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Mixed thick/thin-film thermocouples for thermoelectric microgenerators and laser power sensor

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This work presents the fabrication of thermopiles with high output voltage. A series of mixed thick/thin-film thermopiles were performed – one of the arms of the thermocouples was screen-printed (PdAg- or Ag-based thick-film layers), the second was made of magnetron sputtered semiconductor (compositions based on Ge). The output parameters (thermoelectric force E_T [V], internal resistance R_i [Ω], output electrical power P_{out} [W]) of the structures were characterized using a self-made automatic measurement system. The best parameters were achieved for TSG/PdAg (TSG – Ge doped by Sb and Ta) and WSG/Ag (WSG – Ge doped by Sb and W) structures. Generated output voltage per single thermocouple was about 20 mV and output electrical power – 0.55 μW, when temperature difference between hot and cold end was 100 K. Also, the influence of activation process on output parameters was investigated (structures were put into high temperature to initialize recrystallization and grain growth process). The possibilities of using of such structures as thermoelectric microgenerators or sensors were considered. TSG/PdAg-based structures were used to prepare laser power sensor. The level of generated thermoelectric force E_T was proportional to the power of the laser beam under investigation. Tests of prototype structures showed that thermoelectric sensors have sufficient resolution and ensure very good repeatability of measurements.

Keywords: thick-film, thin-film, thermoelectricity, microgenerator, sensor, thermocouple, thermopile.

1. Introduction

When ends of two different materials, A and B, are connected together and the junctions are put into different temperatures the thermoelectric force E_T appears between connection points and the current flows in the circuit [1, 2]. This effect is illustrated in Fig. 1.

Applications of thermocouples in sensor systems, in cooling devices or in power generation systems are described in the literature very often [3–5]. To multiply

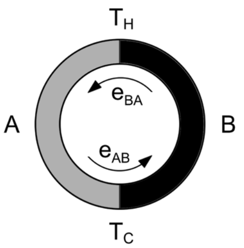


Fig. 1. Thermoelectric effect in the circuit built of two different materials, *A* and *B*.

thermoelectric force E_T thermocouples are connected electrically in series and thermally in parallel. This kind of structure is called a thermopile and its thermoelectric force E_T is expressed as:

$$E_T = n \alpha \Delta T \tag{1}$$

where: n – number of thermocouples in stack, α – Seebeck coefficient of a single thermocouple, ΔT – temperature difference between "hot" and "cold" junction.

To maximize output power P_{out} of such generators thermoelectric power E_T should be as high as possible and internal electrical resistance R_i as small as possible:

$$P_{\text{out}} = \frac{(E_T)^2}{R_i} \tag{2}$$

To compare different thermoelectric materials Seebeck coefficient α [μV/K], electrical resistivity ρ [Ωm] and thermal conductivity λ [W/Km] are combined in the so-called thermoelectric figure-of-merit Z [6]:

$$Z = \frac{\alpha^2}{\rho \lambda} \quad [\mathrm{K}^{-1}] \tag{3}$$

In the case of thermoelectric generators a simplified version of Z, *i.e.*, power factor W, is used:

$$W = \frac{\alpha^2}{\rho} \quad \left[\frac{\mathrm{W}}{\mathrm{K}^2\mathrm{m}}\right] \tag{4}$$

Thick-film thermocouples based on metallic composites were fabricated and widely described by the authors [6–8]. Such structures are able to generate about 7.5 μW of electrical output power for a single thermoelectric junction (when $\Delta T =$ = 100 K) and can also be easily miniaturized [9]. The main problem is insufficient level of generated output voltage – 2.25 mV (α = 22.5 μV/K). On the other hand, in order to supply modern low-power electronic microdevices voltage E ranging from 1 to 1.2 V and at least P ranging from 10 to 50 μW are required. As can be easily calculated to provide appropriate level of voltage about 500 thermocouples should be connected together ($\Delta T = 100$ K). 22.5 μV/K is also often not enough to construct sensible sensors.

