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A Review on Fabrication Methods for Segmented Thermoelectric Structure

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Abstract. Thermoelectric leg made up semiconductor thermoelectric materials fabricated using various techniques. Types of thermoelectric leg is divided into single thermoelectric material or segmented thermoelectric material. The segmented thermoelectric material is the improvement of single thermoelectric material to produce a high performance of thermoelectric device. Previous study shows that electrical contact does give influence to the thermoelectric leg performance. A single thermoelectric leg usually used electrical contact as a connection to n- and p-type thermoelectric leg. The segmented thermoelectric leg also used similar electrical contact to couple the legs. However, there is an interfacial resistance occur in between segmented leg as it formed from different thermoelectric materials. In addition, there is a joining contact in between the segmented materials, which could give effect to the segmented thermoelectric leg. Thus, this study will discuss more on fabrication and the electrical contact in between segmented thermoelectric as the interface layer or joining technique for the segmented leg. A low electrical contact resistance is necessary to produce a high efficiencies thermoelectric device.

INTRODUCTION

Electrical energy from a renewable energy source is becoming choices to be studied because of the climax changes and fossil fuels source might be worn out one day. Thermoelectric energy produced useful electrical current from temperature difference of thermoelectric material. It used a semiconductor thermoelectric material that will convert heat to electrical energy or vice versa. Thermoelectric energy conversion is widely recognized as a promising technology for both electric power generations in term of waste heat recovery and cooling of various electronic devices [1].

The performances of these materials can be shown by its figure of merit, ZT, defined by:

$$ZT = \frac{\alpha^2 \sigma}{\lambda} T \quad (1)$$

where it involved temperature dependence parameters. A good thermoelectric material should have high Seebeck coefficient, α , high electrical conductivity, σ but low thermal conductivity, λ . Efficiency of thermoelectric device related to the ZT value, which is temperature dependent. One approach to enhance the thermoelectric properties in bulk is by tuning or doping techniques [2]. However, the operating temperature for single thermoelectric material typically in narrow range [3,4]. Therefore, the segmentation between the thermoelectric materials should be produced to increase the efficiency of the thermoelectric generator at wider temperature range. The segmented thermoelectric legs constructed by joining different thermoelectric materials in series [5,6]. Segmented thermoelectric generator is one of the advanced thermoelectric structure beside cascaded thermoelectric structure [5,7,8,9]. Segmented structure is better for the application of medium/high temperature power generator compare to cascaded structure which aim for higher power density.

The famous segmented leg was using bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) based material segmentation. Bi_2Te_3 -based material usually used as the low temperature part of segmented leg because it is known to be the best thermoelectric materials, which can perform at temperature range from room temperature to around 550 K. For medium or higher temperature part of segmented leg, there are many materials that can be used such as skutterudite, Zintl phase materials, half-Heusler and lead telluride (PbTe) [10-14]. PbTe -based materials are the perfect material for high temperature part of segmented thermoelectric generators because it has an outstanding performance at temperature range of 650 – 900 K. Before producing thermoelectric leg, the crucial part is how to fabricate the leg so that it can perform efficiently [5]. Previous study shows that electrical contact resistance used in formation of thermoelectric device also gives influence to the performance of the produced leg [15]. In addition, different fabrication technique has been manipulated in order to find the best technique to fabricate the thermoelectric materials. Due to this, this paper review on the fabrication methods that have been used for single and advance structure such as segmented and future improvement being suggested for easy fabrication.

SEGMENTED THERMOELECTRIC

Recently, most research regarding fabrication of thermoelectric material focused on the powder metallurgy process, ball milling followed by sintering process. The spark plasma sintering method has advantages in restricting rate growth and consolidates powder into bulk materials in fast rate²⁰. Thermoelectric material can be divided into two, single and segmented thermoelectric material. Segmented thermoelectric material is one of the alternative ways to increase the efficiency of the thermoelectric material. It is a combination of thermoelectric material that provides high ZT value at difference temperature range so that the segmented materials will work at wide temperature range [15,21-23]. In order to construct a high efficiency segmented thermoelectric material, the compatibility factor is important. A maximum efficiency of thermoelectric material can only be achieved if the relative current density, u is equal to the compatibility factor, s [22]. They stated that if the compatibility factors differ by a factor of two or more, both materials are incompatible to each other which resulting a not efficient segmented thermoelectric material.

