Physical Generation in Thermoelectric Generators

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Abstract

Nowadays humans are facing difficult issues, such as increasing power costs, environmental pollution and global warming. In order to reduce their consequences, scientists are concentrating on improving power generators focused on energy harvesting. Thermoelectric generators (TEGs) have demonstrated their capacity to transform thermal energy directly into electric power through the Seebeck effect. Furthermore, Thermoelectric generators have been found as a viable solution for direct generation of electricity from waste heat in industrial processes. This paper presents in-depth analysis of TEGs, beginning with a comprehensive overview of their working principles such as the Seebeck effect, the Peltier effect, the Thomson effect and Joule heating with their applications, materials used, Figure of Merit, improvement techniques including different thermoelectric material arrangements and technologies used and substrate types.

Keyword: *Thermoelectric generator, Seebeck Effect.*

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1. INTRODUCTION

Thermoelectric power generators are proposed for many applications such as waste heat recovery (as topping cycles) automobile industry and solar thermoelectric power generators. It has been shown that the performance of the thermoelectric power generators is an increasing function of its material figure of merit, $ZT = \frac{\sigma S^2 T}{\kappa}$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the operating temperature and κ is the thermal conducitity. Typical commercial thermoelectric devices are made out of Bi_2Te_3/Sb_2Te_3 for room temperature applications and PbTe for high temperature applications and they have a ZT of around 1. These modules are made out of many p-n legs, which are placed thermally in parallel and electrically in series. As an example, HZ-14 model developed by Hi-Z Company, has 6.27 cm by 6.27 cm ceramic area with 49 p-n pairs of bismuth telluride based semiconductors and a thickness of about 5 mm. The module provides 25 W (5% efficiency) output for a temperature difference of 300 °C. This is equivalent of $\nabla T=$60 °C/mm which is quite large. According to the Goldsmid analysis, the ideal efficiency of the thermoelectric module used in this example (i.e. for a ZT ~ 1 and the temperature difference of 300 °C) is about 10%. Clearly, there is a factor-of-two difference between ideal and practical efficiency, which could be attributed to thermal/electrical contact resistances and non-ideal heat managements (operational conditions). Both issues have been largely studied in the literature in the past. In this work, we would like to address the heat management issue. It has been shown by several authors, that heat loss through sidewalls of thermoelectric legs, result in lowering of the thermoelectric efficiency. The argument here is simple. Opening of heat loss channels, results in less conversion of heat to electricity and therefore lowering the thermoelectric efficiency, a direct conclusion. The purpose of this article is to point to practical issues resulting in cases, wherein opening of heat loss channels, improves the efficiency!

2. LITERATURE REVIEW

Hussam Jouharaa et.al (2021) The temperature difference between two sides of the generator is what determines the operation of TEGs. Fig. 1 explains the theory behind TEGs. If one side of a piece of metal could be heated while simultaneously cooling the other side, electrons surrounding the metal atoms at the hot side will have more energy than the equivalent electrons at the cooler side, this means the hot electrons will have more kinetic energy than those in the cooler side.

Cekmas Cekdin et.al. (2020) Thermoelectric generator (TEG) is a solid-state device that produces electrical energy from the temperature difference applied to TEG. This generator technology was first introduced by Thomas Johann Seebeck in 1821 [27]. Seebeck reports that the thermoelectric potential energy can be developed with the presence of temperature differences in two different materials. As a result, this phenomenon is referred to as the "Seebeck effect". Usually, a large number of TE elements are connected electrically in series and thermally in parallel to increase the TEG output power.

KatrinaA. Morgan et.al. (2019) Flexible thermoelectric generators (TEGs) can provide uninterrupted, green energy from body-heat, overcoming bulky battery confgurations that limit the wearable-technologies market today. High through put production of fexible TEGs is currently dominated by printing techniques, limiting material choices and performance. This work investigates the compatibility of physical vapour deposition (PVD) techniques with a fexible commercial process, roll-to-roll (R2R), for thermoelectric applications. We demonstrate, on a fexible polyimide substrate, a sputtered Bi_2Te_3/GeTe TEG with Seebeck coefcient (S) of 140 µV/K per pair and output power (P) of 0.4 nW per pair for a 20°C temperature diference.

Salama Abdelhady et.al. (2018) The measured efficiencies of modern photovoltaic solar cells that exceed the limit determined by Shockley and Queisser indicate a need for advanced physics to solve such conflict. In other words; the gained potential in photovoltaic cells is generated by the thermal potential of the incident radiation and the difference of the Seebeck coefficients of the materials of its junctions. Such advanced physics may represent a gateway to understand other phenomena in the nature.

