EXPLORING SCREEN PRINTING TECHNOLOGY ON THERMOELECTRIC ENERGY HARVESTING WITH PRINTING COPPER-NICKEL AND BISMUTH-ANTIMONY THERMOCOUPLES

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ABSTRACT

This paper reports the fabrication and testing of copper (Cu) − nickel (Ni) and bismuth (Bi) – antimony (Sb) based thermocouples fabricated using screen printing technology. The transport properties of the printed thermoelectric material were measured in room temperature while the Seebeck voltage and power output of the printed thermocouples were tested under a variety temperature gradient. Initial thermoelectric materials have been integrated in inks and then deposited on substrate by the simple, low-cost and low-temperature operation screen printing technology.

KEYWORDS

Energy Harvesting, screen printing, copper-nickel, bismuth-antimony, thermoelectric generator

INTRODUCTION

Thermoelectric generators (TEGs) can generate electrical energy for autonomous microsystems from a thermal gradient existing in the environment. When there is heat flux along the thermolegs, a voltage will be generated from the thermocouple due to the Seebeck Effect (shown in figure 1). However, the energy transfer efficiency (the ratio of output electrical power to transferred thermal energy) is relatively low for current TEGs (typically around 5%) [1]. Hence, in order to achieve high power output, high density TEG devices are required to be fabricated with aspect-ratios. Compared with other micro machining technologies, such as electrochemical deposition, photolithography and etching [2], screen printing is a low-cost process and easier to realize on large area fabrication, which is essential for practical applications.

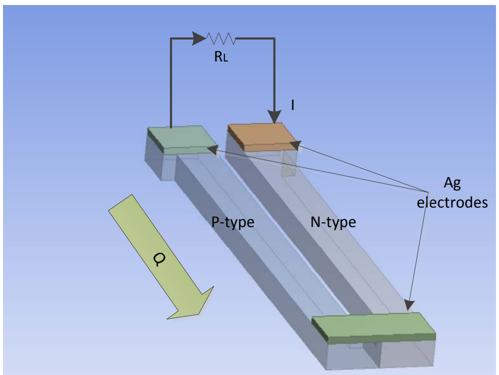

Figure 1: Seebeck schematic of a screen printed TEG with one thermocouple

Screen printing technology involves the deposition of synthesized thermoelectric inks that consist of thermoelectric material powders in a binder and solvent. After that only a curing process is needed. Compared with thin film fabrication technologies, the consumed energy and waste in screen printing process are reduced substantially [3]. In this work, low-cost copper and nickel have been used to explore various screen printed designs and geometries, while bismuth and antimony films are investigated achieve greater performance because they have a higher theoretic Seebeck coefficient [4].

EXPERIMENTAL

Material synthesis

A screen printable paste contains active materials (copper, nickel, bismuth and antimony particles in this experiment) and a binder system. All pastes have been formulated at the University of Southampton.

For p-type copper and n-type nickel thermocouples, 325 meshes copper and nickel flakes (Alfa Aesar) are the active thermoelectric materials. The particles size of 325 meshes is chosen for the empirical studies from other researchers [5]. Moreover, particles with flake shape lie against each other with a greater amount of overlapping surface-area in higher degree of inter-particle contact than nodular or granular particles, which provides more opportunities for electrons hoping from one particle to the next rather than tunneling through the non-conductive binder matrix [6]. A glass binder was used to adhere the adjacent particles and onto the underneath layer. Different percentages of binder were investigated to make paste depend on the trade-off between the electric resistivity and the adhesion of the thick-film and the layer underneath. ESL 400 solvent was used as the vehicle in the ink. This vehicle is removed during a 125 °C drying process before firing the printed pattern in high temperature.

For p-type antimony and n-type bismuth thermocouples fabrication, Sb and Bi powders (Alfa Aesar) are the active thermoelectric materials. The melting points for Bi and Sb are 271.5 °C and 630.6 °C in the Standard atmospheric pressure [4]. The powders in the printed bismuth and antimony thick films will be partly melted to generate a reasonable conductivity after firing process. Normal granular powders were used here to form the printed paste. However, the firing temperature cannot be too high to burn off the binder, then losing the adhesion. Different firing temperatures were investigated to meet these requirements. A two part epoxy resin was used as the binder, while a Butyl carbitol acetate-based thinner was used to dilute the composite with a screen printable viscosity.

Empirically, the ideal viscosity range of the working ink is from 9000 cP to 15000 cP, measured by Brookfield High Shear CAP-1000+ viscosity measuring machine. The triple roll mill was used to mix the particles achieving an even particles distribution.

