FLEXIBLE THERMOELECTRIC POWER GENERATORS BASED ON ELECTROCHEMICAL DEPOSITION PROCESS OF Bi_2Te_3 AND Sb_2Te_3

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ABSTRACT

The harvest of thermal energy using thermoelectric (TE) effect is one of the potential methods for wearable devices. This paper demonstrates a new approach of electrochemical deposition to fabricate flexible thermoelectric generators (FTEGs). Two proposed structures have been developed to compare the performance of the devices. One is the π-type flexible devices with thick thermoelectric cells in micro scale and the other is a new lateral Y-type structure for FTEGs. For the first time, the electrochemical deposition of thermoelectric materials Bi_2Te_3 and Sb_2Te_3 is used to integrate thermoelectric materials inside the flexible structures. The Seebeck coefficients of Bi_2Te_3 and Sb_2Te_3 are -150±20 and 170±20 μV/K, respectively. Additionally, the electrical resistivity of Bi_2Te_3 shows 15±5 μΩm while that of Sb_2Te_3 is 25±5 μΩm. The thicknesses of each thermocouple (TCs) are approximately 100 μm and 200 μm for Y-type and π-type, respectively. With the temperature difference approximately 22°C between human body (around 37°C) and environment ambience (15°C), the lateral Y-type and vertical π-type devices generate maximum powers approximately 3 and 4 $\mu W/cm^2$, respectively.

INTRODUCTION

Body area network (BAN) is a promising technology for ubiquitous applications in residential and medical fields. The widespread implementation of BAN expects self-supplied power sources that are able to provide power for its entire lifespan. Therefore, devices that can scavenge energy from heat waste, are being researched. In which, thermoelectric power generators (TEGs) is one of energy scavengers to convert low-grade heat waste into electrical energy using Seebeck effect. Many efforts have been made on this field [1-8]. In order to enhance the performance of the FTEGs, many obstacles need to be solved. First challenge comes from material issues. Among thermoelectric materials, N-type of Bi_2Te_3 and P-Type of Sb_2Te_3 always keep the attraction due to their highest performances for applications near room temperature [1, 2]. In a case of vertical π-type solid thermoelectric power generators (STEGs), power generators with thicker thermocouples (TCs) cells would theoretically provide better output power for energy harvester. However, the synthesis of thick films of Bi_2Te_3 and Sb_2Te_3 in micro devices is a big challenge so far [3]. The second challenge is the fabrication technique. There are various fabrication means to integrate thermoelectric materials into solid generators, such as, dicing from bulk material [4], and spark-plasma sintering from nano-powders [5], etc. However, these fabrication methods cannot apply to batch-fabrication for FTEGs. In previous works, thin films of Bi_2Te_3 and Sb_2Te_3 are usually deposited on a flexible substrate by co-evaporation and sputtering methods [6, 7]. For these researches, not only the disadvantage of high internal electrical resistance, but also the performance as an energy harvester is low due to the large internal resistance of thermoelectric thin films. The other backward is that in such structures constructed on sustaining substrates, thermal energy is lost through these substrates. That is reason why all best FTPGs to date are based on a print-screening method which shows the possibility to synthesize thick thermoelectric films [8]. However, this method has the disadvantage of low integration density of the TCs cells. The third obstacle is the structure of the device. It is necessary to remove top and bottom sustaining solid substrates for making self-supported flexible structures for FTEGs. In this research, we have developed the fabrication process of FTEGs with Y-type and π-type structures and evaluated their power generation performances. All device's structures are based on electrochemical deposition process of Bi_2Te_3 and Sb_2Te_3 and a sacrificial etching technique of a silicon substrate.

DEVICE STRUCTURE AND WORKING PRINCIPLE

Y type structure

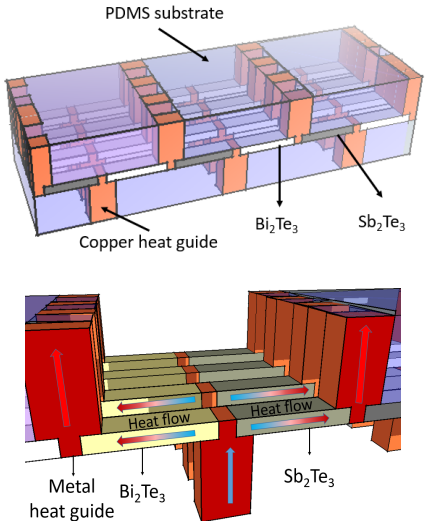


Figure 1. Schematic of lateral Y-type FTEGs

The detailed structure of the proposed device is sketched in Fig. 1. Basically, it consists of N type-bismuth telluride and P type-antimony telluride thermoelectric elements, which are serially connected in a flexible support. Heat guide columns are connected to the junctions of the thermoelectric elements. All thermal heat guides are designed to lead the heat flux vertically from the bottom to top sides of the device.

