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Revision Report 3 on

Fabrication and evaluation of a thermoelectric micro-device on a free-standing substrate

by Jun-ichiro Kurosaki et al.

I would first like to thank the reviewer for his/her effort. My detailed responses are as follows:

Comment: The English language requires minor improvements.
Response: We improved our English writing as you advice.

Fabrication and evaluation of a thermoelectric micro-device on a free-standing substrate

J. Kurosaki, A. Yamamoto, S. Tanaka, J. Cannon, K. Miyazaki, H. Tsukamoto

Abstract

Using shadow masks prepared by standard micro-fabrication processes, we fabricated in-plane thermoelectric micro-devices (4 mm × 4 mm) made of bismuth telluride thin films, and evaluated their performance. We used $Bi_{0.4}Te_{3.0}Sb_{1.6}$ as the p-type semiconductor, and $Bi_{2.0}Te_{2.7}Se_{0.3}$ as the n-type semiconductor. We deposited p- and n-type thermoelectric thin films on a free-standing thin film of Si_3N_4 (4 mm ×4 mm × 4 μm) on a Si wafer, and measured the output voltages of the micro-devices while heating at the bottom of the Si substrate. The maximum output voltage of the thermoelectric device was 48 mV at 373K.

Keyword: Thermoelectricity; MEMS; Micro-device; Bismuth telluride; Waste heat recovery

INTRODUCTION

Recently, energy harvesting has been proposed as a promising method of supplying electric power for autonomous sensor network devices and mobile electrical instruments[1]. The basis of energy harvesting is to gain electric power from unused environmental energy such as heat, light and vibration. For example, it is already in use in some cases in solar-power generation, wind turbine electricity, electrets[2], etc. The micro-generator for energy harvesting is more useful than those of transmissions or batteries[3]. Previously, such generation systems have not been considered to be important in small devices, because those systems are insufficient for power generation. However, they became realizable by a drastic decrease of power consumption of electronic components due to advances in storage of electric power, miniaturization and optimization[4]. Thermoelectric devices have advantages in energy harvesting because they can convert thermal energy into electric energy without any moving parts and fuel. In addition they can generate power from low temperature heat sources[5-7]. The performance of thermoelectric generators was low due to their physical properties; however, improvement of thermoelectric performance with constructed nano-structures have been proposed[8, 9], and it has already been possible to successfully realize these structures[10-14]. Thus, we fabricated an in-plane thermoelectric micro-devices based thin film[15-17] in order to further develop the thermoelectric micro-devices. We chose a thin film method, because it is easily miniaturized and the reported nano-structured thermoelectric devices are based on thin films. Most in-plane type thermoelectric devices are made of silicon germanium[16-18], but the thermoelectric efficiency of silicon germanium becomes important around 1,000 K and is lower at room temperature[5-8]. In this study, we used bismuth telluride ($Bi_{2.0}Te_{2.7}Se_{0.3}$ and $Bi_{0.4}Te_{3.0}Sb_{1.6}$) because they have highest thermoelectric properties at room temperature. Bismuth telluride based thin films can not be applied in wet-processes due to their weak structure[19, 20], so we therefore fabricated the patterned bismuth telluride based thin film by using the flash evaporation method through shadow masks[21]. The shadow masks can be fabricated by using micro-fabrication processes. The overall size of the fabricated thin film devices is 4 mm by 4 mm. We fabricated a free-standing substrate in order to obtain a temperature difference between cool and hot junctions of the thermoelectric devices. The free-standing substrate was fabricated by micro-fabrication techniques, and contains a free-standing thin film of 4 μm in thickness, allowing the structure to obtain a temperature difference in its planar direction. Thus, we can obtain appreciable temperature differences between the hot and the cool junctions of thermocouples deposited on these free-standing substrates as shown in Fig. 1. By heating the bottom of the substrate we were able to measure the output voltage. The measured output voltages were evaluated by estimating the temperature distribution and by using the measured Seebeck coefficient.