Semiconductors (*e.g.*, germanium) are characterized by high electrical resistivity but, at the same time, high α. They are frequently used for construction of sensors based on thermoelectric effect. In this work, we tried to connect advantages of semiconductor-based thermocouples and metal-based ones. As a result, we expect to obtain a thermocouple both with high Seebeck coefficient (that provides high level of generator output voltage) and low internal resistance (that provides appropriate level of electrical output power). Using such thermocouples efficient microgenerators and sensible sensors can be constructed.

2. Test sample fabrication

A series of mixed thick/thin-film thermopiles were fabricated, where one of the arms of the thermocouples was screen-printed using metal-based composites and the second was made of magnetron sputtered semiconductor, (thick-film metallic layers are cheaper than thin film ones). LTCC (low temperature cofired ceramic – tape DP951 from DuPont) were used as substrates. Two circular (28 mm in diameter) or rectangular (30×25 mm^2) LTCC green tapes were put together, laminated and fired to fabricate a single substrate (~280 μm thick). After this the thick-film tracks were screen-printed through 325 mesh stainless screen. PdAg or Ag-based inks were used to provide good electrical parameters. The masks for screen-printing are shown in Fig. 2. Tracks on circular substrates had 200 μm in width and 7 mm in length, on rectangular ones – 200 μm and 23 mm, respectively. Next structures were fired at 850 °C for 1 hour.

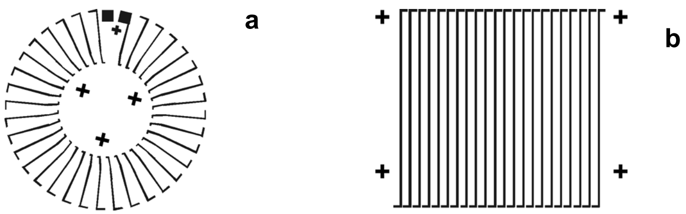


Fig. 2. Masks for screen-printing of PdAg- and Ag-based arms: circular structure (**a**), rectangular structure (**b**).

Six different semiconductive thermoelectric compositions based on germanium, marked AG (Ge:Au), TAG (Ge:Au:Ta), VAG (Ge:Au:V), HAG (Ge:Au:Hf), TSG (Ge:Sb:Te) and WSG (Ge:Sb:W) were used. Thin-film thermocouples arms were made by magnetron cosputtering (through metal mask – Figs. 3**a** and 3**b**). To minimize the resistance of the structures the width of semiconductive tracks was increased – it had 500 μm for rectangular thermopiles and from 500 μm (near the centre of the substrate) to 1000 μm (near the edge) for circular ones. The sputtering process was

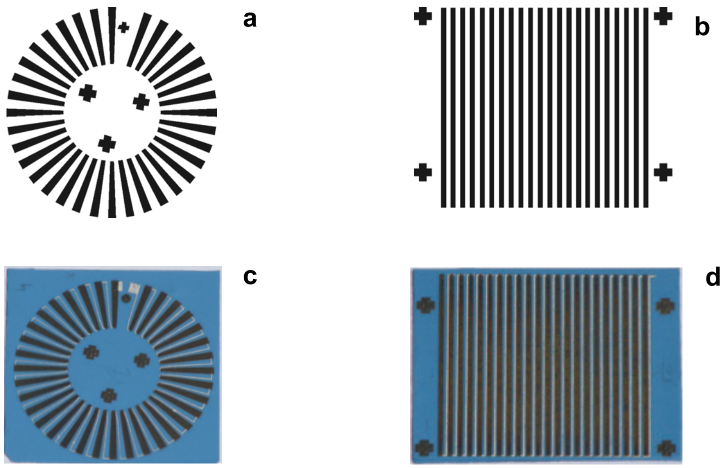


Fig. 3. Masks for magnetron sputtering of germanium-based arms: circular structure (**a**), rectangular structure (**b**). Examples of mixed thermopile on LTCC substrate: circular structure (**c**), rectangular structure (**d**).

performed using a WKM-100 magnetron system (100 mm in diameter) and Dora Power System unit working in unipolar pulse mode (165 kHz). The temperature of the substrate was in the range 300–340 °C. Sputtering times (in argon atmosphere from $3 \cdot 10^{-2}$ to $5 \cdot 10^{-2}$ Pa) were from 40 to 60 minutes and deposition speed – about 170–200 Å per minute. Examples of circular and rectangular thermopiles consisting of 35 and 22 thermocouples, respectively, are shown in Figs. 3**c** and 3**d**.