Univ Pau & Pays Adour et.al. (2017) This review begins with the basic principles of thermoelectricity and a presentation of existing and future materials. Design and optimization of generators are addressed. Finally in this paper, we developed an exhaustive presentation of thermoelectric generation applications covering electricity generation in extreme environments, waste heat recovery in transport and industry, domestic production in developing and developed countries, micro-generation for sensors and microelectronics and solar thermoelectric generators. Many recent applications are presented, as well as the future applications which are currently being studied in research laboratories or in industry. The main purpose of this paper is to clearly demonstrate that, almost anywhere in industry or in domestic uses, it is worth checking whether a TEG can be added whenever heat is moving from a hot source to a cold source.

3. THERMOELECTRIC MODULES

To extend the use of thermoelectricity, it was essential to manufacture standard thermoelectric modules of different sizes, accessible to all. In 1959 the General Electric company commercialized thermoelectric modules composed of 36 couples of bismuth telluride in flat bulk architecture. Nowadays, there are dozens of companies all over the world that manufacture TE modules. Some of these are listed in.

A typical thermoelectric generator (TEG) module consists of between 10 and 100 thermoelectric elements of type n and type p, electrically connected in series and thermally in parallel, and interposed between two ceramic layers, as shown in Figure 1. The p–n pairs are joined by conductive tabs connected to the elements via a low melting point solder (PbSn or BiSn). When a temperature gradient occurs between its two junctions, the TEG converts thermal energy into electrical energy according to the principle of the Seebeck effect. This flat bulk architecture is the most widely used and marketed However, in some applications a flat shape is not practical. This is because of the difficulty in adapting the heat source to the thermoelectric device, which makes it more costly, heavier, and more cumbersome. As a result, other designs are being investigated to overcome these drawbacks, although most of them, like the cylindrical shape [23–25], are still at the laboratory stage. This is the subject of limited studies, unlike thick and thin films and flexible TE devices, which are being developed more effectively [26]. More details on the usefulness of these designs are presented in the following section.

The two ceramic plates serve as a support for the module and as electrical insulation, but their thermal resistance degrades the module's efficiency. From this, some investigations have proposed the concept of a direct contract thermoelectric generation (DCTEG), which is characterized by one of the surfaces of the module being directly exposed to the heat source and the other surface in direct contact with the coolant flow. Several manufacturing technologies for TE modules are reported in the literature. Some examples include foil lithography, the lift-off process, flash evaporation, evaporation thin film, photolithography and etching, screen-printing, sputtering, dispenser printing, the spark plasma sintering technique, direct current (DC) magnetic sputtering and the printing process.

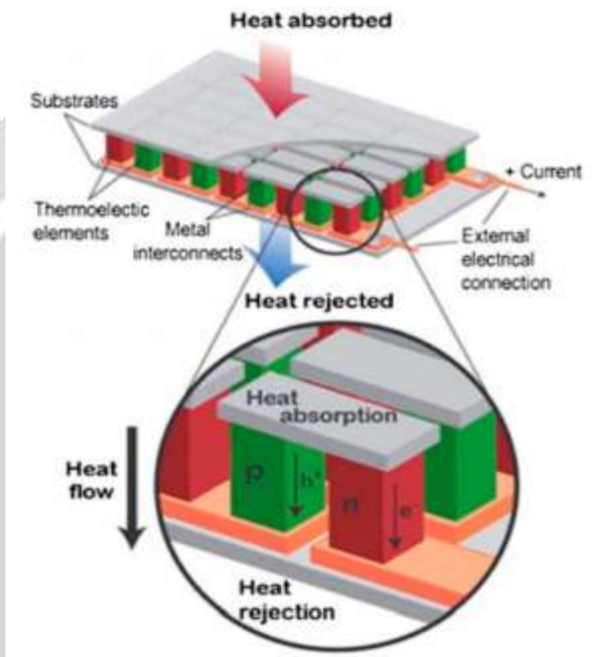

Figure 1: Diagram of a typical thermoelectric device

The critical challenge in the development of TEGs is the degradation of original properties brought on by thermal fatigue, which is in turn caused by thermal expansion and thermal shock. This degradation can be brutal or progressive, and result in a decrease in service life and efficiency. In fact, during the normal operation of TE devices, the shunts are periodically heated and cooled and undergo thermal expansion. The TE materials connected to these shunts can experience different effects of expansion from temperature sources, which cause increased stress at the interface between them. These stresses are generally the main cause of mechanism failure, and consequently the principal reason why TE materials are not sintered and integrated into shunts.

