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Research Article

Porous Graphene Nanoribbons as a Promising Candidate for Thermoelectric Generators -

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ABSTRACT

The field of thermoelectrics has been growing steadily due to its ability to convert heat directly into electricity and to develop cost effective, pollution free forms of energy conversion, aiming at efficiencies as high as possible. Low-dimensional structures have proved to be promising candidates for enhancing the thermoelectric properties of semiconductors. Here, we discuss the idea of implementation of dense arrays of armchair graphene nanoribbons in microfabricated structures to develop planar unileg thermoelectric microgenerators to convert heat flow into electrical energy. This paper is a discussion on energy scavenging to provide power autonomy to devices on a human body i.e., thermoelectric conversion of human heat and thereby summarizes the advantages of this material for commercial use because of its extra ordinary thermoelectric performance.

Keywords: Microgenerator; Nanoribbon; Thermoelectric; Heat; Electricity; Figure of merit

INTRODUCTION

The increasing demand for miniaturized systems where long-lasting operation is desired is driving the development of new technologies to achieve efficient energy generation which require autonomous operation, preferably with no need to replace or recharge batteries for a long time [1]. Although low-power electronics offers a decrease in the power consumption of devices so that the battery lasts for years yet recharging of batteries needs to be performed on a regular or occasional basis which thus needs human intervention. However, the more functions that are implemented in the device, the more power it consumes. The simple solution can be to increase their size in order either to include a bigger battery or to cover a larger area with solar cells. But this would unavoidably make them too bulky to be acceptable in the market for wearable and portable electronics [2]. Although solar cells provide power autonomy but they fail in adverse illumination conditions [3]. Thus, the association of such devices with the use of some kind of energy-recovering system which can work day and night can reveal an interesting approach. Fortunately, one way to generate the electricity base is through the scavenging of waste heat with Thermoelectric Generators (TEGs). They are ideal for small and distributed power generation since they have no moving parts and are completely silent [4]. Several industrial processes need a large amount of heat which is wasted and dispersed in the environment at the end of the productive cycle because it cannot be converted by conventional thermodynamic systems. All these industrial processes could exploit TEGs for recovering most of this otherwise wasted heat.

In 1950s, the research on thermoelectric materials started with bulk semiconductors such as Bi_2Te_3 , PbTe and SiGe for the applications of room temperature, intermediate temperature and high temperature respectively [5]. With relative low ZT of 1, their conversion efficiencies are limited. Later in 1960s solid solutions such as $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$, PbTe-SnTe were formed which leads to better ZT [6]. In 2004, first wearable TEG was produced which could supply power to a wireless sensor node. Torfs realized a wearable wireless EEG system powered by body heat capable of producing 2mW at 23°C and functions autonomously without batteries [7]. A body-heat powered autonomous pulse oximeter device has been designed in 2006 which provides full energy autonomy. Seiko and Citizen have designed a thermoelectric wristwatch based on body heat using thin bulk thermoelectric devices. Although, tellurium compounds exhibit interesting TE properties, but Te being a toxic material, its disposal arises several environmental problems. Moreover, it is a very rare material on the surface of Earth [6].

Over the past two decades, the trend to use low-dimensional thermoelectric materials such as quantum dots, nanowires and nanocomposites which are theoretically predicted to have improved

ZT due to quantum confinement, provides better conversion efficiencies. Davila et al. designed a planar unileg thermoelectric microgenerator using silicon nanowires to convert heat flow from thermal gradients naturally present in the environment into electrical energy which can overcome the technological limitations on the maximum achievable thermo element length [1]. Despite such achievements, the progress in thermoelectric materials for practical applications has been limited. Therefore, there is a great potential to seek novel thermocouple materials with higher ZT which can be used for thermoelectric applications. Several theoretical works have been carried out to investigate the ZT of nanomaterials. Our previous theoretical results have shown that graphene nanoribbon with specially designed pores behave as an efficient thermoelectric material with extremely high ZT [8,9]. Although defects or vacancies are usually considered to be detrimental to the properties of materials and their consequent applications, but generally growth induced defects like point defects or cluster defects do occur as a part of the fabrication process [10]. Therefore, the major reason for employing the porous structures is to utilise the fabrication defects and deformations for design of enhanced thermoelectric devices which help the manufacturers economically.

