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# Improvement of thermoelectric properties of screen-printed $Bi_2Te_3$ thick film by optimization of the annealing process

Ju Hyung We [a], Sun Jin Kim [a], Gyung Soo Kim [b], Byung Jin Cho [a,*]

[a] Department of Electrical Engineering, KAIST, 291 Daehak-Ro, Yuseong, Daejeon, Republic of Korea
[b] Phoenix Materials, 130 Gongdan-dong, Gumi-si, Gyeongsangbuk-do, Republic of Korea

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ABSTRACT

The thermoelectric properties of $Bi_2Te_3$ thick film prepared by a screen-printing technique are investigated to produce a low-cost thermoelectric power generator module. It is shown that thermoelectric properties of the screen-printed $Bi_2Te_3$ thick film can be greatly improved by optimizing annealing conditions. The printed $Bi_2Te_3$ thick film annealed at 500 °C for 15 min in Bi and Te powders ambient, achieves a power factor of 2.1 mW/m $K^2$ and a thermal conductivity of 1.0 W/m K. The ZT value is 0.61 at room temperature.



## 1. Introduction

Bismuth telluride and its alloys are widely used as a thermoelectric material for thermoelectric power generators and coolers that operate near room temperature. The dimensionless figure of merit (ZT) of the conventional bulk-type $Bi_2Te_3$ and its alloys is around 1.0 [1,2]. However, in the mid-1990s, developments in nano technology made significant improvements in thermoelectric efficiency. Several $Bi_2Te_3$ thin films made by co-evaporation [3], sputtering [4,5], and electrochemical deposition [6] were introduced with improved ZT values. The possibility of preparing devices with ZT values of 2.4 at room temperature was demonstrated on the p-type $Bi_2Te_3/Sb_2Te_3$ superlattice material [7].

However, thin-film thermoelectric devices with nanostructures still suffer from problems associated with the production such as long process time, high fabrication cost, and small temperature difference across the thin film, etc. On the other hand, the screen printing technique can overcome the production associated issues because the thermoelectric film can be fabricated in a much cheaper and faster way and the film is thick enough to induce a large temperature difference. It has already been demonstrated that the thermoelectric properties of ZnSb films prepared by the screen-printing technique are comparable to those of bulk ZnSb thermoelectric material [8,9].

In this paper, we present an experimental report on the thermoelectric properties of screen printed $Bi_2Te_3$ thick film. A detailed study on the effect of annealing after screen printing is also described.

## 2. Experimental details

The deposition of $Bi_2Te_3$ thermoelectric films using the screen-printing technique consists of several steps: paste synthesis, screen printing, leveling, drying, and annealing. The paste consists of Bi and Te powders, glass powder, binder, and solvent and their weight compositions are 75%, 2.4%, 2.3%, and 20.3%, respectively. The Bi and Te powders have 99.5% purity and the sizes of the two powder particles are smaller than 3 and 20 μm, respectively. The powder mixing ratio of Bi and Te was 35:65 in atomic percentage. The paste was 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 is to keep the paste's viscosity at a desired level. The solvent is used to mix the powder. The prepared $Bi_2Te_3$ paste was screen-printed on a $SiO_2$/Si wafer or an alumina substrate. The samples were dried at 120 °C for 15 min to remove the solvent. Three steps annealing in a furnace tube is then performed: binder removal step, solidification step, and high temperature annealing step. First, the binder removal step is done at 200 °C for 5 min to remove the organic binder and solvent from the paste. The solidification step is done at 400 °C in a $N_2$ ambient for 30 min for densification of the screen-printed film. Finally, the annealing step is conducted at a higher temperature in a $N_2$ ambient to achieve the best thermoelectric property of the film. Because the annealing step is the most critical process step which determines the Seebeck coefficient and electrical conductivity of the screen-printed film, various annealing conditions are investigated to find out the optimum annealing condition. The morphology of the screen-printed $Bi_2Te_3$ films was analyzed by field emission scanning electron microscope (FESEM, FEI, Sirion, operating voltage: 10 kV) and multi-purpose attachment X-ray diffractometer (MPA-XRD, RIGAKU, D/MAX-2500). The change of the mass of the screen-printed $Bi_2Te_3$ film during the annealing was analyzed by Thermogravimetry Analyzer (TGA, NETZSCH,

* Corresponding author. Tel.: +82 42 350 3485; fax: +82 42 350 8565.
E-mail address: bjcho@kaist.edu (B.J. Cho).