4. THEORY OF THERMOELECTRIC DEVICES

Thermoelectric refers to direct conversion of thermal energy into electricity and vice versa. This chapter presents the thermoelectric effects and the structure of thermoelectric devices. The thermoelectric phenomena, known for over a hundred years, can be employed for heat pumping, temperature sensing and power generation. The latter is the operational mode of interest in this paper; therefore, the main purpose of this chapter is to outline the principles of thermoelectric generators. Understanding the thermoelectric effects is of fundamental importance for the engineering design of any thermoelectric system. This chapter aims at describing the most important effects related to thermoelectrics and the thermoeletric device from a systems point of view. Extensive further reading about the physics, chemistry and microelectronics involved is given in Thermoelectrics Handbook: Macro to Nano. This chapter first covers the definition of the thermoelectric effects; then, the key parameters and design challenges relative to thermoelectric devices are discussed; finally, the steady-state behaviour of thermoelectric devices is analysed.

5. PHYSICAL PHENOMENA OF THERMOELECTRICITY

Four physical phenomena are relevant to the study of thermoelectric devices: the Seebeck effect, the Peltier effect, the Thomson effect and the Joule heating effect. The Kelvin relationships describe an important link between the first three of these effects.

The Seebeck effect

In semiconductors, electrons and holes are considered to be charge carriers when they do not participate in covalent bonds. They can easily be set in motion and the resulting electrical current is measured in terms of the number of electrons moving past a given point in a given time; in the case of the S.I. system, in one second. The measure unity is termed ampere [A] and it equals the movement of 6.25 · 1018 electrons per second. Charge carriers can be set in motion by the flow of heat. Whenever an electrical conductor is placed between two different temperatures, the conductor transfers thermal energy from the warmer side to the colder one, and charge carriers are moved in the same direction. To take advantage of this flux of charge carriers, it is necessary to close the circuit. If a second identical conductor is used, there will be an equal movement of charge carriers in both conductors, which results in no net current flow. By using two dissimilar materials the current in one conductor will not equal that generated in the other, thus resulting in a net continuous current flow; such current is equivalent to the difference of the two thermally-generated currents in the two conductors. The existence of this net current flow indicates that a voltage is created due to the movement of heat, and a direct measurement of this voltage can be taken across the open circuit terminals of the pair. This voltage is referred to as the Seebeck voltage, after the discovery of thermoelectromotive forces by T.J. Seebeck in 1821; however, this thermoelectric phenomenon was initially discovered in 1794 by the Italian physicist Alessandro Volta.

According to this effect, a voltage is produced in a circuit of two dissimilar materials when the two junctions are maintained at different temperatures. The open-circuit thermoelectric potential VOC is obtained from the following equation:

$$V_{OC} = \alpha \Delta T$$

where ΔT [K] is the temperature difference across the two junctions, and α [V/K] is the Seebeck coefficient, which gives the rate of change of VOC [V] with ΔT:

$$\alpha = \frac{\Delta V_{OC}}{\Delta T}$$

α is a ’combined’ coefficient associated with the properties of the materials used and is defined for ΔT → 0. The Seebeck coefficient of the junction between two materials is the difference between the two absolute coefficients and experimental data show that metals’ Seebeck coefficients are very small. On the contrary, however, values in the hundreds of µV/K, negative or positive, are typical for good thermoelectric semiconducting materials.

The Peltier effects

As with the Seebeck effect, another interesting physical effect can be observed due to electrical current flow at the junction of dissimilar materials when the electrons flow across a discontinuity in the energy levels of the conduction bands in the coupled materials.

The Peltier effect was discovered in 1844 by the French physicist J.C.A. Peltier. The Peltier effect states that if a direct current is passed through a circuit of dissimilar materials, one junction will be heated and the other will be cooled. This is the reversed Seebeck effect and it is also polarised in that, if the direction of current flow is reversed, heat absorption and dissipation locations are also reversed. Peltier heating (or cooling) can be interpreted as being due to the change in the average kinetic energy of a charge carrier when it crosses a junction.

The Peltier coefficient, measured for $\Delta T \rightarrow 0$, is labelled π [V] and defined as

$$\pi = \frac{P_P}{I}$$

where PP is the heat-transfer rate from the junction and I is the direct current flowing in the circuit. The Peltier coefficient has the dimensions of voltage and gives the magnitude of the heating or cooling that occurs at a junction of two dissimilar materials.

