Current Progress and Future Challenges in Thermoelectric Power Generation: From Materials to Devices

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Abstract

Thermoelectric power generation represents one of the cleanest methods of energy conversion available today. It can be used in applications ranging from the harvesting of waste heat to conversion of solar energy into useful electricity. Remarkable advances have been achieved in recent years for various thermoelectric (TE) material systems. The introduction of various nanostructures is used to tune the transport of phonons, and band structure engineering allows for the tailoring of electron transport. In this overview, top-down approaches for phonon engineering such as atomic construction of new materials will be reviewed. Bottom-up approaches for electron engineering such as the formation of ordered nanostructures will also be discussed. The assembly of Thermo-Electric power Generating (TEG) devices is still particularly challenging, and consequently, thermal-to-electric conversion utilizing these devices has been realized only in niche applications. In this review paper, we will discuss some of the challenges that must be overcome to enable widespread use of TE devices. These include: thermal stability at the material level, and reliable contact at the device level.

Key words: Thermoelectric Materials; Thermoelectric Devices; Phonon Scattering; Electron Transport; Reliable Contact

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1. Introduction

Thermoelectric power generation (TEG) has been widely investigated as a clean energy conversion technology for the harvesting of waste heat as well as for converting solar energy into useful electricity. The energy conversion efficiency is determined by the Carnot efficiency and dimensionless figure of merit (ZT), in which ZT is defined as $ZT=(S^2\sigma/\kappa)T$, where S , σ , κ , and T are: the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. The utilization of waste heat, such as from ground/aerial vehicles, industrial boilers, power plants, cement plants, etc., has garnered significant interest. During the past fifteen years there has been tremendous growth in thermoelectric (TE) research, in which the number of annual publications increased from 500 to 2000 according to the Web of Science database [1]. Furthermore, significant boosts in the peak ZT over the benchmark value of 1 for many conventional materials have been reported, including Bi_2Te_3 based alloys [2][3][4], PbTe [5][6][7][8], PbSe [9][10], SiGe [11][12], Mg_2X ($X = \text{Si}, \text{Ge}, \text{Sn}$) [13][14], Skutterudite [15][16][17], Clathrate [18], Zintl [19], and half-Heusler [20][21]. These increases have been achieved through nanostructural approaches to phonon transport tuning, and band structure engineering to tailor electron transport. Recently, the Kanatzidis group and his coworkers have claimed a ZT over 2 in the PbTe system, in which they attributed the efficiency enhancement to a hierarchical length-scale phonon scattering scheme. They combined melting-casting (to incorporate nano inclusions) and ball milling-hot pressing (to achieve fine grain size) [22][23]. Recently, a SnSe single crystal has been shown to have a new, record ZT value of 2.6 [24]. It seems that practical applications utilizing TE power generation techniques might just be within reach.

However, there is still a significant need for improvement when we consider the requirements for TEG in real applications. The University of Karlsruhe in Germany in 1988 [25], made the first attempt, applying TEGs with FeSi_2 legs to the automobile. Later, other prototype TEGs for cars had been developed and tested by both industry and academia [26][27]. However, the maximum output power of most reported prototype TEGs was limited to 100 W, preventing any real adoption of this new technique for the commercial automobile. In 2008, IAV (a German engineering company in the automotive industry) developed a prototype TEG for the Volkswagen Golf exhaust pipe. It generated an output power of 600 W at highway speeds [28]. Recently, a Gentherm led team, including BMW and Ford, launched a prototype TEG which

could be integrated into two different passenger vehicles: the BMW X6 and the Lincoln MKT. This prototype TEG with Skutterudite legs generates 700 W of power in bench testing and over 600 W in on-vehicle testing [29]. Even though the power generated provides ~30% of the electricity required for a car's operation, this is still well below the target of 5% fuel efficiency improvement. Similar projects to improve the fuel efficiency of auto vehicles by harvesting waste heat were also launched by other automakers, such as Toyota, Honda, Nissan, GM, etc. However, there are not yet any commercial automobiles with integrated TEGs on the market. The challenge behind this contradiction arises from two difficulties: 1) inadequate mechanical properties and insufficient thermal stability of TE materials, 2) unreliable contact between the TE leg and the electrode. As an example, PbTe is well known as a traditional TE material for intermediate temperatures. However, because of poor mechanical properties it has not been considered favorably as a practical material for TEG in commercial applications. In contrast, Skutterudites get much more attention in the industry, such as from Gentherm [29], GM [30], and Furukawa [31]. However, the thermal stability of Skutterudite at temperatures close to 600 °C is still a concern. Even with its lower ZT value, half-Heusler alloys have much better mechanical properties and thermal stability than PbTe and Skutterudite, and hence get more and more attention as the material with the most promise for power generation applications [32][33].

Another big challenge for TE materials is the reliability of metallized contact layer. Direct soldering of most TE materials is problematic due to either the poor wettability of solder on TE materials or the subsequent reaction/diffusion between the materials. Metalized contact/diffusion barrier layers on the ends of the TE legs improve the wettability of TE materials by solder and prevent the diffusion between the solder and TE material. However, an ohmic contact is necessary to reduce the parasitic loss coming from the extra electrical and thermal resistance at the interface. In this paper, we designate R_c as the electrical contact resistance (unit: Ω) as the extra electrical resistance introduced by the contact/TE interface, which can be obtained by subtracting the calculated material resistance and wiring resistance from the total measured module resistance. The contact resistance includes the effect of contact area. Because different cross-section areas were used in the modules built by different groups, the contact resistance is not suitable for comparing the quality of the contacts. To compare the quality of contacts prepared with different cross-section areas, we designate ρ_c for specific contact resistivity (unit: $\mu\Omega \text{ cm}^2$), which is the reciprocal of the derivative of the current density

with respect to the voltage across the interface, as $\rho_c = (\frac{dJ}{dV})_{V=0}^{-1}$. While investigating the contact for TE materials by measuring the contact resistance, the specific contact resistivity can be estimated by multiplying contact resistance with the cross-section area, $\rho_c = R_c \times A$. Figure 1 shows the effect of specific contact resistivity on the leg efficiency and the output power of a p-type Skutterudite by using the energy balance of one-dimensional heat flow equation. It is clearly shown that the specific contact resistivity significantly reduces the leg efficiency and the output power as well. Simply, the specific contact resistivity ρ_c between the conducting strip and TE material decreases the effective $\langle ZT \rangle_{leg}$ of TE devices according to, [34]

$$\langle ZT \rangle_{leg} = \frac{L}{(L + 2\rho_c \sigma)} \langle ZT \rangle_m, \quad (1)$$

where L and σ are the length of the TE leg and the electrical conductivity of the leg, respectively. $\langle ZT \rangle_m$ is the effective ZT of the TE material between T_h and T_c . For a typical device that has $L \sim 1$ mm, and $\sigma \sim 10^5$ S m⁻¹, ρ_c should be much less than $L/2\sigma \sim 10^{-8}$ Ω m² (10⁻⁴ Ω cm²). Ideally, the specific contact resistivity should be less than 1 μΩ cm². We are still far from this targeted low value for most materials.

Bi₂Te₃ based modules have a long history as commercially available TE solutions for silent cooling, and hence mature fabrication skills exist in industry. However, recent investigations of commercial Bi₂Te₃ based modules under thermal cycling conditions have shown significant performance degradation. Hatzikraniotis et al. has conducted a long-term performance and stability study of a commercial Bi₂Te₃-based module (Melcor HT9-3-25). The cold side was fixed at 24 °C while the hot side was subjected to thermal cycles from 30 to 200 °C [35]. A continuously decreased output power was observed due to the increased resistance and decreased open circuit voltage. The Goodson group at Stanford University conducted a similar thermal cycling test for another commercial Bi₂Te₃ module (Ferrotec 9500/127/060). After 6000 repeated thermal cycles from 30 to 160 °C, the peak output power showed an 11% reduction [36]. Mechanical damage including voids, pores, and cracks, were seen at the interface between the Cu electrode and the Bi₂Te₃ leg, as shown in Fig. 2 [37]. It seems that reliable contact is still an open challenge for TEG devices, even for the conventional Bi₂Te₃ material. Recent work has shed some light on the challenge behind the contact of Bi₂Te₃ for the power generation applications [38]. The main challenge of the Bi₂Te₃-based TEGs comes from the unstable

interface between Ni contact layer and the Bi_2Te_3 , which could result in forming a p-type region in the n-type leg leading to a high contact resistance.

In this review, we will summarize the latest advances in TEG materials and devices paying special attention to new challenges that have arisen. Progress on the materials level will be handled by discussing thermomechanical properties, and thermochemical reliability in addition to the TE properties. The continuous pursuit of higher ZT will be discussed from the phonon engineering and the electron engineering points of view. Phonon engineering is regarded as a top-down approach, e.g., some materials with special crystalline structure have low lattice thermal conductivity comparable to nanocomposites with hierarchical architectures. In contrast, the electron engineering is considered a bottom-up approach, e.g., the self-assembly of ordered nanostructures. For device level progress, we will first discuss challenges regarding the design of a reliable contact, and then narrow our attention to the specific contact design of several materials, including Bi_2Te_3 , PbTe , CoSb_3 , Mg_2Si , etc. In addition, how the contact properties play a role in maximizing the output power generation and its conversion efficiency, will be examined. To conclude, we will discuss the most recent trends in TEG materials and devices.

