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Hybrid composite of screen-printed inorganic thermoelectric film and organic conducting polymer for flexible thermoelectric power generator

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ABSTRACT

TEG (Thermoelectric power generator) modules are attractive energy harvesters, as they can deliver electrical output power from the temperature difference of all sorts of things. Recently, growing interests in self-powered wearable mobile electronics provoke the necessity of flexible TEG modules. However, the technology on flexible TEG modules is still at a very early stage. Here we demonstrate flexible high-performance TEG modules using a screen-printed inorganic thermoelectric thick film and organic conducting polymer hybrid composite. By infiltrating the organic conducting polymer, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), into the micropores of the screen-printed thermoelectric thick film, the flexibility of the module is greatly enhanced without degradation of the output characteristics of the module. This work provides a promising new approach which has the potential to achieve a flexible high-performance TEG module.

1. Introduction

TEG (Thermoelectric power generator), which converts waste heat into electricity, is one of the promising energy harvesting devices [1]. The output performance of the TEG module is determined by dimensionless figure-of-merit (ZT). The ZT (or Z) is the ability of a given material to efficiently produce electrical power from thermal gradient [2]. So far, regarding waste heat recovery and harvesting methods, various ways including structure optimization of the module [3] or system [4], organic rankine cycle [5], transcritical rankine cycle [6,7], thermal energy storage integration [8–12], TEG incorporation [13] have been adopted and studied extensively. In recent years, research on flexible TEG module fabrication has attracted great interest due to the potential new market for self-powered wearable mobile electronics [14]. In fact, because many heat sources (human body, power stations, heating systems, motor vehicles, and so on) have arbitrary shapes, a flexible TEG module helps to have better thermal contact with the arbitrary shaped heat sources. However, conventional inorganic TE (thermoelectric) materials such as bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) are unsuitable for flexible TEG modules because of their brittle material properties. To overcome this problem, some groups have proposed organic [15] or organic-based composite materials [16,17] for flexible TEG modules. However, organic-based flexible TEG modules have limitation of low output performance due to their low figure-of-merit ZT value and high contact resistance. Although some organic-metal [18] or organic-inorganic hybrid composite materials [19,20] for flexible TEG modules with improved performance have been proposed, the output performance is still low compared to that of inorganic-based TEG modules.

In this work, flexible high-performance TEG modules using a screen-printed inorganic TE thick film and organic conducting polymer hybrid composite have been realized. In this new approach, the micropores in the screen-printed TE thick film are filled with an organic conducting polymer, PEDOT:PSS, using a spin-coating and infiltration process. Compared to other methods to prepare organic–inorganic hybrid composites, the proposed method is much simpler, cheaper, and mass-production friendly because it is easy to make a large size film quickly. The feasibility of flexible TEG module operation using body heat has also been demonstrated. This work may open a new route to develop flexible high-performance TEG modules.

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Nomenclature

TEG	thermoelectric power generator
TE	thermoelectric
Bi	bismuth
Sb	antimony
Te	tellurium
Ag	silver
Cu	copper
Bi_2Te_3	bismuth telluride
Sb_2Te_3	antimony telluride
PI	polyimide
PEDOT	PSSpoly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)
DMSO	dimethyl sulfoxide
N_2	nitrogen gas
FESEM	field emission scanning electron microscope
SEM	scanning electron microscope
HMS	Hall-effect measurement system
LFA	laser flash apparatus
n	carrier concentration (cm^{-3})
S	Seebeck coefficient ($\mu V\ K^{-1}$)
|S|	absolute value of the Seebeck coefficient ($\mu V\ K^{-1}$)
ZT	figure-of-merit (dimensionless)
Z	figure-of-merit (K^{-1})
R	electrical resistance (Ω)
K	thermal conductance ($W\ K^{-1}$)
L	length of thermoelectric leg (m)
A	area of thermoelectric leg (m^2)

Greek letters

μ	carrier mobility ($cm^2\ V^{-1}\ s^{-1}$)
σ	electrical conductivity ($S\ m^{-1}$)
κ	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
ρ	electrical resistivity (Ω m)