EXPERIMENT

Many processes for composite thin films have been attempted, such as flash evaporation, MBE[22, 23], MOCVD[24-26], PLD[27, 28], electro-deposition[29, 30], and inkjet printing[31]. We used the flash evaporation method because this method allows us to deposit alloys whilst keeping their composition. We deposited both p- and n-type bismuth telluride based thin films by the flash evaporation method. Our flash evaporation equipment contains a powder vessel with a guide, a tungsten boat for evaporation and a substrate holder in a vacuum chamber[32-35]. The distance between the tungsten boat and the substrate is 30 mm. The tungsten boat contains a slight pocket (50 mm length, 10 mm width, and 2 mm in depth) to prevent the powders from spilling out from the boat. The guide is made from stainless steel and is covered with a Teflon thin film to help the powders to pass smoothly through the tungsten boat. For the flash evaporation, we prepared fine powders of $Bi_{0.4}Te_{3.0}Sb_{1.6}$ (p-type) and $Bi_{2.0}Te_{2.7}Se_{0.3}$ (n-type), and then loaded 5 g of this powder in the vessel, and place the substrate on the holder. The chamber is evacuated to 1.4×10^{-3} Pa. A current of 80 A is then applied, and by gradually tilting the powder vessel, the powders are fed to the heated tungsten boat. In our previous study, the Seebeck coefficients of the deposited bismuth telluride based thin film were 170 μV/K[34] for the p-type and -90 μV/K[35] for the n-type without an annealing process.

We fabricated shadow masks to evaporate the materials with their patterns. The shadow masks are fabricated by using standard micro-fabrication processes as shown in Fig. 2. We prepared a silicon wafer and deposited a silicon nitride thin film on the silicon wafer by plasma enhanced chemical vapor deposition (PECVD). For patterning the configurations of each shadow mask, we spun on photoresists on the silicon nitride thin film, and the photoresists were removed in our arbitrary pattern by exposing in ultraviolet light and developing them. The silicon nitride thin films were etched in the desired patterns using reactive ion etching (RIE). Finally, the remaining silicon in the patterns was etched by soaking in KOH. Each of the fabricated shadow masks have patterns which are appropriate for their respective p/n-type of bismuth telluride and copper electrodes. The materials were deposited through each of the corresponding shadow masks.

We fabricated a substrate which has a free-standing thin film of silicon nitride. The substrate is constructed with a free-standing silicon nitride based thin film on the outside and another silicon wafer sandwiched in between, as shown in Fig. 1. The silicon nitride based thin film has a very small cross-sectional area, so it has a large thermal resistance. Therefore, if we heat at the bottom of the substrate, the thermal conduction will run through the silicon nitride based thin film from the silicon, with the result that a temperature distribution is obtained in the free-standing thin film. The substrate is fabricated by micro-fabrication processes. The processes for fabrication of the substrate are almost the same as the shadow masks as shown in Fig. 2, but in the case of the substrate, unlike the shadow masks, we can fabricate the free-standing thin film by etching the silicon nitride thin film on just one surface. The dimensions of the fabricated substrate are 4 mm (length) × 4 mm (width) × 4 μm (thickness).

The samples of the thermoelectric micro-devices were fabricated on the free-standing substrate by using the three shadow masks (for the p- and n-type thin films and their junctions). The dimensions of the p- and n-type legs are 0.5-1.2 mm (length) × 0.2 mm (width) × 1.0 μm (thickness) and the spacing between the legs is 0.2 mm. Their overall size is 4 mm × 4 mm, and 1.0 μm thick, consisting of 16 (or 8) p/n couples. Figure 3 shows a photo of the samples. We measured the output voltages of the samples to verify the thermoelectric performance while heating at the bottom of the substrate (Fig. 4). The temperature difference between the center and outside in the free-standing substrate was measured by a radiation thermometer (at the center) and a thermocouple (on the outside). We calculated the temperature distribution of the free-standing Si_3N_4 thin film by using commercial software (ANSYS CFX 11.0) to estimate the output voltage. We did not take into account the effects of the thermal conduction through the bismuth telluride based thin film on the performance of the micro-devices, because the thermoelectric thin films are very thin. We apply a constant temperature (373 K) to the bottom of the substrate and a constant heat transfer coefficient on the surface at 16 $W/(m^2 \cdot K)$ as a forced-convection cooling for the boundary conditions. We roughly assumed 300 μV/K thermoelectric power per one p/n pair, based on our past experiences[34, 35].

