

MgSiSn/Mg₂Sn Amorphous–Crystalline Nanocomposites with Enhanced Figure-of-Merit Performance for Efficient Thermoelectric Conversion

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ABSTRACT: Thermoelectric conversion is emerging as an efficient method for transforming waste heat into electricity. Approximately 60% of unrecovered waste heat is below 500 K, necessitating suitable materials. Bi₂Te₃-based compounds, widely commercialized for this purpose, exhibit a figure of merit (zT) of one near room temperature but are expensive and highly toxic. While less toxic and more abundant materials including Mg₂Sn and Mg₂Si are explored as alternatives, their zT values remain considerably low. For zT enhancement, Mg₂Si_xSn_y nanocomposite thin films were fabricated using a combinatorial sputter coating system. Through interfacial engineering and nanocrystallization, this system produced multilayered (ML) Mg₂Si and Sn structures that overcame the trade-off relationship among

Seebeck coefficient, electrical conductivity, and thermal conductivity, achieving zT values of 0.021 and 0.083 at room temperature and 520 K, respectively. ML samples were fabricated on flexible substrates for potential wearable thermoelectric applications. This zT -enhancement strategy can yield high-performance, ecofriendly thermoelectric thin films.

KEYWORDS: Thermoelectric conversion, Sputter coating, Thin film, Coating, Combinatorial technology, Magnesium silicide, Flexible thermoelectric device

1. Introduction

Thermoelectric energy conversion has garnered increasing attention as an efficient method for converting waste heat into electricity, making it a promising technology for energy harvesting across various applications. Approximately 60% of unrecovered waste heat exists at temperatures below 500 K, making low-temperature thermoelectric materials crucial for effective energy harvesting[1]. Among commercially available thermoelectric materials, Bi_2Te_3 -based compounds, which exhibit a figure of merit (zT) of approximately one, are preferred for near-room-temperature applications[2]. However, their widespread adoption is hindered by high cost and toxicity concerns. To address these limitations, researchers have explored alternative thermoelectric materials such as Mg_2Sn - and Mg_2Si -based compounds, which are more abundant and less toxic[3]. However, their relatively low zT values prevent them from serving as effective replacements for Bi_2Te_3 -based materials, making improvements in zT performance a critical research focus. Simultaneously, the rising demand for lightweight, flexible thermoelectric devices particularly for wearable electronics and curved surfaces along with the need for reduced material usage, has spurred interest in the development of thin-film thermoelectric materials. However, these thin-film materials generally exhibit poorer performance than their bulk

counterparts. Recent advancements in deposition and evaluation techniques have enabled the optimization of the composition and introduction of doping elements into Mg_2Sn - and Mg_2Si -based thin films, improving their zT values[4-34]. Although Mg_2Si and Mg_2Sn have long been researched as thermoelectric materials, their low electrical conductivity and high thermal conductivity result in a relatively low zT value. To improve the zT values of these materials, researchers have added doping elements that enhance electrical conductivity; alternatively, they have partially substituted the Si sites with doping elements having a larger atomic radius than Si to reduce thermal conductivity.

The efficiency of thermoelectric materials is evaluated using zT , a dimensionless parameter defined as $zT = (S^2 \sigma / \kappa)T$, where S denotes the Seebeck coefficient (SC, $S = DV/DT$), σ denotes electrical conductivity (EC), κ represents thermal conductivity (TC), and T signifies absolute temperature. TC (κ) comprises two components: electronic TC (κ_{el}) and lattice TC (κ_{lat}). Among these, κ_{el} is related to EC (σ) through the Wiedemann–Franz law: $\kappa_{\text{el}} = L\sigma T$, where L denotes the Lorentz number. Consequently, optimizing one parameter to enhance zT often leads to compensatory changes in another, leading to a trade-off.

One approach to improving zT performance involves utilizing nanocomposite thin films with low-dimensional structures, which enhance zT performance by leveraging the quantum and classical size effects of electrons and phonons[35-37]. In such structures, the SC is expected to increase owing to the steepening of the density of states (DOS) slope near the Fermi level with decreasing dimensionality. Under these conditions, TC is also expected to decrease owing to enhanced phonon scattering caused by an increase in interfacial density. If Mg_2Si - and Mg_2Sn -based thermoelectric materials can exhibit high zT values using this approach, then thermoelectric devices can be fabricated from environmentally friendly, inexpensive materials.

The development of novel thermoelectric materials requires a film-coating system that can efficiently and reproducibly generate various materials with controlled nanostructures. We have developed a combinatorial sputter coating system (COSCOS), which can precisely control the film-coating parameters and automatically fabricate multiple samples with different crystal, nanostructures, and compositions; additionally, we have used it to develop novel materials for thermoelectricity[38, 39], thermal management[40-50], tribology[51-57], and other applications.

The objective of this study is not to identify materials with the highest zT values but to verify whether nanostructure control can overcome the trade-off relationship among the three parameters governing thermoelectric performance, thereby enabling the application of the proposed approach to thermoelectric materials with high zT values or to develop new thermoelectric materials. For this purpose, we fabricate nanocomposite thin films composed solely of Mg, Sn, and Si— widely available elements—and simplify material structures using COSCOS. Notably, this technique offered high control over material nanostructures, enabling improvements in zT through low-dimensional and interfacial effects.

2. Experimental procedure

2.1 Sample fabrication apparatus

Nanocomposite thin films composed of Mg, Sn, and Si were fabricated using a combinatorial sputter coating system (COSCOS), as depicted in **Fig. 1**. Notably, the COSCOS is a system widely used for material development across various fields. It enables a streamlined research and development process, from material discovery to device fabrication, facilitating the rapid identification of high-performance materials and their integration into industrial applications. The sputtering method offers control over numerous experimental parameters, including working pressure, gas composition, partial pressure of mixed gases, radio frequency (RF) power, substrate temperature, substrate–target distance, and bias voltage. By modifying these parameters, thin