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TG209F3) with ramping rate of 10 °C/min. 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 whose temperature is kept at room temperature. From the measurement of the temperature difference and the output voltage of both sides of the sample at various temperature differences, 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 Keithley 2700 equipment simultaneously. The electrical conductivity was measured by the Hall-effect measurement system (Ecopia, HMS-3000).

## 3. Results and discussion

Fig. 1a and b show SEM images of the screen-printed $Bi_2Te_3$ film (a) before and (b) after annealing at 500 °C for 10 min in a $N_2$ ambient, respectively. The annealing was done in a reduced pressure of 110 mmHg. This pressure was selected experimentally to avoid both oxidation and excess evaporation of Te. When the pressure was close to 1 atm, the oxidation of the film happened. On the other hand, when the pressure was too low, an excess evaporation of Te was observed. The image of screen-printed $Bi_2Te_3$ film before annealing shows a bunch of particles with various sizes and shapes, while that after annealing shows rock-like clusters that are rounded and bonded together. The XRD analysis in Fig. 2 confirms that the particles in Fig. 1a are Bi and Te, and the clusters in Fig. 1b are $Bi_2Te_3$ compound. This result indicates that the high temperature annealing process is essential to turn a simple mixture of Bi and Te into the desired $Bi_2Te_3$ compound.

The dependence of the annealing temperature on the thermoelectric properties of the screen-printed $Bi_2Te_3$ film is shown in Fig. 3a and b. After the solidification step, the annealing temperature ramped up to 450–550 °C. Once the temperature reached to the set point, it immediately ramped down with no dwelling time at the top temperature. The results show that the electrical conductivity and the Seebeck coefficient of the screen-printed $Bi_2Te_3$ film are quite sensitive to the annealing temperature. The electrical conductivity ($\sigma$) reaches the maximum ($2.6 \times 10^4$ S/m) by 500 °C annealing, while the Seebeck coefficient ($S$) gradually increases with the annealing temperature, as shown in Fig. 3a. The negative number of Seebeck coefficient indicates that the screen-printed $Bi_2Te_3$ sample is n-type. The power factor ($S^2\sigma$) also reaches the maximum (0.48 mW/m $K^2$) by 500 °C annealing. However, this value is about 1 order of magnitude lower than that of the previous reported $Bi_2Te_3$ thin film by a co-evaporation method [3]. Such a low power factor of $Bi_2Te_3$ may be attributed to the deficiency of Te in $Bi_2Te_3$ film due to the evaporation of Te during annealing process, as the similar phenomenon is also found in Ref. [10–13]. Fig. 4 shows the change of the mass of the screen-printed $Bi_2Te_3$ film during annealing at different temperatures. The sample was analyzed under 760 mmHg in a $N_2$ ambient with ramping rate of 10 °C/min. The first drop of the mass observed at 150–200 °C is due to the evaporation of binder in the film. Once the binder is removed, the mass remains almost constant up to 450 °C. Beyond 450 °C, the mass starts to decrease rapidly, due to the evaporation of Te at high temperatures. Beyond 500 °C, the electrical conductivity decreases rapidly in Fig. 3a. Such a sudden degradation of the electrical conductivity after higher temperature annealing is believed to be due to the excess evaporation of metal powder which is evidenced in Fig. 4. Some research groups have successfully prepared $Bi_2Te_3$ films with a high thermoelectric power factor by controlling the substrate temperature and flux of reactants or

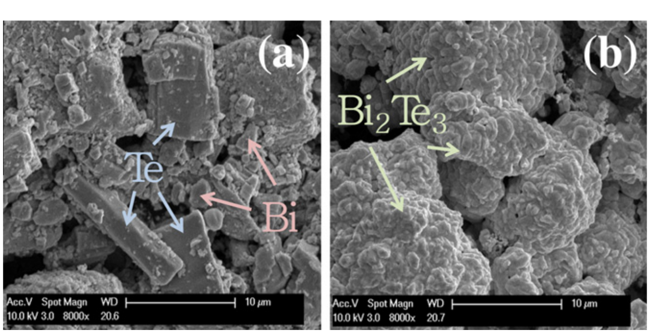


**Fig. 1.** SEM images of screen-printed $Bi_2Te_3$ film (a) before and (b) after annealing at 500 °C for 10 min in a $N_2$ ambient. The ramping rate of annealing process was 10 °C/min.

