# Low-dimensionalization enhancing the thermoelectric performance of higher manganese silicide

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Higher manganese silicide (HMS) is a candidate thermoelectric (TE) material at medium temperature due to its non-toxicity, abundance, and competitive price. The focus on improving the TE performance of HMS is to decrease the thermal conductivity. Low-dimensionalization techniques, such as nanocrystallization, embedding quantum dots (QDs) and thin film formation are effective strategies to decrease the lattice thermal conductivity by enhancing the phonon scattering on interfaces. Additionally, the Seebeck coefficients also can be improved due to the energy filtering effect via the interface barrier, and correspondingly increasing the power factor of HMS. The TE performance of HMS can be enhanced due to synergistically optimized electrical and thermal properties.
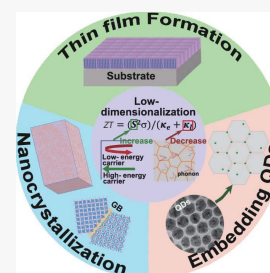
Thermoelectric (TE) technology has gradually attracted widespread attention due to the continuous increase in global demand for reducing carbon-based fuel dependence and energy waste.[1–4] The TE material is widely used in solid-state refrigeration and thermoelectric power generation due to the interconversion between heat and electricity.[5,6] The TE performance can be estimated by the dimensionless figure of merit (*ZT*), $ZT = S^2 \sigma T / \kappa_{tot}$, where S, σ, T and κ_{tot} are the Seebeck coefficient, electrical conductivity, absolute temperature and total thermal conductivity (the sum of lattice thermal conductivity (κ_l) and electronic thermal conductivity (κ_e)), respectively.[7,8] Apparently, excellent TE materials possess high power factors ($PF = S^2 \sigma$) and low κ_{tot}. Obviously, it is a challenge that these parameters are strongly coupled in a conflicting manner.[9] At medium temperature, higher manganese silicide (HMS) has become a candidate due to its naturally abundant, eco-friendly and low-cost.

Currently, the *PF* ($PF = S^2 \sigma$) of HMS based material has reached up to ~18 μW cm⁻¹ K⁻²[10], which is higher than those of SnSe (~10 μW cm⁻¹ K⁻²)[11] and Cu₂Se (~12 μW cm⁻¹ K⁻²)[12] based materials. Whereas, the κ_{tot} of HMS (~2.9 W m⁻¹ K) is much higher than that of SnSe and Cu₂Se based materials, resulting in a relatively low *ZT* value (~0.4 at 873 K)[13,14]. Consequently, the key to enhancing the TE performance of HMS material is decreasing the κ_{tot}. Low-dimensionalization is an effective strategy to reduce κ_l, which also can retain or even enhance the electrical properties simultaneously. When the size of the material decreases to the nanometer, the density

of state (DOS) near the Fermi energy level (E_F) will be increased, correspondingly improving the Seebeck coefficient. The size effect and interface scattering effect on phonon transmission can decrease the κ_l. In this perspective, we should focus on the low-dimensionalization techniques, including nanocrystallization, embedding quantum dots (QDs) and thin film formation, for enhancing the TE performance of HMS.

Grain size is an important parameter in determining the TE performance of HMS. Conventionally, HMS powders are ground into micron-sized particles by planetary ball-milling, which are then sintered to form dense ceramics. It has been demonstrated that the κ_l of HMS ceramics is largely reduced by reducing the grain size to the nanoscale.[15] The κ was reduced by ~30% after wet ball milling using n-hexane, in which the grain size is refined adequately.[16] Therefore, reducing the grain size is an effective approach to enhance the TE performance of HMS. However, the grain size of HMS ceramics prepared by conventional ball-milling is limited to less than 100 nm due to the limitation of force, residence time and energy during milling. Therefore, more advanced ball-milling techniques, such as high-energy ball-milling and cryogenic ball-milling are needed to achieve the nanocrystallization of HMS.

The TE performance of HMS can also be improved by embedding quantum dots (QDs) in the matrix. The size of QD is lower than or comparable with the phonon mean free path of HMS (~33 nm), which can effectively reduce κ_l. Moreover, embedding QDs could produce various defects in the HMS matrix, enhancing the phonon scattering over the full frequency range. In addition, carrier concentration can be regulated by the charge transfer effect as shown in Fig. 1[17]. The optimized carrier concentration is located at about 10²¹ cm⁻³ (Fig. 1a), which can be slightly adjusted using the difference of work

