Nanostructured Thermoelectric Thin Films for Low-Grade Waste Heat Recovery

Amrita Singh[1] and Malini S[2]
Associate Professor[1], Department of Physics[1]
Post Graduate Student[2], Department of Physics[2]
Acharya Institute of Graduate Studies, Bengaluru, India

Abstract: *: The increasing demand for energy and the ongoing waste-heat discharge from industrial, transportation, electronic and domestic systems have raised the urgency to develop efficient waste-heat recovery technologies. In particular, a portion of the waste heat that has been regarded as low-yield and of low value is low-grade waste heat with a small temperature difference and near ambient temperature. Thermoelectric generators provide a route for direct conversion of thermal energy to electrical power via use of the Seebeck effect. However, thermoelectric materials often show poor performance at low temperature due to the intrinsic correlation between electrical conductivity, Seebeck coefficient and thermal conductivity. Nanostructured thermoelectric thin films present an attractive opportunity to address this challenge by enabling simultaneous modulation of charge-carrier and phonon transport via grain-boundary engineering, defect engineering, interface engineering, quantum confinement, energy filtering and band-structure modification. This review describes the underlying principles of nanostructured thermoelectric thin films and investigates the relations between structure, carrier transport, phonon scattering and thermoelectric performance. The main classes of thermoelectric materials that have been explored for low-temperature applications are Bi2Te3-based compounds, Sb2Te3, Bi2Se3, SnSe, Cu2Se, oxide thermoelectrics, Mg-based compounds and half-Heusler materials. Physical and chemical fabrication approaches such as magnetron sputtering, thermal evaporation, pulsed laser deposition, chemical vapor deposition, atomic layer deposition, molecular beam epitaxy and solution processing are critically compared. Strategies for enhancing the thermoelectric figure of merit are investigated on the basis of nanostructuring, doping, defect-engineering, band-convergence, superlattice formation and interface engineering. The review highlights that future research on thermoelectric thin films should be focused on the combination of nanoscale transport engineering and scalable thin-film fabrication, while the low-grade heat sources with reasonable temperature differences should be exploited for achieving practical power generation.*

Keywords: Nanostructured thermoelectrics; thin films; low-grade waste heat; Seebeck coefficient; phonon scattering; transport engineering.

I. INTRODUCTION

Modern energy systems generate large amounts of energy as waste heat. Industrial furnaces, engines, power plants, chemical processes, electronic devices and many other technologies create thermal energy that is often released into the environment without being used for any other purpose. This unwanted energy is called waste heat.

The temperature of waste heat varies widely. High-temperature waste heat can be relatively easily converted into other forms of useful energy using conventional heat engines or heat exchangers. However, vast amounts of low-temperature heat exist from which conventional technologies are too expensive or impractical to extract useful energy.

This has made the scavenging of low-grade waste heat an important area of research.

Thermoelectric generators (TEGs) offer an attractive solution by directly converting a temperature difference into electricity without requiring moving parts.

Seebeck effect:

Consider a material with hot side T_H and cold side T_C.

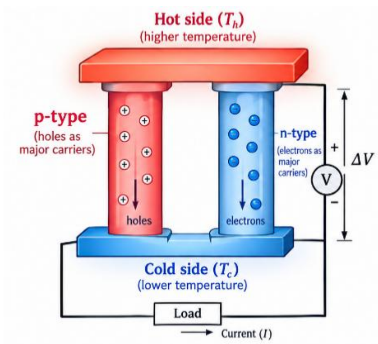
Charge carriers diffuse from the hot region toward the cold region.

This produces an electrical potential difference:

$$\Delta V = -S\Delta T.$$

Figure of merit,

$$ZT = \frac{S^2 \sigma T}{k}$$



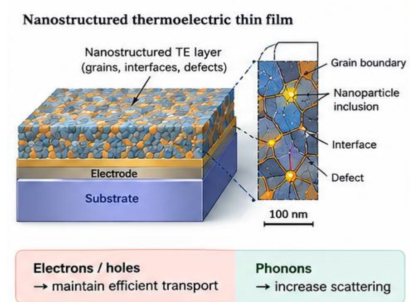


Fig. 1 Thermoelectric Effect Fig. 2 Nanostructured thermoelectric thin film

II. THIN FILMS

2.1 Why Nanostructured Thin Films?

Bulk thermoelectric materials have relatively large dimensions and thus provide only limited control over carrier and phonon transport. Dimensional reductions down to the nanometre or micrometre scale introduce additional interfaces, grain boundaries and surfaces. These structures can be used to selectively influence heat and charge carriers.

