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A REVIEW ON THE POTENTIAL OF SILICON NANOWIRES (SINWS) IN THERMOELECTRIC ENERGY HARVESTERS

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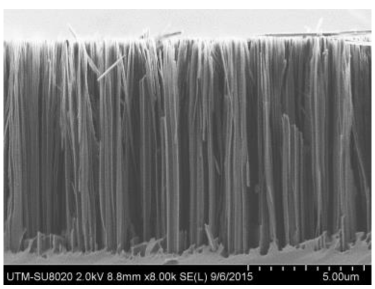
Graphical abstract



Abstract

There are various types of micro-scale energy harvesters (EH) that have been reported by many researchers around the world such as photovoltaic cells, piezoelectric transducers, electromagnetic transducers, thermoelectric and others. Energy harvester that harvest ambient energy which exists naturally or produced by mankind or machines, are able to be an alternative source for low-power devices such as mobile phone, laptop, health implant and many more. Thermoelectric is an energy harvester that converts heat waste from any sources such as vehicle engines, laptops or human body into electricity. Numerous kind of thermoelectric materials including metals and semiconductors have been investigated by researchers that produce different performances and efficiencies. Recently, researchers are looking forward to nanostructured semiconductors such as nanoribbons, nanotubes, nanowires and quantum dots as a potential to increase the figure of merit (ZT) and efficiency of thermoelectric EH. This paper reviews on silicon as the second most abundant element on earth and commonly used in electronic components is possible to be used as thermoelectric material. Silicon in bulk has high thermal conductivity which is less desirable for thermoelectric application. However, many studies regarding nanostructured silicon such as silicon nanowires have been carried out with promising results in reducing thermal conductivity.

Keywords: Energy harvester, thermoelectric, semiconductors, silicon nanowires

1.0 INTRODUCTION

Energy harvesting or sometimes called energy scavenging is a process that converts ambient energy into electricity for small low-powered wireless electronic devices such as laptop, mobile phone, wristwatch, wireless sensor networks and healthcare implant. Methods of harvesting ambient energy such as light, temperature vibration or movement have been explored for many years by using various energy conversion materials or structures. This technology has attracted the attention of many researchers nowadays because of the latest advancement in low power electronic devices along with more effective energy capturing and storage management, giving the technology a high potential for a wide number of applications. It has been predicted that the total market for energy harvesting devices will increases to $2.6 billion in the next 10 years [1]. The application of energy harvester (EH) as a substitute to a conventional batteries contributes several benefits such as less maintenance cost, therefore less need to replace batteries which can be inconvenient and time consuming task. It is also an environmental friendly technology that reduces the risk of chemical pollution from the disposal of batteries which contain dangerous chemicals include acid, lead, lithium and mercury which are harmful to the environment and human health.

In this paper, Section 2 discusses on common types of micro-scale EHs such as photovoltaic cells, piezoelectric and radio frequency (RF) wave harvester while Section 3 will focus more on thermoelectric EH. The material selection criteria is important for thermoelectric EH and is described in Section 4, whereas some of the prototype devices invented by other researchers will be discussed in Section 5. The potential of silicon nanowires which can be used in thermoelectric application will be explained in the last section of this paper.

2.0 TYPES OF MICRO-ENERGY HARVESTER

There are several types of EH that are commonly used for small autonomous devices for example; photovoltaic cells that harvest solar energy, electromagnetic and piezoelectric EH that harvest vibration and motion, radio-frequency (RF) EH that harvests RF radiation, and thermoelectric EH that harvests heat. Photovoltaic EH which dominates most of the market for consumer application, harvests solar energy and then is stored in a charge-integrating capacitor during period of darkness [2]. Radiation from the sun on the Earth's surface able to provide power density approximately about 100 mW/cm^3. Photovoltaic cells offer the best solution for outdoor application that needs to function during the day with power density roughly around 14 000 µW/cm^3. On the contrary, indoor lighting only able to provide power density as low as 10-20 µW/cm^3 which is not a good choice for indoor application [3, 4]. Table 1 shows the comparison on power density measured in different condition and environment.

