Improving the Performance of Thermoelectric Materials by Atomic Layer Deposition-based Grain Boundary Engineering①

LI Shuan-Kui ZHU Wei-Ming
XIAO Yin-Guo② PAN Feng②
(*School of Advanced Materials, Peking University Shenzhen Graduate School, Shenzhen* 518055, *China*)

ABSTRACT Thermoelectric materials can directly achieve the conversion between heat and electricity, providing a clean and reliable way to alleviate energy crisis. However, the wide use of thermoelectric materials is subjected to their low energy conversion efficiency. Grain boundary engineering is considered as an effective strategy to improve thermoelectric performance, particularly for the most polycrystalline thermoelectric materials in bulk state. Recently, the precise controlling over the microstructure and composition of grain boundary at atomic scale has been achieved by atomic layer deposition (ALD) technology, which has been confirmed in various thermoelectric materials, such as $Bi_2Te_{2.7}Se_{0.3}$, $Bi_{0.4}Sb_{1.6}Te_3$, and ZrNiSn. Importantly, it is demonstrated that the decoupling between three key thermoelectric parameters, i.e. Seebeck coefficient, electrical conductivity and thermal conductivity, can be realized by ALD-based grain boundary engineering. Moreover, these key parameters can be optimized simultaneously toward the desired direction, which is extremely important for improving the thermoelectric performance. In this review, the relevant progress on the grain boundary engineering by ALD-based strategy is reviewed and some prospects are proposed.

Keywords: grain boundary engineering, atomic layer deposition, thermoelectric materials;
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1 INTRODUCTION

Thermoelectric (TE) materials, which could achieve the conversion between heat and electricity, provide a new approach to overcome the worldwide energy crisis[1]. Although thermoelectric owns many advantages compared to conventional thermal-energy-conversion strategies, the wide commercialization is limited by its low energy conversion efficiency[2]. The performance of TE materials is characterized by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, κ, and T are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Therefore, high ZT requires high σ, large S, and low κ. Unfortunately, due to their complex interrelationships, tuning the above key TE parameters simultaneously is quite difficult, and thus it hardly yields remarkable enhancement of ZT[3, 4]. By taking advantage of nanotechnology developed in recent years, the ZT values of various TE materials are rapidly increased, which mainly attributes to the lower κ caused by phonon scattering at the grain boundaries. Therefore, grain boundaries play a crucial role in the carrier and phonon transport in bulk TE materials. Grain boundary engineering is the most promising strategy to improve the performance of known TE materials, which has been widely confirmed by experiments and theoretical calculation[5, 6]. For TE materials, especially those with nano-structural characters, the high density of grain boundaries plays a significant role in determining the overall transport properties. However, designing idea grain boundaries to significantly increase the S and simultaneously reduce the lattice thermal conductivity (κ_L) without deterioration of the carrier mobility is difficult to be realized experimentally[7]. Nevertheless, compared to atomic defects and nanoscale domains, grain boundary engineering provi-

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② Corresponding authors. E-mails: y.xiao@pku.edu.cn (Prof. Xiao Yin-Guo) and panfeng@pkusz.edu.cn (Prof. Pan Feng)

des more degrees of freedom in scattering engineering, such as the thickness, microstructure, and composition. For example, the potential barrier with optimized height and size could be introduced at the grain boundaries, which is expected to increase *S* by energy filtering effect as well as quantum size effect, as theoretically predicted and experimentally demonstrated in many systems, including BTS/SS[8] and BTS/ZnO[9]. Meanwhile, grain boundary displays multiple effects on phonon transport, which is the primary cause of the ultralow κ_L in the most reported nanostructured TE materials[10-12]. Therefore, by designing idea grain boundaries, it is possible to simultaneously optimize the carrier/phonon transport behavior, which is of great significance for the development of high-performance TE material. However, only few experimental studies have been made to explore the influence of grain boundaries on the carrier/phonon transport behavior in bulk TE materials, because it is difficult to control over the thickness, microstructure, and composition of grain boundaries at atomic-scale by traditional approach.