In 2009, Vikhor and Anatyshuk investigated the factors affecting the segmented thermoelectric generator [24]. They reported that the efficiency of double-segmented legs was about 7.5%, which higher than the efficiency of legs made from the homogeneous material. Thermoelectric generator had been improved by using segmented thermoelectric material [25]. They show that their segmented thermoelectric model has peak efficiency at about 11.9% and produce a higher steady voltage. The studies of solar hybrid systems with thermoelectric generators found that the power generated has quadratic temperature dependency. A thermoelectric energy conversion system at mid-temperature used segmented bismuth telluride thermoelectric generator system shows that system operated at mid-temperature could significantly improve the efficiency of the device [26]. Moreover, a theoretical modelling of segmented thermoelectric device has been performed to improve the thermal efficiency [27]. They revealed that the Seebeck coefficient of segmented thermoelectric generator conserved larger values of electrical load resistance compared to the traditional thermoelectric generator.

Segmented thermoelectric generators proved to have a wider range of working temperature and higher efficiency than conventional thermoelectric device [23]. Furthermore, a study on waste recovery of diesel engine using segmented and traditional thermoelectric generators shows that the main factor affecting the performance of both generators is the temperature of heat source [28]. An analysis study of segmented thermoelectric performance described that due to low electrical contact resistance across segmented leg, a high strength of segmented thermoelectric leg can be achieved. Experimental study on medium temperature application of segmented thermoelectric material was done in 2016 by fabricating the multistage thermoelectric generators [29].

Nanocrystalline Synthesized

Thermoelectric materials have been fabricated in various ways. A lot of work has been done in fabricating nanoparticle and nanocomposites [16]. There is several alternative method used to synthesis nanotubes or nanocrystalline thermoelectric material such as mechanical and chemical alloying methods, microwave-assisted synthesis, solvothermal-reduction synthesis technique and electrodeposition [17]. Electrodeposition is a simple process with high deposition rates, which can achieve up to tens of μm , but resultant films present low ZT. In addition, the product structure of this technique needs an expensive template with special structure to depend on. Meanwhile, solvothermal-reduction synthesis requires long reaction rate and high pressure [18]. The

microwave-assisted synthesis has the advantage of providing a higher reaction rate, faster volumetric reaction and shorter reaction compared to conventional heating techniques [18,19].

The microwave-assisted polyol technique limiting the particle growth because of the ability of the solvent used to coordinate at particle surface. Despite of that, the solvent has a high boiling point and high solubility due to the high polarity of solvent used (multivalent alcohol – ethylene glycol (EG)). This process which used polyol agent provides a low cost efficiency, short reaction time and low temperature compared to other chemical process [20]. The 30 minutes of reaction time was reported for preparation of bismuth telluride single crystal of nanotube or nanocrystalline using microwave-assisted which is much more shorter than reaction time that is needed for hydrothermal and solvothermal techniques (6 to 26 hours). However, this material have to undergo the sintering process before the thermoelectric properties of this material can be studied [18].

Fabrication of Segmented Thermoelectric Generators

Fabrication techniques for thermoelectric generator had been carried out years ago. Most of research done used sintering method by Spark Plasma Sintering, SPS because this method known to be effective method in fabricating thermoelectric. A lead free thermoelectric generator which used oxide-based material was fabricated in 2001 using sintering method [30]. They reported that the p-type thermoelectric material $\text{Ca}_{2.75}\text{Gd}_{0.25}\text{Co}_4\text{O}_9$ was constructed using SPS under pressure of 50 MPa at 1073 K for 5 min while the n-type material $\text{Ca}_{0.92}\text{La}_{0.08}\text{MnO}_3$ was constructed using conventional sintering method. After that, the sintered samples undergo annealed under O_2 condition at 1173 K for 20 hours to eliminate carbon on the surface. The resistivity obtained for n- and p-type thermoelectric material was 7.8 $\mu\Omega$ and 6.6 $\mu\Omega$ respectively. In 2012, fabrication of the material of Mg_2Si by a Plasma-activated Sintering (PAS) using monobloc sintered under pressure of 30 MPa at 1113 K for 11 min. The Ni electrode is sintered simultaneously with the thermoelectric material provided 6 m Ω of contact resistivity. The overall resistance of sintered sample was about 10.5 m Ω [31].