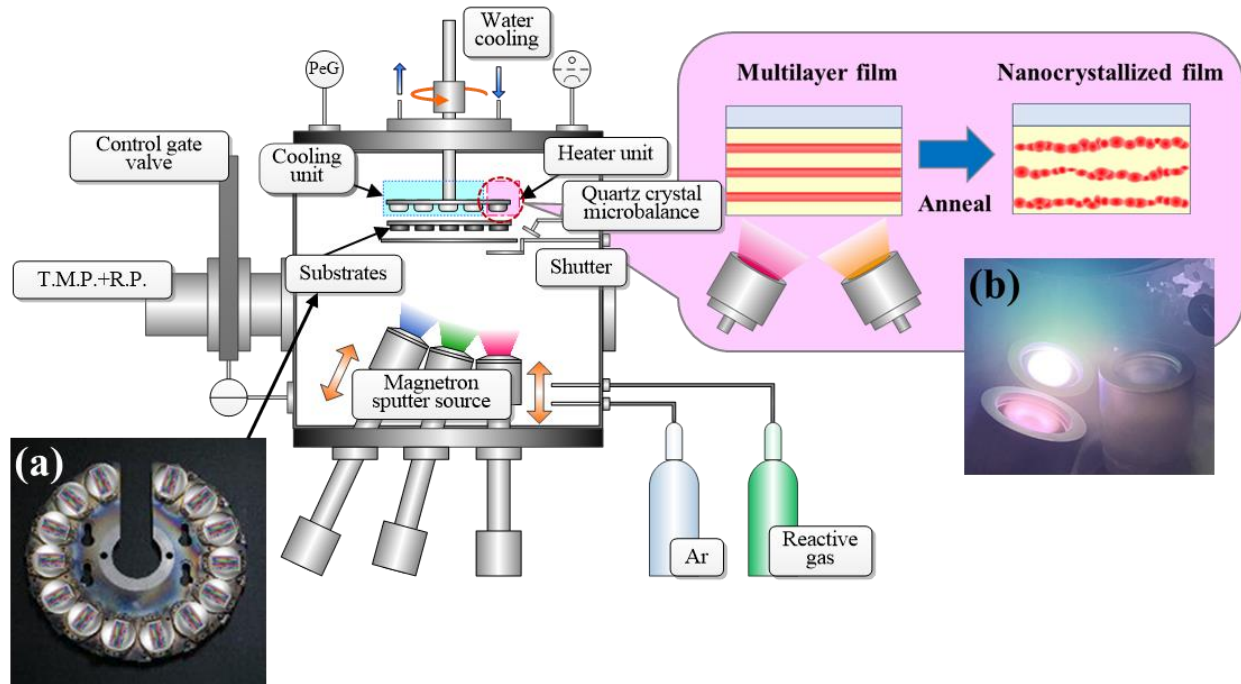


Fig. 1. Schematic illustration of the COSCOS.

films with varying properties can be produced. Furthermore, even when desirable material properties are achieved, ensuring reproducibility in thin-film fabrication is crucial for conducting fundamental research and advancing practical applications. However, the need to control multiple experimental parameters and the lack of reproducibility in thin-film fabrication have been identified as major challenges in the sputtering process. To address these issues and enable high-throughput material discovery, we introduced the basic concept of the COSCOS, which applies combinatorial technology to sputter coating. Unlike conventional combinatorial techniques, the COSCOS was designed to streamline the entire process, from rapid material discovery to industrial-scale applications, including device fabrication.

The COSCOS primarily consists of a vacuum chamber, multiple sample holders, sputter cathodes, a vacuum pumping system, and an automated valve control system. A large front hatch in the vacuum chamber allows for efficient sample loading and unloading. The chamber is evacuated using a high-capacity turbomolecular pump (Shimadzu Model TMP-803LM(0), 800 L/s), achieving a vacuum of up to 2×10^{-6} Pa without the need for chamber baking.

Generally, during chamber baking, contamination from the chamber walls affects the substrate surface, making it difficult to achieve reproducible sample fabrication. To address this, various commercially available and custom-developed magnetron sputter cathodes are used to supply material elements, in combination with RF and direct current (DC) power supplies as needed. This setup allows for the deposition of a wide range of materials, including metals, ceramics, semiconductors, and polymers. To enhance the reproducibility of sputter-coated films, the vacuum chamber pressure is monitored using a capacitance manometer (CM) during sputtering. This system is integrated with a gate valve controller for feedback control, ensuring a stable sputtering gas pressure. The CM is specifically used owing to its ability to withstand 100% oxygen environments, as filament-based vacuum gauges cannot operate under high oxygen concentrations due to filament burnout. Additionally, the multi-sample holder (**Fig. 1(a)**) enables the simultaneous preparation of multiple samples, with up to 14 samples typically processed in a single vacuum evacuation. **Fig. 1(b)** presents a photograph of the vacuum chamber interior with its front door open. Here, discharge occurs from the three magnetron sputter cathodes positioned at the bottom of the chamber. The sample exchange mechanism is located at the top, while the sputter cathodes are at the bottom. A mask plate is placed at the bottom of the sample exchange mechanism, ensuring that only one sample is coated at a time. Once the coating process is completed, the multi-sample holder rotates, positioning the next sample for deposition. Heat transfer between individual sample fixtures and the multi-sample holder is minimized using alumina spacers, allowing only the sample at the coating position to be heated to approximately 1273 K. During this heating process, the remaining 13 samples are continuously water-cooled, maintaining the temperature rise for non-coated samples within 80 K. A thermocouple, in contact with both the sample holder and the heater, performs feedback control to maintain a constant set temperature. Additionally, a DC bias voltage of up to 1200 V can be applied to the sample. The substrate–target distance is adjustable using a motor-driven linear positioning mechanism. Coating parameters, including sputter gas pressure, gas composition, partial pressure, sputter power, substrate temperature, substrate–target distance, and bias voltage, can be configured and remotely controlled via an external control system. The control system allows manual implementation of individual system functions and real-time monitoring of system status. Once the predefined process recipe is initiated, the coating procedure runs fully automatically. Real-time monitoring of film thickness, temperature, and gas pressure during coating is possible, with

all data recorded in a log file. These data, along with the results of sample property evaluations, are stored in a database and integrated with materials informatics technology to facilitate the discovery of new materials. Overall, this automated fabrication process offers several advantages. First, the system is capable of producing thin films with a relatively large area, facilitating their use in various applications. Automation also reduces the workload on researchers, allowing them to focus on other tasks while experiments are underway. Additionally, reproducibility is improved by eliminating human variability in the process. In summary, this approach dramatically improves the efficiency of materials development, enabling systematic exploration of thin-film materials with novel properties and facilitating performance optimization—tasks that previously required considerable time and effort. Although not attempted in this study, the fabricated thin-film thermoelectric materials can be integrated with electrodes to produce thermoelectric devices using the device fabrication mode of the COSCOS. This capability highlights the COSCOS as an efficient system for rapid thermoelectric material exploration and device fabrication.

2.2 Fabrication of nanomaterials

Nanocomposite Mg, Sn, and Si thin films were fabricated using the COSCOS with two sputter cathodes. The films were deposited at room temperature onto microelectromechanical system (MEMS) sample tips (**Fig. 2**) for thermoelectric property measurements, with a floating potential applied during the coating process. For sputter coating, Mg₂Si (diameter: 50 mm, thickness: 6 mm, 99% purity, Kojundo Chemical Lab. Co., Ltd.) and Sn (diameter: 50 mm, thickness: 6 mm, 99.999% purity, Kojundo Chemical Lab. Co., Ltd.) sputter targets were used with high-purity argon gas (99.999%) at a working pressure of 0.4 Pa. The RF power was set to 60 W for the Mg₂Si target and 100 W for the Sn target during ML sample preparation. The target–sample distance was fixed at 190 mm, and pre-sputtering was performed for 15 min. ML thin films were fabricated by alternating layers of Mg₂Si and Sn in three different configurations: 18 nm/2 nm, repeated 143 times ($18/2 \times 143$; hereafter 18/2); 18 nm/4 nm, repeated 136 times ($18/4 \times 136$; hereafter 18/4); and 18 nm/8 nm, repeated 63 times ($18/8 \times 63$; hereafter 18/8). The total thicknesses of these samples were 2860, 2992, and 1638 nm, respectively. These films were then coated onto microelectromechanical system sample tips for thermoelectric measurements.

Film thickness was initially monitored using a conventional quartz crystal thickness monitor and later precisely determined by transmission electron microscopy (TEM). A non-ML thin film with the same elemental composition as the $18/2 \times 143$ sample was also prepared by fixing the RF power for the Sn target at 100 W while varying the RF power for the Mg_2Si target. Additionally, to assess the applicability of the $18/2 \times 143$ nanostructured sample for flexible thermoelectric devices, a thin film was deposited on a polyimide substrate.