Nanostructuring can therefore help to overcome the fundamental trade-off between electrical and thermal transport. Reviews on nanostructured thermoelectrics have highlighted that reductions in lattice thermal conductivity due to multiscale phonon scattering are among the dominant reasons for improved thermoelectric performance.

Thin-film advantages

Thermoelectric thin films typically range in thickness from tens of nanometres to several micrometres. It reduces material consumption and has short thermal diffusion lengths. It is compatible with microfabrication and can be flexible to use. It enhances interface-to-volume ratio and shows potential quantum-confinement effects. It can be integrated with microelectronic devices.

III TRANSPORT ENGINEERING IN NANOSTRUCTURED THERMOELECTRIC FILMS

3.1 Seebeck coefficient

The Seebeck coefficient is a measure of the voltage generated per unit temperature difference:

$$S = -\Delta V/\Delta T$$

The sign of S provides information about the dominant charge carriers. Negative S generally indicates n-type conduction while positive S generally indicates p-type conduction.

For a simplified semiconductor model, thermopower is strongly related to carrier concentration and electronic structure. Consequently, doping is one of the most important methods of controlling Sand σ.

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3.2 Electrical conductivity

Electrical conductivity is given by

$$\sigma = ne\mu$$

where, n is the carrier concentration, e is the electronic charge and μ is the carrier mobility.
Thus, increasing carrier concentration or mobility can increase electrical conductivity.

3.3 Thermal conductivity

Total thermal conductivity can be represented approximately as

$$\kappa = \kappa_e + \kappa_L$$

where, κ_e is the electronic thermal conductivity and κ_L is the lattice or phonon thermal conductivity.
For many semiconducting thermoelectrics, reducing κ_L is particularly important.
Nanostructuring introduces grain-boundary scattering, interface scattering, defect scattering, nanoparticle scattering, strain-induced scattering and point-defect scattering.
This can shorten phonon mean free paths.

IV MATERIALS FOR NANOSTRUCTURED THIN FILMS

TABLE I CHARACTERISTICS OF THIN FILM MATERIALS

Material	Low-grade heat suitability	Major advantage	Main challenge
Bi_2Te_3	Excellent	Mature, high performance near room temperature	Te dependence
Sb_2Te_3	Excellent	Strong p-type material	Te/Sb concerns
Bi_2Se_3	Good	n-type layered material	Optimization
SnSe	Good	Lead-free, low lattice thermal conductivity	Anisotropy
Cu_2Se	Good	Very low lattice thermal conductivity	Stability
Oxides	Moderate–good	High stability	Lower mobility
$Mg_3(Sb,Bi)_2$	Moderate–good	Te-free	Film processing
Half-Heuslers	Moderate	Robust	Higher thermal conductivity

V FABRICATION OF NANOSTRUCTURED THERMOELECTRIC THIN FILMS

5.1 Magnetron sputtering

Magnetron sputtering is particularly attractive because it provides good control of film thickness, deposition rate, composition, substrate temperature, working pressure, target power and film texture.
In sputtering, energetic ions generated in an Ar plasma bombard a target. Atoms ejected from the target are transported to the substrate and form a thin film.
A typical process is:

RF magnetron sputtering has already been demonstrated for fabrication of $Bi_2Te_3$and Sb_2Te_3 thermoelectric thin films.

5.2 Thermal evaporation

Thermal evaporation involves heating a source material under high vacuum to evaporate and subsequently condense on a cooler substrate.
It is beneficial due to simple equipment, high vacuum environment, low substrate damage and good film purity.

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However, maintaining stoichiometry can be challenging for multi-component thermoelectric materials because component elements can have different vapour pressures.

5.3 Pulsed laser deposition

In pulsed laser deposition (PLD), intense laser pulses are fired at a target and produce a plasma plume. The material from the plume subsequently condenses onto the substrate.

PLD offers relatively good stoichiometric transfer.

It also helps in crystalline-film growth, oxygen atmosphere control and multilayer fabrication.

It is particularly useful for research-scale studies, although scale-up to large-area fabrication can be challenging.

5.4 Chemical vapor deposition

Chemical vapor deposition (CVD) involves gaseous precursors that react or decompose near a heated substrate.

It is useful for conformal films, large-area deposition, nanowires, 2D materials and controlled interfaces.

5.5 Atomic layer deposition

Atomic layer deposition (ALD) is based on sequential surface reactions.