Later, a study on manipulating 0 – 4 percentage mol concentration of SrTe for PbTe-SrTe thermoelectric material was done by doping with 2 percent mol of Na. The samples were fabricated in the form of ingot by melting for over 10h at 1323 K and quenching to room temperature at 297 K. Later, the ingots undergo powder processing and sintered with Spark Plasma Sintering at 823 K for 10 min under pressure of 60 MPa in argon atmosphere [32]. The maximum ZT value that can be achieved when using the above steps was nearly 2.2 at 915 K compared to the ZT value of nearly 1.7 at 800 K of the ingot sample. This proved that the uses of SPS can increased the performance of thermoelectric samples produced. Other than that, a SnSe sample was first synthesized in the form of ingot at 1223 K for over 9.5 hours then soak for 6 hours followed by furnace-cooling at room temperature before heated up to 1223 K over 9.5 hours by vertical Bridgman crystal and cooled to room temperature with moving sample at a rate of 2 mm/h [33]. The ZT value reported was 2.62 at 923 K with a lower lattice thermal conductivity of 0.23 $\text{Wm}^{-1}\text{K}^{-1}$. It is a high ZT value for a low thermal conductivity material.

All of the mentioned above basically for single thermoelectric material. Generally, fabrications of segmented thermoelectric material are same as single thermoelectric material. This is because to form a segmented thermoelectric leg, the single legs will be formed first followed by joining the legs together. Interestingly before the fabrication of segmented sample, researchers tend to calculate their performance first by using finite element model. This is to ensure that the segmented thermoelectric sample can be used and save the cost. On the other hand, simulation of segmented thermoelectric generator was constructed to determine the performance of the generator without fabricate the generator in order to avoid material waste. The simulation also used to validate and manipulate the properties of the manufactured samples to calculate the module performance. In 2014, the segmented n-type 0.01 and 0.055 mol% PbI_2^- doped $(\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{0.92}(\text{PbS})_{0.08}$ were fabricated using hot pressed for 30 min under pressure of 25 MPa at 1073 K [34]. The ingots were milled using agate mortar and pestle before pressed. The result obtained from the tested sample will be used in COMSOL finite-element to simulate the further performance of the device by manipulating boundary conditions, applications and geometries.

Later in 2015, generator model that contains segmented thermoelectric leg of p-type of BiSbTe/MgAgSb/K-doped PbTeS/SnSe and n-type of Cu-doped BiTeSe/AgPbSbTe/SiGe was simulated to obtain its performance. This modelling method used ANSYS simulation [35]. They reported that this high performance generator used Cu interface with electrical contact resistance of $1 \times 10^{-8} \Omega\text{m}^2$. Thermal analysis of segmented thermoelectric generators using MATLAB can provide useful information for segmentation. This is shown by simulation of the modified segmented n-type of $\text{Ag}_{0.8}\text{Pb}_{1.9+x}\text{SbTe}_{20} / \text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and p-type $\text{Ag}_{0.9}\text{Pb}_9\text{Sn}_9\text{Sb}_{0.6}\text{Te}_{20} / \text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$. From the thermal analysis, the efficiency and output power of thermoelectric device can be determined. Therefore, the findings will gives the useful information on segmentation ratio over the operating condition to have maximum efficiency and power output [36]. This shows that simulation of thermoelectric leg to obtain the module performance is necessary in verifying the experimental test techniques.