As a layer-by-layer deposition technique, ALD can be used to deposit highly uniform film on materials with Å-scale thickness control via sequential surface-limiting vapor precursor chemical reactions, which is generally used in semiconductor industry[13]. The key feature of this process is that both surface reactions with the precursor and counter-reactant are self-limited, which prevents the deposition of more than one atomic monolayer per full cycle[14, 15]. Compared to traditional method, ALD has many advantages, such as atomic scale control of film thickness, high conformity on structures with irregular morphology, low process temperature and excellent scalability. The idea of modifying the grain boundaries of TE material via ALD was reported by Li et al. in 2016 for the first time[9]. The results demonstrate that ALD is a promising approach to modify the grain boundaries of TE material, which could significantly improve the *ZT*. Recently, the ALD-based grain boundary engineering strategy applied for improving the performance of TE materials has been presented by different groups[16]. In this perspective, we provided a brief review on recent progress in this field. The motivation of this work is to explore an ALD based general approach in designing and controlling the grain boundary of TE materials, which will finally contribute to the development of high performance TE materials.

2 GRAIN BOUNDARY CHARACTERISTICS

The core idea of the grain boundary engineering is to modify grain boundaries in order to reduce κ without detriment to σ by taking into account the difference scattering lengths of carrier and phonon. Moreover, considering that the thickness of introduced ALD layers is only about few nanometers, the quantum-confinement effects play an important role in determining the electrical transmission characteristics[17]. By ALD-based grain boundary engineering, a band offset between the host matrix and ALD layer could be introduced, which can filter lower-energy carriers or minor charge carriers and lead to increasing *S*. According to the calculation results[18], the contribution of low-energy carriers to *S* is negative, while the higher energy carriers contribute positively and mostly for high *S*. However, the carriers grain boundary scattering will not only filter lower-energy carriers but also reduce the mobility. Given that the width of barrier layers is comparable to that of quantum well, the quantum confinement effect could also influence the electrical properties, which is quite similar to the effect of the superlattice film demonstrated recently[19, 20]. Thus, by optimizing the potential barriers at grain boundaries, the *S* can be maximized while σ will be maintained or increased, leading to a significantly improved power factor (σS^2).

Actually, the prominent features of ALD technology make it particularly suitable for the application in engineering the grain boundary of TE materials. Firstly, as a technology widely applied in industry, ALD could be used to deposit common semiconductors layer on the matrix (such as metallic oxide and metal sulfide)[14], which means the chemical composition at grain boundary is controllable. For a thermoelectric material, the height and width of potential barriers at grain boundaries could be precisely regulated by tuning the composition and thickness of ALD layer, which is crucial for optimizing the energy filtering effect. Moreover, through controlling the thickness of ALD layer comparable to the effective de Broglie wavelength of carriers, the reduction of the carrier mobility could be negligible and the quantum confinement effect will contribute to the electrical properties. Another critical aspect of grain boundary engineering is to introduce different phonon scattering centers, resulting in low thermal conductivity. Similar to Rayleigh scattering, phonons with different wavelengths could be scattered by scattering centers with similar scales;

the high-frequency phonons can be scattered by point defects; intermediate-frequency phonons can be scattered by stacking defects or nanograins; while low-frequency phonons can be scattered by grain boundaries[21-23]. By ALD-based grain boundary engineering, the scattering centers with different scales could be introduced to the TE materials, and the κ_L could be suppressed accordingly. Accompanied by introducing ALD layer on grain boundaries, the point defects such as vacancies and heteroatoms, edge dislocations and nanoprecipitates may also form near the grain boundary, which all contribute to the reduced κ_L. Furthermore, the theoretical calculation indicates that the atomic scale interface roughness is one of the reasons for the reduced κ, which is the more obvious feature for the ALD-modified grain boundaries. Apart from the suppressed κ_L, the bipolar thermal conductivity can also be reduced by grain boundary engineering. It is well known that the bipolar thermal conductivity originates from the thermal motion of the minority and majority carriers[24]. By designing grain boundary which can preferentially scatter minority carriers, the bipolar thermal conductivity could also be reduced. According to above discussions, it is obvious that the effects of grain boundary engineering can be used to modify the carrier and phonon transport behavior. It should be possible to decouple the three key thermoelectric parameters and simultaneously modify all of them toward the desired direction by ALD-based grain boundary engineering, which is crucial for improving the performance TE materials.