Table 1 Power density measurement in different conditions [4]

Condition	Outside (noon)	4 inch from 60 W bulb	15 inch from 60 W bulb	Indoor lighting
Power Density (µW/cm^3)	14 000	5 000	567	6.5

Motion or vibration energy which is also exists in nature can be harvested through a converter such as piezoelectric, electromagnetic (inductive) and electrostatic (capacitive) transducer [3, 5-9]. Among these converters, piezoelectric converter is the most attractive choice because of no requirement for external voltage source which is easy to integrate with micro-electromechanical system (MEMS) [5, 10-13] and the piezoelectric coupling is minimized [14]. Despite of its ability to harvest vibration in many environments, however, the frequency spectrums are complex and it depend on the nature of the machine and surroundings [15]. While it is true that piezoelectric is capable to be integrated into MEMS, there is an issue on compatibility of piezoelectric with standard CMOS processes, making it less potential for integration with microelectronic compared to electrostatic converter [16].

Another source of energy harvesting is through radio-frequency (RF) waves. This energy is currently transmitted from billions of radio transmitter around the globe. By harvesting RF waves from ambient sources, this will open up the possibilities of wireless charging of low-powered devices such as mobile phones, wireless sensor networks and more to be explored in future. Passive devices such as electronic ID tags and smart cards are powered by nearby sources that transmit RF energy. These devices receive the energy through RF harvesting receiver and convert it into DC to power its electronic systems [17]. In spite of its potential for wire-free charging technology, this method is impractical for a large network of wireless node especially in a closed space. A large amount of radiation is required to power the nodes and the entire space will be flooded with the radiation which probably lead to a health risk [16].

Thermoelectric EH is another method of harvesting heat flow or temperature gradient that present in nature or human-made settings as an alternative approach to deal with global issue on reducing the dependence on fuels. This EH will be discussed more in Section 3.

3.0 THERMOELECTRIC ENERGY HARVESTER

It is predicted that the market of thermoelectric EH will increase over US$ 950 million in the next 10 years [18]. Figure 1 shows the market forecast of thermoelectric EH for some application sectors such as wireless sensor networks (WSN), militaries, space exploration, healthcare and electronics for three years. The graph suggests that there will be a great increase in demand of thermoelectric application mainly in WSN and electronic consumer. Apart from that, the America's space agency, NASA uses thermoelectric EH to power their Mars rovers besides solar cells whenever the source of light in space is limited [1]. Many well-known car companies are currently developing a waste heat recovery systems by converting heat waste from engines and exhaust into electricity to power vehicle's electrical systems [1, 18].

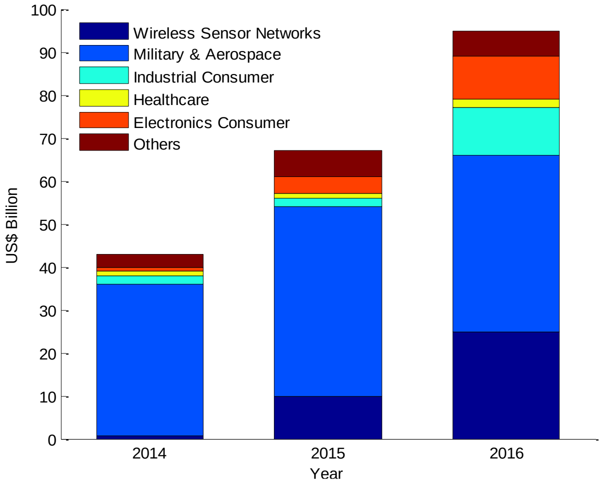


Figure 1 Market Forecast and Applications for Thermoelectric Energy Harvesters [18]

3.1 Working Principle of Thermoelectric EH.

A physicist known as Thomas Johann Seebeck who in 1821 noticed that when there are two dissimilar metals connected and exposed to a temperature difference i.e. electrically in series and thermally in parallel, the needle of a magnet is deflected [19]. The thermoelectric effect is a phenomenon that occurs either a temperature difference creates voltage (also known as Seebeck effect) or an electrical voltage applied creates a temperature difference (known as Peltier effect).