PDMS (Polydimethylsiloxane) is used as a base material for the flexible support because of its good flexibility and low thermal conductivity (0.2 W/mK [8]). Metallic barrier contacts are employed to reduce the internal electrical resistance. Herein, the multilayers of the metallic contact of Ti-TiN-Au-Cu are formed between TCs cells and heat guides. This device structure with TCs embedded by a thick polymer layer with low thermal conductivity can reduce the heat loss along vertical direction. Hence, the temperature difference along lateral direction is generated, and more thermal energy will be scavenged than that of conventional vertical π-type structure if the device thickness is thin.

π-type structure

In the case of previous TEGs structures, if a thermal resistance exists in the heat guide, the temperature gradient is generated along this region (Fig. 2(a)) [1-7]. Therefore, the harvested temperature is much smaller than the actual temperature difference of heat sources because a large heat loss occurs through these sustaining substrates [8]. With proposed structure (Fig. 2(b)), the sustaining substrate is eliminated, therefore, the heat loss is significantly reduced and more thermal energy can be harvested. Instead, a self-endurance structure with PDMS has been used. On the other hand, the electrochemically deposited thermoelectric materials are also employed for possibility of synthesizing TCs with thicknesses up to approximately few hundreds micrometers.

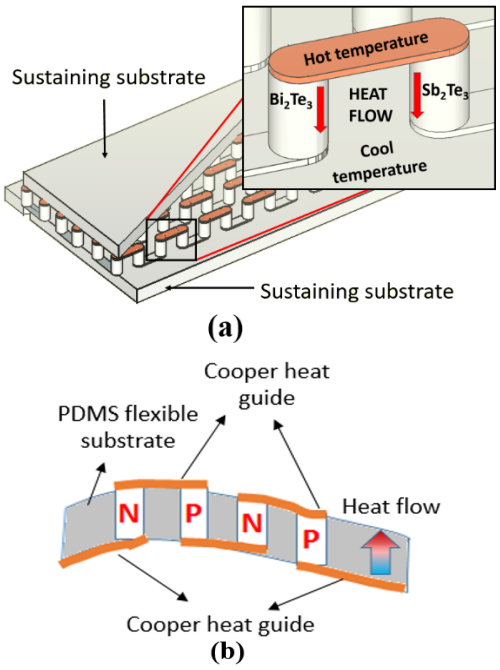


Figure 2. (a) Structure of conventional vertical -type FTEGs. (b) Self-endurance vertical -type FTEGs.

THERMOELECTRIC MATERIALS SYNTHESES

Both N-type bismuth telluride (Bi_2Te_3) and P-type antimony telluride (Sb_2Te_3) are synthesized by electrochemical deposition. The details of the deposition method are described in our previous paper [9]. Highly oriented Bi_2Te_3 and Sb_2Te_3 thick films are successfully synthesized with high Seebeck coefficients and low electrical resistivities. The material properties are summarized in Table. 1.

Table 1. Thermoelectric properties of Sb_2Te_3 and Bi_2Te_3.

	Thermocouples cells	
	Sb_2Te_3	Bi_2Te_3
Seebeck coefficient (μV/K)	170	-150
Electrical resistivity (μΩm)	25	15
Power Factor (W/mK^2)	$11.2x10^{-4}$	$15x10^{-4}$