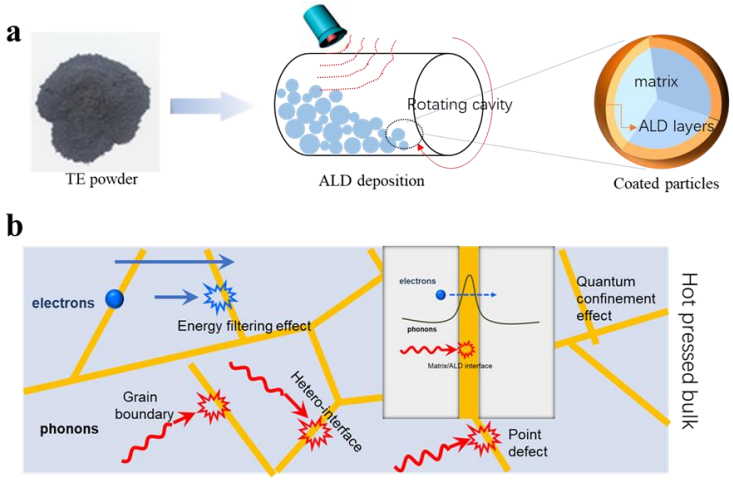

Fig. 1. (a) A schematic of the grain boundary engineering strategies based on ALD. (b) Some effects influence the the carrier/phonon transportation behavior at grain boundaries

3 PROGRESS OF ALD-BASED GRAIN BOUNDARY ENGINEERING

Modifying the grain boundaries by ALD-based strategy is a highly effective way to improve the performances of TE materials. In this section, we will introduce how this ALD-based grain boundary engineering strategy improves the performance of TE materials by giving some typical examples. To explore the relationship between grain boundary and the electron/phonon transportation behavior, ALD technology is introduced for the first time by Li et al. in n-type $Bi_2Te_{2.7}Se_{0.3}$ (BTS) TE materials[9]. An ultrathin n-type zinc oxide (ZnO) layer is deposited on the BTS nanoparticle surface using diethylzinc (DEZ) and H_2O as ALD precursors by a continuous-flow ALD reactor equipped with a vertical stainless rotating sample chamber (Fig 1a). Fig. 2a～c shows high-resolution transmission electron microscope (HRTEM) images of the BTS powder coated by ZnO layer with different thickness. It is found that the ZnO layers are amorphous and uniformly coated on the particles. As observed, the thickness of ZnO layer follows a good linear relation with the total cycle number, and the growth rate is around 1 Å per ALD cycle. The detailed microstructure and composition of the hot pressed bulk sample are also analyzed by TEM, as shown in Fig. 2d～f. Due to the diffusion of Te from the inside of BTS grain to the ZnO/BTS interface, the sawtooth ZnO/BTS interface with 2 nm ZnO amorphous layers could be observed in the sample after 20 ALD cycles. Moreover, the Te nanodot with a small size of ~2 nm at the ZnO/BTS interface is clearly observed in the sample after 60 ALD cycles. To demonstrate the impact of grain boundary on phonon/carries transport behaviors, Fig. 2g and h show main thermoelectric properties at 300 K for samples with different thickness of ZnO layers. It

indicates that either too thin or too thick ZnO layer can be detrimental to carrier transport. The sample after 20 ALD cycles possesses $S^2\sigma$ of 25.1 μW/(cmK^2) derived from the slightly changed σ (361 S/cm) and strongly enhanced S (−261 μV/K). The energy-filtering effect and the Te precipitation are employed to explain the grain boundary-determined carrier transport behavior. Briefly, designing of the grain size (d) and grain boundary potential barrier to satisfy the relationship that λ_p (momentum relaxation length) < d < λ_e (energy relaxation length), S may be improved without hurting σ much, which results in a net improvement in $S^2\sigma$. On the other hand, by suppressing the κ_{bi} and κ_L via introducing ZnO layer at the grain boundary, an ultralow value of thermal conductivity is successfully achieved. As a consequence, the highest ZT reaches 0.85 at 390 K for the sample after 20 ALD cycles, which is ~80% higher than that of pristine BTS. These findings reveal that the decoupling of thermoelectric parameters can be achieved by controlling the microstructure and composition in atomic scale, which is crucial to improve thermoelectric performance. The above ALD-based grain boundary engineering is simply extended to other TE materials by Kim, S. K. et al[16]. An extremely thin ZnO layer is coated on the surface of $Bi_{0.4}Sb_{1.6}Te_3$ powders by similar ALD-based strategy, and numerous heterogeneous grain boundaries were generated after high-temperature sintering. Due to phonon scattering at heterogeneous grain boundaries, κ_L is significantly decreased. Meanwhile, by tuning the thickness of ALD layers, the carrier transport is modulated, resulting in a high σS^2. The ZT value reveals an approximately 45% improvement compared to the uncoated sample.