Device fabrication

The thickness of the active thermoelectric lays can be built up by drying each layer then subsequently depositing another layer. A polyester screen with 325 mesh was used for deposition.

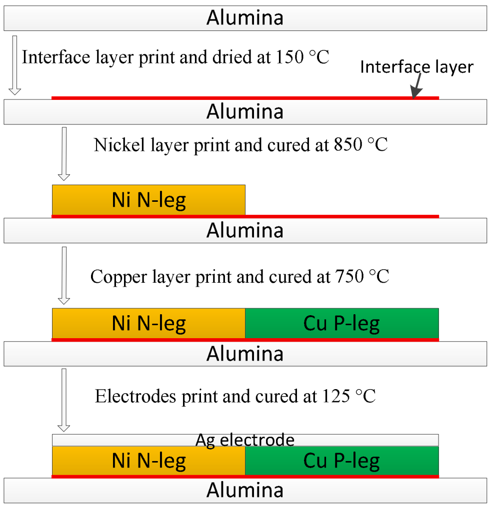

Figure 2: Fabrication process of screen printed TEGs

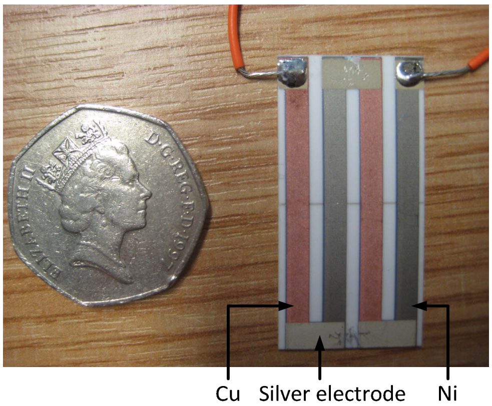

Figure 3: Images of printed thermocouples on alumina substrate

For the Cu-Ni thermocouples, a dielectric composition was deposited onto the alumina substrate firstly to improve the adhesion of the Ni thick-film. The printed dielectric layer was dried at 125 °C before printing the nickel. This drying process was also applied to drive out the solvents in the active thermoelectric patterns in order to build up the thickness of the Ni and Cu layers. Following by the interface layer printing, 2 layers of nickel paste were deposited on the dried dielectric layer, with 2 depositions for each layer. After 850°C firing in nitrogen, another 2 layers of copper were deposited on the fired dielectric layer and fired at 750 °C. Finally, a silver electrode layer was printed to make the electric connections between the thermolegs. The fabrication process is illustrated in figure 2 and the final layout of the printed thermocouples is shown in figure 3. The conductive wires were soldered to the two ends of the thermocouples. The dimension of each thermoleg is 39.8 mm × 3 mm and with a thickness of 11.2 μm for Copper and 1.5 μm for Nickel. The distance between two adjacent thermolegs is 2 mm.

For Bi-Sb thermocouples, there was no adhesion problem between the active thermoelectric material layer and the alumina substrate. Hence, the interface layer was not required. The low melting point of Bi and Sb meet a firing temperature of 250 °C [4]. Initially, after firing the printed bismuth thick-film is not conductive when simply tested by multimeter. The reason is that the heavy bismuth powders sink down to the bottom of the pattern during the printing process, leaving a non-conductive epoxy matrix on the top of the pattern. A polishing process after firing removes this thin polymer layer from the film, exposing the melted bismuth underneath (shown in figure 4). Other processed for Bi-Sb TEG device fabrication was the same as for the Cu-Ni TEG.

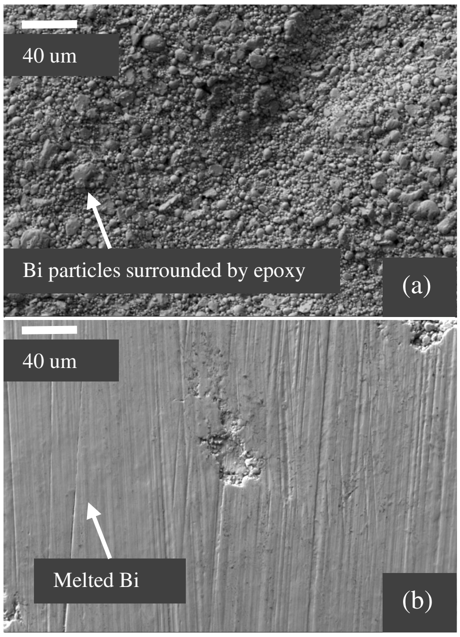

Figure 4: Scanning electron microscope images of (a) Bi/epoxy composite film before polish and (b) Bi/epoxy composite film after polish.