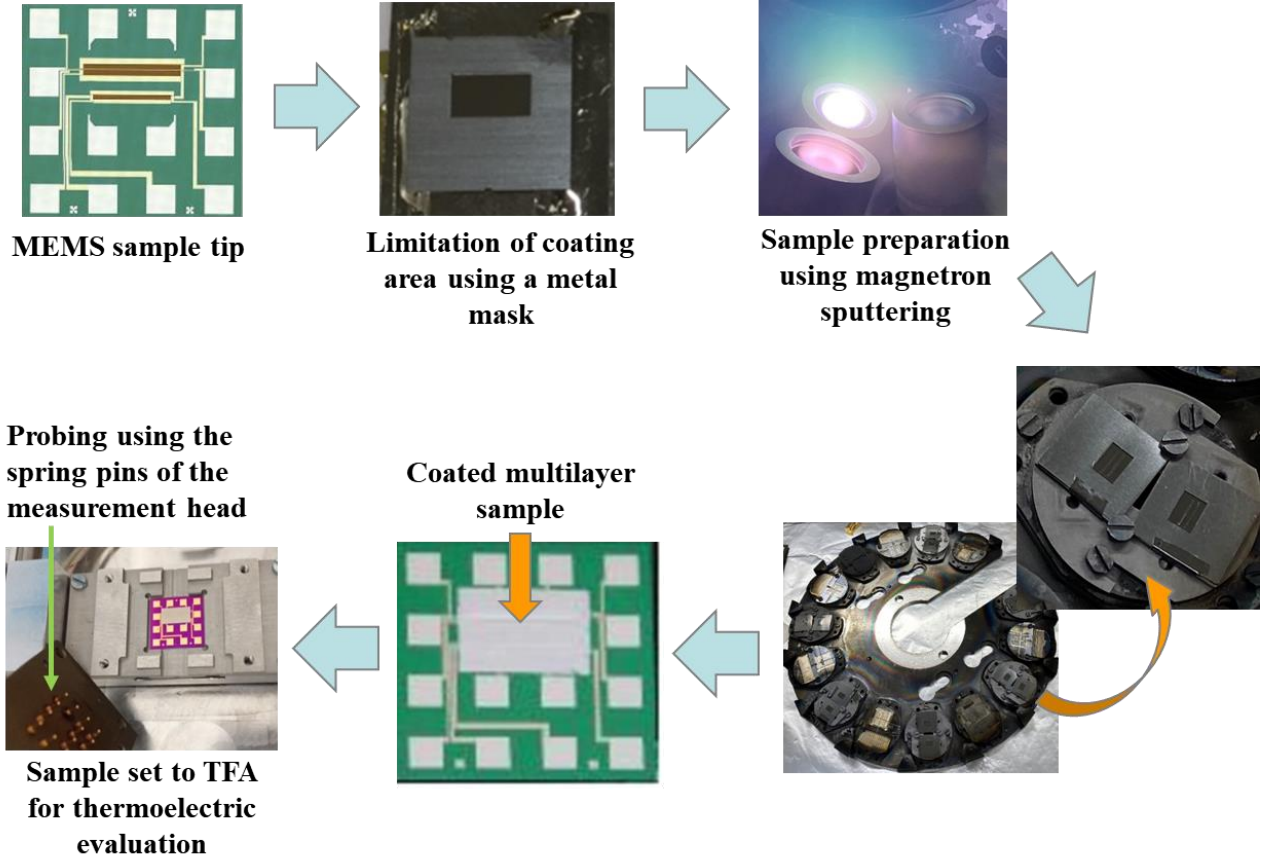


Fig. 2. Fabrication and thermoelectric property assessment of $\text{Mg}_2\text{Si}/\text{Sn}$ nanocomposite thin films using the COSCOS.

2.3 Characterization

The crystal structure, multilayer arrangement, material composition, and elemental distribution of the thin films were analyzed using TEM (JEOL JEM-ARM200F) with energy-dispersive X-ray spectroscopy and electron diffraction. The in-plane thermoelectric properties of the samples, including the Seebeck coefficient, electrical conductivity, and thermal conductivity,

were assessed using a thin-film analyzer (TFA) (LINSEIS TFA). Measurements of additional thermoelectric parameters such as carrier density, mobility, Hall coefficient, and heat capacity were obtained from the same sample to ensure consistency and improve measurement reliability. The thermoelectric samples were deposited on a designated area of the MEMS sample tips using a metal mask in the COSCOS (**Fig. 2**). After removing the mask, the sample tip was inserted into the TFA system. Fourteen test probes were then connected to the electrodes of the MEMS sample, allowing automated thermoelectric property analysis. Further details on the analysis method are available in previous reports[58].

Details regarding the thermoelectric measurement apparatus are provided in **Fig. 2**. During thermoelectric property measurements under heating, the initial sample nanostructures underwent modifications, leading to corresponding changes in thermoelectric performance. We investigated the relationship between these structural transformations and thermoelectric property variations to acquire insights for improving zT values. For comparison, a reference sample with the same elemental composition as the 18/4 sample but without an ML structure was also prepared.

3. Results and discussion

Subsequently, the thermoelectric properties of the nanostructured samples (18/2, 18/4, and 18/8) and the non-nanostructured reference sample (labeled Normal in the figure) were analyzed, as depicted in **Fig. 3**. The corresponding results, displayed in **Fig. 3a**, reveal that the 18/4 and 18/8 samples exhibited higher SC values than the Normal and 18/2 samples. After annealing, the SC of the 18/4 sample reached its maximum of $167 \mu\text{V/K}$, approximately 13 times higher than that of the annealed Normal sample ($13 \mu\text{V/K}$). The SC values of all samples except 18/2 increased after annealing, with the most pronounced increase observed in the 18/4 sample. This suggests that the initial ML structure underwent changes during annealing, as will be discussed