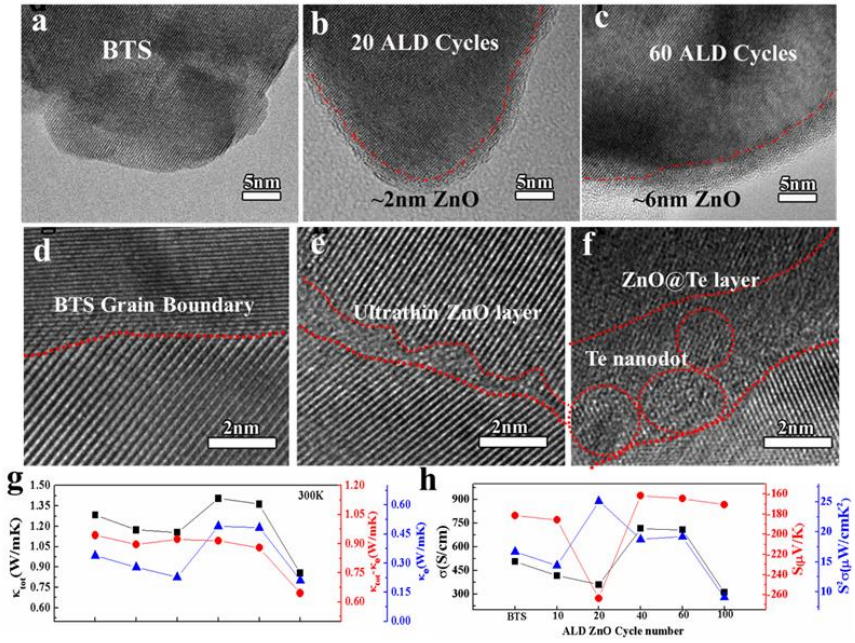

Fig. 2. HRTEM images of the BTS samples with different ALD cycles. (a) As-prepared BTS, (b) 20 ALD cycles, (c) 60 ALD cycles. HRTEM images of the ultrathin ZnO layer modified the BTS grain boundary with different ALD cycles. (d) pure BTS, (e) 20 ALD cycles, and (f) 60 ALD cycles. Thickness of ALD ZnO layer (corresponding to the ALD cycle namber) is dependent on the (g) thermal and (h) electronic transport properties at 300 K. Reproduced with permission[9]. Copyright 2017, Elsevier

Due to the amorphous nature and ultrathin thickness of the ALD coating layer, the chemical reaction between coating layer and matrix may occur during sintering process, which aslo could be used to reconstruct the grain boundary and optimize the TE transport properties. For example, in the case of BTS, the oxygen-related impurities could be accurately controlled by the ALD-based solid phase diffusion strategy, which results in the simultaneously enhanced S and σ as well as the suppressed κ[25]. As shown in Fig. 3a, a TiO_2 layer deposited on the BTS powder surface by ALD is the source of the oxygen-related impurities in hot pressed sample. By precisely controlling the thickness of TiO_2 layer at atomic scale, the formation of oxygen-related impurities in the sample can be tuned, which is crucial to the carrier/phonon transport behavior. It is found that for the sample with thin TiO_2 layer, the oxygen-related impurities mainly exist in the form of O-related dislocation clusters, which can be unambiguously identified by HR-TEM