Printed Thick-films and Device Characterization

The efficiency of a TEG depends on the figure of merit Z of the materials ($Z=\alpha^2/(\rho\cdot\lambda)$, where α is the Seebeck coefficient, ρ is the electrical resistivity, and λ is the thermal conductivity). Hall Effect measurements were performed to test the transport properties of the printed thick films, including resistivity, using a commercial Hall Effect measurement system (HMS 3000 from Ecopia). The Seebeck coefficients of all the material samples were measured using custom-made equipment to determine the voltage output of the material for a given temperature difference (ΔT).

The Seebeck voltage of the printed sample devices were tested by a bespoke set-up shown in figure 5. Once the device reached steady state with a temperature gradient, the Seebeck voltage of the device was measured using a digital multimeter. Peltier modules from European Thermodynamics provided a thermal gradient across the device. The temperature gradient was measured using a Tenma digital thermometer with dual type K input. The gap between the two peltiers was fixed at 2 cm. The power output can be calculated out from the voltage across a variable load resistance in series.

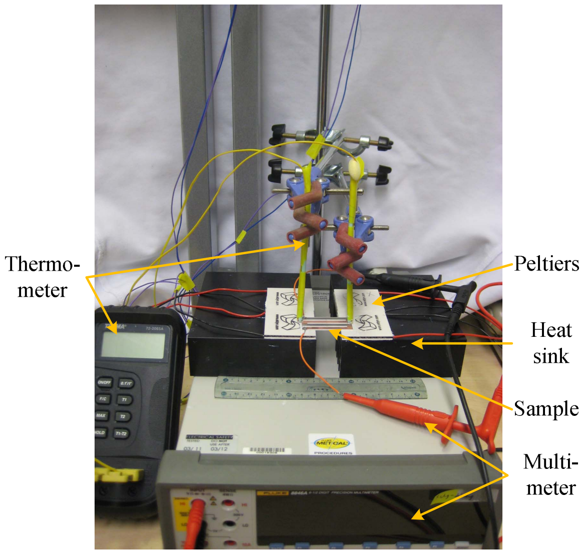

Figure 5: Seebeck voltage measurement setup

RESULTS

Thermoelectric properties of printed thick-films

The experimental resistivity and Seebeck coefficient are listed in table 1.

The negative sign of Seebeck coefficient indicates that the nickel and bismuth acting as n-type material in a thermocouple, while the positive α value means that the copper and antimony are p-type thermolegs. The absolute value of Seebeck coefficient of bulk nickel (-19.5 μV/K) is larger than that of thick-film nickel (-13 − -17 μV/K). However, the Seebeck coefficient of bulk copper (1.83 μV/K) is smaller than that of thick-film copper (3 μV/K). This is due to the other ingredients in the pastes which change the Seebeck coefficient of the film. Therefore, it can be assumed that the glass binder has a positive Seebeck coefficient which increases the α values of both nickel and copper films.

Table 1: Transport properties and Seebeck coefficient of Cu, Ni, Bi and Sb

	Cu	Ni	Bi	Sb
ρ (Ω·cm)	6.4×10^{-5}	4.86×10^{-4}	7.26×10^{-2}	1.24×10^{-3}
Bulk ρ (Ω·cm)	1.71×10^{-6}	7.12×10^{-6}	1.07×10^{-4}	3.9×10^{-5}
α (μV/K)	3	-13 ~ -17	-57~ -60	23 ~ 25
Bulk α (μV/K)	1.83	-19.5	-70	40

Also, it can be seen that the tested ρ and α are both less than those of bulk. All the values are measured at room temperature. Although bismuth and antimony have a higher seebeck coefficient, the high resistivity limits the improvement of power factor ($\alpha^2\sigma$). For example, the power factor of the nickel thick-film is 0.035 – 0.06 mW/cm·K^2, while that of bismuth thick-film is only about 0.004 – 0.005 mW/cm·K^2.

Device Characterization

Figure 6 shows the generated voltage and current of two Cu-Ni thermocouples when there is a temperature difference applied across the device. Both can be considered as linear curves. After linear fitting in Matlab, at a temperature difference of 60°C, the voltage is 3.0 mV and the current is 28.2 μA. For single Cu-Ni thermocouple, the generated voltage is about 1.5 mV. This compares favorably with a Ni/Chrome and Ni/Panipol based thermocouples fabricated with a screen printing process by Duby and Ramsey, whose one 40 mm long thermocouple generated 1 mV voltage with a 80°C temperature difference [6].