Subscripts

p	p-type thermoelectric leg
n	n-type thermoelectric leg

2. Experimental

2.1. Paste synthesis

The paste consists of 75% of metal powders (Bi, Sb, and Te), 2.4% of glass powder, 0.2% of binder, and 22.4% of solvent in their weight compositions. The metal powders have 99.5% purity and the sizes of the metal powder particles are smaller than 5 μm. The powder mixing ratio of Bi and Te was 35:65 while the ratio of Sb and Te was 40:60 in atomic percentage. The pastes were thoroughly mixed for 24 h using ball-mill equipment. The purpose of the glass powder is to increase the adhesion between the substrate and the paste so that the paste would not be delaminated after annealing. The binder maintains the paste's viscosity at a desired level and the solvent is used to mix the powders. The synthesized Bi_2Te_3 paste has viscosity of 40 Pa s while Sb_2Te_3 paste does 65 Pa s.

2.2. Screen-printed thermoelectric thick film formation

The deposition of Bi_2Te_3 (n-type) and Sb_2Te_3 (p-type) TE thick films using a screen-printing technique consists of several steps: screen printing, drying, and annealing. The prepared paste was screen-printed on a flexible PI (polyimide) film substrate by using a 150 mesh screen. After that, the samples were dried at 120 °C for 10 min to remove the solvent. Two-step annealing in a furnace tube was then performed: a binder removal step and a high temperature annealing step. First, the binder removal step was performed at 260 °C for 10 min in a vacuum ambient to remove the organic binder from the paste. The annealing step was then conducted at 450 °C under 110 mm Hg in a N_2 ambient to achieve the best TE properties of the film. This pressure was carefully selected experimentally to avoid oxidation and excess evaporation of Te. When the pressure was close to 1 atm, the film was oxidized. On the other hand, when the pressure was too low, excess evaporation of Te was observed.

2.3. Thermoelectric transport characterization

The morphology of the screen-printed thick films was analyzed by field emission scanning electron microscope (Sirion, FESEM, operating voltage: 10 kV). The Seebeck coefficient was measured by connecting one side of the film to a hot metal block and the other side to a heat sink which is kept at room temperature. By varying and measuring the temperature differences across both sides of the sample and measuring the output voltage, the Seebeck coefficient can accurately be obtained from the slope of the data curve in the plot of temperature difference versus output voltage. The temperature difference and output voltage were measured by a Keithley 2700 equipment simultaneously. The electrical conductivity was measured by the standard Van der Pauw method using a Hall-effect measurement system (Ecopia, HMS-3000) and the thermal conductivity was measured by the standard laser flash method using a Laser Flash Apparatus (NETZSCH, LFA 447).

2.4. Area ratio optimization for the TEG module

To maximize the output power density of a TEG module, the area ratio of p-type and n-type TE legs must be optimized because the TE legs have different electrical and thermal properties. The figure-of-merit Z of a TEG module can be defined as follows:

$$Z = \frac{(S_p - S_n)^2}{R \cdot K}, \tag{1}$$

where S is the Seebeck coefficient, R is the electrical resistance, and K is the thermal conductance of the module. The subscripts 'p' and 'n' represent the p-type and the n-type TE leg. The electrical resistance (R) and thermal conductance (K) are defined as follows:

$$R = \frac{L_p \cdot \rho_p}{A_p} + \frac{L_n \cdot \rho_n}{A_n} \tag{2}$$

$$K = \frac{\kappa_p \cdot A_p}{L_p} + \frac{\kappa_n \cdot A_n}{L_n}, \tag{3}$$

where L is the length, ρ is the electrical resistivity, κ is the thermal conductivity, and A is the area of the TE leg. The figure-of-merit Z is maximized when the product RK is minimized. To minimize RK, the differentiation value of RK respect to A_n/A_p should be zero.

$$\mathrm{RK} = \left(\frac{L_p \cdot \rho_p}{A_p} + \frac{L_n \cdot \rho_n}{A_n}\right) \cdot \left(\frac{\kappa_p \cdot A_p}{L_p} + \frac{\kappa_n \cdot A_n}{L_n}\right) \tag{4}$$

Suppose the length of the TE legs is the same ($L_p = L_n$). Then,