Figure 2 shows the theory of electron mobility in a thermoelectric device. Considering a metal rod such as copper is heated at one side and cooled at the other side, this creates a temperature difference at two ends. The electrons at the hot side gains more energy, accelerate faster than electrons at the cold side. The electrons at the hot side diffuse towards the cold end, leaving behind the positive metal ions at the hot end. The net diffusion of electrons stops when electric field is built up between positive ions and electrons. Eventually, this situation develops a potential difference between two ends or also known as Seebeck voltage.

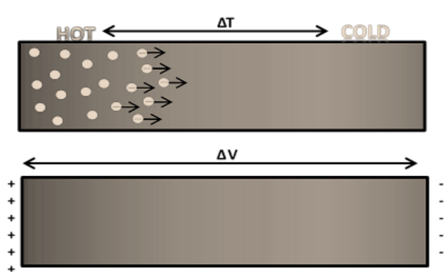


Figure 2 Electron mobility of thermoelectric in metals [20]

The voltage difference across the metal rod as a result of a temperature difference is known as Seebeck effect [20]. Seebeck coefficient is used to measure the Seebeck effect is given by;

$$S = \frac{\Delta V}{\Delta T} \tag{1}$$

where
S = Seebeck coefficient
ΔV = Potential difference, [V]
ΔT = Temperature difference, [K]

However, this single piece of metal rod only produce a very small voltage. By connecting these metal rods in series may increase a little voltage but the wire that connects them also will produce an opposite voltage which may reduces Seebeck voltage. To solve the problem, we may use any material that has one type or majority of conducting particle such as semiconductor material. As shown in Figure 3, when heat is applied at one end while the other end is kept cold, the majority carriers (electrons) at the hot side of n-type material diffuse to the cold side i.e. the same concept as in Figure 2. While in p-type material, the positive carriers (holes) at the hot side will diffuse to the cold side creating a negative end at the hot side.

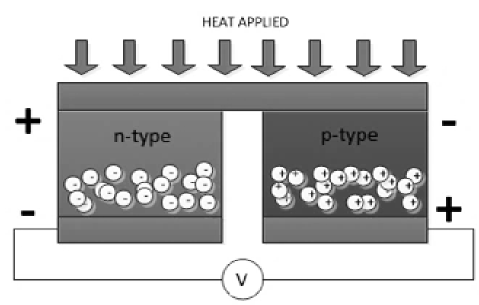


Figure 3 Semiconductor Material

4.0 THERMOELECTRIC MATERIAL

The thermoelectric material selection is very important to provide a high efficiency thermoeletric device. A good material should be good in conducting electricity in order to minimize Joule heating, poor thermal conductivity to preserve the heat at the junction and maximum Seebeck coefficient to produce required voltage. It is also stated that in order to achieve this simultaneous optimization, a trade-off will exist due to both electrons and electric current present in thermoelectric materials. The electrons and current also carry undesirable heat which will reduce the Seebeck effect as the electrical conductivity increases. All these properties can be linked together in one equation called the dimensionless figure of merit, ZT which is given by [21]:

$$ZT = \frac{\sigma S^2}{\kappa} T = \frac{S^2}{\rho\kappa} T \quad (2)$$

where
S = Seebeck coefficient
σ = Electrical conductivity
ρ = Electrical resistivity
κ = Thermal conductivity
T = Absolute temperature

The advantage of ZT is that it can be measured on a single leg without constructing the whole device and the bigger value of ZT means better thermoelectric material but when the value reaches towards infinity, the thermoelectric device asymptotically approaches the Carnot efficiency limit [22]. Equation (2) is only suitable for single material but not for thermoelectric device or module that consists of an array of thermocouples (with two types of material). The ZT for a thermoelectric device or module especially for semiconductor materials is normally written as in (3) where all parameters are comprised with both types of materials (i.e. p-type and n-type material) excluding temperature.

$$ZT = \frac{(S_p - S_n)^2}{(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}} T \quad (3)$$

Figure 4 shows the graph of ZT as a function of temperature in Kelvin of current state-of-the-art bulk thermoelectric material. Numerous bulk materials are being studied by researchers to give some promising results as shown in Figure 4. A few ways can be used to increase the value of ZT in order to maximize the efficiency of thermoelectric device such as by reducing κ or increasing either σ or S.