DEVICE FABRICATION

Y-type structure

The fabrication process is described in Fig. 3. It begins from a 300 μm-thick silicon substrate coated with 500 nm-thick SiO_2 by plasma enhanced chemical vapor deposition using TEOS (TetraEthOxySilane Si $(OC_2H_5)_4$). To prepare the seed layer for the electrochemical deposition of thermoelectric materials (Bi_2Te_3 and Sb_2Te_3), a 10 nm-thick Cr film as an adhesion layer is formed by sputtering, and then a 150 nm-thick Au film is formed by sputtering both at room temperature (Fig 3. (a)). On this seed layer, a photoresist with 100 μm thickness is coated and patterned by photolithography. The wafer is exposed to O_2-plasma with an RF power of 130 W for 5 min for the pretreatment process. Then, N type-bismuth telluride followed by P type-antimony telluride films with thicknesses of 100 μm are formed by the electrochemical deposition method (Fig. 3 (b)). Samples are then annealed at 250°C to increase the Seebeck coefficient and electrical conductivity. Subsequently, barrier metallic contacts which consist of Ti-TiN-Au-Cu multilayers are deposited by sputtering via a stencil mask at room temperature (Fig. 3 (c)). Copper heat guide columns are then formed on the barrier metallic contacts by electroplating. The thickness of the copper layer is 300 μm. This copper layer plays the role of not only guiding the heat flux, but also interconnection between TCs cells (Fig. 3 (d)). The front side of the device is completely filled by PDMS. PDMS is chosen due to its excellent flexibility and low thermal conductivity in comparison with copper (0.2W/mK versus 385W/mK). The back side of the wafer is patterned and etched by deep RIE to create a mold for thermal heat guides (Fig. 3 (e)). The thermal conductive glue with a high thermal conductivity of 35 W/mK (EPO-TEK EK1000) is refilled into the created mold by a screen printing method (Fig. 3 (f)). The rest of the backside wafer consists of Si-SiO_2-Cr-Au, respectively, is removed by plasma etching and ion beam milling processes again (Fig. 3 (g)). At the last process, PDMS is poured into

the backside and the fabrication of the FTEGs is completed (Fig. 3 (h)), as shown in Fig. 4.

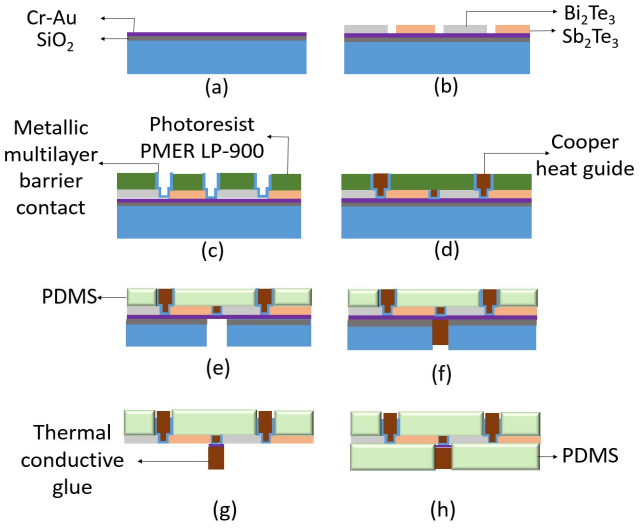
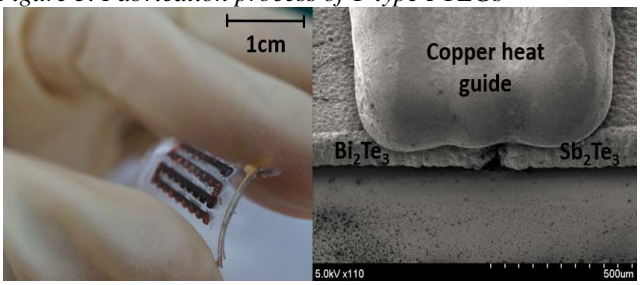


Figure 3. Fabrication process of Y-type FTEGs



(a) **(b)**

Figure 4. Fabricated device of Y-type FTEGs. (a) Titled view. (b) SEM-cross section view