A simplified cycle is:

Repeated cycles produce highly-controlled films.

ALD is particularly attractive for ultrathin thermoelectric layers, interfaces, and multilayer structures.

An important 2026 review identifies ALD, molecular beam epitaxy, CVD, magnetron sputtering and solution-based approaches among the essential routes for the fabrication of inorganic thermoelectric thin films.

5.6 Molecular beam epitaxy

MBE is a highly-controlled vacuum deposition method that is used to produce crystalline multilayers and quantum structures. It is important in quantum wells, superlattices, epitaxial interfaces and controlled layer thickness.

The early theoretical work of Hicks and Dresselhaus motivated the use of quantum-well structures to modify thermoelectric transport, and these experimental studies investigated such structures using molecular-beam epitaxy.

Solution processing

Solution-based methods include spin coating, spray coating, inkjet printing, electrodeposition and chemical synthesis.

These techniques can reduce processing costs and enable flexible or large-area devices. However, their principal challenges include film uniformity, residual solvents, crystallinity, and precise control of composition.

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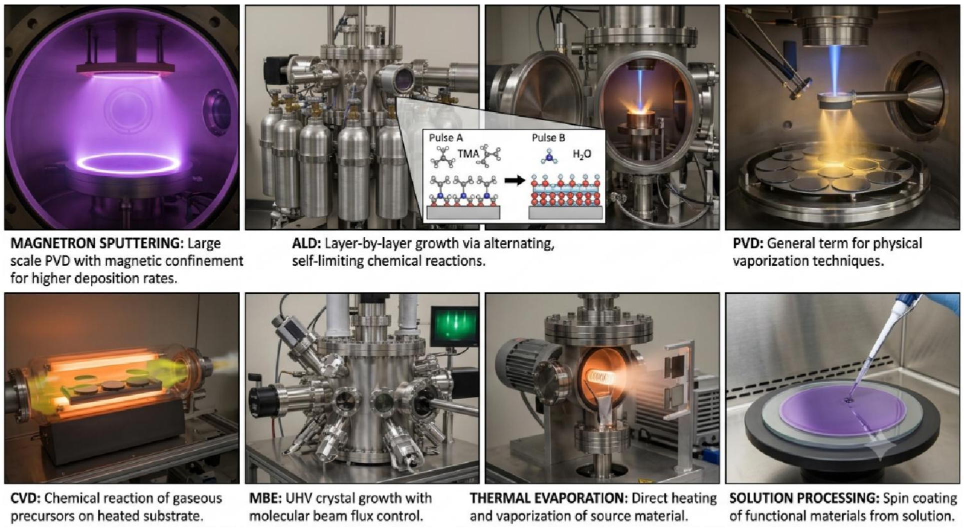

Fig. 3 Thin film fabrication techniques

VI CHARACTERIZATION OF THERMOELECTRIC THIN FILMS

A complete investigation requires structural, morphological, electrical, thermal and thermoelectric characterization.

TABLE III CHARACTERISTICS OF THIN FILM MATERIALS

Property	Technique	Information obtained
Crystal structure	XRD	Phase and crystallinity
Surface morphology	AFM	Roughness and grain structure
Microstructure	SEM/TEM	Grain boundaries and interfaces
Composition	EDS/XPS	Elemental and chemical composition
Thickness	Profilometry/ellipsometry	Film thickness
Electrical transport	Four-probe method	Electrical conductivity
Seebeck coefficient	Seebeck measurement	Thermopower
Thermal conductivity	TDTR/3ω methods	Thermal transport
Optical properties	UV–Vis/ellipsometry	Optical response
Temperature dependence	Variable-temperature measurements	Transport evolution

VII. LOW-GRADE WASTE HEAT RECOVERY

Low-grade waste heat typically refers to the thermal energy that is low-temperature and often challenging to utilize by conventional heat engines for economical electricity production.

The sources of waste heat can be categorized as:

i. Industrial sources like exhaust gases, furnaces, process equipment, heat exchangers, hot pipelines.
ii. Transportation like automobile exhaust, engine surfaces, braking systems.
iii. Electronics like processors, power electronics, data-centre equipment.
iv. Human/environmental sources like body heat, solar-heated surfaces, ambient temperature gradients.

Thin films are particularly attractive in the case of low-temperature differentials as they can be placed close to the heat source.

VIII. RECENT RESEARCH ADVANCES

Research in the past few years has shifted from simply discovering new materials with high ZT to transport engineering and device integration.