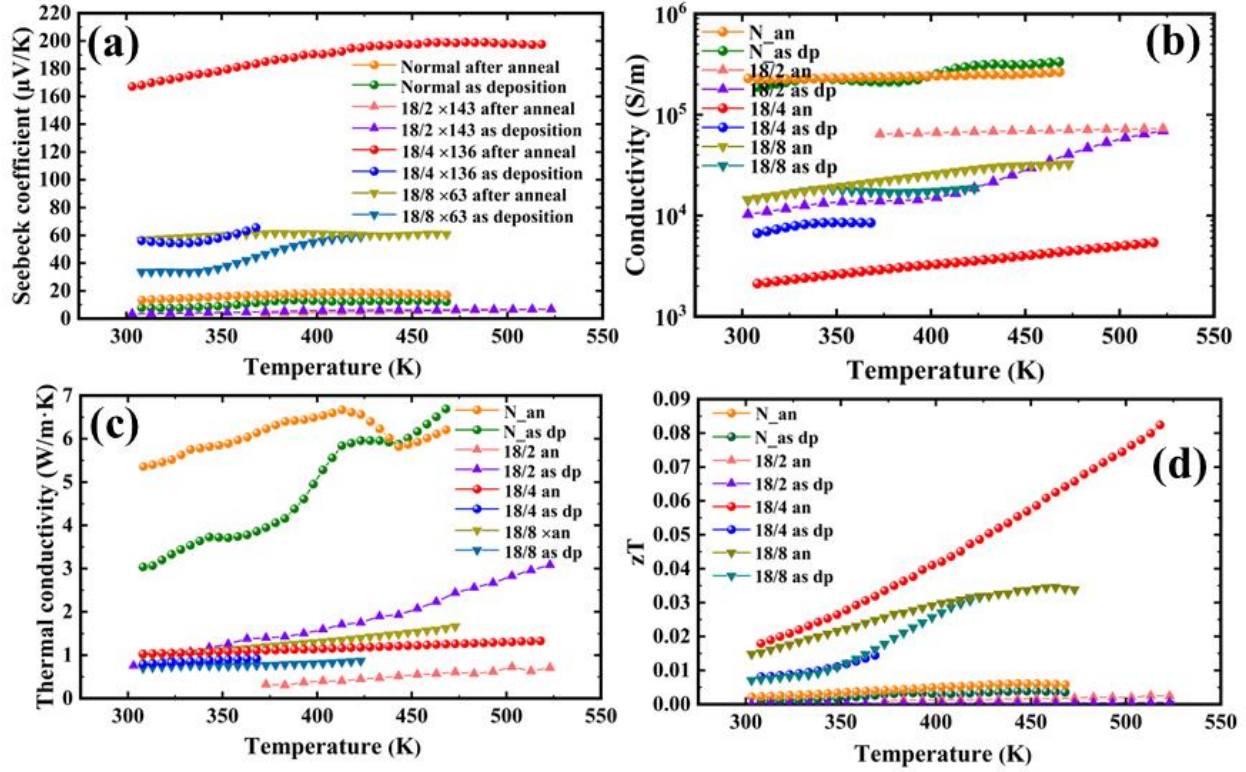


Fig. 3. Temperature dependence of the thermoelectric properties of Mg₂Si/Sn nanocomposite thin-film samples (18/2, 18/4, and 18/8) and the non-nanostructured reference sample (denoted as "Normal" in the figure): (a) Seebeck coefficient (S), (b) electrical conductivity, (c) thermal conductivity, and (d) figure of merit (zT).

later. In contrast, the SC of the 18/2 sample was lower than that of the Normal sample. Similarly, the EC values of all ML samples (18/2, 18/4, and 18/8) were also lower than those of the Normal sample across the entire temperature range, as illustrated in (Fig. 3). Additionally, annealing decreased the EC of the 18/4 sample but increased the EC of the 18/2 and 18/8 samples.

The EC of the Normal sample, remained nearly unchanged. As illustrated in Fig. 3c, the TC values of all ML samples were substantially lower than that of the Normal sample. Specifically, for the 18/4 sample, TC increased slightly after annealing but remained around 1 W/mK. In contrast, the TC values of the 18/2 and 18/8 samples decreased after annealing, with the lowest value of 0.3 W/mK observed for the 18/2 sample at 373 K, which was remarkably low compared

to the typical values observed for conventional Mg_2Si -based materials. **Fig. 3d** presents the temperature dependence of zT values. Notably, the zT values of the 18/4 and 18/8 samples were higher than those of the Normal and 18/2 samples. Further, annealing increased the zT value of the 18/4 sample by approximately 2.3. Compared to the Normal sample, this zT represented an increase of nearly tenfold. These results demonstrated that the ML samples achieved substantial improvements in thermoelectric performance. To simplify the graph, only data obtained during the heating phases before and after the annealing of each sample were shown. The actual data were more complex; for example, the data of sample 18/4 were collected during 10 cycles of the heating and cooling phases (**Fig. 4**). At the start of evaluation, temperature was limited to approximately 400 K or lower to avoid sudden changes in the nanostructure and to investigate

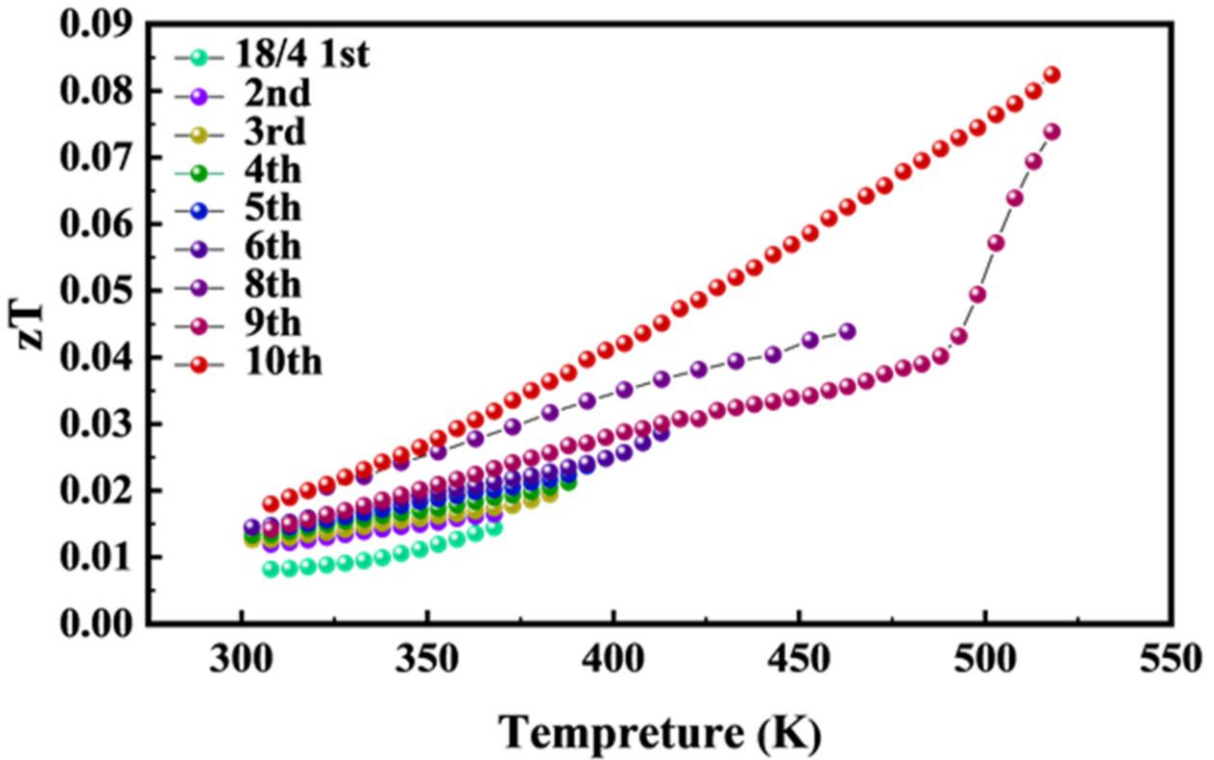


Fig. 4. Ten repeated cycles of the temperature dependence of the figure of merit (zT) of a $\text{Mg}_2\text{Si}/\text{Sn}$ nanocomposite thin-film sample (18/4).

the detailed correlation between nanostructure differences and thermoelectric properties. The samples could be evaluated even after 10 repeated cycles, confirming their stability.

The temperature dependence of the zT value for an $18/2 \times 143$ nanostructured sample was measured via 10 cycles of heating and cooling. To avoid complicating their display, only data obtained during the temperature rise are shown. In addition, data acquisition failed during the seventh cycle. The thermoelectric characteristics improved through repeated measurements. The sample remained suitable for evaluation even after 10 measurements, confirming its sufficient stability. To suppress rapid changes in the nanostructure caused by high-temperature heating, the initial maximum temperature was set low (368 K during the 1st cycle, 383 K during the 2nd cycle, 388 K during the 3rd cycle, and similarly up to the 10th cycle). Gradual nanostructure variations caused by sample heating during multiple thermal–electric property evaluations clearly changed the zT value. As shown in the graph, the zT value improved through consecutive measurements.