(Fig. 3b～3d). Due to multiple roles of oxygen-related dislocation clusters, including electron donors, electron energy filters and phonon blockers, the simultaneously enhanced *S* and σ as well as the suppressed κ are achieved, and *ZT* is significantly improved, as shown in Fig. 3e～3g. Importantly, decoupling between these three key thermoelectric parameters is achieved only by tuning the oxygen-related impurities at atomic scale, which is difficult to be achieved by the traditional approach. Recently, a similar approach has been developed in $ZrNiSn_{0.99}Sb_{0.01}$ thermoelectric material by tuning the Zr vacancy at grain boundaries[26]. By adjusting the potential energy barrier and carrier concentration, the decoupling between *S* and σ is achieved, leading to a large improved power factor. The introduced Zr vacancy interface and ZrO_2 nanoparticles are also effective in achieving a very low lattice thermal conductivity. As a result, a maximum *ZT* of 1.13 is obtained, approximately 35% improvement compared to the ZNSS matrix.

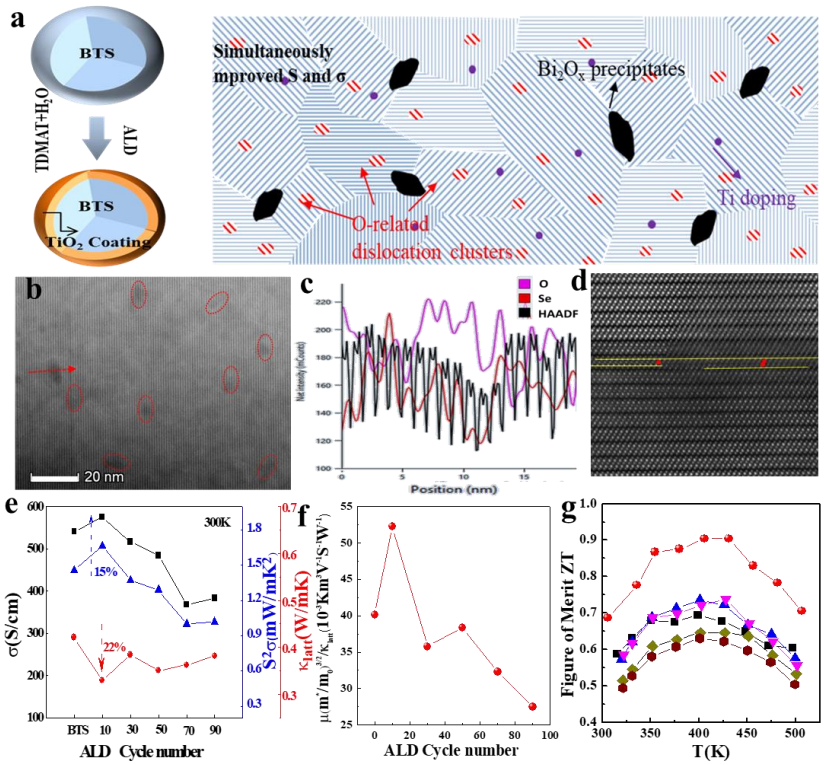

Fig. 3. A schematic of controlling the oxygen doping in BTS thermoelectric material via ALD based solid phase diffusion strategy and the microstructure of the bulk sample. (b) HAADF-STEM image. (c) Elemental line scanning and (d) HAADF-STEM image (taken along the *a* axis of BTS) of O-related dislocation clusters area noted in (b). (e) Electrical conductivity, lattice thermal conductivity and power factor at 300 K, (f) $\mu(m_*/m_0)^{3/2}/K_l$ of all the ALD coated BTS samples as a function of ALD cycle count. (g) Thermoelectric figure of merit ZT of the BTS sample after different ALD cycles. Reproduced with permission[25]. Copyright 2020, Royal Society of Chemistry

Overall, ALD-based grain boundary engineering offers simple and effective way to achieve the decoupling modulation of the three TE parameters, which has been widely confirmed by the experiments in many material systems. In comparison with conventional techniques, the core advantage of this approach is the atomic scale regulation of composition or microstructure. Moreover, as a widely industry technology, ALD can be easily implemented with the existing TE material preparation technology. ALD-based grain boundary engineering is a new strategy to decouple the three TE parameters and to optimize these parameters, providing an efficient avenue for designing high performance TE material.