Therefore, we propose a thermoelectric generator based on porous armchair graphene nanoribbon with improved thermoelectric parameters which can offer better conversion efficiencies and of course exhibit better performance over other commercially used tellurium based bulk semiconductors like bismuth telluride Bi_2Te_3 etc. The first section of the paper deals with the design of a TEG. The second section of the paper discusses the major problems encountered in the design by using Bi_2Te_3 and discusses theoretically how the choice of GNR as the thermoelectric material can help overcome them. The focus of our application area is to target the waste body heat i.e. to make use of the natural temperature difference between the human body and the environment to generate electricity which can be used for low-power applications e.g., health monitoring systems. It involves placing one side of the thermoelectric module into contact with the skin of the human body and the other in direct contact with ambient air. The major challenge for this application is the few-degree temperature difference and low thermal conductivities of body and air which decreases the thermoelectric conversion efficiencies. The article therefore proposes the use of armchair graphene nanoribbon to be a better and promising material over other existing materials.

Thermoelectric generator

Requirements: The schematic thermal circuit of a thermoelectric generator placed on the human skin is illustrated in figure 1. The human body T_{body} with an average temperature of around 37°C with the surrounding air T_{air} at 22°C form natural thermal generator located

on the body between the points T_{skin} and $T_{interface}$ (the interface layer of air) where R_{body} and R_{air} are the thermal resistances of the human body and air respectively. A thermoelectric generator with resistance R_{TEG} placed in contact with the skin plays the role of a thermal load on this generator [2]. The heat flow W is calculated as:

$$W = (T_{body} - T_{air}) / (R_{body} + R_{air} + R_{TEG}) \tag{1}$$

The product of this heat flow by the thermal resistance of the thermopile gives real thermal gradient on the TEG as [2]:

$$\Delta T_{TEG} = (T_{skin} - T_{interface}) = R_{TEG} (T_{body} - T_{air}) / (R_{body} + R_{air} + R_{TEG}) \tag{2}$$

Design: The design concept of the device presented here correspond to a single thermocouple fabrication as a test structure for development of a complete thermoelectric microgenerator [11]. The designed device, based on unileg planar architecture, consists of a suspended silicon platform connected to a silicon mass through arrays of armchair graphene nanoribbons acting as the thermoelectric material. An integrated heater has been placed on the top of the suspended platform which thus works as the hot junction while the silicon mass acts as the cold junction as illustrated in figure 2 [1].

The proposed design is simply a test structure to prove the thermoelectric concept. One-leg architecture has been chosen since it simplifies the fabrication process when compared with two-leg architecture although the fabrication details are beyond the scope of the paper. From an electrical point of view, the change in the width

and density of the nanoribbons is equivalent to a change in the width/thickness of a standard thermocouple strip, while the serial linkage of multiple nanoribbon arrays is equivalent to a change of its length [11].

From the perspective of device engineering, it is important to increase the output power. The maximum efficiency of power generation is one of the used indicators for device performance because it represents generated power per unit of heat flux. The equation of power generation efficiency is [12]:

$$P = \eta Q \tag{3}$$

$$\eta = P/Q = \eta_c \cdot \frac{\sqrt{1+Z_{dev}T-1}}{\sqrt{1+Z_{dev}T+\frac{T_C}{T_H}}} \tag{4}$$

Where $Z_{dev} T$ is the ZT of the device, T_H and T_C are the hot-side and cold-side temperatures respectively and η_c is the Carnot efficiency given by:

$$\eta_c = \frac{T_H - T_C}{T_H} \tag{5}$$

Therefore, in order to maximize the recovered electric power, there is a need to maximise the efficiency which in turn is dependent on ZT.

Miniaturization

On an average, a single thermocouple of Bi_2Te_3 occupies an area of 7mm and Seebeck Coefficient of 0.2 mV/C, the total TEG area is of the order of 2-3 cm for small power applications [3]. The market trend is towards adding more functionality which creates the need to generate more voltage and power. This, in turn requires more number of thermocouples which will make the device bulky. Various techniques have been designed to make the device compact. However, the fragility of bismuth telluride limits its further miniaturizing, so it is not possible to decrease the size further which is the need for today electronics.

While the device proposed in this paper has a dimension of a few nanometres resulting in much compact size than the existing thermoelectric materials. Also, our theoretical study on graphene nanoribbons under twisted deformation are shown to exhibit Seebeck Coefficient of as high as 0.34 mV/C [9] which is almost double than that of bismuth telluride exhibiting 0.2 mV/C. Hence for a certain temperature difference, more voltages can be attained even with a lesser number of thermocouples in case of graphene nanoribbons as compared to BiTe. Therefore, further miniaturization can be achieved which has proved to be impossible using existing thermo materials.