2. Material-level Progress in Thermoelectric Power Generation

The recent improvements in ZT (from 1 to about 2) are quite significant and welcome development. However, mechanical strength and chemical stability are equally crucial to TE applications, but these aspects received only limited attention. Considering the working condition of TEG, the stress in most cases is induced by the large temperature difference between the hot and cold side. Mechanical problems become severe thermomechanical issues. Similarly, normal chemical stability issues become thermochemical issues. In this section, a few examples of efforts to improve the thermomechanical and thermochemical performance of TEG materials will be discussed, followed by new progress in thermoelectric performance.

2.1 Thermomechanical Performance

The mechanical properties parameters such as Young's modulus (E), shear modulus (G), and Poisson's ratio (ν) describe the elastic response of a solid to the imposed mechanical stress, while in the inelastic region, the fracture strength σ_f and fracture toughness K_c are important parameters. Thermomechanical properties play an important role in the fabrication and reliable operation of TEG materials. Both conventional materials Bi_2Te_3 and PbTe compounds are brittle

in nature. Consequently, the yield of acceptable quality legs during the cutting process can be low due to edge chipping. Secondly, the TE materials also need sufficient mechanical hardness to prevent surface damage during handling. Thirdly, TE materials need significant toughness to prevent failure from thermal fatigue or thermal shock during the repetitive heating and cooling cycles they experience in practical applications. Enhancement of strength and hardness will improve the yield of the leg production during cutting and packing process, while improved toughness will enhance the longevity of the TEG module. Table 1 summarizes the thermomechanical properties of selected TE materials, including Bi_2Te_3 , PbTe , PbSe , PbS , CoSb_3 , Zn_4Sb_3 , $\text{Ca}_3\text{Co}_4\text{O}_9$, Mg_2Si , half-Heusler and SiGe [39]-[50].

2.1.2 Strength

In the elastic region, the mechanical strength is usually represented by elastic modulus. The Young's moduli for selected materials are summarized in Table 1. Among all the TE materials, Bi_2Te_3 (32 MPa) [39] and PbTe (27-58 MPa) [41][44] are the weakest, while half-Heusler (225 MPa) [49] is the strongest. Most TE materials are of the solid solution form, such as the n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ which is a solid-solution between Bi_2Te_3 and Bi_2Se_3 . For such binary solid-solution systems, an empirically linear or parabolic model was used to describe the compositionally dependent elastic modulus. Ren et al. extended such a model to have four compositional variations and successfully applied it in the LAST system [51]. In the non-elastic region, the mechanical strength is governed by the critical stress that results in either: yield of ductile materials, or fracture in brittle materials. Bi_2Te_3 and its alloys have the longest history of utilization for direct energy conversion, and hence received early attention for the mechanical strength. The bending fracture strength of the ingot made by conventional zone-melting growth or Bridgman method is only 10-20 MPa [52][53]. Low mechanical strength not only caused failure during leg cutting but also limited the degree of miniaturization possible for cooling modules in the microelectronics. One of the reasons for the weak mechanical strength is the crystalline structure containing van der Waals' bonds, which allow easy cleavage along the *ab*-plane. Polycrystalline Bi_2Te_3 , formed by grinding and hot pressing, shows a significantly enhanced fracture strength of up to 50-80 MPa [52][53]. It is also found that the mechanical strength of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ made by the angular extrusion method is enhanced with decreased grain size from $\sim 20\text{ }\mu\text{m}$ to $\sim 1\text{ }\mu\text{m}$, fitting the well-known Hall-Petch relationship [54]. Furthermore, the anisotropic crystalline structure of the Bi_2Te_3 leads to plate-like grains. The re-orientation of

the randomly distributed grains into a texture was widely confirmed to be an effective route for the improved TE properties. Zhao et al. reported that such a texture in Bi_2Te_3 also improves the mechanical bending fracture strength from 62 MPa to 120 MPa [55].

Besides reducing the grain size, there are many other ways that could be used to improve the mechanical strength, for example, adding nano particles or nano wires to prevent crack propagation [39][40][56]. However, such strategies have a limitation, i.e., the improved mechanical strength is very often at the expense of the ZT value. One of the more successful examples is the addition of nano-TiN in $\text{CoSb}_{2.875}\text{Te}_{0.125}$ [56]. It was found that a 1.0 vol.%TiN increased the flexural strength and fracture toughness of $\text{CoSb}_{2.875}\text{Te}_{0.125}$ by 31% and 40%, respectively. The TiN nano particles slightly decreased both the electrical resistivity and thermal conductivity but the ZT value was nearly unchanged, and this was attributed to the pinning effect of TiN nanoparticles as shown in Fig. 3.

2.1.3 Hardness

If the TE leg is too soft, the surface is easily damaged during handling or device assembly process. Table 1 shows the hardness of commonly used TE materials, which indicates that SiGe and half-Heusler rank on the top of the list having hardness of 14 GPa. CoSb_3 and Mg_2Si come to the next, having hardness of 4~6 GPa, which is good enough to survive the typical industrial handling. Zhang et al. at the University of Vienna conducted a wide ranging investigation of the mechanical properties of filled Skutterudites [57]. They found that the hardness could be increased by partially substituting Fe with Co or Ni in the $\text{R}_y(\text{Fe}_{1-x}\text{M}_x)_4\text{Sb}_{12}$ based filled-Skutterudites. However, if the content of the Co or Ni exceeded $x = 0.2$, the hardness began to decrease. Furthermore, they found that the relationship between the hardness and the modulus for the filled Skutterudites follows a general trend: the material having higher modulus has higher hardness, as shown in Fig. 4.

PbTe and Bi_2Te_3 are the softest TE materials with the hardness of only 0.3-0.4 GPa and 0.7 GPa, respectively, and these materials are very susceptible to surface damage and hence need special care. According to the work by Li et al. at Tsinghua University, the addition of nano SiC was an effective in improving the hardness of Bi_2Te_3 from 0.6 to 0.8 GPa [39][58]. Kavei reported that 0.1 mol% Nd_2Te_3 resulted in a 40% enhancement in hardness [59]. Such enhanced hardness, due to the alloying effect was also observed in the PbTe-PbSe , PbTe-PbSe , and PbSe-PbS systems [43]. Additionally, it is worth noting that the hardness is sensitive to the porosity of

the material, e.g., a 1% relative density decrease from 99.6% to 98.6% caused >10% decrease of hardness in the filled Skutterudite [57].

2.1.4 Toughness

TEG modules intended for waste heat recovery in an automotive application must be able to withstand not only at least ten thousand cycles of cold start-up and hot shut down, but also the mechanical vibration due to uneven roads. It is a challenge to make TEG module capable of surviving an environment where they are subjected to such thermal and mechanical fatigue cycles and shocks [60][61][62]. The accumulation of damage due to the micro crack growth under repetitive thermal or mechanical loading results in eventual failure [35][36]. For a brittle material, the fracture strength is typically dependent on the pre-existing flaw length, i.e., $\sigma_f \sim 1/a_c^{0.5}$ where a_c is the length of the largest flaw. The fracture toughness K_c reflects the flaw tolerance [42],

$$K_c = Y\sigma_f (\pi a_c)^{0.5} \quad , \quad (2)$$

where Y is the dimensionless geometric factor. Materials with high K_c can bear higher thermal or mechanical loads. Among the TE materials in Table 1, PbTe shows the lowest toughness of 0.35 MPa m^{0.5}, while Ca₃Co₄O₉ has the highest toughness of 2.8 MPa m^{0.5}. The toughness of other materials falls in a narrow range between 0.8~1.2 MPa m^{0.5}.

Thermal shock due to sudden heating and cooling during typical automobile operation is an extreme condition that the TE material must survive. Since even only one thermal shock inducing thermal stresses above material's yield or fracture criteria causes fatal damage and/or a failure of the material, the thermal stress resistance by thermal impact is important as a conservative design parameter of TEG. Based on the thermoelastic approach, the thermal stress resistance R by thermal shock is given as [42][63],

$$R = \frac{\sigma_f (1-\nu) \kappa}{\alpha E} \quad , \quad (3)$$

where α is the coefficient of thermal expansion (CTE). In order to avoid the nucleation of crack, it is desirable that candidate materials have high thermal conductivity and low CTE since generally the ratio of the fracture strength to Young's modulus of a material has a little variation. Unfortunately, there is still a lack of data regarding thermal fatigue and thermal shock of devices using novel TE materials with various nanostructures in the open literature [42].

2.2 Thermochemical Performance

The thermochemical performance is related to the thermal or chemical stability of the atomic defects, dislocations, and grain boundaries of the material. The typical thermal stability of TE material includes the sublimation and diffusion of the atoms (such as surface oxidization and inside bloating), and the motion of the dislocation and grain boundary (such as creep), which significantly reduces the working temperature of materials. The conventional materials, containing the elements with high vapor pressure (such as Pb, Ge, Te, Sb, Sn, etc.), usually have high sublimation rates at the working temperature of the corresponding TE material. As an example, the sublimation rate is $9.4 \times 10^{-2} \text{ g cm}^{-2} \text{ h}^{-1}$ at 500°C for n-type PbTe, and $1 \text{ g cm}^{-2} \text{ h}^{-1}$ for the p-type TAGS [64]. These values are far too high compared with a sublimation rate of $\sim 1 \times 10^{-7} \text{ g cm}^{-2} \text{ h}^{-1}$, the maximum rate allowed in order to achieve the target of a maximum of 5% reduction of the cross-section of the TEG leg over 10 years operation. Table 2 gives the sublimation rate of selected materials measured by JPL. A coating of SiO_2 and Si_3N_4 to suppress the sublimation of TAGS/PbTe and SiGe was early used in the Radioisotope Thermoelectric Generator (RTG). In addition, an Ar environment instead of the physical coatings also reduced the sublimation rate. The drawback of the cover gas of Ar is that it can reduce the sublimation rate only by a factor of 5. On the other hand, the coatings of SiO_2 and Si_3N_4 thin layer can be consumed rapidly. A SiO_2 -based aerogel was found to reduce the sublimation rate of Skutterudite samples by 700-fold from $\sim 2 \times 10^{-2}$ into $3 \times 10^{-5} \text{ g cm}^{-2} \text{ h}^{-1}$ [65]. The inherent micro-meso porous structure of aerogel is expected to prevent permeation of the heavy atom vapor which has a mean free path of centimeters. Additionally, the low thermal conductivity and electronic conductivity due to the high porosity have a negligible effect on heat flux loss and does not cause the electronic shorts. The same group also developed coating materials [66][67][68], for Skutterudites, $\text{La}_{3-x}\text{Te}_4$, and $\text{Yb}_{14}\text{MnSb}_{11}$, to suppress the sublimation. However, they did not release the details about the composition and synthesis process.