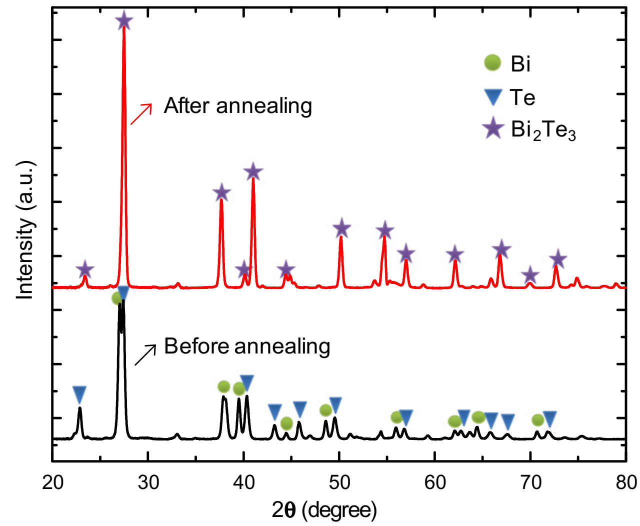


**Fig. 2.** X-ray diffraction patterns of the screen-printed $Bi_2Te_3$ film before and after annealing.

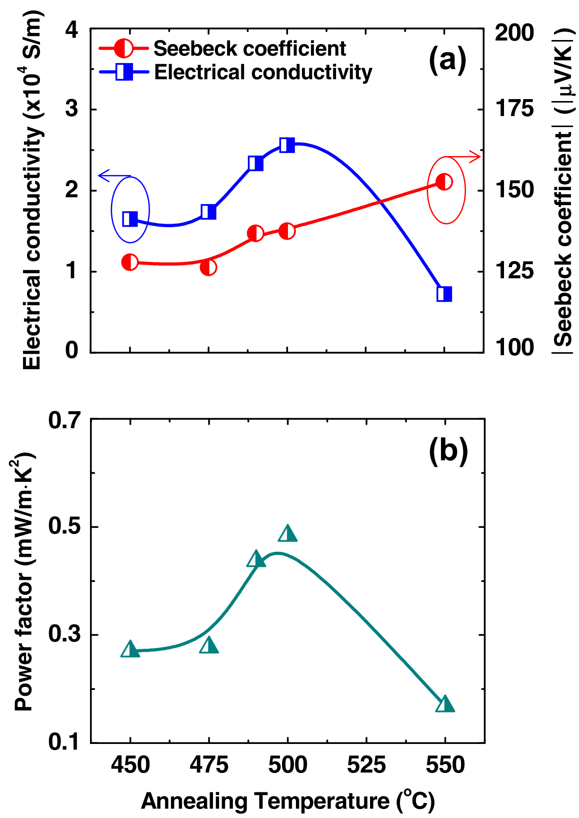


**Fig. 3.** Thermoelectric properties of the screen-printed $Bi_2Te_3$ film as a function of annealing temperature. (a) The electrical conductivity, the absolute of the Seebeck coefficient, and (b) the power factor of the screen-printed $Bi_2Te_3$ film.

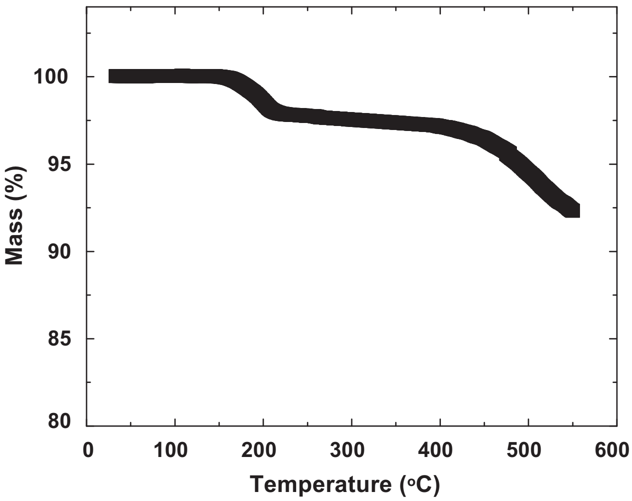


**Fig. 4.** The change of the mass of the screen-printed $Bi_2Te_3$ film during annealing at different temperatures. The ramping rate was 10 °C/min.