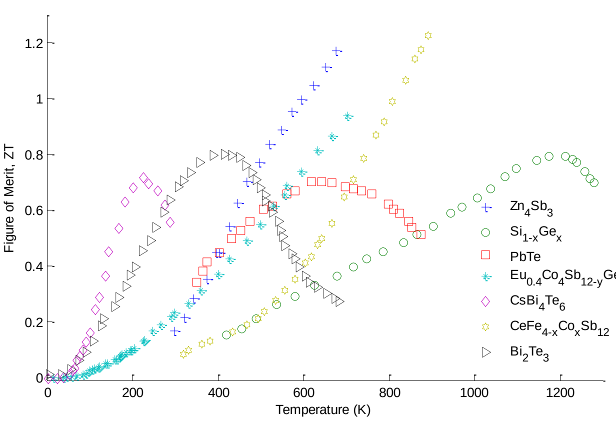


Figure 4 Current Bulk Thermoelectric Materials [23]

However, there is a big challenge to achieve maximum ZT because changing one parameter in ZT usually affects others [24]. This is because of the electrical conductivity, σ is bounded with κ according to the Wiedemann-Franz law;

$$LT = \frac{\kappa}{\sigma} \quad (4)$$

where
L = Lorentz constant
T = Temperature
κ = Thermal conductivity
σ = Electrical conductivity

Metal has a low Seebeck coefficient with only a few μV/K while semiconductors typically have high Seebeck coefficient around 100 μV/K. The electrical conductivity of metal is large in the order of 10^6 $(\Omega cm)^{-1}$ compared to semiconductor which is usually lies between 10^{-4} and 10^4 $(\Omega cm)^{-1}$. The higher value of ZT also can be obtained with some semiconductors than other metals [25]. There are several types of metal thermocouples such as copper- nickel, chromel-alumel (Type K), iron-constantan (Type J), chromel-constantan (Type E), nicrosil-nisil (Type N) and others. On the other hand, bismuth telluride (Bi_2Te_3) and Antimony Telluride (Sb_2Te_3) are the most commonly used semiconductor in thermoelectric sectors.

5.0 THERMOELECTRIC DEVICES

A number of studies on thermoelectric with various kind of materials were done by many researchers. Different material produces different performance in terms of output voltage, or power. A model of a vertical micro-thermoelectric with thermoleg length of 150 μm was designed using metal thermocouple pair i.e. copper-nickel. The thermoleg was insulated and fabricated in a 190 μm thick flexible polymer as shown in Figure 5. This model is able to generate a power of 12.0 ± 1.1 nW/cm² for a temperature gradient of 0.12 K at the model interface and equivalent to the thermoelectric efficiency factor of 0.83 μWK^{-2}cm^{-2}. It is also concluded that the output power per unit area are not dependent to the number of thermolegs and its cross-sectional area. However, the insulation area around thermolegs should be minimized and the cross-sectional area of thermolegs must be increased in order to assist in achieving low contact resistance which increases the output power.

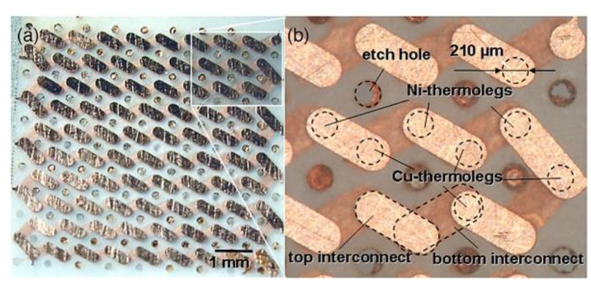


Figure 5 Microscopic image of thermoelectric device. (a) 90 Cu-Ni thermocouples fabricated on polymer. (b) Enlarge image of the thermocouples [26]. Copyright 2006, Elsevier