To investigate the reasons underlying the observed zT increase for the $18/4$ sample, transmission electron microscopy (TEM) and electron diffraction (ED) analyses were performed, as depicted in **Fig. 5** and **Fig. 6**. A well-ordered ML structure was observed near the substrate of the $18/4$ sample, as illustrated in **Fig. 5a**. However, toward the surface, the structure became scaly and disordered, as illustrated in **Fig. 5b**. This transformation is attributed to the effect of increasing temperature within the film during sputter deposition and the stress induced by lattice mismatch. After annealing, the overall film structure became more uniform, as depicted in **Fig. 5c**. In contrast, the periodic structure of the interface became less distinct, and tiny crystal grains, ranging from several nanometers to approximately 20 nm in diameter, formed (**Fig. 5d**). **Fig. 7** presents elemental mapping images of the samples obtained using energy-dispersive X-ray

spectroscopy (EDX). As illustrated in **Fig. 7a**, in the as-deposited state, despite the alternating deposition of Mg_2Si and Sn, Mg was uniformly distributed throughout the film, whereas Si and Sn formed a distinct periodic structure. After annealing, as illustrated in **Fig. 7b**, Mg species

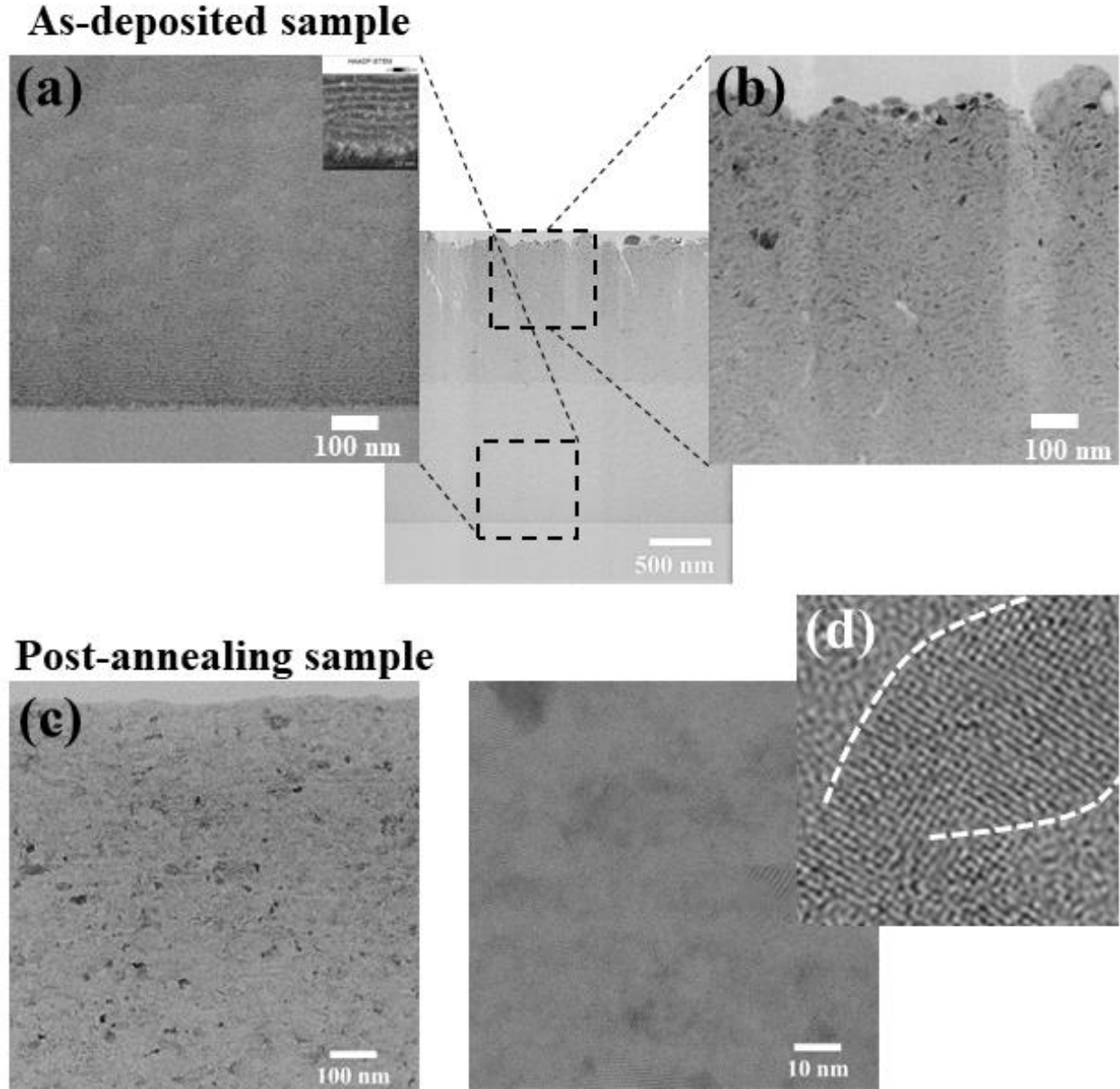


Fig. 5. Transmission electron microscopy images of an $\text{Mg}_2\text{Si}/\text{Sn}$ nanocomposite thin-film sample (18/4). (a) A superlattice-like structure is observed in the region near the substrate in the as-deposited sample. (b) The superlattice interfaces are clearly visible, exhibiting a well-defined periodic structure, though the layers become curved near the surface. (c) In the annealed sample, the interfaces appear faint and show signs of disruption. (d) Nanocrystalline domains are dispersed across the entire region, with some areas exhibiting torn interfaces.