Power level

For the case of a TEG placed on a human skin, there is a limited difference in temperature between the hot source (i.e., the human body at an average temperature of 37°C) and the cold source (ie the ambient air at a temperature of 22°C). Further, the thermal resistance of the body and ambient high is higher than the thermocouple resistance which leads to poor thermal coupling. As a result, it leads to a very low temperature gradient with the actual temperature difference of much smaller than the 12°C at the thermoelectric generator terminals according to Equation 2 and hence low productivity [2].

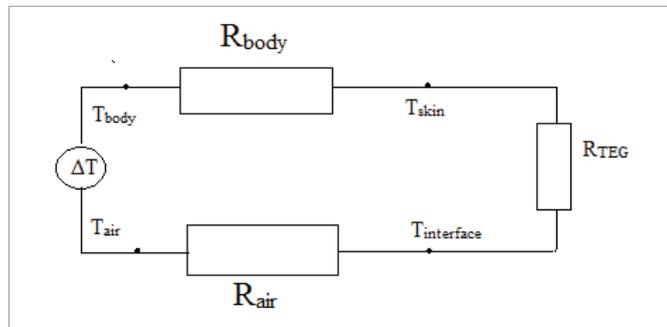


Figure 1: Thermal circuit of a thermoelectric generator placed on a human skin [2].

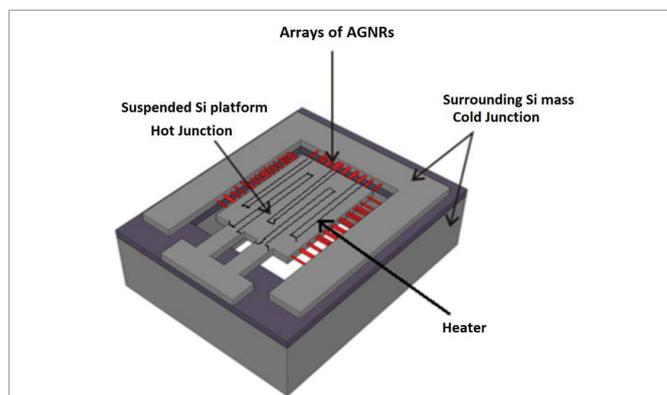


Figure 2: Designed device consisting of arrays of graphene nanoribbons as the thermoelectric material, based on unileg planar architecture.



In order to improve the thermal gradient on the thermopile, its thermal resistance should be increased as compared to that of body and air. The most logical way to do so is in case of bulk material Bi_2Te_3 is to decrease the cross section of the thermocouple leg which in turn is impossible due to its miniaturization limits [3]. Therefore, in addition to higher figures of merit which can generate more power from low temperature gradients, there is a need to evolve thermoelectric materials with increased thermal resistance so that the ratio $R_{\text{TEG}}/(R_{\text{body}} + R_{\text{air}})$ must be maximised for efficient thermal coupling. For achieving these objectives, our design based on porous graphene nanoribbons under certain deformations are capable of extending ZT from unity to as high as 74 with thermal conductivities of the order of few pW/K [9]. This improvement in ZT leads to better conversion efficiencies as stated by Equation 4 and therefore more amount of generated power. Here the physical characteristics of the designed device which includes radiator, heat sink and the body location are assumed to be almost same with the existing commercial thermogenerators which contributes to same amount of heat flux.

Economic benefits

Because of the low ZT of the existing thermoelectric materials, the fabrication cost of the device is not economical. High production costs of thermopiles prevent spreading of the applications [13]. Therefore, there is a need to cut down the cost per device to compete successfully with batteries on the market. Moreover, the existing bulk semiconductors which primarily uses Te causes several environmental problems because of its toxic nature. A better alternative to this material could be our proposed nanodevice which because of its features can bring vast economic and environmental benefits. In addition to dramatic improvements in thermoelectric efficiency over the bulk materials, the nanostructures can be fabricated through relatively inexpensive processing techniques and can be assembled into a variety of desired shapes for device applications.

Another important advantage is that the self-induced defects and deformations which occur during fabrication process can be turned into utility for the design of enhanced thermoelectric devices, thereby cutting down the manufacturing costs.

CONCLUSION

Ordered arrays of porous armchair graphene nanoribbons in a planar architecture is a design solution for improving the thermoelectric conversion of TEGs in harvesting applications that can overcome the technological and economical limitations to promote their widespread adoption for environmental benefits. The

comparison ensemble demonstrates an enhancement in conversion efficiencies with the ability to generate sufficient voltage to drive the electronics even from low temperature gradients. Thus our paper suggests that graphene nanoribbon is a better choice which can replace the existing thermoelectric materials made of Bi, Te and Sb compounds.

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