A high flexibility thermoelectric module that consists of hundred pairs of antimony-bismuth (Sb-Bi) thermocouples as shown in Figure 6 was developed by using a simple low-cost process [27]. The micro materials Sb and Bi are formed by galvanostatic method from acid electrolytes. This module is able to generate an output voltage of 250 mV at a differential temperature of 30 K with Seebeck coefficient of 8.4 mV/K. The module designed is thin and flexible, giving a capability to be shaped to suit various application conditions. Besides, another thermoelectric device that uses both n-type and p-type polysilicon are designed fabricated by a CMOS-compatible process. The device with the size of 1cm x 1cm and 5 K temperature difference is maintained across the cold and hot sides are able to produce the open-circuit voltage of 16.7 V and maximum output power of 1.3 μW under a matched resistance [28].

Furthermore, a thermoelectric device is proposed by using thin films of n-type Bi_2Te_3 and p-type Sb_2Te_3 that uses Seebeck effect which converts heat into electricity [29]. The device is fabricated by using microsystem technique and suitable for electronics integration. The experimental results of this device gives an absolute Seebeck coefficient in the range of 150-250 μV/K, lower than in [27]. The maximum output power of 20 μW is obtained when the thermoleg length of 4 mm for 1 cm^2 Bi_2Te_3 – Sb_2Te_3 thermoelectric device. Besides that, the ZT of Bi_2Te_3 and Sb_2Te_3 films obtained at room temperature are 0.84 and 0.5 respectively. It is also concluded that based on the measurements, the films show thermoelectric properties that are as good as the other studies for the same material in bulk form [29].

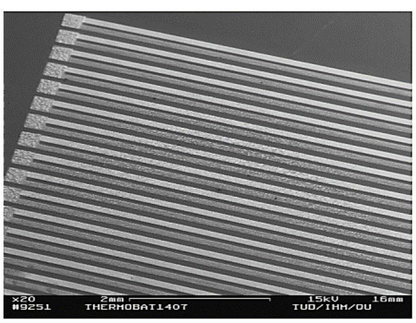


Figure 6 A part of thermoelectric module with Sb-Bi pairs [27]. Copyright 2001, IOP Publishing

6.0 SILICON NANOWIRES (SiNWs) IN THERMOELECTRIC ENERGY HARVESTERS

Silicon as the most abundant material and widely used semiconductor has a large industrial infrastructure for low-cost and high-yielding process [30], easy to integrate with current microelectronic devices [31] and environmental friendly. Bulk Silicon has a relatively high thermal conductivity around ~150 $Wm^{-1}K^{-1}$ at room temperature [32] contributing ZT of 0.01 at 300K. On the other hand, semiconductor nanowires as shown in Figure 7 can be formed to enhance thermoelectric efficiency where the temperature of maximum efficiency may be altered by varying the doping and the nanowire size [24].

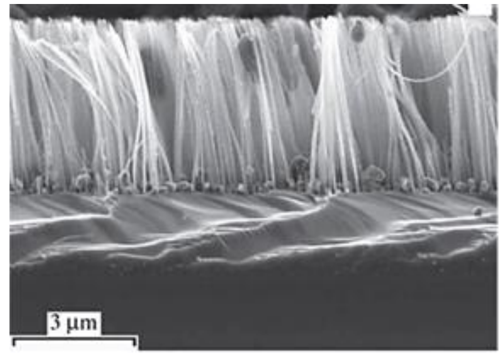


Figure 7 SEM image of Silicon Nanowires created from metal-assisted chemical etching (MACE) process [33]. Copyright 2010, Wiley