Sublimation has an additional, serious effect besides the reduction of the cross-section of the TEG leg itself. The departure of atoms from the surface leaves a concentration gradient of corresponding vacancy defects, which can continuously diffuse into the matrix and cause the degradation of TE performance, significantly reducing the expected lifetime of the material. In PbTe, Pb vacancies aggregate together to form vacancy plates which significantly reduce mechanical strength at temperatures higher than 500°C [69]. In the PbTe system, Si can play an

important role in reducing grain size and consequently the density of the Pb-depletion plates, leading to higher mechanical strength that helps the sample to bear the compress force without yield during the measurement as shown in Fig. 5 [70]. In some cases, atomic vapor released into the voids (known as bloating) results in structural failure [71]. Additionally, dislocation and grain boundary motion also decreased the efficiency and reliability of the TEG modules [72].

The chemical stability of TE materials is affected by two major issues: 1) the diffusion of oxygen and nitrogen from the air into the TE materials, 2) TE materials react with the oxygen and nitrogen in the air at high temperature. Both cases cause significant deterioration of the TE performance. One of the solutions is sealing the TEGs with argon. Chemical stability can also be changed with varying dopant concentrations as well as the incorporation of nanostructures. A well-known example is the AZ series of Mg alloys. Even though pure Mg is very active, it becomes stable in air after the addition of 3 wt.% Al and 1 wt.% Zr. If TE materials such as Skutterudite and Mg_2Si could be in air without argon protection, it would be a tremendous advance that would significantly reduce the cost of TEG materials. Another way to improve chemical stability is through surface coating. For example, the improved oxidation resistance of Skutterudite coated with composite glass, which shows good stability at 550 °C in air [73]. Brostow et al. reported that aluminum isopropoxide $[\text{Al}(\text{OC}_3\text{H}_7)_3]$ significantly improved the stable working temperature of Bi_2Te_3 [74].

2.3. Thermoelectric Performance

Advances in thermoelectric performance of TE materials can be viewed as the pursuit of higher ZT . There are many excellent review papers and book chapters [75]-[85] that pay specific attention to particular materials, such as PbX ($\text{X} = \text{Te}, \text{Se}, \text{S}$), CoSb_3 , half-Heusler, Mg_2Si , and oxides, or focus on special fabrication routes, such as melting-casting metallurgy, ball milling-hot pressing metallurgy, and heavy plastic deformation. This section, will review the latest advances grouped by thermal transport type: phonon engineering and electron engineering.

2.3.1 Phonon Engineering: A Top-down Approach

Nano Grains and Nano Inclusions. The heat conducted by the phonons is an energy loss in the TEG conversion process that should be suppressed as much as possible. Nano grains, nano inclusions and nano particles, are widely accepted strategies to reduce the phonon mean free path ($\kappa=1/3C_v v l$), reducing the lattice thermal conductivity, and improving the ZT value

[86]-[88]. Figure 6 compares the ZT s of conventional-bulk, and nanocomposite TE materials made by ball milling and hot pressing (SiGe [11][12], half-Heusler [89][90], Bi_2Te_3 [2][4]). The nanocomposite made by this powder metallurgy method has some general features [91]: 1) a wide distribution range of grain size from hundreds nanometers to several nanometers, 2) nano-inclusions due to the compositional fluctuation, and 3) secondary phase nanoparticles at grain boundaries. Among these features, the increase in total grain boundaries due to the reduced grain size, play the most important role in suppressing the propagation of phonons. Due to the significantly reduced lattice thermal conductivity, a 30-40% enhancement of ZT in all the three material systems has been observed in both p- and n-type materials. It should be noted that the average grain size in different materials could be different due to the different grain growth behaviors and also the ratio between the hot pressing temperature (T_{HP}) and the melting point (T_m), i.e., T_{HP}/T_m . In order to obtain good carrier mobility, the ratio of T_{HP}/T_m needs to be close to 0.8-0.9. However, at such high hot-pressing temperatures, grain growth occurs in both the half-Heusler (powder: tens of nanometers; bulk: hundreds of nanometers) and Bi_2Te_3 (powder: tens of nanometers; bulk: micrometers) systems. How to suppress the grain growth without reducing carrier mobility is still an open challenge in most materials. Another general route widely used to reduce the thermal conductivity is to form nano inclusions by melting and quenching. This approach utilizes the phase separation that occurs when a single-phase liquid turns into a two-phase solid [83][84]. According to the different phase diagrams, there are four precipitate-types: 1) matrix encapsulation, 2) nucleation/growth, 3) eutectic decomposition, and 4) spinodal decomposition, as shown in Fig. 7 [92]-[95]. By using such routes, the ZT of n-type PbTe ($ZT=1.4$ at 880K [96]) was improved by including AgSbTe₂ to 1.8 at 800 K [5], while that of the p-type PbTe ($ZT=1.4$ at 880K [97]) was improved to 1.5 at 650 K by including Ag₂Te [93], to 1.7 at 650K by including NaSbTe₂ [98], to 1.7 at 800K by including SrTe [99], and to 1.8 at 800 K by including PbS [100]. Similar TE performance improvements were also observed in PbSe [101], PbS [102][103], CoSb₃ [15][104], half-Heusler [105], and Mg₂Si [106] systems. Besides the melting-quenching method, nano inclusions were also formed by direct ball milling and hot pressing, such as the PbTe with AgSbTe₂ [107]. Recently, the combination of melting and quenching with ball milling and hot pressing was found to be able to further reduce the thermal conductivity down to 0.5 for PbTe with SrTe, yielding a ZT value over 2.0 [22]. There

seems to be not much room left for further improvement since the lattice thermal conductivity is already very small for these materials.

Callaway's phenomena model [108] were widely used to fit lattice thermal conductivity with the various scattering centers for phonon-phonon scattering, alloying scattering, nano inclusions scattering, and grain boundary scattering [109]-[111]. However, it has some limitations in terms of understanding detailed phonon transport, such as: 1) which phonon mode is more sensitive to a special scattering center, 2) whether the amorphous limit is reasonable, or reachable through the nano approaches, 3) why Si is more sensitive to grain boundary scattering than PbTe, and 4) why AgSbTe₂ is not sensitive to the alloying effect. The answer to these questions should be related to the phonon mean free path distribution. Recent theoretical [112][113] and experimental [114][115] works have given some new understanding about the propagation of phonons. The distribution of the phonon mean free path is much wider than previously expected. As an example, the phonon mean free path of Si can expand from several nanometers to tens of micrometers, and this is the reason why Si is very sensitive to the grain boundary scattering. Furthermore, direct measurement of phonon spectrum by neutron scattering has also uncovered some new mechanisms for the intrinsic low lattice thermal conductivity, e.g., soft phonon nature due to the anharmonic interaction between the LA and TO phonons [116].

Atomic construction. In addition to the approach of artificially introducing new phonon scattering centers, there are also efforts being made to create new crystalline structures based on Skutterudite, Clathrate, and Zintl complexes [117]. Recently, re-investigations of two simple compounds found high ZT values of 1.5-1.6 for Cu₂Se [118][119] and 2.6 for SnSe [24] due to the low lattice thermal conductivity of 0.4 W m⁻¹ K⁻¹ for Cu₂Se and 0.23 W m⁻¹ K⁻¹ for SnSe at 700 °C. Cu₂Se is an ionic conductor at high temperature, which has a thermal stability problem [120]. However, the decreasing C_v from 3R to 2R due to the partial melting of Cu-lattice is still fundamentally interesting, and suggestive of another possible way to reduce the lattice conductivity in addition to reducing the phonon mean free path. Stabilizing the mobile ionic atom in the sublattice, however, is another challenge. SnSe has a highly anisotropic orthorhombic structure as compared with its counterpart cubic SnTe, or PbSe. The exceptionally low lattice thermal conductivity in SnSe has been attributed to anharmonicity according to the first principles calculation [24]. If these exceptional properties are confirmed by others, this finding could lead to a new trend, searching for novel TE materials with anharmonic bonding..