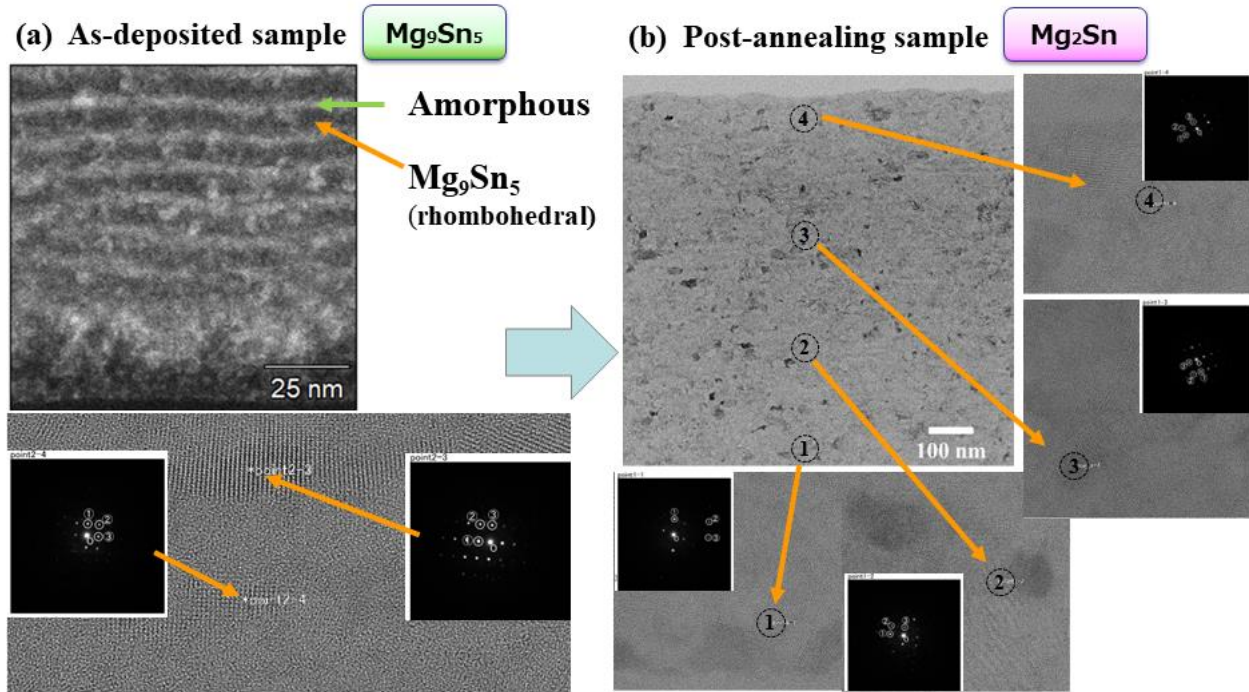
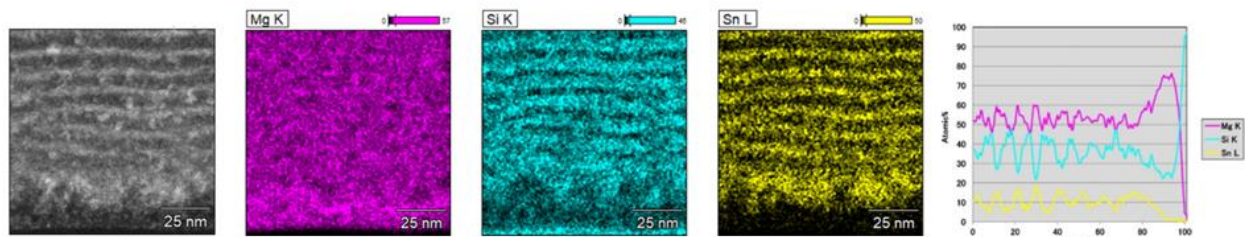


Fig. 6. Electron diffraction analysis of the Mg₂Si/Sn nanocomposite thin film labeled as 18/4. (a) The as-deposited multilayer film consisted of Mg₉Sn₅ nanocrystals embedded in an amorphous matrix. (b) After annealing, the Mg₉Sn₅ nanocrystals transformed into Mg₂Sn nanocrystals with diameters ranging from a few nanometers to approximately 20 nm.

(a) As-deposited sample



(b) Post-annealing sample

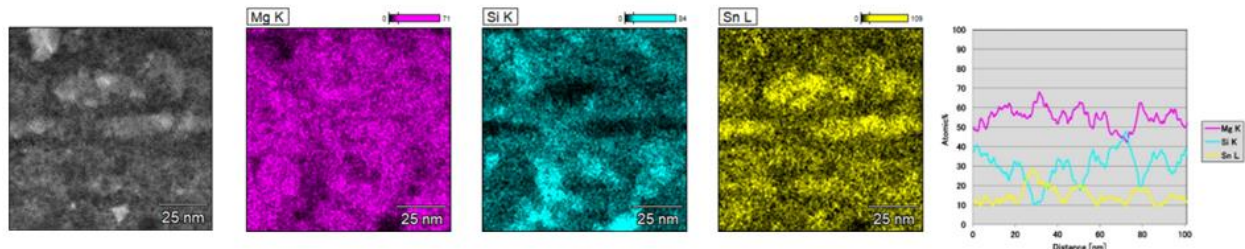


Fig. 7. Elemental mapping images obtained via energy-dispersive X-ray spectroscopy. (a) In the as-deposited sample, despite the alternating deposition of Mg₂Si and Sn, Mg was uniformly distributed throughout the film, while Si and Sn formed a distinct periodic structure. (b) After annealing, Mg migrated toward the Sn regions, becoming more separated from the Si regions. Consequently, the periodic structure was largely preserved, although some interfaces were disrupted.

increasingly migrated toward Sn, separating from Si. Consequently, the periodic structure of the sample was largely retained, although some interfaces were disrupted.

The crystal structure of the 18/4 sample, analyzed using ED, is presented in **Fig. 6**. In the as-deposited state, tiny Mg_9Sn_5 nanocrystals were embedded in the amorphous layers of the ML 18/4 sample (**Fig. 6a**). Upon annealing, these Mg_9Sn_5 nanocrystals transformed into Mg_2Sn nanocrystals. Additionally, annealing led to grain growth, as evidenced by the appearance of crystal sizes ranging from a few nanometers to approximately 20 nm.

The following discussion focuses on factors contributing to the increase in the zT value of the 18/4 sample. Initially, the 18/4 sample had an ML structure composed of 18-nm-thick Mg_2Si layers and 4-nm-thick Sn layers. Subsequent annealing led to the formation of a nanocomposite thin film, where numerous Mg_2Sn microcrystals were dispersed within an amorphous MgSiSn matrix. **Fig. 8a** illustrates the temperature-dependent carrier density of the 18/4 sample before and after annealing. Notably, the as-deposited sample reached its maximum carrier density of $1.8 \times 10^{26} \text{ m}^{-3}$ at 338 K. However, after annealing, the carrier density increased with temperature across the entire measurement range, rising from $0.3 \times 10^{26} \text{ m}^{-3}$ at 308 K to $0.94 \times 10^{26} \text{ m}^{-3}$ at 518 K. Despite this temperature-dependent increase, the overall carrier density in the annealed sample was lower than that in the as-deposited sample. **Fig. 8b** presents the temperature-dependent Hall coefficient of the 18/4 sample. The as-deposited 18/4 sample exhibited a low Hall coefficient of $4 \times 10^{-8} \text{ m}^3/\text{C}$, whereas the annealed sample exhibited a higher value of $2.1 \times 10^{-7} \text{ m}^3/\text{C}$ at 308 K, which decreased with increasing temperature, reaching $6.6 \text{ m}^3/\text{C}$ at 518 K. Further, the temperature-dependent carrier mobility of the 18/4 sample is presented in **Fig. 8c**. For the as-deposited sample, mobility increased from $3.1 \text{ cm}^2/\text{Vs}$ at 308 K to $4.2 \text{ cm}^2/\text{Vs}$ at 368 K. However, for the annealed sample, mobility remained nearly constant at approximately 3.7