RESULTS AND DISCUSSION

We measured the output voltages of the samples on the free-standing substrate at room temperature while heating at the bottom of the substrate as shown in Fig.5. The maximum output voltage was 48 mV at a temperature difference of 13 K. The measured 48 mV corresponds to 16 nW electric power, because the electrical resistance of the fabricated micro-device was 72 kΩ. Takashiri et al. describe how annealing in hydrogen improves the Seebeck coefficient of bismuth telluride based thin films to 254.4 μV/K (p-type) and -179.3 μV/K (n-type)[20, 35]. The output power of the micro-device can be improved by annealing processes at the present stage. The numerically calculated temperature distribution of the free-standing substrate is shown in Fig. 6. It is only at the edge of the free-standing thin film that a large temperature difference is observed, and therefore thermoelectric thin films are necessary only at the edge of the free-standing thin film for efficient in-plane thermoelectric devices. We calculated the output voltages of the device from the temperature distribution of the sample. The estimated output voltages are shown in Fig. 5 with experimental results. The calculation results agreed well with the experimental results.

CONCLUSIONS

We fabricated the in-plane thermoelectric micro-devices on a free-standing Si_3N_4 thin film. We deposited Bi_2Te_3 thin films by the flash evaporation method through the shadow masks, without any wet processes, due to mechanical weakness of the Bi_2Te_3 films. These films are peeled off from the substrate when we apply the wet etching processes to make micro-structures. The in-plane thermoelectric micro-devices consist of 16 p/n (or 8 p/n) couples of legs with copper electrodes. The dimensions of p- and n-type legs are 0.5-1.2 mm (length) × 0.2 mm (width) × 1.0 μm (thickness) and the spacing between the legs is 0.2 mm. We measured the output voltages of the devices while heating at the bottom of the substrate. The maximum output voltage was 48 mV at 373 K. The results showed that the fabricated devices can generate electricity just by being placed on a hot plate, and the free-standing substrate becomes a good thermal resistor. The micro-device is fabricated by as-grown films, and therefore the device performance will be improved by annealing processes after the device fabrication processes. The temperature distribution of the free-standing substrate without thermoelectric films was numerically calculated, and the output voltages of the device calculated from the temperature distribution agreed well with experimental results. The performance of the device can be evaluated from numerically calculated temperature distributions of the thin film.