In 2006, Koumoto et al. proposed the concept of nanoblock integration into a layer-structured hybrid crystal. The layered $\text{Na}_x\text{Co}_2\text{O}_4$ could be regarded as a hybrid crystal of ordered CoO_2 nanosheet and disordered Na nanosheet. The CoO_2 nanosheet serves as an electronic transport layer and hence shows a high power factor, while Na nanosheet works as phonon scattering boundary to give a low thermal conductivity. The layered Cu_2Se is also considered as “natural superlattice” with an ordered selenium layer and a disordered copper layer [121]. In 2014, Morelli et al. proposed a way to construct a highly ordered diamond-like compound, e.g. using Zn^{2+} and Se^{2-} to form the diamond-like compound ZnSe , and further replacing the two Zn^{2+} with Cu^{1+} and In^{3+} to form CuInSe_2 , or replacing three Zn^{2+} with two Cu^{2+} and one Sn^{4+} to form Cu_2SnSe_3 [122]. Similarly the natural mineral Tetrahedrite is also considered as a highly ordered diamond-like compound with Cu^{1+} , Zn^{2+} , Sb^{3+} , and S^{2-} . Such highly ordered diamond-like compounds would have a semiconductor behavior as the total charge is equal to zero [123]. Of the highly ordered diamond-like group of compounds, those having group-V elements (As, Sb, Bi) as a construction ion with a charge of 3+, such as AgSbTe_2 , CuSbSe_2 , and Cu_3SbSe_3 , have an intrinsically low thermal conductivity. The lone pair s-electrons are believed to introduce strong lattice anharmonicity [124]-[127]. Besides tuning at the metal site, we could also tune the nonmetal site by using two chalcogen elements. The new compounds BiCuSeO [80] and BiAgSeS [128] can also be considered as highly ordered diamond-like compounds. Recently, a theoretical work suggested the intrinsic low thermal conductivity of IV–VI, $\text{V}_2\text{–VI}_3$ and V materials is related to the resonant chemical bonding. Such resonant bonds cause optical phonon softening, strong anharmonic scattering, and large phase space for three-phonon scattering processes [129]. New insights on the relationship between resonant bonding and low thermal conductivity will help the development of better TE materials by direct atomic construction.

2.3.2 Electron Engineering: Bottom-up Approach

Atomic scale. Most state-of-the-art TE materials fall into the category of degenerated semiconductors with optimized carrier concentrations on the order of 10^{19} cm^{-3} - 10^{20} cm^{-3} depending on the carrier effective mass. The optimization of the carrier concentrations is closely related to maximization of the power factor, i.e., $PF = S^2\sigma$. Fundamentally, the optimized power factor is connected with the weighted mobility $(m^*)^{3/2} \mu$ [130]. In multi-valley, the carrier

effective mass is $m^* = N_v^{2/3} (m_1 m_2 m_3)^{1/3}$, where N_v is the degenerated valley number. m_1 , m_2 , and m_3 are the effective masses along the axes of symmetry within each valley. The concept of weighted mobility was also applied to understand why Bi_2Te_3 and PbTe have good TE performance. One of the reasons is the high N_v due to the highly symmetric structure. For quite a long time, the attention of the TE community has been focused on phonon engineering through the rattling atoms or nanostructures. The method of boosting the TE performance through tuning the band structure did not get nearly as much attention. In 1996, Caillat et al. noted an increased m^* with increased carrier concentration in both n and p-type CoSb_3 [131], in which the author attributed it to the contribution of the non-parabolic band following Kane's model. In 2002, Dyck et al. reported a significantly increased m^* from $4 m_0$ to $7 m_0$ with increased Ni in $\text{Ba}_y\text{Co}_4\text{Sb}_{12}$ which finally resulted in the PF_{max} increase from 41 to $58 \mu\text{W cm}^{-1} \text{K}^{-2}$, in which the rate of change of m^* with increasing carrier concentration with Ni is much larger than that in Ni-free samples [132]. However, the authors still think that the increased m^* is due to the non-parabolic band. Similarly improved PF was also observed in Ni doped $\text{Ca}_y\text{Co}_{14}\text{Sb}_{12}$ [133]. However, the first-principles calculation supports a different explanation, one which suggested an additional carrier pocket formed in the conduction band due to the d -orbital of Ni and provided a new fast transport channel for electrons [134]. Later, Liu et al. clarified that the improved PF due to the additional carrier band could be observed, since the band edge difference is less than $5 k_B T$ based on a multi-band model [135]. These works clearly demonstrate that the PF could be improved by introducing impurity energy bands through doping to increase m^* . These research results did not get widespread attention, however, until Heremans published the Tl-doped PbTe work in 2008 [6]. Later, a similar effect was also found in $\text{Bi}_2\text{Te}_3\text{:Sn}$ [136], PbSe:Al [137], PbTe:Mn [138], and SnTe:In [139]. Another band structure tuning method at the atomic level is the band convergence related to alloying. In 2011, Pei et al. utilized this effect in the valence band of PbTe-PbSe system and achieved a ZT value of 1.8 in $\text{PbTe}_{0.85}\text{Se}_{0.15}$ by using Na as the acceptor [7]. Zhang et al. confirmed the same idea in PbTe-PbSe by using K as acceptor and got a peak ZT of 1.6 in $\text{PbTe}_{0.75}\text{Se}_{0.25}$ [140]. Similar band convergence was also identified in $\text{Mg}_2\text{Sn-Mg}_2\text{Si}$ system with the composition of $\text{Mg}_2\text{Sn}_{0.7}\text{Si}_{0.3}$ [14][141]. Recently, a similar effect was found in $\text{Mg}_2\text{Sn-Mg}_2\text{Ge}$ system with the composition $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, which shows a ZT of 1.4 at 450°C [142]. Now, band structure tuning has been widely accepted as an effective strategy for improving electronic transport.

Nano Scales. The key to nano scale tuning for electron transport is to reduce the energy potential at the grain boundary and interface between nano inclusion/particle and the matrix. The negative influence of the grain size on mobility is well known even at the micron scale range in FeSi₂ [143], CoSb₃ [144], and Bi₂Te₃ [145]. The hot pressing temperature impacts not only the reduction of grain size, but also the concentration of intrinsic defects (such as the tellurium vacancy in Bi₂Te₃) that can affect carrier mobility. However, Nakagawa et al. observed that carrier mobility decreased from 1758 to 271 cm² s⁻¹ V⁻¹ as the grain size decreased from 40 μm to 2 μm while the carrier concentration remained relatively constant [144]. The decreased carrier mobility is likely related to dangling bonds at the grain boundary. Bulk materials made by the chemical powder metallurgy method, are notorious for having poor electrical conductivity as a result of grain boundary scattering. Residual molecules (from precursor compounds) or absorbed oxygen (from air) on the surface of the nano blocks decompose and leave some C or O defects at the grain boundary after the powders are sintered. Such C or O defects act as charge carrier trapping centers and significantly reduce the carrier mobility [82]. One of the solutions is to add an additional surface treatment to the nano blocks before sintering. Recently, Liu and Guo et al. have used such a strategy to get a significant enhancement in the TE performance of Bi₂S₃ made from chemically derived nano networks [146].

Nano inclusion is a widely used approach to reduce thermal conductivity for the purpose of boosting *ZT*. However, nano inclusions scatter phonons as well as charge carriers. Generally, nano inclusions with crystalline structure similar to the matrix exhibit less charge carrier scattering compared with those inclusions with different crystalline structure. This is why the *ZT* of PbTe nanocomposite was enhanced from 1.4 to 1.6-1.8 with coherent nanoinclusions, e.g. SrTe, AgSbTe₂ and NaSbTe₂, but only 1.4-1.5 with incoherent nanoinclusions, e.g. Sb and Ag₂Te. Figure 8 shows that the carrier mobility of PbS matrix varies with different nano inclusions, including CdS, ZnS, CaS, and SrS [147]. Generally, the carrier mobility for both n- and p-type PbS decreases with an increased amount of the second phase from 1% to 4%. Interestingly, the carrier mobility of p-type PbS with 1% CdS shows a higher value (~180 cm² s⁻¹ V⁻¹) than that with 1% SrS (~125 cm² s⁻¹ V⁻¹). The author attributed it to the energy difference in the valence band between the inclusion phase and matrix phase. However, such a “rule” is not applied to the n-type PbS. To understand this dilemma we may need to consider the interface of the nano inclusion phase and the matrix phase as a semiconductor-semiconductor heterojunction.

The nano inclusion scattering of the electrons is related to the energy barrier owing to carrier re-distribution at the interface. The degree of charge carrier transfer is related to not only the band edge difference but also the Fermi energy. The position of Fermi level is mainly determined by the doping concentration. Due to the formation energy difference, the concentration of dopant atoms can be different between the inclusion phase and the matrix phase. Actually, He et al. has observed such non-uniform distribution of Na in the PbTe-PbS system by atom-probe tomography, in which the partitioning coefficient of $\text{Na}^{\text{PbS}}/\text{Na}^{\text{PbTe}}$ could be as large as 10 [95].

Meso Scales. The accepted phonon scattering centers in nanocomposites include the dopant or alloying atoms, nano inclusions, grain boundaries, and pores. Grain boundary modification, or alloyed nano inclusion, are examples of techniques that can be used to decrease the potential barrier. On a meso-scale, an “ordered nanocomposite”, can reduce the negative impact of phonon scattering centers on electronic transport [87]. The key concept is to reconstruct the electron transport channel by changing nanostructures with un-defined morphology, random size distribution, and disordered configuration, into ones with well-defined morphology and ordered arrangement. This idea was also resonant by others [88]. The re-orientation of random grains in Bi_2Te_3 is one of the most successful examples of this strategy [148] [149]. Our novel process of multiple time repeated pressing improved the power factor close to that of the single crystals. An improved power factor was also reported in BiCuSeO materials by re-orienting random grains [150]. Modulation doping is another method that can be used to achieve an ordered nanocomposite [87].