π-type structure

The sacrificed silicon wafer with multilayers of SiO_2-Cr-Au is prepared as same as the fabrication process of Y- type structure (Fig 5. (a)). Continuously, a 200 nm-thick film of copper is deposited by sputtering method for electroplating of thick copper interconnection electrodes (~100 µm in thickness) in the next step (Fig 5. (b)). The 150 nm-thick film of Au is covered upon the wafer surface. This Au thin film works as a protective film during electrochemical deposition of thermoelectric materials (Fig 5. (c)). A pretreatment process using O_2 plasma with an RF power of 130 W for 5 min is also used before electrochemical deposition process. N type-bismuth telluride together with P type-antimony telluride films with thicknesses of 200 µm are grown and then annealed at 250°C (Fig 5. (d)). The sustaining substrate with PDMS is then filled in the front side of the device by spinning coating process at speed of 1500 rpm for 20 seconds (Fig 5. (e)). Top electrodes with multi-metallic contacts, which consist of Ti-TiN-Au-Cu multilayers, are deposited by sputtering via a stencil mask at room temperature (Fig 5. (f)). Eventually, the sacrificed substrate of Si-SiO_2-Cr-Au is removed by plasma etching and ion beam milling processes (Fig 5. (g)). The completed device is shown in Fig. 6.

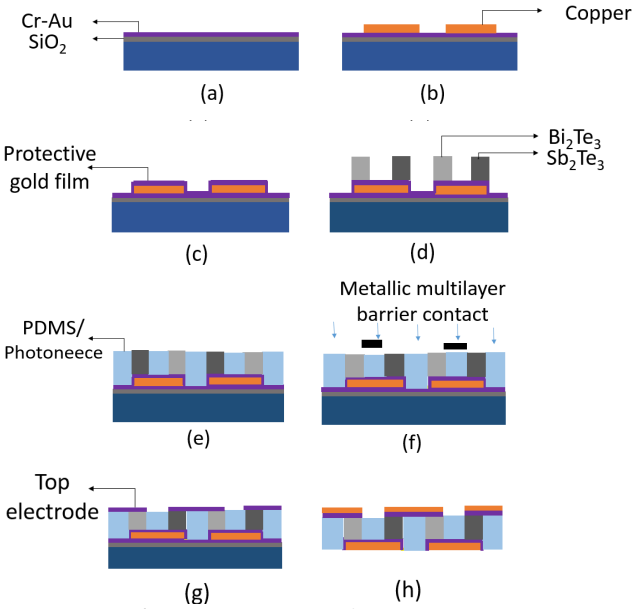
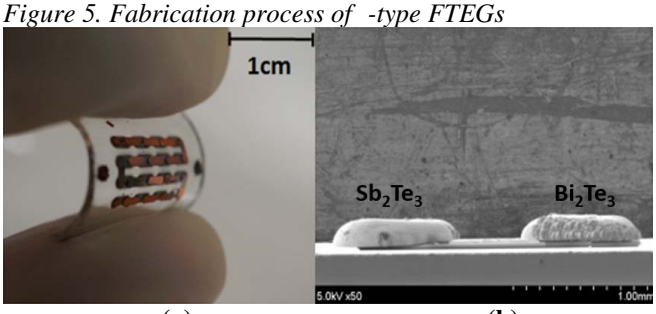


Figure 5. Fabrication process of -type FTEGs



(a) **(b)**

Figure 6. Fabricated device of -type FTEGs. (a) Titled view. (b) SEM-cross section view

DEVICE EVALUATION

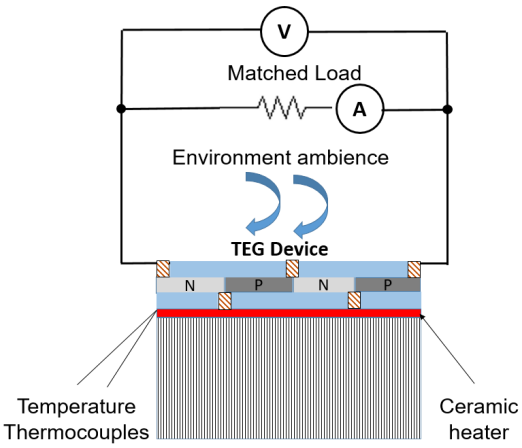


Figure 7. Experimental setup for evaluation of the thermoelectric devices.

The experiment setup for the evaluation of the device is shown in Fig. 7. The FTEG is mounted on a ceramic heater which works as a heat source for the measurement. The temperature of the ceramic heater can be controlled by a power source. The other side of the device is exposed to

ambient atmosphere with a temperature of 15°C to examine the performance. Temperatures are measured with a thermocouple mounted at the top of the ceramic heater substrate.

