zheng, W. Li, S. Lin, Z. Chen, Y. Wang, X. Xu, H. Yu, Y. Chen, and B. Ge, *Adv. Electron. Mater.* 2, 1600019 (2016).
58. Z. Liu, N. Sato, W. Gao, K. Yubuta, N. Kawamoto, M. Mitome, K. Kurashima, Y. Owada, K. Nagase, C.H. Lee, J. Yi, K. Tsuchiya, and T. Mori, *Joule* 5, 1196 (2021).
59. Q. Guo, W. Zhang, Z. Liu, X. Fu, S.L. Tonquesse, N. Sato, H.W. Son, K. Shimamura, D. Berthebaud, and T. Mori, *ACS Appl. Mater. Interfaces* 13, 8574 (2021).
60. Y. Miyazaki, H. Hamada, H. Nagai, and K. Hayashi, *Materials* 11, 926 (2018).
61. B. Ge, J. Hu, Z. Shi, H. Wang, H. Xia, and G. Qiao, *Nanoscale* 11, 17340 (2019).
62. Y. Pei, H. Wang, and G.J. Snyder, *Adv. Mater.* 24, 6125 (2012).
63. H. Zhu, C. Xiao, and Y. Xie, *Adv. Mater.* 30, 1802000 (2018).
64. J. Shuai, J. Mao, S. Song, Q. Zhu, J. Sun, Y. Wang, J. Ran He, G. Zhou, D.J. Chen, and Z.R. Singh, *Energy Environ. Sci.* 10, 799 (2017).
65. B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M.S. Dresselhaus, G. Chen, and Z. Ren, *Science* 320, 634 (2008).
66. T. Zhu, Y. Liu, C. Fu, J.P. Heremans, J. Snyder, and X. Zhao, *Adv. Mater.* 29, 1605884 (2017).
67. T. Yamane, N. Nagai, S. Katayama, and M. Todoki, *J. Appl. Phys.* 91, 9772 (2002).
68. S.D. Sharma, K. Bayikadi, S. Raman, and S. Neeleshwar, *Nanotechnology* 31, 365402 (2019).
69. M. Pokharel, H. Zhao, Z. Ren, and C. Opeil, *Int. J. Therm. Sci.* 71, 32 (2013).
70. T.Y. Kim, C.H. Park, and N. Marzari, *Nano Lett.* 16, 2439 (2016).

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