The Thomson effects

The Thomson effect was discovered in 1854 by the British physicist William Thomson (Lord Kelvin). This effect states that there is reversible absorption or liberation of heat (in excess of the Joule dissipation I 2R) in a homogeneous material simultaneously exposed to a thermal gradient under the passage of an electric current. The heat absorbed by the conductor when the current flows toward the higher temperature is

$$P_T = \tau I\Delta T$$

where τ [V/K] is the Thomson coefficient. Both the Seebeck and Peltier coefficients are defined for junctions between two conductors, while the Thomson coefficient is a property of a single conductor. Thus, the Peltier and Seebeck coefficients can only be determined for pairs of materials whereas the Thomson coefficient is directly measurable for individual materials. The Thomson effect is frequently excluded from the analysis of thermoelectric devices because usually much smaller than the Joule heating [92, 93]. However, its contribution can be significant for large temperature differences [94, 95].

The Kelvin relationships

The Peltier coefficient is related to the Seebeck coefficient by the following relationship:

$$\pi = \alpha Tj$$

where Tj is the temperature at the junction. This result is widely substantiated through experimental evidence and hence the assumption of reversibility appears valid. Eq. 3.5 constitutes a simple way to determine π and allows Eq. 3.3 to be re-written as

$$PP = \alpha ITj$$

The Thomson coefficient is related to the Seebeck coefficient by the following relationship:

$$\tau = T_{AVG}\frac{d\alpha}{dT}$$

where T_{AVG} is the average temperature of the material.

6. ANALYSIS

Thermoelectric generators (TEGs) can provide constant power for flexible electronic platforms. Using the body's warmth, they do not rely on solar power, unlike photovoltaic generators, or on the user's fitness, unlike electromagnetic induction generators. TEGs could be combined with sensors and displays to enable a fully flexible integrated circuit to achieve commercialization viability. However, there are still challenges that are holding back this technology from fully entering the market. These include limited efficiencies at body range temperatures, large-area scaling and mass production compatibility.

The efficiency of thermoelectric materials are measured by a unit less value known as the figure of merit, ZT, defined by Eq. (1), where σ, S, T and κ are the electrical conductivity, Seebeck coefficient, temperature and thermal conductivity, respectively. In order to increase ZT, thermal conductivities have been lowered by harnessing 2D and nano-structured material properties. However, the majority require complex fabrication techniques that are extremely challenging to perform on a large-area, mass production scale. Alternatively, the efficiency can be raised using scalable techniques by increasing the electrical conductivity and Seebeck coefficient, collectively known as the power factor (PF), which are linked to the materials' physical properties and defined by Eq. (2). This can be done by discovering new materials or optimising existing ones through techniques such as alloying or doping, where doping can also be used to tune the semiconductor type.

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

$$PF = \sigma S^2$$

In the commercial world, roll-to-roll (R2R) systems are used to create large areas of high-throughput fexible coatings, and can be used to manufacture fexible electronics. Rolls of fexible materials, referred to as a web,

Table 1. Atomic concentration of elements and thermoelectric properties of sputtered Bi2Te3, SnTe and GeTe thin films. Error bars represent uncertainty of measurement for EDX, Seebeck coeffcient and resistivity. Te power factor uncertainty is calculated by error propagation

	Film Compositional Results				Film Electrical Results			
Target Material	Bi %	Sn %	Ge %	Te %	Seebeck Coefficient (μV/K)	E Resistivity (mΩ-cm)	Power Factor ($\mu W/cm\text{-}K^2$)	Semi-conductor type
Bi_2Te_3	43 ± 2	—	—	57 ± 2	−50.6 ± 1.0	0.50 ± 0.05	5.1 ± 0.6	n
SnTe	—	53 ± 2	—	47 ± 2	26.0 ± 1.0	0.20 ± 0.05	3.4 ± 0.9	p
GeTe	—	—	54 ± 2	46 ± 2	47.9 ± 1.0	0.27 ± 0.05	8.5 ± 1.6	p

are gradually unwound, coated and rewound, with the coated processes potentially consisting of multiple steps/ layers. Web speeds may be, for example, up to hundreds of metres per minute, allowing a high-throughput manufacturing process. Inkjet printing is a well-known technique that is scalable and compatible with R2R but has many limiting factors; the ink must maintain low surface tension, low viscosity, and have the nanomaterial well dispersed. This creates challenges with synthesizing inks, limiting material choices, and can lead to non-uniform films with poor density and electrical conductivity, limiting power factors. Sputtering, a type of PVD, is an alternative, scalable and R2R compatible technique that offers high quality films from a huge array of materials with the ability to tightly control material properties, enabling PFs of materials to be tuned.