3. Results

The profilograms of sample structure (Ge:Au) are presented in Fig. 4. The thickness of the semiconductive, magnetron sputtered AG layer is about 3 μm (all fabricated semiconductive tracks were 0.6–3 μm thick – these differences were caused by different cosputtering process times). Metal-based layers were much thicker – from 10 to 20 μm depending on the ink used (Ag-based composites formed thicker layer than PdAd-based ones).

Fabrication of thicker tracks was purposeful as it causes a decrease of the structure internal resistance and, according to Eq. (2), an increase of generated output power level. It is important in the case of microgenerator construction, where very high resistivity of semiconductive tracks is a serious problem. The thicknesses and phase compositions (specified by X-ray diffraction technique) of selected semiconductive tracks are presented in Tab. 1.

The semiconductive materials have poor thermoelectric properties directly after sputtering process. Their internal structure is disordered, which causes small Seebeck

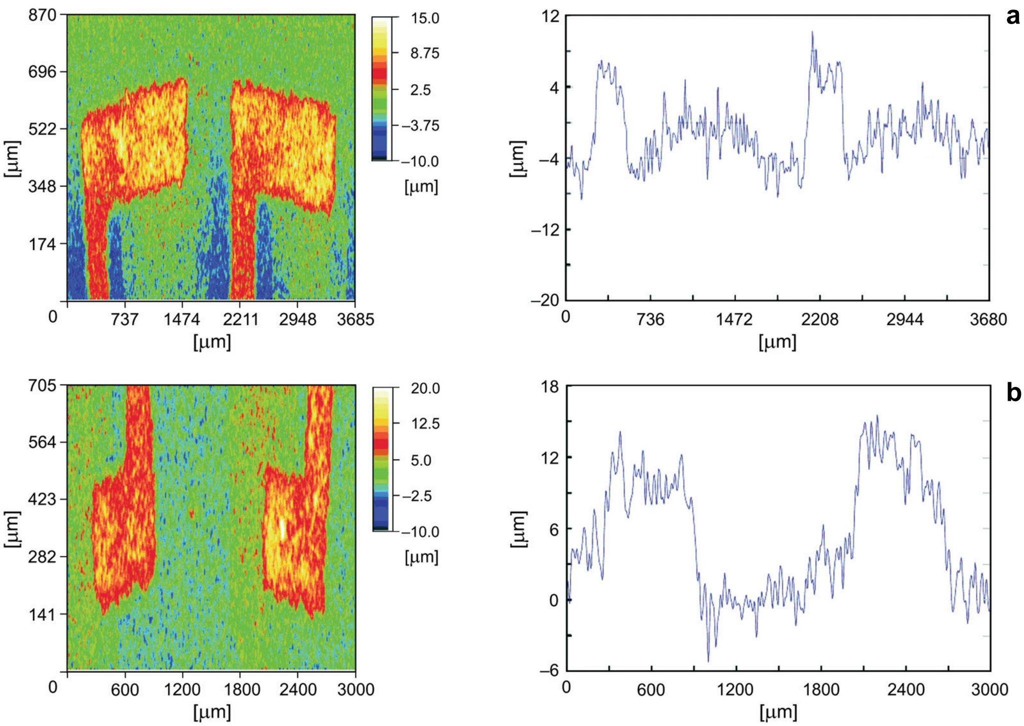


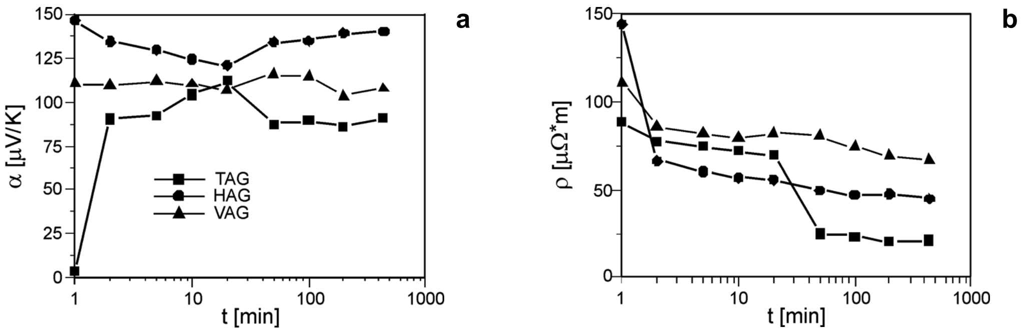
Fig. 4. Profilograms of circular PdAg/AG thermopile on LTCC substrate: cold junction near the edge of the substrate (**a**), hot junction near the centre of the substrate (**b**).