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Figures

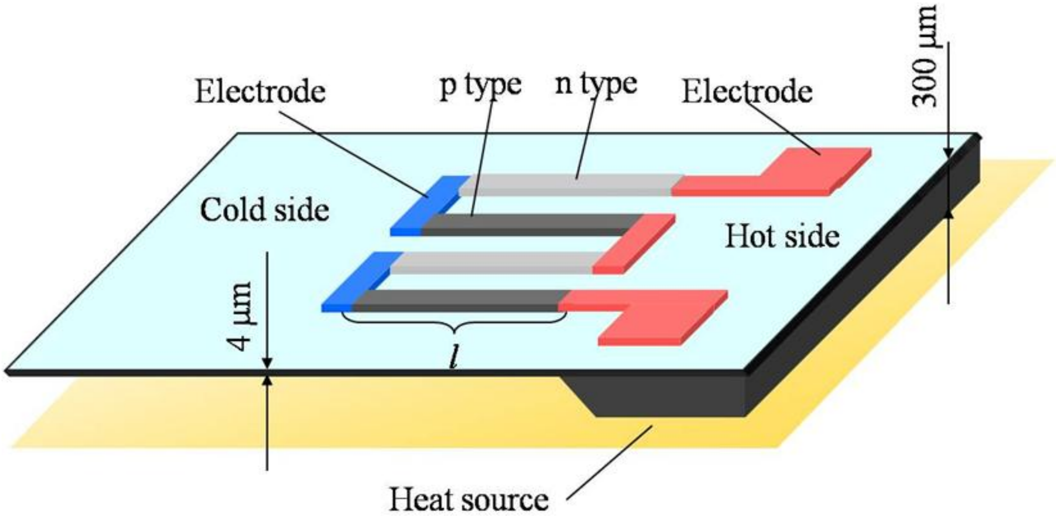

Fig. 1 Schematic of an in-plane thermoelectric micro-device

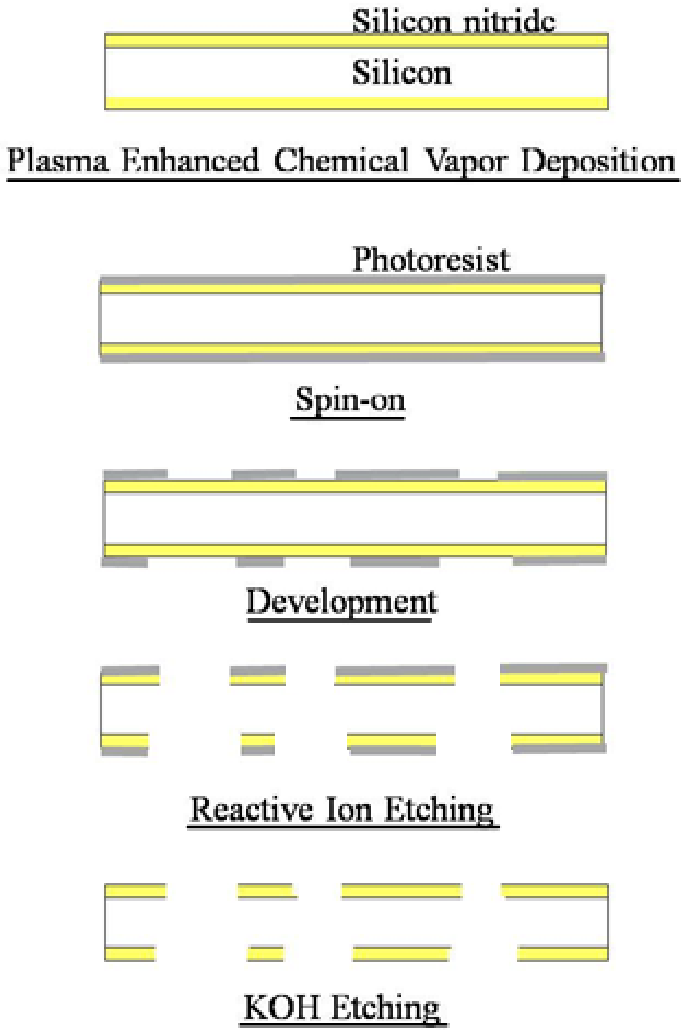

Fig. 2 Micro-fabrication processes for making a shadow mask of Si with Si_3N_4.