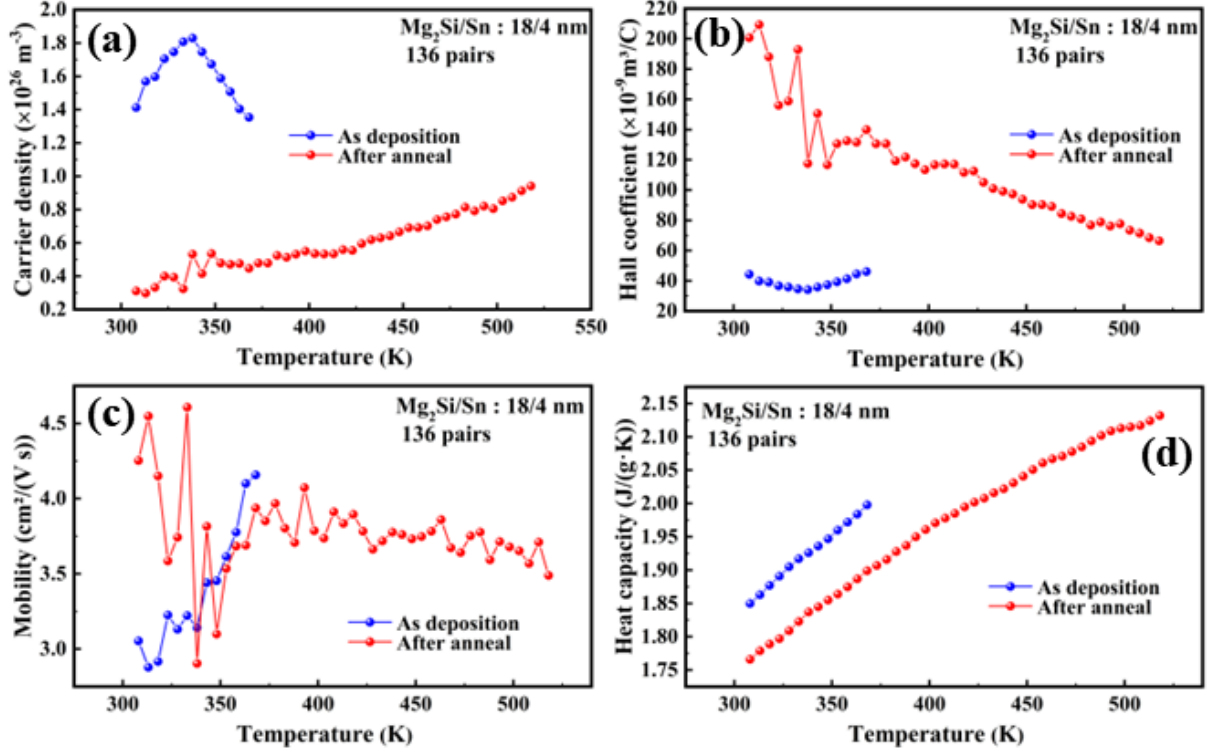


Fig. 8. Temperature dependence of the carrier properties and heat capacity of the $\text{Mg}_2\text{Si/Sn}$ nanocomposite thin-film sample 18/4: (a) carrier density, (b) Hall coefficient, (c) mobility, and (d) heat capacity.

cm^2/Vs . Finally, **Fig. 8d** illustrates the temperature-dependent heat capacity of the 18/4 sample, which increases linearly with temperature. Specifically, before annealing, heat capacity rose from 1.85 J/gK at 308 K to 2.00 J/gK at 368 K, whereas after annealing, it increased from 1.77 J/gK at 308 K to 2.13 J/gK at 518 K. **Fig. 9** illustrates the changes in electronic TC (κ_{el}) and lattice TC (κ_{lat}) for the ML 18/4 sample and Normal (non-multilayered) sample. The results indicated that multilayering reduced κ_{el} and κ_{lat} . In the as-deposited state, the κ_{lat} values of the ML sample were notably low, measuring 0.74 W/mK at 308 K and 0.84 W/mK at 368 K. Annealing led to an increase in these κ_{lat} values; however, they remained low, measuring 1.0 W/mK at 308 K and 1.26 W/mK at 518 K. Further, the κ_{el} values of the as-deposited 18/4 sample ranged from 0.05 W/mK at 308 K to 0.08 W/mK at 368 K and further decreased after annealing,

reaching as low as 0.02 W/mK at 308 K and 0.07 W/mK at 518 K. In contrast, κ_{el} and κ_{lat} were higher for the Normal sample, ranging from 1.5 to 4.2 W/mK. Overall, the increase observed in κ_{el} for the annealed sample was attributed to progressive crystallization. These results demonstrated that multilayering was highly effective in suppressing TC.

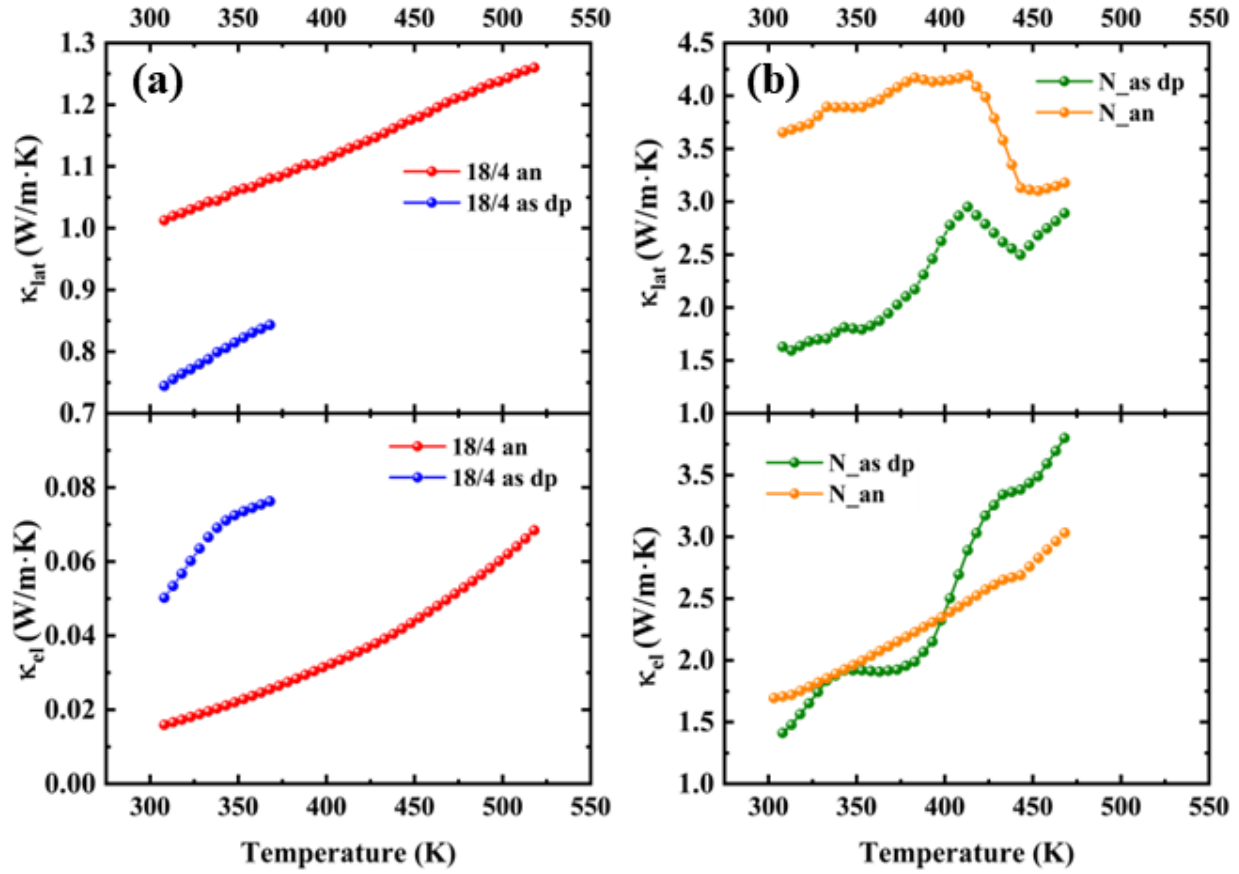


Fig. 9. Electronic thermal conductivity (κ_{el}) and lattice thermal conductivity (κ_{lat}) of the Mg_2Si/Sn nanocomposite thin-film sample 18/4 and the non-nanostructured reference sample ("Normal"). (a) κ_{el} and κ_{lat} for the 18/4 sample. (b) κ_{el} and κ_{lat} for the reference sample. Multilayering effectively reduced both κ_{el} and κ_{lat} .