T a b l e 1. Thickness and phase composition of selected semiconductive tracks.

Material	Phase composition			Thickness
WSG	Ge: 93 at.%,	Sb: 2.5 at.%,	W: 4.5 at.%	3 µm
TSG	Ge: 85.5 at.%,	Sb: 2.5 at.%,	Ta: 12 at.%	3 µm
VAG	Ge: 89.7 at.%,	Au: 7.8 at.%,	V: 2.5 at.%	0.9 µm
HAG	Ge: 88.6 at.%,	Au: 8.2 at.%,	Hf: 3.2 at.%	0.7 µm

coefficient and high resistivity. Proper activation process is required to improve thermoelectric parameters – structure should be put into high temperature to initialize recrystallization and grain growth process. The influence of activation time (at 600 °C) on thermoelectric parameters is presented in Fig. 5. The measurements of Seebeck coefficient and electrical resistivity were made at a temperature of 180 °C, power factor W was calculated according to Eq. (4).

As can be seen, a noticeable improvement of α and ρ starts after 50 min. Activation process seems to have the largest influence on TAG tracks. Power factor W for this



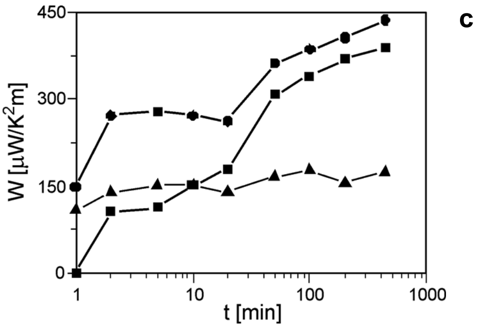
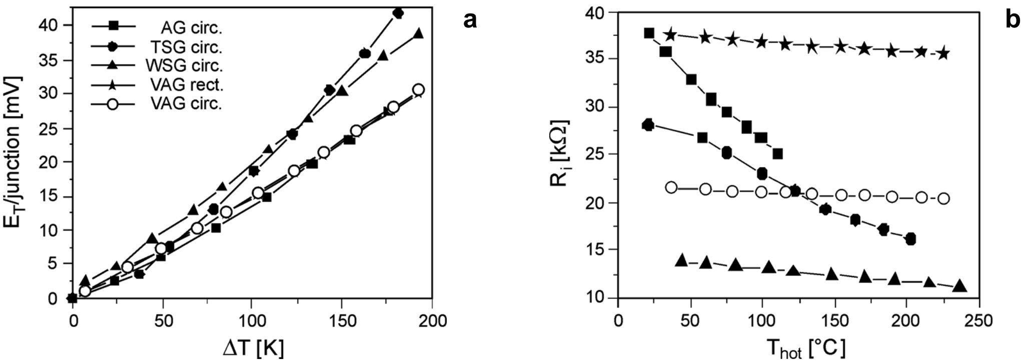


Fig. 5. Influence of activation time at 600 °C on thermoelectric parameters (measurements at the temperature of "hot" ends about 180 °C for three different semiconductive materials): Seebeck coefficient (**a**), resistivity (**b**), power factor (**c**).