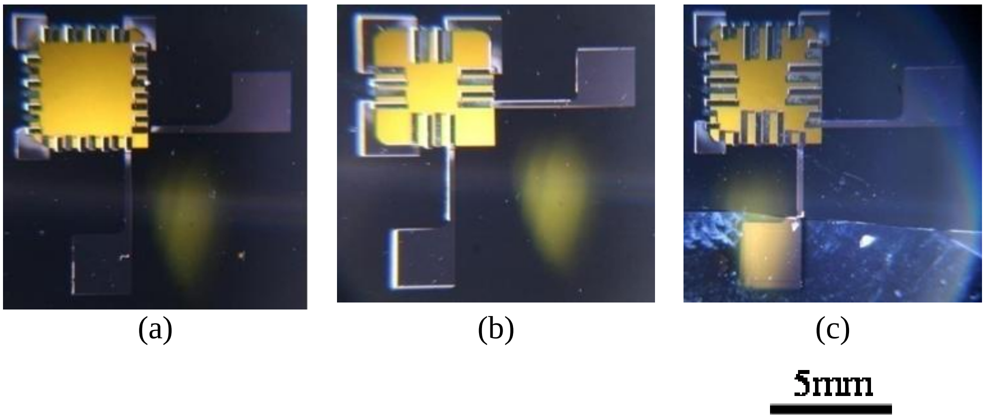

Fig. 3 Photo of fabricated thermoelectric micro-generators on a glass substrate with leg length: (a) 0.5 mm (16 p/n pairs), (b) 1.2 mm (8 p/n pairs), (c) 1.2 mm (8 p/n pairs) and 0.5 mm (8 p/n pairs).

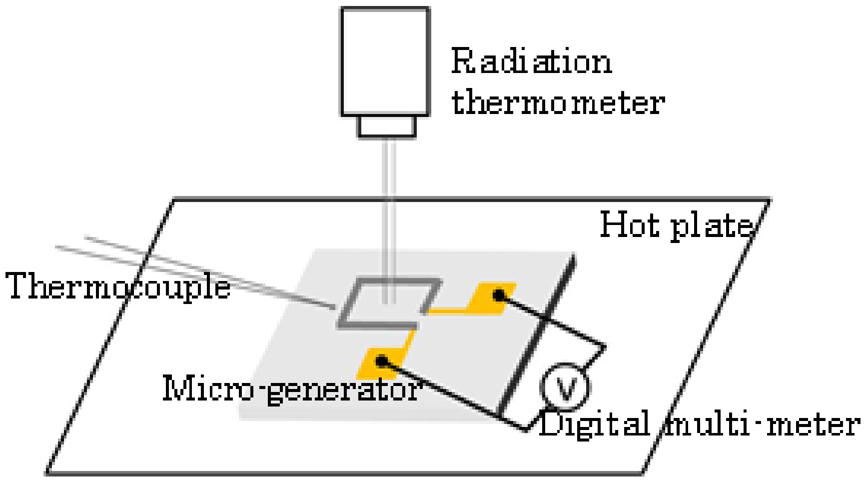

Fig. 4 Experimental setup for output voltage measurement of the micro-generators on a free-standing substrate