Moreover, a design segmented thermoelectric generator had been reported in 2014 where both of the segmented n- and p-type used SPS [37]. The n-type segmented sample Bi doped $\text{Mg}_2\text{Si}/\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ was crushed into powder using ball milling followed by SPS under pressure of 50 MPa at 1023 K for 3 minutes. The p-type thermoelectric material sample HMS / $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ was pressed with 30 MPa at 1173 K for 15 minutes in vacuum. The joining material used was silver (Ag) solder and Cu electrode which provide an electrical contact resistance of $< 50 \mu\Omega\text{cm}^2$. The materials used were light-weight and cost effective based material. In addition to, Ag foil was also used as joining material for segmented thermoelectric material of Ca349 and HH. It also was being used as electrode to couple p- and n-type thermoelectric leg. In 2015, the joining process was done using brazing technique by SPS under 20 MPa at 973 K for about 10 minutes [38]. They described that after the joining process, there was no changes in both material characteristics. Furthermore, multistage thermoelectric generators were fabricated using fast vacuum soldering process [29]. The p- and n-type leg material was $\text{Pb}_{0.94}\text{Sr}_{0.04}\text{Na}_{0.02}\text{Te}/\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and $\text{Pb}_{0.94}\text{Ag}_{0.01}\text{La}_{0.05}\text{Te}/\text{Bi}_2\text{Te}_3$ respectively coupled together with $\text{Pb}_{95}\text{Sn}_5$ solder paste. They reported that average ZT value obtained was 1.9 and 1.4 for both p- and n-type PbTe based material for temperature range of 600 K to 900 K. Meanwhile for room temperature to 500 K temperature range, BiTe based material has the average ZT of 0.9. They reveal that this method gives a good electrical contact between the materials.

In 2016, the segmented n-type $\text{Bi}_2\text{Te}_3/\text{PbSe}_{0.5}\text{Te}_{0.5}$ and p-type $\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3/\text{Zn}_4\text{Sb}_3$ legs of a thermoelectric generator fabricated using one-step spark plasma sintering (SPS) [39]. The n-type segmented leg was produced from powders where the powders were milled with ball milling then it was tightly pressed in carbon die partially. After that the carbon die was sintered using SPS under pressure of 50 MPa at 673 K. The sintered samples were cut into cube-shaped with dimension of $3 \times 3 \times 3.7 \text{ mm}^3$ using wire-electrode and polished with sand papers. The p-type segmented samples were prepared with similar steps. N- and p-type legs were coupled using Cu electrode soldered with Sn – 95 Pb solder. They found that the interfacial resistance in between the segmented gives major influence to the electrical resistance of thermoelectric legs. The interfacial electrical resistance measured between p-type segmented legs was 224.8 m Ω lead to drastic increased in electrical resistance of segmented leg up to 30 times larger than single leg. Meanwhile, the segmented n-type has doubled electrical resistance compared to the bulk counterpart because it was measured at high temperature. This was due to the small interfacial electrical resistance of 89.9 m Ω compared to the segmented p-type. They expected to have power output of 165.9 mW and efficiency up to 1.53%. However, due high interfacial electrical resistance the maximum power output obtained was 48.9 mW with efficiency of 0.48% at temperature difference of 296 K.

Recently, a module based on bismuth telluride/skutterudite segmented material has been fabricated using one-step sintering hot pressing technique [40]. The Ni foil was used as interfacial layer between bismuth telluride/skutterudite, which has small interfacial resistance of $40 \mu\Omega\text{cm}^2$, causes the loss of efficiency $< 2\%$ from simulated result. The sintering process was carried out for n- and p-type skutterudite at 953 K and 923 K respectively for 1.5 hours under pressure of 60 MPa. After that, the bismuth telluride sample was soldered to skutterudite sample using tin-based solder. The fabricated module was able to achieve up to 12.0% in efficiency under temperature difference of 541 K. they also reported that by a suitable structure design and fabrication techniques, the measured efficiency can reaches up to 96.5 % of the theoretical efficiency which based on the performance of each thermoelectric material used. Thus, it proves that to have a high efficiency of thermoelectric generators, the electrical contact resistance in between segmented legs need to be as small as possible so that it will not affect the performance of the leg and device.

CONCLUSION

All in all, most fabrications of thermoelectric material either for single or segmented leg are using the Spark Plasma Sintering (SPS) method by using graphite die. The graphite die is used as graphene is known to have high thermal conductivity with the maximum pressure of 60 MPa. Therefore, the process conducted under pressure of 20 MPa to 50 MPa at temperature range of 773 K to 1373 K for about 5 – 30 minutes time. This method also conducted under Argon atmosphere. SPS technique is the best method for the time being because it consumes less time compared to the conventional sintering method. Most importantly, it helps in improving the performance of fabricated thermoelectric materials. Contact material is needed in reducing the thermal loss of thermoelectric material. A low electrical contact resistance will help segmented thermoelectric material to perform in high efficiency condition. As for now, Cu was used as the electrode and Ag as the interface or joining material of segmented and electrode.

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