8.1 Defect engineering

Point defects, such as vacancies and substitutional atoms, can alter carrier concentration, carrier mobility, band structure and phonon scattering. The recent $Mg_3(Sb,Bi)_2$ thin-film work illustrates the use of controlled defects and doping to manipulate carrier type and transport.

8.2 Interface engineering

Interfaces are important because they can simultaneously affect electrons and phonons. A carefully designed interface can scatter phonons and filter undesirable carriers while maintaining adequate electrical conductivity.

8.3 Flexible thermoelectrics

Flexible thermoelectrics are increasingly important for wearable sensors and distributed electronics. The flexible Bi_2Te_3 device described above represents an example of combining high thermoelectric performance with mechanical flexibility.

8.4 Tellurium-free materials

Because of concerns about tellurium supply and the temperature limitations of Bi_2Te_3, recent research is increasingly exploring:Mg_3Sb_2, MgAgSb, SnSe, Mg_2Sn and oxide thermoelectrics. A recent Nature Reviews Materials review specifically highlights Te-free materials and device-level strategies for low-temperature energy harvesting.

8.5 Artificial intelligence and computational design

A particularly emerging direction is the use of computational methods and machine learning to identify compositions and deposition parameters that produce desired combinations of S, σ and κ. The 2026 review of inorganic thermoelectric thin films identifies AI-driven optimization, hybrid fabrication strategies and multifunctional device engineering as emerging directions.

IX. CHALLENGES

9.1 Electrical-thermal transport trade-off

Enhancing the electrical conductivity often leads to increased electronic thermal conductivity. Thus, a preferable balance of all three transport properties is to be achieved for a high ZT .

9.2 Contact resistance

Due to the low thickness of thin films, their cross-sectional area is limited, which increases the contact resistance. This effect reduces the output significantly if the interface is poorly formed.

9.3 Film stability

Repeated thermal cycling leads to grain growth, cracking, delamination, interdiffusion, and oxidation.

9.4 Scalability

Most of the fabrication methods allow obtaining high-quality thin films but are not scalable for large-area manufacturing.

9.5 Material sustainability

Many promising thermoelectric materials include Pb or Te, which imposes the importance on developing materials with respect to the following characteristics: Performance, Abundance, Toxicity, Stability, Cost (PATS).

9.6 Device-level considerations

A high ZT value is not sufficient for a good thermoelectric generator, since mechanical and electrical connections, heat exchangers, and other components also contribute to the overall efficiency. According to recent studies, the thermoelectric generator's performance can be improved through downscaling and optimization of the geometry and integration of thermoelectric modules with heat exchangers.

X. FUTURE ENHANCEMENT

Future research efforts are likely to be focused on multifunctional, flexible and structured thermoelectric thin films.

Potential future directions include multilayer thermoelectric superlattices, quantum-confined structures, gradient-composition films, defect-engineered materials, 2d thermoelectric materials, flexible and stretchable generators, AI-assisted deposition optimization, Te-free thermoelectrics, printed thermoelectric devices, hybrid thermoelectric–photovoltaic systems, self-powered IoT sensors and large-area waste-heat harvesting surfaces

2026 literature shows a growing convergence between thin-film fabrication, low-dimensional transport, flexible electronics and intelligent optimization.

XI. CONCLUSION

Nanostructured thermoelectric thin films are a key technology for harvesting low-grade heat and converting it into electricity. The main challenge for designing efficient thermoelectric materials is related to the figure of merit. A possible way to manipulate all the parameters of ZT is offered by the use of materials with reduced dimensionality, grain boundaries, interfaces, and quantum confinement.

Beyond the optimization of the thermoelectric properties, other factors should be considered for engineering of thermoelectric thin-film systems. The choice of fabrication methods plays an essential role in the discussed area, with magnetron sputtering being the most promising technique for controllable deposition of thermoelectric thin films. Atomic layer deposition, molecular beam epitaxy, and solution-based processing can be used for fabrication of ultrathin interfaces and heterostructures or low-cost large-area processing, respectively.

Recent progress in the field of thermoelectrics includes the fabrication of flexible Bi_2Te_3 films, defect-engineered $Mg_3(Sb,Bi)_2$, Mg_2Sn, and tellurium-free thermoelectric materials and devices, which suggests that the field has entered a stage of deliberate design of electronic and phonon transport at multiple length scales and the development of novel thermoelectric systems for integrated energy harvesting.

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