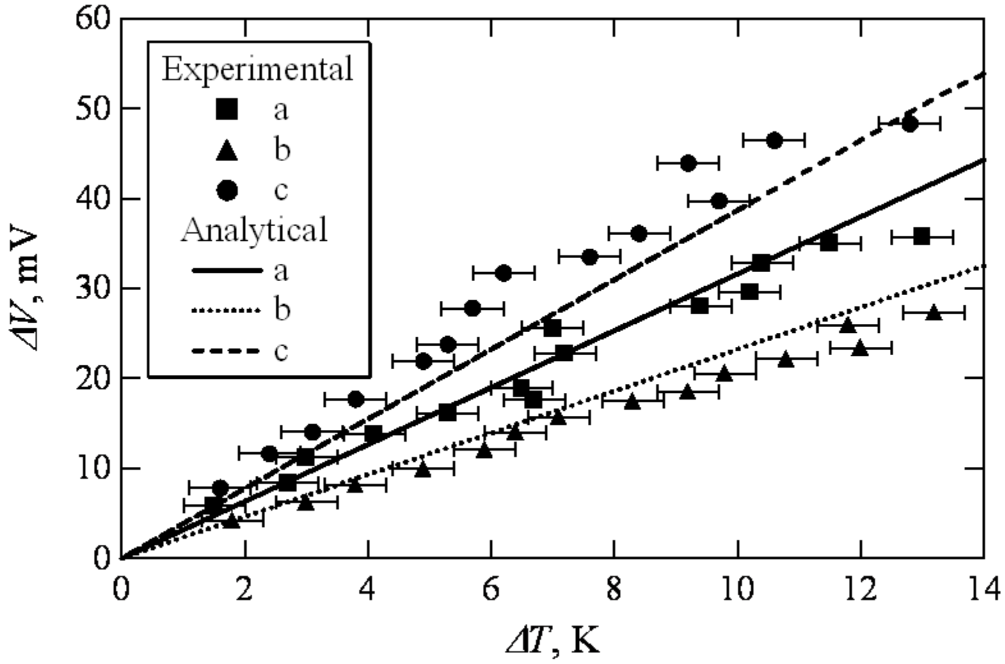

Fig. 5 Experimental results and calculated results for output voltages of micro-generators on a free-standing substrate, markers: experimental results, lines: calculated results.

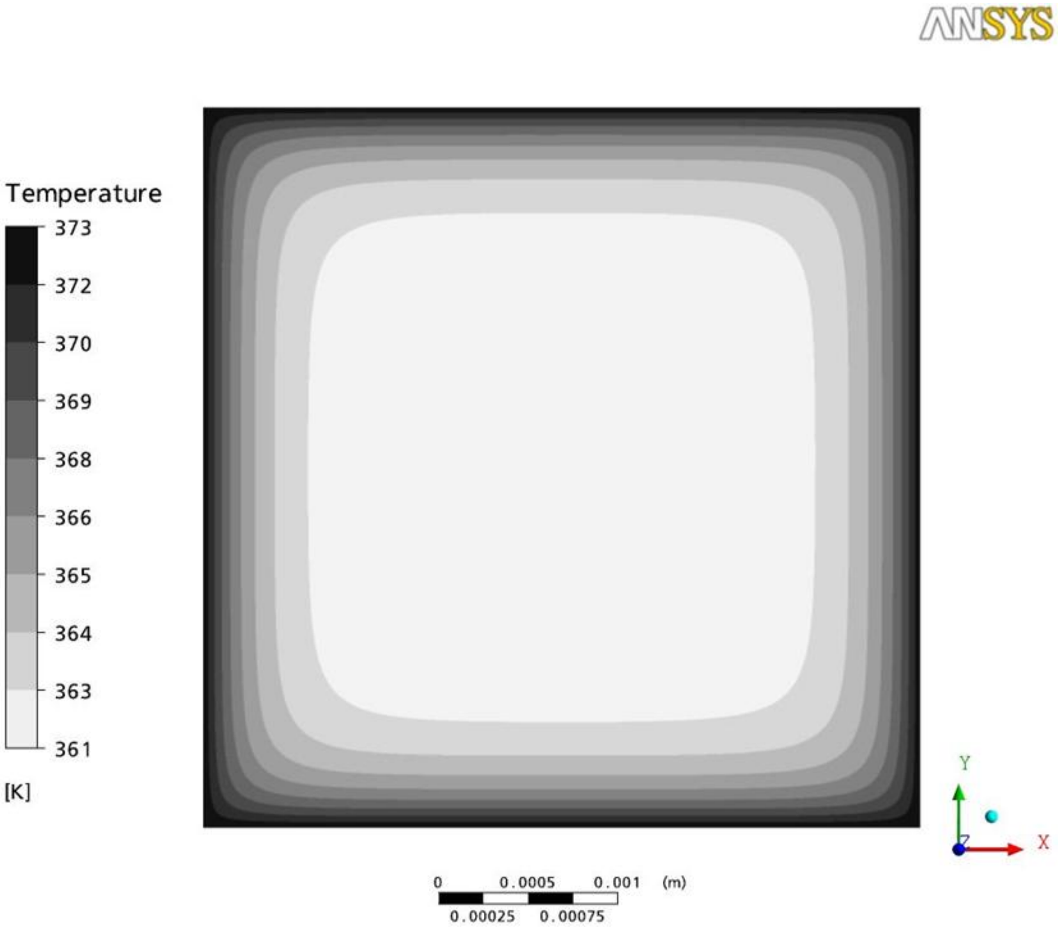

Fig. 6 Calculated temperature distribution of a free-standing thin film heated at 373K