4 CONCLUSION AND OUTLOOK

In summary, we outline recently the progress on synergistic optimization of TE performance by ALD-based grain boundary engineering. Most excitingly, all of such work preliminarily realized the decoupling optimization of

three TE parameters due to the atomic scale regulation of composition or microstructure. From the above research results, we envision that the ALD-based grain boundary engineering could be a general route to improve TE performance, which could be extended to a wide range of material systems. However, as an emerging strategy, there is still much work to be done in this challenging field. First, the relation between the composition/microstructure of grain boundaries and the carrier/phonon transportation behavior should be intensively studied. Moreover, the combined effect of grain size and grain boundary engineering on the carrier/phonon transportation behavior should be investigated, which may maximize the TE performance. As a powerful grain boundary modification strategy, ALD-based approach may contribute to the development of high performance TE material of great significance.

REFERENCES

(1) Snyder, G. J.; Toberer, E. S. Complex thermoelectric materials. *Nat. Mater.* **2008**, 7, 105–114.

(2) Ding, Y.; Qiu, Y.; Cai, K.; Yao, Q.; Chen, S.; Chen, L.; He, J. High performance n-type Ag_2Se film on nylon membrane for flexible thermoelectric power generator. *Nat. Commun.* **2019**, 10, 841.

(3) Novak, T. G.; Kim, K.; Jeon, S. 2D and 3D nanostructuring strategies for thermoelectric materials. *Nanoscale* **2019**, 11, 19684–19699.

(4) Rodenkirchen, C.; Cagnoni, M.; Jakobs, S.; Cheng, Y.; Keutgen, J.; Yu, Y.; Wuttig, M.; Cojocaru-Mirédin, O. Employing interfaces with metavalently bonded materials for phonon scattering and control of the thermal conductivity in TAGS-*x* thermoelectric materials. *Adv. Funct. Mater.* **2020**, 30, 1910039.

(5) Minnich, A. J.; Dresselhaus, M. S.; Ren, Z. F.; Chen, G. Bulk nanostructured thermoelectric materials: current research and future prospects. *Energy Environ. Sci.* **2009**, 2, 466–479.

(6) Neophytou, N.; Kosina, H. Optimizing thermoelectric power factor by means of a potential barrier. *Journal of Applied Physics* **2013**, 114, 044315.

(7) Kim, R.; Lundstrom, M. S. Computational study of energy filtering effects in one-dimensional composite nanostructures. *Journal of Applied Physics* **2012**, 111, 024508.

(8) Li, S.; Liu, X.; Liu, Y.; Liu, F.; Luo, J.; Pan, F. Optimized hetero-interfaces by tuning 2D SnS_2 thickness in $Bi_2Te_{2.7}Se_{0.3}/SnS_2$ nanocomposites to enhance thermoelectric performance. *Nano Energy* **2017**, 39, 297–305.

(9) Li, S.; Liu, Y.; Liu, F.; He, D.; He, J.; Luo, J.; Xiao, Y.; Pan, F. Effective atomic interface engineering in $Bi_2Te_{2.7}Se_{0.3}$ thermoelectric material by atomic-layer-deposition approach. *Nano Energy* **2018**, 49, 257–266.

(10) Fang, H.; Wu, Y. Telluride nanowire and nanowire heterostructure based thermoelectric energy harvesting. *J. Mater. Chem. A* **2014**, 2, 6004–6014.

(11) Li, S.; Fan, T.; Liu, X.; Liu, F.; Meng, H.; Liu, Y.; Pan, F. Graphene quantum dots embedded in Bi_2Te_3 nanosheets to enhance thermoelectric performance. *ACS Appl. Mater. Interfaces* **2017**, 9, 3677–3685.

(12) Tan, G.; Zhao, L.; Kanatzidis, M. G. Rationally designing high-performance bulk thermoelectric materials. *Chem. Rev.* **2016**, 116, 12123–12149.