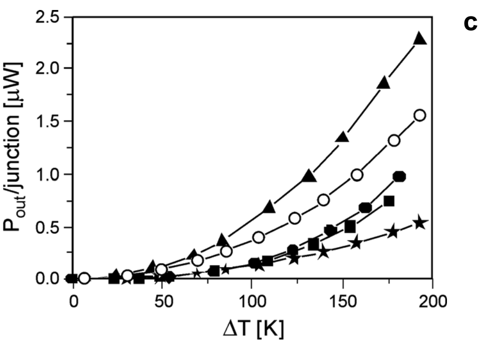


Fig. 6. Electrical and thermoelectric properties of mixed thermopiles: output electrical power E_T per single junction as a function of temperature difference (**a**), resistance of thermopile as a function of hot junction temperature (**b**), output power P_{out} per single junction as a function of temperature difference (**c**).

material is increased 3 times after 1 hour activation. Seebeck coefficient is increased at the beginning, but then decreased by about 25 μV/K (to the level just before activation) when resistivity decreased. In the case of HAG and VAG compositions α is increased and ρ is decreased after 50 min. But for VAG the changes are smaller. Based on the above observations one hour activation process was applied for fabricated thermopiles.

Characteristics of the electrical and thermoelectrical properties of examples of mixed (thick/thin-film) thermopiles are given in Fig. 6. AG, TSG, WSG and VAG thermopiles, fabricated on circular substrates have been chosen. Also, one structure on rectangular LTCC is presented to show the differences in output parameters. As can be seen all structures have high thermoelectric power E_T, however at the same time also high internal resistance.

The best parameters, as far as microgenerators are considered, were observed for Ag/WSG thermopile. The output voltage generated by a single thermocouple was 20 mV for 100 K temperature difference. The output power was 0.55 μW at the same time. As can be easily calculated only 50 thermocouples are required to achieve a useful level of output voltage (1 V). They can supply nearly 30 μW of electrical power.

Thermocouples based on TSG and WSG seem to be best for the construction of sensors. But also AG, VAG and HAG have Seebeck coefficients at a suitable level and can be used in practice.

Thermoelectric parameters of all fabricated structures are summarized in Tab. 2. Values measured when the temperature of "hot" ends was 180 °C are shown. Also, the output voltage and output electrical power generated by thermopiles are given – PdAg (for AG, TSG, WSG) or Ag (for VAG, HAG) thick-film inks were used for the second arm.

T a b l e 2. Thermoelectric and electric parameters of all fabricated structures (temperature of "hot" ends – 180°C); output voltage E_T and output electrical power P_{out} generated by whole thermopiles (C – circular substrate, R – rectangular substrate).

Thermopile	AG	TAG	VAG	HAG	TSG	WSG
Shape	C	C	C / R	C / R	C	C
Number of junctions	35	—	35 / 22	35 / 22	35	35
α [μV/K] (thin-film layer)	155	90	150	140	220	200
ρ [μΩm] (thin-film layer)	195	25	70	50	130	90
W [μW/K^{2}m] (thin-film layer)	123	324	321	392	372	444
E_T [V] (whole thermop. ΔT = 100 K)	0.48	—	0.52 / 0.33	0.49 / 0.31	0.66	0.7
P_{out} [μW] (whole thermop. ΔT = 100 K)	5.2	—	13 / 3.1	10.3 / 1.4	5.6	19.6

4. Laser power sensor

TSG/PdAg-based structures were used to prepare a prototype of laser power sensor. A thermopile was located on radiator in such a way that the edge of the substrate (with "cold" thermoelectric junctions) was in good thermal contact with the radiator, while the centre of the substrate (with "hot" thermoelectric junctions) was hanged in air (Fig. 7). Cold water circulation inside the radiator ensures stable temperature of "cold" junctions when the laser beam heats the centre of the substrate. As a result, thermoelectric force E_T appears between the thermoelectric junctions. The level of E_T is proportional to the power of the laser beam investigated. The sensitivity of TSG/PdAg thermopile (consisting of 35 thermocouples) is about 5 mV/K.