3. Device-level Progress in TEG

3.1 TEG Efficiency

The maximum conversion efficiency of a TEG is derived from temperature independent TE properties as [151],

$$\eta_{\max} = \eta_{\text{Carnot}} \frac{\sqrt{1 + Z_M \bar{T}} - 1}{\sqrt{1 + Z_M \bar{T}} + \frac{T_c}{T_h}}, \quad (4)$$

where η_{Carnot} , T_h , T_c , and $\bar{T}$ are the Carnot efficiency $[(T_h - T_c)/T_h]$, the hot side temperature, cold side temperature, and the average temperature, respectively. Z_M is the module figure of merit

defined as $(S_p - S_n)^2 / (KR)$, in which K and R are the thermal conductance of an n-p pair in thermal parallel and the electric resistance of an n-p pair in electrically series, respectively. The subscript n and p denotes n-type and p-type. It is noted that $\sqrt{1 + Z_M \bar{T}}$ is the optimized ratio of an external to an internal load for the maximum efficiency. As a load is matched, the efficiency at which the output power generation is maximized is expressed as [152],

$$\eta_{P_{\max}} = \eta_{Carnot} \left[2 - \frac{1}{2} \eta_{Carnot} + \left(\frac{4}{Z_M T_h} \right) \right]^{-1}. \quad (5)$$

These formulas are only valid for constant TE properties without considering the effect of thermal/electric contact resistance, parasitic losses, and Thomson effect on the efficiency. Moreover, Eq. (5) is not complete when considering a practical TEG design that includes the role of heat exchangers, since the temperature drop between a heat source/sink and hot/cold side of a leg in an actual TEG is not negligible. This is because maximum power generation doesn't take place at a unit ratio of impedance matching at a limited heat flux from a heat source [153][154]. In order to more accurately predict the performance of TEGs including the effects ignored in the equations above, the temperature dependence of TE properties should be taken into account. The 1-D governing equation of the energy balance in a differential element is [155],

$$\frac{d}{dx} \left(\kappa(x) \frac{dT(x)}{dx} \right) + J^2 \rho(x) - JT(x) \frac{dS(x)}{dx} - \varepsilon \sigma_{sb} \frac{W}{A} (T^4(x) - T_\infty^4) = 0, \quad (6)$$

where J , ε , and σ_{sb} are the current density, the emissivity and the Stefan-Boltzmann constant, respectively; W and A are the perimeter and the cross-sectional area of a leg, respectively. The terms from left to right in Eq. (6) represent the conduction heat, Joule heat, Thomson heat, and heat loss by radiation, respectively. The TE properties in Eq. (6) are shown as a function of a spatial position x , since the temperature is position dependent, for example, T_h at $x = 0$ and T_c at $x = L$ (length of TE leg) when one considers a TE leg only. To solve Eq. (6), an iterative method is applied to a discretized differential element until the current density and thermal boundary conditions are converged. The thermal/electric contact resistances are included in the iterations as additional differential elements. The efficiency is obtained by computing the ratio of the output power density to the input heat flux q_h as,

$$\eta_{TEG} = \frac{JV_L}{q_h}, \quad (7)$$

where V_L is the potential drop across a load.

The temperature dependent efficiency of various n-type and p-type materials is plotted in Fig. 9a based on the numerical calculation described above, in which the cold side temperature is kept at 50°C while the hot side temperature is ramped up to the materials' maximum operational temperature. The heat loss by radiation is ignored in this prediction. Fig. 9b shows the measurement data of assembled modules consisting of Bi₂Te₃ for low temperature up to $\Delta T = 150^\circ\text{C}$, and Skutterudite or Mg₂Si/MnSi for intermediate temperature up to $\Delta T = 600^\circ\text{C}$. The calculated efficiency of each single n-type and p-type Bi₂Te₃ is 7~9% at $\Delta T = 150^\circ\text{C}$ with $T_C = 50^\circ\text{C}$ as shown in Fig. 9a [2][156] while the module based on Bi₂Te₃ legs yields 4.5% at the same temperature condition [157]. For the modules based on Skutterudites, the measured efficiency is in the range from 6 to 10.7% at $\Delta T = 500\sim 570^\circ\text{C}$ [31][158][159] while the predicted efficiency of typical Skutterudite materials are 9~13% [16][17][160]. The lower measured module efficiency compared with the efficiency of each homogeneous material is mainly caused by the degradation of the output power due to the effect of intermediate layers between the TE material and the heat source as well as heat losses. The electric and thermal contact resistances play an important role in maximizing the electric output power and module efficiency as shown in Eq. (8) and (9) [161],

$$P_{\max} = \frac{S^2}{2\rho} \frac{A \cdot N (T_H - T_C)^2}{(\gamma + l) \left(1 + 2\lambda \frac{l_c}{l} \right)^2}, \quad (8)$$

$$\eta = \eta_{\text{Carnot}} \left[\left(1 + 2\lambda \frac{l_c}{l} \right)^2 \left\{ 2 - \frac{1}{2} \eta_{\text{Carnot}} + \left(\frac{4}{Z_m T_H} \right) \left(\frac{l + \gamma}{l + 2\lambda l_c} \right) \right\} \right]^{-1}. \quad (9)$$

where the TE properties of n-type and p-type are identical and assumed to be independent of temperature, in which $\gamma = 2\rho_c/\rho$ and $\lambda = \kappa/\kappa_c$ where κ_c , A , and N are the thermal contact conductivity, total cross sectional area of TE legs, and the number of n-p pairs in a module, respectively; l and l_c are the length of a leg and thickness of a contact layer, respectively. It is noted that larger γ and λ lead to decreasing efficiency as well as decreasing maximum power generation. Larger γ increases the internal electric resistance of a module [162] and larger λ decreases the net temperature difference across a leg resulting in a reduced TE voltage [163].

Another possible source of degradation of module efficiency is parasitic heat loss through convection and/or radiation. This leads to lower voltage generation or can require more thermal input depending on boundary conditions. However, the effect of parasitic heat loss is highly dependent on a measurement set-up and its constraints for the heat management, and a commercial TEG [33] using a technology for encapsulating a module is available for minimizing the effect of parasitic heat dissipation. Thus, the effect of the electric/thermal contact resistance at the interfacial layers is the intrinsic primary issue for designing a TEG with maximum performance.

Conventionally, peak ZT is used to evaluate the usability of TE materials. From the device-level view, the high peak value of ZT at a certain temperature does not guarantee high output power and efficiency. In contrast, the average $\langle ZT \rangle_m$ over the working temperature range is more reasonable index. For example, $\text{In}_4\text{Se}_{3.8}$ [164] and SnSe [24] have high ZT peak at high temperature end, but have a rather low value near room temperature. However, recent numerical calculations suggest that even the average ZT is still not sufficient to predict a correct power generation and its conversion efficiency since it doesn't reflect the accumulation of its properties through the temperature gradient [165]. Thus, it is necessary to examine the output power and conversion efficiency of a material based the numerical methods or accumulated characteristics under a realistic temperature gradient instead of a direct use of TE properties measured over small temperature differences at each nominal temperature.

3.2 General Considerations for the Contact Design

In a real-world TEG module, the p and n-type legs are connected in series electronically by a soldered conducting strip, as shown in Fig. 10. For most good TE materials, either direct soldering onto the interconnect is difficult, or the solder reacts with the TE material and degrades quickly at the working temperature [169]. A metalized contact layer is needed between TE elements and interconnects. Contact materials with high thermal and electrical conductivity are favorable for high device performance. In addition, reducing the contact resistivity between the contact layer and TE leg is also very important. Ebling et al. reported large loss of average ZT and power output arising from poor contact both experimentally [170] and in simulation [171]. The perfect contact material should have all of the following characteristics: 1) high electrical conductivity, 2) high thermal conductivity, 3) a matched CTE with the TE elements, 4) the ability to be made very thin to reduce total electrical and thermal resistances, 5) low contact

resistance at the interface between the contact layer and the TE layer, 6) stability at the working high temperature, 7) an ability to form strong mechanical bonds with the TE layer, and 8) higher yield strength the solder at operating temperature.

There are several ways to prepare a contact layer on TE legs. For low temperature applications, sputtering, electroplating / CVD methods allow the preparation of a very thin layer ($< 5 \mu\text{m}$) of contact material on a properly prepared TE leg. For high temperature applications, the contact layer can be joined to the TE material by hot-pressing. The latter way usually is capable of making relatively thick contact layers at low cost and works better as diffusion barrier at high temperatures. In the cases where these two methods are not applicable, conducting paste can be used to bond TE legs to the conducting strip for a limited time. In general, there are three major criteria to consider when choosing contact material for a specific TE material.

3.2.1 Match of Coefficient of Thermal Expansion

Among the requirements for contact layer, high electrical and thermal conductivities are not difficult to achieve for metal or alloy contacts. Matching CTE between contact and TE materials is usually the first and most important challenge researchers need to deal with, especially for those TE materials working at intermediate to high temperature. A system with a significant CTE mismatch is going to experience high interfacial stresses and consequently have a high risk of *in situ* fracture of the device. Since many current applications are under circumstances where maintenance is not easy, such as spacecraft, reliability has become the most important characteristics a TEG needs to have. Therefore, a measurement of CTE is needed for both TE materials and contact materials from room temperature to the working temperature [172][173]. When there is a CTE mismatch between the contact and the TE material, the system needs to be carefully engineered to meet lifetime requirement. For instance, the relative thickness between two materials could change the magnitude of interface stresses [173]. The tolerable range of CTE mismatch depends on the mechanical properties of both contact and TE materials.