A study has shown that SiNWs specifically with diameter of 50 nm instead of using bulk silicon shows hundredfold reduction in thermal conductivity, κ with same Seebeck coefficient and electrical conductivity as in bulk, thus increases ZT to 0.6 at room temperature as shown in Figure 8 [30]. In nanostructured thermoelectric material such as SiNWs, the spectral distribution of phonons which is responsible for thermal conductivity in material at room temperature is quite extensive. This is due to a large rate of phonon-phonon Umklapp scattering scales as phonon frequency, ω^2 which have a long mean free path and contribute importantly to κ at room temperature. Umklapp scattering happens when the sum of the wave vectors results from the interaction of three or more electron or phonon waves is not equal to zero. It is also expected that the κ of Si decreases by rational unification of phonon scattering elements at several length scales and report that roughened SiNWs can reduces thermal conductivity to ~1.6 $Wm^{-1}K^{-1}$ without altering the power factor such that ZT approximately 1 at room temperature. Furthermore, the roughness surface of SiNWs plays a main role by altering phonon transmission through these confined structures and it is possible to increase ZT with optimized doping, reduced diameter and roughness control [30].

An electro-thermal simulator was developed in [34] to solve the electron and phonon Boltzmann transport equations (BTE) and to calculate ZT in SiNWs. It is found that ZT in SiNWs was 50-70 times higher than in bulk Silicon due to massive reduction in thermal conductivity with increasing spatial confinement. Researchers also concluded that the electron and phonons that control thermal conductivity will entirely determine the Seebeck coefficient while decreasing nanowire cross section will reduce both electrical and thermal conductivity. However, the reduction of thermal conductivity in SiNWs is few times greater than the decrease in electrical conductivity if compared to the bulk value. The simulation work has shown that the ZT in SiNWs increases to a maximum value ZT of 0.65 as the cross sections of 8 x 8 nm^2 reduces to 4 x 4 nm^2 at 300K and then the ZT drops drastically for cross section smaller than 4 x 4 nm^2 due to strong reduction in electrical conductivity.

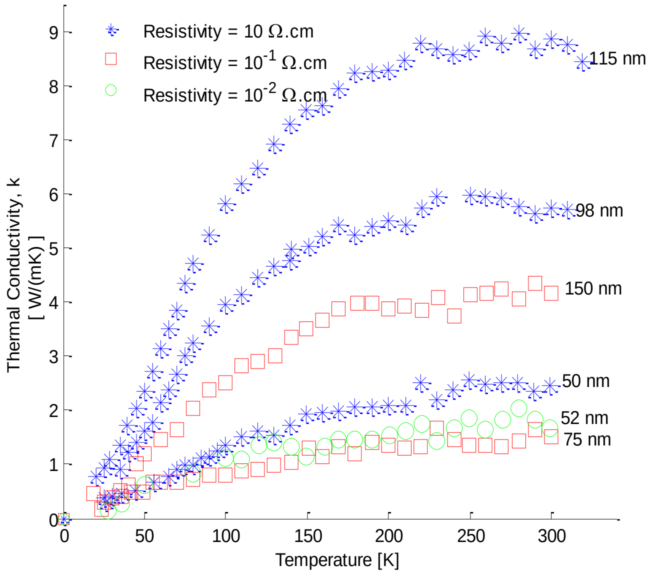


Figure 8 Thermal conductivity versus Temperature of a SiNWs produced on different resistivity of Silicon wafer which associates with the doping concentration [30]

Besides that, researchers in [35] studied the vertical SiNWs fabricated with top-down process using Inductive-Coupled-Plasma (ICP) cryogenic dry etching method with diameters down to 180 nm and selected height between 1 to 10 micrometer. The electrical resistivity of single SiNW with various diameters were measured using scanning electron microscope (SEM) equipped with nano-manipulators while a Wollaston-wire-based 3ω technique was used to measure thermal conductivity. The researchers came out with promising results where n-type SiNW with diameter of 230 nm contribute a large Seebeck coefficient (350 ± 20 μV/K) and reduced thermal conductivity (9 ± 2 $Wm^{-1}K^{-1}$) with respect to the bulk Si.

7.0 CONCLUSION

Based on the studies of thermal conductivity in SiNWs, the reduction of thermal conductivity opens up the potential for SiNWs to be used in thermoelectric energy harvesting. Reduction in thermal conductivity helps to improve the important parameter for thermoelectric i.e. the dimensionless figure of merit, ZT and thus improve the efficiency of the device to harvest ambient heat.

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