The prototype of laser power sensor was tested using Aurel NAVS-30 laser system. This system enables regulation of the laser beam power by changing activation current I [A]. The smallest possible change of I (0.1 A) causes the rising (or falling) of output signal generated by the sensor by about 2.5 mV.

In Figure 8, E_T generated by thermopile versus time is presented (for 4 different activation currents I). There are distinct differences between generated output signals

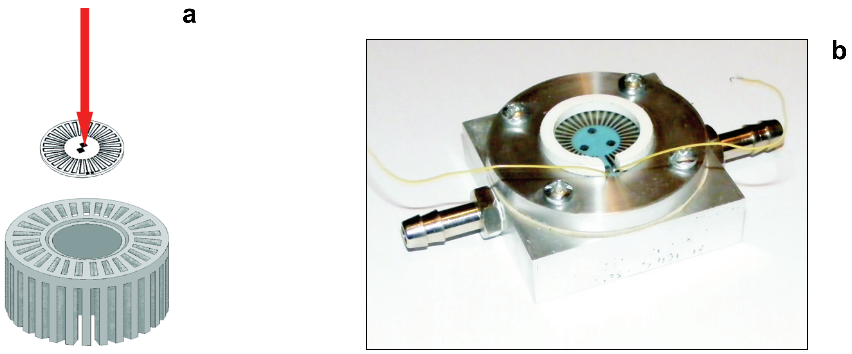


Fig. 7. Laser power sensor: location of thermopile on the radiator (**a**), sensor module (**b**).

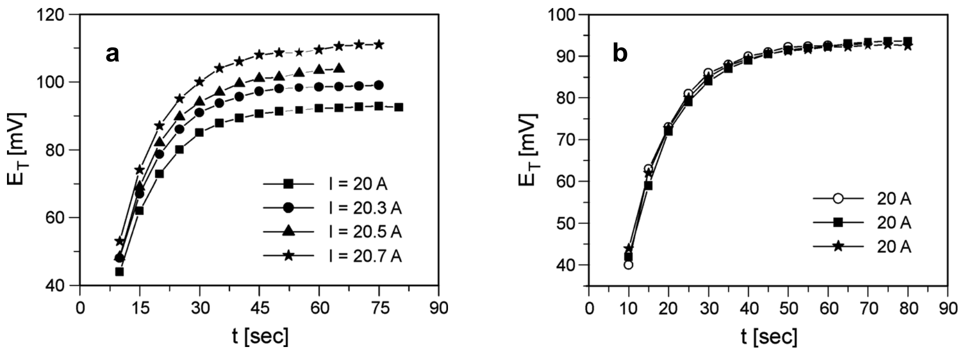


Fig. 8. Voltage response of laser power sensor to activation: different power of radiation (**a**); the same power of radiation (**b**).

depending on *I* level (Fig. 8**a**). This proves that sensor resolution is appropriate for this laser system. Also, the repeatability of measurements is very good (Fig. 8**b** – multiple tests gave similar results).

The auto-correction of a small displacement of structure (or imprecise placement) is an important advantage of the sensor module presented. If laser beam hits exactly the centre of thermopile, all thermocouples generate the same level of E_T, and the whole thermopile – nE_T. But even a small displacement of beam causes that the levels are different. The circular shape of the fabricated thermopile and linearity of the characteristics of the thermocouples (temperature differences between "cold" and "hot" junctions is lower than 50 °C, so characteristic are nearly-linear) causes that the total output signal is still nE_T.

5. Summary

Mixed thick/thin-film thermopiles have high Seebeck coefficient, much higher than metal-based ones – it exceeds 200 μV/K. Thanks to this the construction of generators and sensors with high output voltage level is quite easy. On the other hand, the resistivities of deposited layers are still high and should be decreased to improve generated output power. 30 μW provided by 50 thermocouples (when $\Delta T = 100$ K) is enough to supply some low-power devices, but should be increased to widen the application range of such structures. The influence of different dopes on Seebeck coefficient and electrical resistivity has been presented in this paper.

Tests of prototype structures showed that thermoelectric sensors have sufficient resolution and ensure very good repeatability of measurements.

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