Ravi et al. [173] reported CTE studies for several high temperature TE materials. Besides the linear thermal expansions of different materials, they also found that filled Skutterudite and SiGe both exhibited permanent length changes over the measurement runs. Permanent length changes in a module give rise to additional compressive stresses on the leg or tensile stress on the counter leg depending on boundary constraints, which could affect the reliability of TE modules. A group of interesting materials for use as contacts is Mo-Cu or W-Cu alloys. Mo and

W are bcc metals with very low CTE ($\sim 4.5 \times 10^{-6} \text{ K}^{-1}$) while Cu is an fcc metal with a high CTE ($\sim 16.5 \times 10^{-6} \text{ K}^{-1}$). The CTE of the alloys change continuously with composition change. For example, the CTEs of Mo-Cu alloys with Mo/Cu volume ratio of 90:10, 80:20, 70:30, 60:40, and 50:50 are 6.59, 7.65, 8.50, 9.87, and $11.21 \times 10^{-6} \text{ K}^{-1}$, respectively. So these alloys can be used to match many TE materials with different CTEs as long as there is no severe reaction between them.

If a contact material with a matched CTE is not available, the interface stress can be reduced with additional buffer layers. A good example is in PbTe modules. Fe has been identified as a good contact material for PbTe. However, the CTE of PbTe is about $23 \times 10^{-6} \text{ K}^{-1}$ and independent of temperature from room temperature to 550 °C while Fe has a CTE of $12 \times 10^{-6} \text{ K}^{-1}$ at room temperature and slightly increases with temperature. To reduce the interface stress, a mixture layer comprised of Fe and PbTe powder was inserted in between the Fe contact layer and the PbTe, with acceptable results [174][175].

3.2.2 Bonding and Interface Reaction

A minor reaction between the TE materials and the contact barrier layers is conducive to a strong bond. W is chosen as contact material for SiGe device because the CTE matches that of SiGe. However, due to the very high melting point of W, the bond between W and Si can be very weak. Therefore, a graphite buffer layer is often inserted in between because it bonds well to both SiGe and W [176].

On the other hand, severe reactions between contact and TE materials should be avoided. Interface reactions at working temperature could result in the formation and growth of intermetallic compounds and subsequent increase in contact resistance [38]. Cracks or voids will also appear at the interface and eventually cause failure of the contact [178][179]. Reaction at the contact bonding or leg preparation step for n-type Bi_2Te_3 proved troublesome. Ni has been proven as a good contact material for p-type Bi_2Te_3 . However, when applied to the n-type leg, the contact resistance is two orders of magnitude higher. Detailed investigations show that at the same hot-press temperature, Ni diffuses quickly into n-type Bi_2Te_3 layer and forms a thick p-type region. The combined effect of Te deficiency and Ni doping results in a wide p-type region, and consequently a high contact resistivity ($\sim 210 \mu\Omega \text{ cm}^2$). To solve this problem, a barrier layer was inserted between Ni and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ to neutralize the acceptor center generated from the interface reaction [38]. A similar method was used for modules consisting of TAGS-85 or GeTe

legs. Since the contact material, Fe, diffuses into these TE materials quickly and results in rapid degradation of the contacts, a SnTe layer was inserted as a diffusion barrier [174][180]. Of course, an extra layer is going to consume ΔT . The thickness of the buffer layer should always be minimized to reduce the parasitic loss.

3.2.3 Specific Contact Resistivity

Besides considering CTE matching and interface reaction problems, the band alignment between the contact layer and the TE material is necessarily considered to minimize the specific contact resistivity. This is basically a metal-semiconductor contact problem. Many of the solutions from the semiconductor industry can be borrowed here. The specific contact resistivity of a metal-semiconductor contact is related to both barrier height and doping concentration [181][182].

According to the ideal Schottky-Mott theory, the barrier height is related to the work function and electron affinity of these materials. Work function (ϕ) and electron affinity (χ) are defined as the required energy to remove an electron from the Fermi level (E_F) and from the bottom of the conduction band (E_C), respectively, to a position just outside the material (vacuum level). First, let's consider the contact between a metal and an n-type semiconductor. When they are separate, the work function of the metal (ϕ_m) is larger than that of semiconductor (ϕ_{sn}), as shown in Fig. 11a. When the metal surface is in intimate contact with the n-type semiconductor, the electrons on the conduction band of the semiconductor have higher energy compared with the electrons on the Fermi level of the metal and will diffuse into metal at the interface, consequently leaving a depletion layer with positive charge (donor ions). The electrons that entered the metal will negatively charge the metal surface. When the whole system reaches thermal equilibrium, the Fermi levels on both sides will line up. Relative to the Fermi level in the metal, the Fermi level in the semiconductor is lowered by an amount equal to the difference between the two work functions, as shown in Fig. 11b and Fig 12a. The built-in electric field formed at the interface will create a rectifying energy barrier that prevents electron diffusion from the semiconductor side to the metal side, and is called a Schottky barrier. The Schottky barrier height of such a metal-semiconductor contact is a function of the work function (ϕ_m) of the metal and the electron affinity (χ) of the n-type semiconductor by Schottky-Mott relationship [183][184]:

$$\phi_{B,n} = \phi_m - \chi \quad (10)$$

The case where ϕ_m is smaller than ϕ_{sn} is rather different, the resulting band bending at the interface is shown in Fig. 12b. If such a contact is biased, so that electrons flow from the semiconductors to the metal, they encounter no barrier. If it is biased so that electrons flow in the reverse direction, the comparatively high concentration of electrons in the region where the semiconductor bands are bent downwards behaves like a cathode which is capable of providing enough electrons. The current is then determined by the bulk resistance of the semiconductor. Such a contact is an ohmic contact. Similarly, for a p-type semiconductor, when $\phi_m < \phi_{sp}$, a Schottky barrier forms at the interface (Fig. 12c), while an ohmic contact forms, if $\phi_m > \phi_{sp}$ (Fig. 12d). The specific contact resistivity of the ohmic contact should be small [185]. In the semiconductor industry, $\phi_m > \phi_{sp}$ is very rare for p-type semiconductors, due to the large band gap of the semiconductors. So currently, there are few experimental results reported for this combination. However, it is more likely for this situation to occur in the TE field, since most state-of-the-art TE materials are semiconductors with small band gaps.

In fact, the discussion we made above is for ideal conditions. Experimentally, the barrier heights of metal-semiconductor systems are found to be, in general, determined by both the work functions and the interface states [181]. In covalent compounds, the interface states create interfacial Fermi level pinning that makes the barrier height independent of or very weakly dependent on the metal work function [186][187][188]. While for ionic materials, the barrier height is strongly dependent on the work function of the metal. The reason is that these materials exhibit a low density of active surface states at the interface and consequently the Fermi level is unpinned [189][190]. Among the state-of-the-art TE materials, SiGe, PbTe, CoSb₃, and Bi₂Te₃ have covalent bonds, so the barrier heights of the contacts on these materials are expected to be weakly dependent on different contact metals. P-type filled Skutterudite, half-Heusler, TAGS-85 and MgAgSb are more like ionic compounds. Specific contact resistivity is expected to be more variable when different metals are bonded to these materials. Generally, matching the work functions of contact and TE materials should give us smaller specific contact resistivity.

The carrier concentration of the semiconductor also plays a very important role on the specific contact resistivity. Besides changing the work function of the semiconductor, the higher carrier concentration also changes the carrier transport mechanism. A rough criterion can be set by comparing the thermal energy kT to E_{00} which is defined as

$$E_{00} = \frac{q\hbar}{2} \sqrt{\frac{N}{m^* \epsilon_s}}, \quad (11)$$

where N , m^* , and ϵ_s are carrier concentration, effective mass, and permittivity of the semiconductor respectively. For low to moderate doping levels ($kT \gg E_{00}$), thermoionic-emission over the barrier dominates the carrier transport. For higher doping level ($kT \approx E_{00}$), thermoionic-field emission, which is tunneling of thermally excited carriers, dominates the carrier transport. With even higher doping level ($kT \ll E_{00}$), field emission, which is a pure tunneling process dominates. Since the current from field emission is much higher than the current from the other two processes, high carrier concentration is favorable for low specific contact resistivity. Most state-of-the-art TE materials have optimized carrier concentrations of 10^{19}cm^{-3} or even higher. Field emission dominates the carrier transport at the contact of TE leg. The relationship of the specific contact resistivity ρ_c and carrier concentration could be simplified into Eq. (12).[181]

$$\rho_c \propto \exp\left(\frac{q\phi_B}{E_{00}}\right), \quad (12)$$

where ϕ_B is the barrier height. According to Eq. (12), the higher the carrier concentration of the TE material, the lower the specific contact resistivity. Taylor et al. increased the carrier concentration on the surface of Bi_2Te_3 legs (both n and p-type) by ion implantation. Then put Ni contacts on the legs for the specific contact resistivity measurement. Their results, as shown in Fig. 13, are consistent with the theoretical analysis shown above [191]. This work demonstrates an easy way to reduce the specific contact resistivity without changing the contact material.