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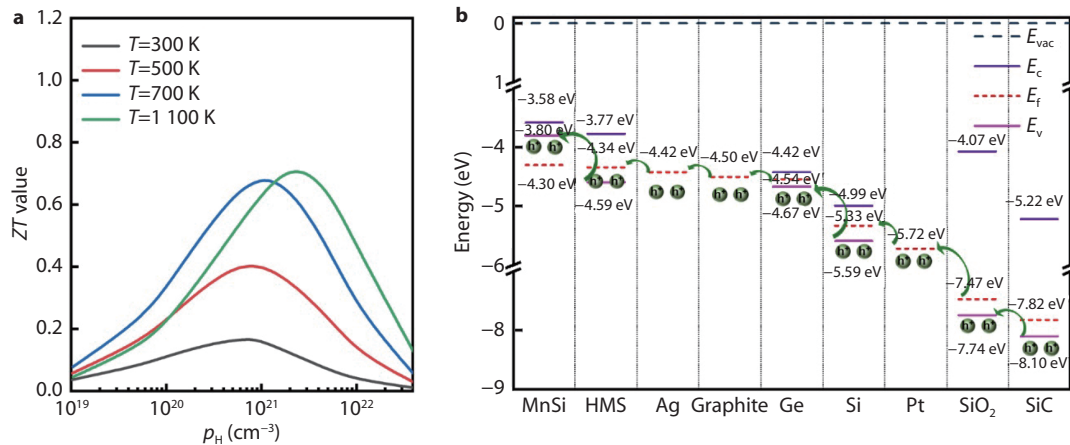
Fig. 1 **a** Optimized carrier concentration of polycrystalline HMS at different temperature calculated based on the single parabolic band model[17]. Copyright 2018, Wiley. **b** Energy/barrier potential difference and charge transfer among the MnSi, Ag, Graphite, Ge, Si, Pt, SiO$_2$, SiC nanoprecipitates and HMS matrix.

function[18–20], leading to the transfer of holes from low energy level to high energy level. It is noticeable that the E_F can be regulated by element doping experimentally, and correspondingly, the direction of charge transfer also can be reversed. Furthermore, the barrier between the matrix and QDs can scatter the low-energy carriers[21], enhancing the S value. Thus, synchronously enhanced electrical and thermal properties have been achieved *via* embedding QDs in HMS.[18,22] It is noteworthy that the energy band on the interface between the HMS matrix and QDs should match well, and the embedded QDs should be of physical and chemical stability within the temperature range of the HMS, and without volatilization or reaction. Furthermore, the distribution of quantum dots in HMS should be uniform, which is significant for optimizing the TE performance of HMS.

In addition, the TE performance of HMS can be further enhanced by forming thin films. Forming thin film has been regarded as a breakthrough to decouple the correlations between electron and phonon transport.[23] The κ of the thin film was significantly reduced compared with the bulk material.[24,25] On the one hand, thin film formation can enhance the phonon scattering and reduce κ_l by adjusting the size and distribution of the micro and nano structures owing to the difference in the mean free path of carriers and phonons. Furthermore, effective strategies including the formation of orientation regulation[23], two-dimensional electron gas (2DEG) system[26], superlattice structure[27], and strain engineering[28] can be performed in HMS thin film, achieving the quantum confinement effect, energy filtering effect, band structure tuning and interface engineering for enhancing the TE performance. The increased DOS near E_F and the energy filtering effect of the interface barrier on low energy carriers could produce an improvement in S value, inspiring significant improvement of electrical properties. Therefore, forming thin film as an effective method to improve TE performance can optimize the electron and phonon transport synergistically. It is worth mentioning that thin film is more compatible with modern semiconductor technology and has irreplaceable advantages in the construction and application of TE micro and nano devices.[29] Consequently, HMS thin film formation is ne-

cessary for improving the TE performance and application of HMS in the modern semiconductor field.

Overall, low-dimensionalization techniques, such as nanocrystallization, embedding quantum dots (QDs) and forming thin film, are effective approaches to enhance the TE performance of HMS. As Fig. 2 displays, these techniques can effectively reduce κ primarily due to the enhanced phonon scattering on interfaces. Additionally, the Seebeck coefficients can be improved due to the energy filtering effect derived from the interface barrier, thus increasing the *PF* of HMS. The simultaneously optimized electrical and thermal properties can significantly improve the TE performance of HMS. Based on the present perspective, future research might focus on further exploring the potential of these low-dimensionalization techniques for improving the TE properties of HMS.
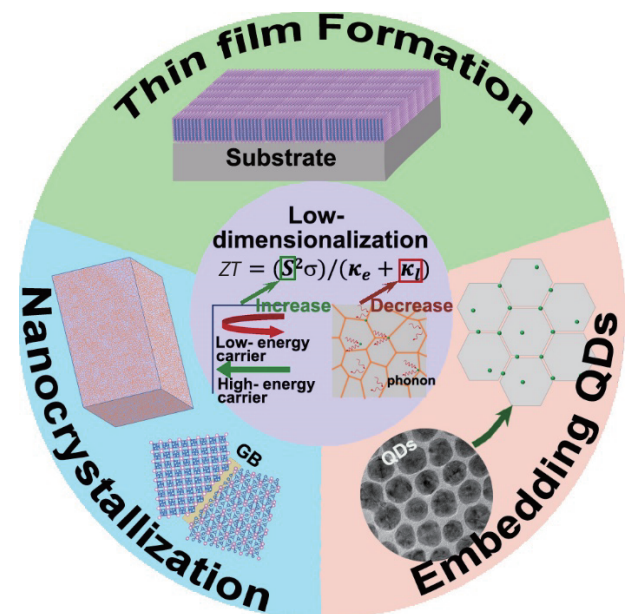
Fig. 2 Schematic diagram of low-dimensionalization techniques including nanocrystallization, embedding QDs and forming thin film.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The manuscript was drafted by Qing Wang and revised by Prof. Zhiliang Li and Shufang Wang. All authors had approved the final version of the manuscript.

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