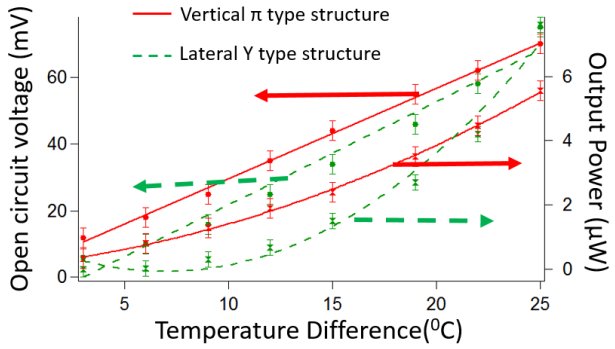


Figure 8. Comparison of generated voltage and output power

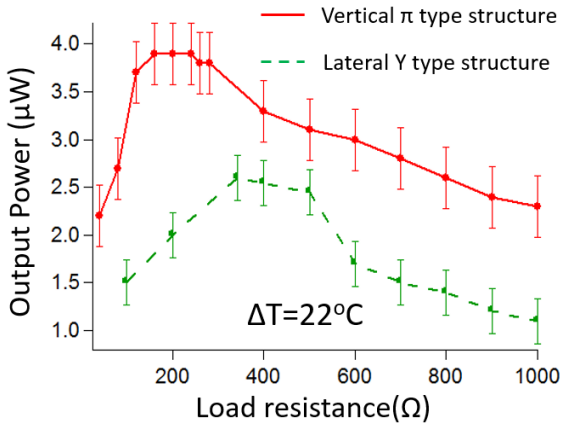


Figure 9. Output power and internal electrical resistance under temperature difference between human body and environment ambient (T=22°C)

The open-circuit voltage is measured for the device with 24 pairs of TCs under heating the bottom side. Figure 8 illustrates the open-circuit voltage and power density as a function of applied temperature difference. In which, the Y-type structure shows higher generated voltage while the π-type structure has better internal electrical resistance. The internal electrical resistance of the π-type structure is evaluated to be 150 Ω, which is two times smaller than that of the Y-type lateral structure. The temperature dependence on the output power is calculated with the match load resistance and measured voltage. From evaluations of the open-circuit voltage and power density, it is seen that the Y-type structure can harvest more thermal energy at small temperature difference than that of π-type structure. The power generation performance of the fabricated device is evaluated under the temperature difference between human body (37°C) and environment ambient (15°C) as shown in Fig. 9. As the result, the Y-type structure achieves an output power density of 3 μW/cm^2, which corresponds to a power factor P/ T= 136 nW/K^2. The π -type structure scavenges less temperature difference than that of Y-type structure. However, the output power is slightly improved due to small internal electrical resistance. The output power density of the π -type structure is approximately 4 μW/cm^2 with power factor of 181 nW/K^2.

CONCLUSION

This work has demonstrated a new fabrication of FTEGs based on electrochemical deposition. The advantages of new Y-type and π-type structures have been proved to optimize device performance significantly. As a result, the Y-type structure is able to harvest more thermal energy at low temperature difference than that of π-type structure while the π-type structure has better internal electrical resistance. With the temperature difference between human body (around 37°C) and environment ambience (15°C), the lateral Y-type and vertical π-type devices can generate approximately 3 and 4 μW/cm^2, respectively.

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REFERENCES

[1] C. Schumacher, et al., *Adv. Energy Mater,* 2013, *3*, pp. 95–104.
[2] C. V. Manzano, et al., *Nature Scientific Report,* 2016, 6, 19129.
[3] R. Roth, et al., *Journal of Microelectromechanical Systems*, 2014, 23, pp. 961-970.
[4] M. Kishi, et al., *Proc. 18th International Conference on Thermoelectrics,* 1999, pp. 301–307.
[5] G. Delaizir, et al., *Sensors & Actuators: A. Physical*, 2012, 174, pp. 115-122.
[6] L. Francioso, et al., *Journals of Power Sources*, 2010, 196, pp. 3239-3243.
[7] L. Francioso, et al., *Proc. Advances in Sensors and Interfaces,* 2013, pp. 104-107.
[8] S. J. Kim, et al., *Journal of The Royal Society of Chemistry,* 2015, **7**, pp. 1959-1965.
[9] N.H. Trung, et al., *Proc. 18th IEEE Nano/ Micro Engineered and Molecular Systems*, Sendai, Japan, (April 2016).

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