3.3 State-of-the-art in Contact Design

3.3.1 Skutterudite

Filled-Skutterudites show promising physical and mechanical properties for power generation using intermediate temperature heat sources such as automobiles. Therefore, quite an effort has been focused on studying the TE power generation modules using filled-Skutterudites material. In 2001, Caillat et al. tried Ni and Nb as the electrode by adding metal powder on the top of the Skutterudites legs during hot-pressing [192]. They found that Ni is not appropriate as a contact material for p-type Skutterudites due to the CTE mismatch and Nb could be a good

choice as electrode material for Skutterudites with a specific contact resistivity lower than $5 \mu\Omega \text{ cm}^2$. Zhao et al. used Ti foil as buffer layer to join CoSb_3 and Mo-Cu alloy contact with an effective contact resistivity of $20\text{-}30 \mu\Omega \text{ cm}^2$ [178][193]. It is worth noting that this contact resistivity was calculated using the total voltage change across the Ti layer, so it includes the contact resistances on two interfaces (CoSb_3/Ti and $\text{Ti}/\text{Mo-Cu}$) and the resistance of Ti layer, as shown in Fig. 14. It is not the actual contact resistivity at one specific interface that can be interpreted using the theory introduced in section 3.2.3. However, it is useful to evaluate the total extra contact resistance introduced by adding a buffer layer. So we define the total contact resistivity calculated using a similar method by multiplying the total extra resistance by the cross-sectional area as effective contact resistivity. It was also found that an intermetallic compound layer formed at CoSb_3/Ti interface, the thickness of which increases with thermal aging and caused further increase of contact resistance at the contact interface. Recently, Zhao et al. used W-Cu alloy to replace Mo-Cu as the contact material for CoSb_3 . Since Ti is still used as buffer layer, the effective contact resistivity is similar and the reaction between Ti and CoSb_3 is still a problem [194]. In 2012, Fleurial et al. used Ti as metal contacts for both n and p-type filled Skutterudite, with a Zr layer in between as diffusion barrier. The specific contact resistivity between Zr and Skutterudite was reported to be $19 \mu\Omega \text{ cm}^2$ [179]. An intermetallic compound layer also formed at the Zr/CoSb_3 interface after aging test. Guo et al. reported using arc-melted Co-Fe-Ni alloys as electrodes as well as diffusion barriers in filled Skutterudite modules [195]. Although no specific contact resistivity data was reported for these legs, the interface was reported to be very stable after prolonged thermal aging and cycling tests. Muto et al. used CoSi_2 for the n-type and Co_2Si for the p-type electrodes for Skutterudite [159]. The specific contact resistivities at the interface for both types are around $1\text{-}2 \mu\Omega \text{ cm}^2$. However, due to the high melting point of CoSi_2 and Co_2Si , a complicated procedure has to be used to produce crack free leg samples. Furthermore, the electrical and thermal conductivity of Co_2Si is relatively low compared with other materials reported.

3.3.2 PbTe

Currently, Fe is chosen as the contact metal for both p-type and n-type PbTe legs. The CTE of PbTe is about $18 \times 10^{-6} \text{ K}^{-1}$, while Fe has a CTE of $\sim 12 \times 10^{-6} \text{ K}^{-1}$. The mismatch causes stress at the interface and hence cracks form and grow in the legs. To solve this problem, Singh et al. reported adding a $\sim 200 \mu\text{m}$ thick PbTe/Fe mixture layer (50%PbTe+50%Fe) between the

Fe PbTe layers on the p-type side [174]. On the n-type side they used TAGS-85 as TE material and added a SnTe layer between the TAGS-85 and the Fe contact layers to prevent reaction between TAGS-85 and Fe. The average specific contact resistivity they reported was about $7.6 \mu\Omega \text{ cm}^2$. In 2012, Leavitt et al. filed a patent for a segmented module using PbTe based material on both the p-type and n-type legs. They used a similar method to solve the thermal expansion mismatch between TE material and Fe contact layer. The mixture layers were about 1 mm thick and consisted of 75%PbTe and 25% Fe by weight [175].

3.3.3 Bi₂Te₃

Ni has been used as contact material for ingot Bi₂T₃ for a long time. For cooling applications, a barrier of nickel (0.5-1 μm) is coated on the Bi₂Te₃ surface to block inter-diffusion, followed by a protective layer of gold on nickel for soldering. These thin contact layers are usually prepared on Bi₂Te₃ using sputtering, electrodeless plating, or a combination of these two methods. In the case of sputtering, nickel atoms are likely to bond to each other and grow into three-dimensional islands due to the poor wettability between nickel and Bi₂Te₃. [196] To improve the quality of the contact, a chromium layer of a few tens of nm thick can be deposit on the surface of Bi₂Te₃ first to improve the wettability. Then a nickel layer of several hundred nm can be sputtered on this chromium layer.

For power generation applications, due to the higher operating temperature (200-250 °C) of the TEG, a nickel barrier layer with 0.5-1 μm cannot effectively block inter-diffusion in the TEG [197]. Recent studies indicated that the thickness of the Ni barrier layer for TEG needs to be at least several μm [198][162]. Sputtering is costly and time consuming. Furthermore, the bonding strength of sputtered Ni layer on Bi₂Te₃ is only 8 MPa, which is too low for TEG applications. Currently, thermal spray is the most common method to fabricate thick Ni contact on Bi₂Te₃-based alloys with large grain size for TEG. However, thermal spraying Ni on nanostructured Bi₂Te₃ leads to cracks propagating randomly along the grain boundaries because of low thermal conductivity and disordered grain textures. Feng et al. developed a chemical treatment assisted electroplating technique [196]. With this method, Bi₂Te₃ based material is pre-treated with functionalized self-assembled 3-mercaptopropyl-trimethoxysilane (MPS), which not only provides strong covalent binding but also creates more nucleation sites for even distribution of nickel electroplating. Then, a 5 μm thick layer of nickel and 3 μm thick layer of gold are electroplated onto the pre-treated surface. This technique is very cost-effective. The specific

contact resistivity observed on both p and n-type samples is around $1 \mu\Omega \text{ cm}^2$ or even lower. However, the bonding strength is still not satisfactory. To achieve better bonding, Liu et al. prepared even thicker Ni contact layer by directly hot-pressing Ni powder layer onto Bi_2Te_3 powder layer [38]. The interface between the Ni layer and the p-type Bi_2Te_3 is strong and clean with a specific contact resistivity $< 1 \mu\Omega \text{ cm}^2$. However, a severe reaction happened between Ni and n-type Bi_2Te_3 during hot-pressing, which caused a two orders of magnitude higher specific contact resistivity on the n-type leg. To solve this problem, a $\sim 100 \mu\text{m}$ thick buffer layer ($\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with 1% SbI_3) was prepared between the Ni and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ layer. Satisfactory bonding strength (16 MPa) and a specific contact resistivity of $1 \mu\Omega \text{ cm}^2$ can be achieved in this manner.

3.3.4 Mg_2Si

Due to the poor TE properties of p-type Mg_2Si , the reported modules are either unileg consisting of only n-type Mg_2Si legs **Error! Reference source not found.** or with other p-type TE materials, such as NaCo_2O_4 as the p-type leg to match [200]. Ni is used as contact material for n-type Mg_2Si because of the matched CTE. Furthermore, Ni is durable and does not react with Mg_2Si seriously at the working temperature. Direct hot-press bonding methods are used for leg preparation. However, the specific contact resistivity between Ni and commercial Mg_2Si is quite large, estimated to be $\sim 100 \mu\Omega \text{ cm}^2$. In the case of Sb-doped Mg_2Si as the TE material, the specific contact resistivity calculated from the total contact resistance in the module dropped to $32 \mu\Omega \text{ cm}^2$ [201]. Sb-doped Mg_2Si has a higher electron concentration, a good example of reducing the specific contact resistivity by increasing the carrier concentration of semiconductor. Even with the reduced specific contact resistivity, however, the sum of wiring resistance and contact resistance still contribute about 20 – 40% of the total module resistance, greatly degrading the performance of the TE module. So it is still a big challenge to make contact layers to these materials with the specific contact resistivity below $1 \mu\Omega \text{ cm}^2$.

3.3.5 Oxides

$\text{Ca}_3\text{Co}_4\text{O}_9$, NaCo_2O_4 , CaMnO_3 , LaNiO_3 , SrTiO_3 , In_2O_3 , and BiCuSeO have attracted lot of attention as TE oxides. Most oxide TEGs currently fabricated use $\text{Ca}_3\text{Co}_4\text{O}_9$ or NaCo_2O_4 based material as p-type leg and CaMnO_3 or LaNiO_3 based material as n-type leg. The performance of these modules is much lower than expected because of: 1) high contact resistance at oxide/metal contact junctions, 2) cracking or exfoliation due to the very different CTE

between oxide and metal, and 3) the difficulty of having both p-type and n-type from the same parent compound. High working temperatures also makes the conventional contact materials and fabrication procedures less viable. The first successful oxide TE module was fabricated by Funahashi et al. in 2004, who used the mixture of silver paint and 6 wt% oxide powder to join conducting strip and oxide TE materials, and reduced the contribution of contact resistance to the total internal resistance of the module from 56.8% to 12.5% [202]. Since then, most of the contacts in oxide modules with other TE oxides legs were assembled using the same technique [203][204][205]. Ni [206] and Fe-Cr alloy [207] have also been tested as contact materials for $\text{Ca}_3\text{Co}_4\text{O}_9$. Although the Fe-Cr alloy was better than Ni, the reaction between the contact metals and the oxide at work temperature caused an increase of internal resistance. Arai et al. [208] used a mixture of Ni and SrRuO_3 powder (6:4 in volume fraction) as the buffer layer between Ni and NaCo_2O_4 and greatly reduced the electrical resistivity of the TE element, although the effective contact resistivity between Ni layer and NaCo_2O_4 is still very high, it was estimated to be $6 \times 10^5 \mu\Omega \text{ cm}^2$.