The power output versus load resistance was measured with 8 thermocouples. The voltage across the load increased with the increasing load resistance, while the maximum output power appeared when the load resistance matched the TEGs resistance. The power output P is calculated by $P=V^2/R$, where V is the voltage across the load resistance and R is the load resistance. For a single screen printed Cu-Ni thermocouple, the maximum power output is 10.3 nW at a temperature difference of 20°C (From figure 7).

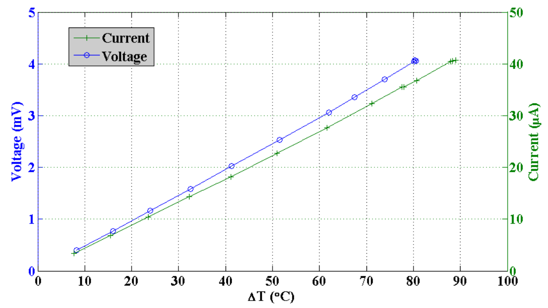

Figure 6: Generated Seebeck voltage of two printed Cu-Ni thermocouples

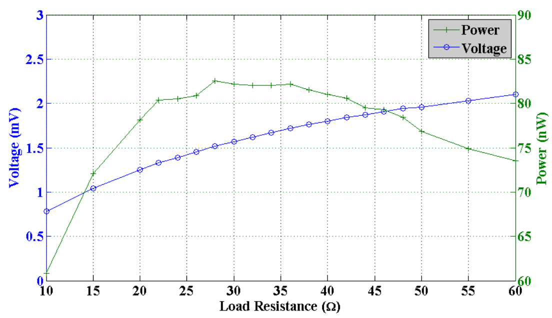

Figure 7: Power output and voltage of the 8 thermocouples as a function of load resistance at a 20K temperature difference

For the printed Bi-Sb TEGs, the average thickness of Bi thermolegs after polishing was 105.2 μm, while that of Sb thermolegs was 78.9 μm. A single Bi-Sb thermocouple generated a voltage of 5 mV with a temperature difference of 20°C (figure 8), compared with 1.5 mV generated for a single Cu-Ni thermocouple. However, maximum power of single Bi/Sb thermocouple is only 9.0 nW (calculated from figure 9) due to the high resistivity of Bi/Sb thick film.

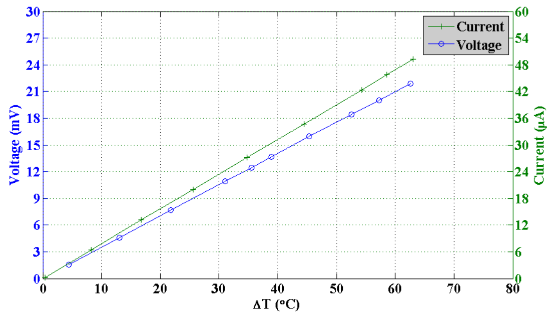

Figure 8: Generated Seebeck voltage of 4 printed Bi-Sb thermocouples

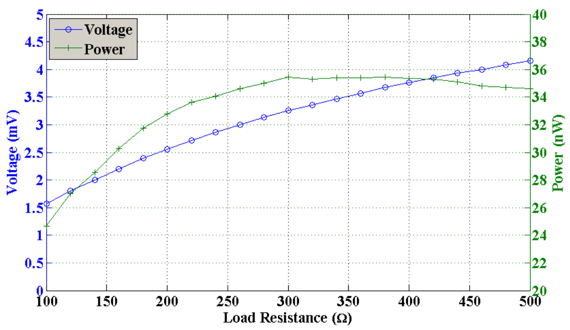

Figure 9: Power output and voltage of the 4 Bi-Sb thermocouples as a function of load resistance at a 20K temperature difference

DISCUSSION AND CONCLUSION

This work demonstrates that screen printed technology can be used to fabricate TEGs. The ease of processing and device fabrication with printed materials provides deployment advantages over copper and nickel as thermoelectric materials. In this work, the adhesion issue of Ni high temperature cuing thick-film on alumina substrate was successfully solved by adding a dielectric interface layer.

The power output per single thermocouple of Bi-Sb TEG is smaller than that of Cu-Ni TEGs. The power output of Bi-Sb thermocouples presented in this work is currently limited by their high electric resistivity. From $P=V^2/R$, even though the generated voltage increased, a larger increase in resistance produces a net reduction in the power output of the device. The strongly oxidizing nature of semimetals Bi and Sb might explain the high resistivity. Power output and Z value may be improved by, e.g., optimizing the device design, fabrication and materials processing parameters.

We are also investigating Bi_2Te_3 and Sb_2Te_3 based thermoelectric active materials in screen printable inks for their higher figure of merit in room temperature [7]. Future work will explore this material for screen printing, TEGs fabrication and continued optimization of materials and design.

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