To date, published research reporting on sputtered flexible TEGs is limited, often showing only small-scale one of prototypes or requires complex photolithography or post-processing steps, making it less attractive for use in an R2R environment. Alternatively, papers are focused on the material itself and do not take into account the up-scaling of flexible generators.

In this work we investigate the suitability and potential of using PVD techniques with R2R for high-throughput manufacturing of flexible TEGs. We demonstrate sputtering as a viable technique for producing a flexible TEG, first by screening materials (section i) and then by selecting two materials to produce a flexible TEG prototype (section ii). To investigate PVD/R2R compatibility for thermoelectric applications, we investigate thermoelectric properties of R2R sputtered Bi2Te3 for the first time (section iii). Further to this, we highlight that higher PFs can in fact be tuned by reducing deposition times, demonstrating PVD/R2R's potential as a high-speed, low-cost commercial system for flexible electronics. Identifying faster deposition times as beneficial, we use a novel high-deposition rate PVD technique, virtual cathode deposition (VCD), to make a TEG prototype for the first time (section iv). VCD offers deposition speeds of more than 1μm/min whilst maintaining substrate temperatures to below 60 °C, making it fully compatible with a large array of low temperature flexible substrates and has potential to be the future of high-throughput flexible electronic manufacturing via R2R.

TEG cell model

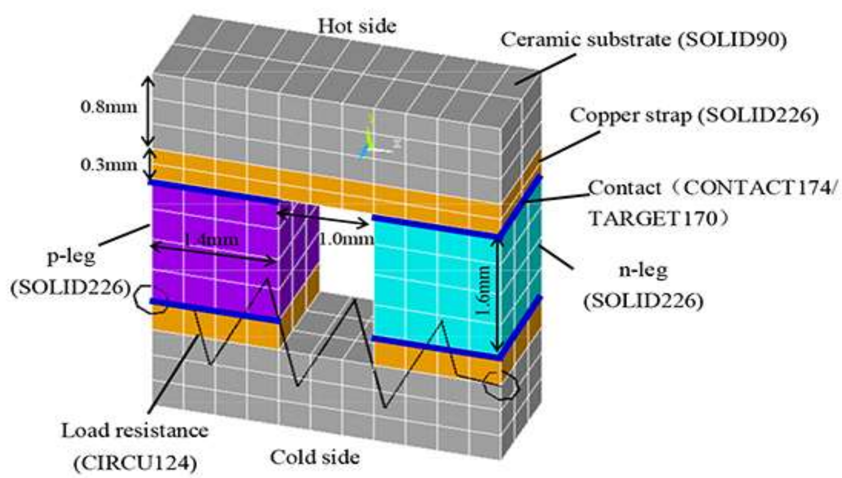

Figure 2: The geometry of TEG cell in ANSYS and its mesh.

By software simulation, TEG performance can be achieved both in thermal and in electrical aspects. But it is not direct to cognize and understand the influence of thermoelectric effects, when compared with the above physical model. In this part, TEG cell model is set up by ANSYS, and geometry and meshing methods are illustrated in Figure 2. Thickness and cross-sectional area of thermoelements are 1.6 mm and 1.4 mm × 1.4 mm, respectively. Other geometry parameters are shown in Figure 2. Thermoelectric module consists mainly of p-n thermoelements, current-conducting copper straps and ceramic substrates for heat conducting and electric insulation. Thermoelements and copper strap are meshed by element SOLID226 in ANSYS. This type of element contains 20 nodes with voltage and temperature as the degrees of freedom. It can simulate 3D thermal-electrical coupling field. Element SOLID90 is used to mesh ceramic substrate. It has 20 nodes with temperature as the degree of freedom. Load resistance is simulated by element CIRCU124. Contact properties of the leg-strap junction are implemented with element pairs CONTACT174/TARGET170. Detailed finite element formulations in ANSYS are introduce, and the range of contact thermal conductivity and electrical resistivity is explicated.

7. CONCLUSION

The built one-dimensional model, which is validated by test results, can calculate TEG output power and energy efficiency accurately. By simplifying this model, it is convenient to analyze influences of different thermal and electrical parameters on TEG performance. At last, ANSYS simulation considering thermal contact and radiation effects for TEGs is introduced briefly, and basic APDL codes are shared. It can be seen that although much effort has been made to develop direct solar thermal power generation technologies, the conversion potential and practical applications are still not widely used. In order to make full use of its advantages and develop practical civil devices, more effort should be devoted to material research, structure optimization, and practical application development.

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