Collectively, the results discussed so far indicated that the thickness of the ML film, optimization of the interfacial structure between layers through annealing, and controlled dispersion of Mg_2Sn microcrystals within the amorphous matrix were key factors contributing to

the improvement in zT . As illustrated in **Fig. 3b**, TC decreases considerably with annealing, likely owing to phonon scattering induced by the introduction of interfaces and the formation of amorphous–crystalline hybrid structures[59-69]. If the ML structure were entirely regular and ordered, phonon scattering would be limited to its narrow interfaces. However, in reality, interface scattering and the mixed amorphous–microcrystalline state of constituent materials in the ML structure contributed to the reduction in TC.

Phonon scattering is known to be effective at the interfaces between amorphous and crystalline materials. In terms of charge carrier properties, our results reveal that the optimized ML structure of the 18/4 sample substantially improves its SC while minimizing the reduction in its EC (**Fig. 3a** and **3b**). This enhancement is attributed to nanostructuring-induced modifications in the DOS, which improve the SC[70-75]. Additionally, the energy filtering effect may have facilitated selective transport of carriers with specific energy levels[76-104]. In summary, optimizing the thickness of the ML film, its interfacial states, and its nanocrystalline–amorphous structure enables effective tuning of both carrier and phonon scattering, ultimately leading to an improvement in zT performance.

In addition to the Mg, Sn, and Si nanocomposite thin films, ML samples were also fabricated on flexible polyimide polymer substrates for potential



Fig. 10. Photograph of the Mg_2Si/Sn nanocomposite thin-film sample deposited on a flexible polyimide substrate for potential application in flexible thermoelectric devices. The film demonstrated strong adhesion and mechanical stability, remaining intact without peeling even when the substrate was bent.

applications in thin-film thermoelectric devices. As depicted in **Fig. 10**, the ML samples on polyimide remained intact even when the substrate was bent, demonstrating sufficient adhesion strength and film rigidity for flexible device applications.

Table 1 lists the zT or power factor (PF) values reported for $Mg_2Si_xSn_y$ thermoelectric materials. The zT values of bulk Mg_2Si and Mg_2Sn were 0.0016 at 323 K and 0.013 near room temperature. By optimizing the Si:Sn composition ratio, the zT value of bulk $Mg_2Si_{0.4}Sn_{0.6}$ was increased to 0.03 at 323 K and 0.28 at 300 K. Thermoelectric thin films, which generally exhibit lower crystallinity than bulk materials, tended to have considerably lower zT values. However, in 2019 and 2021, Safavi et al. obtained zT values of 0.1 and 0.0007 for nondoped $Mg/Sn = 1.78$ and $Mg_2Si_{0.35}Sn_{0.65}$ thin films at 300 K through composition optimization. Additionally, Byeon et al. reported a zT of 0.0124 for an $Mg_{1.9}(Si,Sn)$ thin film. Notably, the abovementioned studies evaluated the SC, EC, and TC data of identical thin-film samples under consistent environmental conditions for zT determination. One of the primary reasons for the lack of reports on the zT performance of thermoelectric thin films is the difficulty in measuring TC under consistent conditions. In this study, zT and PF values of 0.021 and $7.1 \times 10^{-5} \text{ W/mK}^2$ at 323 K and 0.083 and $2.1 \times 10^{-4} \text{ W/mK}^2$ at 520 K, respectively, were achieved for an $MgSiSn$ -based amorphous thin film containing Mg_2Sn nanocrystals. These zT values are approximately 30 times higher than those of non-nanostructured $Mg_2Si_{0.35}Sn_{0.65}$ thin films and approximately 10 times higher than those of thin films with the same composition as the Normal sample in this study. These results demonstrate that the controlled fabrication of nanostructures is an effective approach for enhancing zT .

Table 1. Comparison of zT values between $Mg_2Si_xSn_y$ materials reported in previous studies and this study.

Year	Compound	Type	zT @ 300K	zT_{max}	PF (W/mK ²)	Author
2006	Mg ₂ Si (Bulk)	n	0.0016 (323K)	0.13 (653K)		Aizawa et al. ⁴
2006	Mg ₂ Sn (Bulk)	p	0.013 (323K)	0.013 (323K)		Aizawa et al. ⁴
2006	Mg ₂ Si _{0.4} Sn _{0.6} (Bulk)	p	0.03 (323K)	0.13 (653K)		Aizawa et al. ⁴
2006	Mg ₂ Si _{0.4} Sn _{0.6} (Bulk)	p	0.28	1.1 (800K)		Zaitsev et al. ⁵
2015	Mg ₂ Si	n	---	---	7×10^{-7} (323 K) 3.5×10^{-5} (723 K)	Tani et al. ¹⁰
2018	Mg ₂ Si	n	---	---	7.6×10^{-6} (300 K)	Yazdi et al. ¹²
2019	Mg ₂ Sn	p	---	---	8.5×10^{-4} (519 K)	Tani et al. ¹⁵
2019	Mg/Sn = 1.78	p	0.1	0.26 (473 K)	---	Safavi et al. ¹⁴
2021	Mg ₂ Si _{0.35} Sn _{0.65}	p	0.0007	0.0042 (473 K)	---	Safavi et al. ¹⁹
2023	Mg _{1.9} (Si,Sn)	p	0.0124	0.0143 (360K)	---	Byeon et al. ²⁴
2025	a-MgSiSn /nc-Mg ₂ Sn	p	0.021	0.083 (520 K)	7.1×10^{-5} (300 K) 2.1×10^{-4} (520 K)	This Study
2025	Mg ₂ SiSn _{0.04}	p	0.0022	0.0061 (430 K)	4.0×10^{-5} (300 K) 7.7×10^{-5} (520 K)	This Study

4. Conclusions

This study aimed to improve the performance of thermoelectric materials in converting waste heat below 500 K into usable energy—a regime where existing commercial alternatives, such as Bi_2Te_3 , encounter limitations owing to high cost and toxicity. To this end, the study examined Mg_2Si -based materials composed of abundant, low-toxicity elements that could serve as viable alternatives. The objective was to improve zT by leveraging the low-dimensional and interfacial effects of nanocomposite thin films. The SC reached its maximum in specific multilayer configurations, attaining considerably higher values than the standard composition after annealing. EC generally decreased in ML samples but was slightly enhanced by annealing. In contrast, TC was substantially reduced through multilayering, demonstrating the effectiveness of this approach in suppressing heat flow. The enhancement in zT was primarily attributed to the formation of Mg_2Sn nanocrystals within the amorphous MgSiSn matrix following annealing. TEM and EDX analyses revealed notable annealing-induced structural changes, including elemental redistribution and grain growth, which played a crucial role in improving thermoelectric properties. Additionally, flexible thermoelectric devices were successfully fabricated and tested, confirming that these materials can be incorporated into wearable electronics without performance degradation. Ultimately, this study demonstrates the feasibility of achieving near-bulk performance in thin-film MgSiSn thermoelectric materials. As such, nanostructure control can dramatically improve the zT s of thermoelectric materials with ubiquitous elemental systems, in which zT is low for practical applications. In the future, the possibility of creating nanostructures that can improve zT in bulk materials through doping and composite material processes should be investigated. This will lead to the applications of these nanostructures in wearable devices and other thermoelectric power-generation devices. Overall,

the present findings suggest that the proposed approach can contribute to the development of high-performance thermoelectric materials with improvements in zT .

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