4. Challenges and Trends

4.1 High ZT is Not the Only Concern

Pursuing high ZT , especially the high peak ZT , through the application of various phonon engineering and electron engineering schemes, has been a focus of the whole TE community. However, for practical applications, a high peak ZT within a narrow temperature range is not good enough since it will not result in a high efficiency. In addition, the efficiency is not the only concern, and high output power density is as important as efficiency when the capacity of the heat source is large (such as solar heat), or the cost of the heat source is not a big factor (such as waste heat from automobiles, steel industry, etc.). The output power density ω is defined as the output power W divided by the cross-sectional area A of the homogenous leg, *i.e.*, $\omega = W/A$, which is proportional to $PF = S^2\sigma$ by

$$\omega = \frac{1}{4} \frac{(T_h - T_c)^2}{L} PF \quad (13)$$

Eq. (13) contains two main parts: the square of the temperature difference divided by leg length and material $PF = S^2\sigma$. Clearly, in order to achieve higher power density for a given heat source and temperature boundaries, we have to either increase the PF or decrease the leg length.

However, decreasing the leg length can have severe consequences: 1) increase of large heat flux that will increase the cost of the heat management at the cold end, 2) increase of the ratio R_c/R and consequently an increase in the parasitic loss and subsequent decrease in output power generation, 3) increase of the thermal shear stress leading to device failure, etc. Therefore, the best approach is to increase the power factor PF of TE material and then optimize its corresponding physical designing parameters. Since PF is a pure material parameter, we can use it as a criterion for searching for new TE materials for high output power.

4.2 Reliable Contact is a Big Challenge

The difficulty of making reliable contacts for TEG is that we need to fulfill all the requirements described in the section 3.2 at the same time. Furthermore, due to the complexity and diversity of TE material systems, a good contact material for one material may not be a good choice for another one. Each specific application requires specific investigation and design because they may have different requirements and environments. A good example is Bi_2Te_3 modules. The cooling and power generation applications have different working temperatures. Thus we need to prepare contacts differently. Finally, the evaluation of system stability requires prolonged aging and thermal cycling tests, and thus is very time consuming.

4.3 Hierarchical Requirements for the TEG

For TEG to be competitive devices for power generation applications, we need consider at least three requirements: efficiency, effectiveness and reliability. Fig. 15 shows a summary for the hierarchical requirements at the material-level, device-level, and system-level as an “E-E-R” mountain. In order to advance TEG technology, focus must be shifted from “ ZT ” to the whole mountain.

5. Summary

In this review, the latest progress in TEG technology at both material and device levels was summarized. At the material-level, efforts to improve the thermomechanical and thermochemical properties of TEG material were reviewed. Top-down approaches for phonon engineering (such as the atomic construction of new materials) and bottom-up approaches for electron engineering (such as forming ordered nanostructures) were examined. For device-level progress, challenges relating to the metallization layer for conventional TE materials such as

CoSb₃, PbTe, Bi₂Te₃, Mg₂Si, and Oxides were analyzed. Finally, new challenges to advance the TE technology were discussed.

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Table 1, The Young's modulus E, Poisson's ratio ν , fracture strength σ_f , Hardness H_V , Toughness K_C , coefficient of thermal expansion α , and thermal shock resistance R for selected TE materials.

Materials	E (GPa)	ν	σ_f (MPa)	H_V (GPa)	K_C (MPa m ^{0.5})	α (10 ⁻⁶ K ⁻¹)	R (W m ⁻¹)
Bi ₂ Te ₃	32 ^[39]		62 ^[39]	0.62 ^[39]	1.1 ^[39]	-	-
Bi ₂ Te _{2.7} Se _{0.3}	52	-	-	2	-	14-16	-
Bi _{0.4} Sb _{1.6} Te ₃	46	0.25 ^[40]	-	1		16-18	-
PbTe	27.7 ^[41] 57.5 ^[43]	0.22 ^[42] 0.293 ^[43]	50 ^[42]	0.39- 0.43 ^[43]	0.35 ^[42]	20 ^[42]	77 ^[42]
PbSe	36.9 ^[41]			0.57- 0.58 ^[44]			-
PbS	39.3 ^[41]			0.71- 0.91 ^[44]			-
Zn ₄ Sb ₃	71.7 ^[45]	0.26 ^[45]	56.6 ^[45]	2.1 ^[45]	0.8 ^[45]		
Ca ₃ Co ₄ O ₉	84 ^[46]		320 ^[46]	2.5 ^[46]	2.8 ^[46]	8-18 ^[46]	
CoSb ₃	148 ^[47]			6.0 ^[47]			-
Yb _{0.35} Co ₄ Sb ₁₂	164 135 ^[42]	0.20 ^[42]	111 ^[42]	8.0	1.7 ^[42]	11 ^[42]	227 ^[42]
Ce _{0.45} Nd _{0.45} Fe ₃ .5Co _{0.5} Sb ₁₂	154		-	6.0			-
Mg ₂ Si	117 ^[48]	0.18 ^[48]	-	5.0-5.6 ^[48]	1.2-1.3 ^[48]		-
Half-Hesuler	225 ^[49]		-	13 ^[49]			-
Si _{0.8} Ge _{0.2}	143 ^[50]	0.23 ^[50]	-	14.5 ^[50]	0.98- 1.03 ^[50]		-

Table 2, Sublimation rate of selected materials, [65]-[68]

	Temperature (°C)	Sublimation rate (g cm ⁻² h ⁻¹)
TAGS	500	~1
PbTe	500	~9.4 x10 ⁻²
n- Skutterudites	600	5.16x10 ⁻³
	700	2.15x10 ⁻²
p- Skutterudites	600	4.12x10 ⁻⁴
	700	2.7x10 ⁻³
SiGe	1000	4.8x10 ⁻⁵
La _{3-x} Te	1000	8x10 ⁻³
Yb ₁₄ MnSb ₁₁	1000	1x10 ⁻³

Figures

Fig. 1. Effect of contact resistance on leg efficiency and output power of a p-type Skutterudite as a function of the temperature difference between hot side and cold side: (a) the efficiency, (b) the output power.

Fig. 2. SEM images of the interface of an individual TE leg and a copper interconnection. (a, c) before, and (b, d) after thermal cycling showing the failure of the device. The thermal cycling is found to introduce a high density of voids, pores, and crack in the vicinity of the interface. *Ref.* [37].

Fig. 3. Effect of TiN on the mechanical strength of $\text{CoSb}_{2.875}\text{Te}_{0.125}$. (a) SEM image of the fractured surface, (b) pinning effect of TiN particle on the crack propagation, and (c) fracture strength *Ref.*[56].

Fig. 4. Vickers hardness HV as function of modulus for filled Skutterudites. (a) Young's Modulus and (b) Shear Modulus. The unit of the hardness HV is kgf/mm², 1kgf/mm²=9.8 MPa. Ref. [57].

PbTe

PbTe:2%Si

Fig. 5. Softening issue of PbTe at high temperature and solution to increase the thermal mechanical strength. Photograph (a), SEM image (b), and TEM image (c) of PbTe. Photograph (d), SEM image (e), and TEM image for strengthened PbTe by addition of 2% Si. *Ref. [70]*

Fig. 6. Summary of the improved ZT and decreased lattice thermal conductivity due to the nano approach through ball milling and hot pressing route in SiGe, Half-Heusler, and Bi_2Te_3 systems.

Fig. 7. Strategy for the formation of nanostructures from melting-casting route. (a) matrix encapsulation, (b) nucleation/growth, (c) eutectic decomposition, (d) spinodal decomposition

Fig. 8. Effect of nano inclusions CdS, ZnS, CaS and SrS on the carrier mobility of PbS, and connection with the DFT band alignment. *Ref. [147].*

Fig. 9. (a) Numerically predicted efficiency of various p-type and n-type TE materials at $T_c = 50^\circ\text{C}$, where the temperature dependence of TE properties is taken into account: p1-Ref. [17], p2-Ref. [166], p3-Ref.[2], p4-Ref. [7], p5-Ref. [18], p6-Ref. [20]; n1-Ref. [142], n2-Ref. [16], n3-Ref. [21], n4-Ref. [156], n5-Ref. [160], and (b) experimentally measured efficiency of TE modules: a-Ref. [158], b-Ref. [157], c-Ref. [159], d-Ref. [167], e-Ref. [31], our result-Ref. [168].

Fig. 10. The configuration of a practical TE module and the stacking layers between the TE leg and the conducting strip.

Fig. 11. Energy band diagram of metal/n-type semiconductor contact. (a) in separated systems, and (b) connected into one system

Fig. 12. Barriers of metal-semiconductor contact for different types of semiconductors and different relative work functions. n-type: (a) $\phi_m > \phi_{sn}$ (rectifying); (b) $\phi_m < \phi_{sn}$ (ohmic); p-type: (c) $\phi_m < \phi_{sp}$ (rectifying); (d) $\phi_m > \phi_{sp}$ (ohmic).

Fig. 13. Specific contact resistivity for (a) bulk samples and (b) film samples, determined before (open symbols) and after (solid symbols) in implantation. *Ref. [191]:*

Fig. 14. The electrical contact resistivity of the $\text{CoSb}_3/\text{Ti}/\text{W}_{80}\text{Cu}_{20}$ TE element. *Ref.* [194]

Fig. 15. Hierarchical requirements for the TEG: Efficiency-Effectiveness-Reliability Mountain.