(13) DeCoster, M. E.; Chen, X.; Zhang, K.; Rost, C. M.; Hoglund, E. R.; Howe, J. M.; Beechem, T. E.; Baumgart, H.; Hopkins, P. E. Thermal conductivity and phonon scattering processes of ALD grown PbTe–PbSe thermoelectric thin films. *Adv. Funct. Mater.* **2019**, 29, 1904073.

(14) Väyrynen, K.; Vihervaara, A.; Hatanpää, T.; Mattinen, M.; Heikkilä, M. J.; Mizohata, K.; Räisänen, J.; Ritala, M.; Leskelä. M. Nickel germanide thin films by atomic layer deposition. *Chem. Mater.* **2019**, 31, 14, 5314–5319.

(15) Warburton, R. E.; Young, M. J.; Letourneau, S.; Elam, J. W.; Greeley, J. Descriptor-based analysis of atomic layer deposition mechanisms on spinel $LiMn_2O_4$ lithium-ion battery cathodes. *Chem. Mater.* **2020**, 32, 5, 1794–1806.

(16) Kim, K. C.; Lim, S. S.; Lee, S. H.; Hong, J.; Cho, D. Y.; Mohamed, A. Y.; Koo, C. M.; Baek, S. H.; Kim, J. S.; Kim, S. K. Precision interface engineering of an atomic layer in bulk Bi_2Te_3 alloys for high thermoelectric performance. *ACS Nano* **2019**, 13, 6, 7146–7154.

(17) Mao, J.; Liu, Z.; Ren, Z. Size effect in thermoelectric materials. *npj Quant Mater.* **2016**, 1, 16028.

(18) Hicks, L. D.; Dresselhaus, M. S. Effect of quantum-well structures on the thermoelectric figure of merit. *Phys. Rev. B* **1993**, 47, 12727–12731.

(19) Harman, T. C.; Taylor, P. J.; Walsh, M. P.; LaForge, B. E. Quantum dot superlattice thermoelectric materials and devices. *Science* **2002**, 297, 2229–2232.

(20) Harman, T. C.; Spears, D. L.; Manfra, M. J. High thermoelectric figures of merit in PbTe quantum wells. *J. Electron. Mater.* **1996**, 25, 1121–1127.

(21) Zhu, T.; Fu, C.; Xie, H.; Liu, Y.; Zhao, X. High efficiency half-heusler thermoelectric materials for energy harvesting. *Adv. Energy Mater.* **2015**, 5, 1500588.

(22) Shi, X. L.; Tao, X.; Zou, J.; Chen, Z. G. High-performance thermoelectric SnSe: aqueous synthesis, innovations, and challenges. *Adv. Sci.* **2020**, 7,

1902923.

(23) Li, S.; Xin, C.; Liu, X.; Feng, Y.; Liu, Y.; Zheng, J.; Liu, F.; Huang, Q.; Qiu, Y.; He, J.; Luo, J.; Pan, F. 2D hetero-nanosheets to enable ultralow thermal conductivity by all scale phonon scattering for highly thermoelectric performance. *Nano Energy* **2016**, 30, 780–789.

(24) Hwang, J.; Kim, H.; Han, M. K.; Hong, J.; Shim, J. H.; Tak, J. Y.; Lim, Y. S.; Jin, Y.; Kim, J.; Park, H.; Lee, D.; Bahk, J.H.; Kim, S. J.; Kim, W. Gigantic phonon-scattering cross section to enhance thermoelectric performance in bulk crystals. *ACS Nano* **2019**, 13, 8347–8355.

(25) Li, S.; Chu, M.; Zhu, W.; Wang, R.; Wang, Q.; Liu, F.; Gu, M.; Xiao, Y.; Pan, F. Atomic-scale tuning oxygen-doped $Bi_2Te_{2.7}Se_{0.3}$ to simultaneously enhance seebeck coefficient and electrical conductivity. *Nanoscale* **2020**, 12, 1580–1588.

(26) Zhang, Y.; Li, S.; Liu, F.; Zhang, C.; Hu, L.; Ao, W.; Li, Y.; Li, J.; Xie, H.; Xiao, Y.; Pan, F. Zr vacancy interfaces: an effective strategy for collaborative optimization of ZrNiSn-based thermoelectric performance. *J. Mater. Chem. A* **2019**, 7, 26053–26061.