Thermoelectric Peltier micromodules processed by thin-film technology

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Abstract. In this paper we consider the structure and manufacturing technology of thermoelectric Peltier micromodule consisting of 288 thermocouples enclosed between two silicon wafers. Method for obtaining thermoelements i.e. the method of electrochemical deposition from an electrolyte solution, has been proposed. Elemental and structural analysis of the obtained semiconductor thermoelements of bismuth telluride and antimony telluride has been carried out. The obtained composition is 39.5% Bi-60.5% Te for Bi₂Te₃ and 39% Sb-61% Te for Sb₂Te₃.

1. Introduction
A large number of studies have been focused on research and development of micro capacity devices with low power and high output voltage to replace bulky batteries with a limited lifetime. Among the available power sources there has recently been much interest for thermal-to-electrical energy conversion, i.e., thermoelectric power generation, due to its attractive characteristics such as no moving parts, long lifetime and high reliability for low-power applications. Continuous complication and miniaturization of opto-, radio- and microelectronic elements along with the increase in device performance leads to rise in operating temperature which contributes to active development of cooling systems for electronic devices [1]. Thermoelectric Peltier thin-film micromodules can be used either for power generation or for cooling microelectronic devices, as well as for effective heat removal from electronics components, since they have high refrigeration power depending on the number of thermocouples in the module with a small device size [2-4].

2. Micromodule structure
The proposed thin-film Peltier micromodule consists of 288 thermocouples (576 thermoelements) and contact layers formed between two silicon wafers. Each of the pairs consists of an element of bismuth telluride (n-type conductivity) and antimony telluride (p-type). All semiconductor thermoelements are connected sequentially. Tin is used as an intermediate layer for joining wafers. The micromodule is mounted onto a printed circuit board with an aluminum base, and a radiator is mounted on the top of the micromodule. Figure 1 shows the device diagram (left) and the general view (right).
Figure 1. Thermoelectric Peltier micromodule structure [5].

3. Thermoelectric module manufacturing process

In order to make bottom substrate with thermoelements, 0.03-μm-thick Cr and 1-μm-thick Cu were sequentially sputtered on silicon wafer with dielectric oxide layer, as shown in Figure 2, a. After that, lift-off photolithography with 1-μm-thick Ti was used to form bottom electrodes, that was also used as a seed layer for further electrochemical deposition (Figure 2, b). AZ P 4620 photoresist of 28-30 μm thickness was used to form mask for thermoelectric elements deposition in developed holes (Figure 2, c). Bismuth telluride Bi$_2$Te$_3$ was deposited from nitric acid aqueous solution consisting of 1 M HNO$_3$, 9 mM Te, 7 mM Bi at constant current density of 5.3 mA/cm$^2$ until it reached 25 μm thickness (approx. 2.5 hours), as shown in Figure 2, d. After that, photoresist was removed and then applied over again to form a mask for antimony telluride deposition (Figure 2, e, f). Antimony telluride was also deposited in nitric acid aqueous solution, consisting of 1 M HNO$_3$, 0.1 M C$_4$H$_6$O$_6$, 7 mM Te, 12.5 mM Sb and 60 mg/l of sodium lignosulfonate at the same current density for a same deposition time (Figure 2, g). Then, mechanical polishing was done to obtain smooth and flat surface of thermoelements. Metallization etching was conducted to form bottom Ti-covered electrodes. After that, 3-μm-thick Sn bump was formed on top of each thermoelement by magnetron sputtering and lift-off photolithography for further assembly.

Top substrate was produced by using same technics of sputtering, photolithography and etching to form Ti-covered electrodes with Sn bumps on top of them. Top substrate was then flip-chip bonded to a bottom substrate with a maximum force of 5 kN for 15 minutes and cooled down under applied external pressure of 500 N.

Assembled thermomodule was then mounted on a PCB with an aluminum base using Epo-tek thermocative glue. To make an electric contact, conductive wires were bonded on the electrodes of thermomodule and PCB. After that, aluminum radiator was mounted on the top of thermomodule using thermopaste to obtain good thermal contact (Figure 3).
Figure 2 (a – j). Thermoelectric Peltier micromodule fabrication process: (a) sputtering of Cr/Cu metallization; (b) formation of Ti electrodes; (c) photoresist patterning; (d) electrochemical deposition of Bi$_2$Te$_3$; (e) photoresist removing; (f) photoresist patterning; (g) electrochemical deposition of Sb$_2$Te$_3$; (h) mechanical polishing and photoresist removing; (i) metallization etching; (j) Sn bumps patterning.

Figure 3 (a, b). Assembled thermoelectric Peltier thin-film micromodule: (a) mounted on a PCB without radiator; (b) final assembly.
A key feature of the proposed technological process is the formation of semiconductor functional layers by the method of electrochemical deposition, which significantly increases the overall manufacturability of the product in comparison with bit-by-bit assembly, allows the composition of precipitated compounds to vary easily and in a wide range, changing the composition of the electrolyte, contributes to increase of thermocouple density on a unit of area, which increases the efficiency of the thermal module.

4. Results
Analysis of the images obtained with an electron microscope showed that the resulting thermoelements have a close-packed structure with crystal sizes ranging from 4 μm (bismuth telluride) to 10 μm (antimony telluride), as illustrated in Figure 4.

![Figure 4](image_url)

**Figure 4 (a, b).** Electrodeposited bismuth telluride and antimony telluride: (a) general view; (b) thermoelements prior to planarization.

Elemental composition of the compounds is close to the given stoichiometric and constitutes 39.5% Bi-60.5% Te for Bi₂Te₃ and 39% Sb-61% Te for Sb₂Te₃ (Figure 5).

![Figure 5](image_url)

**Figure 5(a, b).** Ratio of components in deposited thermoelements, obtained by energy-dispersive X-ray spectroscopy: (a) bismuth telluride; (b) antimony telluride.

Testing of manufactured generator samples was carried out with a temperature differences from 25 to 100K, as it shown in Figure 6. The values of the external load ranged from 10 Ohm to 10 kOhm. During the experiment, the output voltage was measured on the load; the output power and current were calculated. The voltage-current characteristics and the dependence of the output power on the current for various temperature differences of the generator sides were prepared. It has been shown that the range of power is from 3 μW to 56 μW while the temperature difference is mentioned above.
Figure 6 (a, b). Measured characteristics of thin-film Peltier micromodule: (a) current-voltage characteristics; (b) current-power characteristics.

5. Conclusion

Microminiature Peltier thermomodules, manufactured according to thin-film technology, have a number of advantages that distinguish them from analogs manufactured with the help of bit-by-bit assembly, namely: miniaturization and wide integration possibilities. In this paper a design and a description of the manufacturing process of microminiature Peltier thermomodule using the electrochemical deposition of functional semiconductor layers were presented, the results of the surface morphology analysis and the elemental composition of the obtained compounds, measured characteristics of assembled micromodule were shown.

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