post-annealing in a controlled vapor pressure of Te [11–13]. Similarly, Bi and Te powders were placed around the sample in the annealing chamber so that the ambient gas may contain Bi and Te powders during the annealing process. The vapor pressure of Bi and Te at 500 °C is about $7.5 \times 10^{-5}$ and $7.5 \times 10^{-1}$ mmHg, respectively. Therefore, the main evaporating element is Te. The elements will be evaporated until the partial pressure of Te in the ambient reaches to the steady state at the annealing temperature.

Fig. 5 shows the thermoelectric properties of the samples annealed at 500 °C for 0 or 5 min with and without Bi and Te powders. Here, 0 or 5 min annealing means the dwelling time at the top temperature is zero or 5 min, respectively. The result shows that the thermoelectric properties do not show any meaningful difference by the presence of Bi and Te powders during the annealing when the dwelling time is zero. However, as the dwelling time increases, the electric conductivity shows a large difference by the presence of Bi and Te powders. The absence of Bi and Te powders during annealing ambient causes the decrease of the electrical conductivity. On the contrary, the presence of Bi and Te powders increases the electrical conductivity. A change in electrical conductivity results in the change of thermoelectric power factor in the same manner, because the Seebeck coefficient has negligible

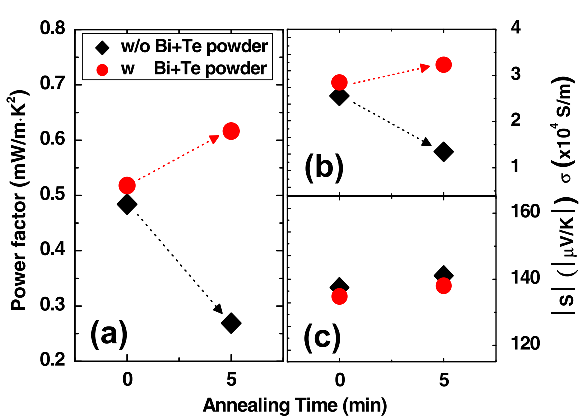


**Fig. 5.** Thermoelectric properties of the screen-printed $Bi_2Te_3$ film annealed at 500 °C with and without Bi and Te powders in the annealing ambient. (a) The power factor, (b) the electrical conductivity ($\sigma$), and (c) the absolute value of the Seebeck coefficient ($|S|$) when the annealing time is 0 or 5 min.

changes. The result indicates that the presence of Bi and Te powders in the annealing ambient suppresses the evaporation of those elements during the annealing or supplies the lost elements by the evaporation. Since we now know that annealing at 500 °C in Bi and Te powders ambient provides a good result, we did further investigation on annealing time in the same condition.

Fig. 6 shows the thermoelectric properties of the screen-printed $Bi_2Te_3$ annealed at 500 °C in Bi and Te powders ambient for various annealing time. In this result, the annealing time means the dwelling time at 500 °C. The sample annealed at 500 °C for 15 min has a power factor of 2.1 mW/m $K^2$, which is about 1 order of magnitude higher than that of the sample annealed at 500 °C without Bi and Te powders in Fig. 3b. The thermal conductivity of the samples was also measured using the method described in Ref [14]. The measured thermal conductivity is in the range of 0.9–1.1 W/m K, as shown in Fig. 6b, and it does not show a strong dependence on the annealing time. The thermal conductivity of the screen-printed $Bi_2Te_3$ films is lower than that of the previous reported bulk or thin-film $Bi_2Te_3$ (1.3–3.3 W/m K) [15,16]. The lower thermal conductivity is attributed to the high porosity of screen-printed $Bi_2Te_3$ film, as can be seen in the SEM image in Fig. 1. This porosity originates from the evaporation of the organic vehicle from the paste during the annealing process. Although thermoelectric power factor of the screen-printed $Bi_2Te_3$ film is slightly lower than that of the previously reported bulk or thin-film $Bi_2Te_3$ (3.5–5.8 mW/m $K^2$), the lower thermal conductivity of it can com-

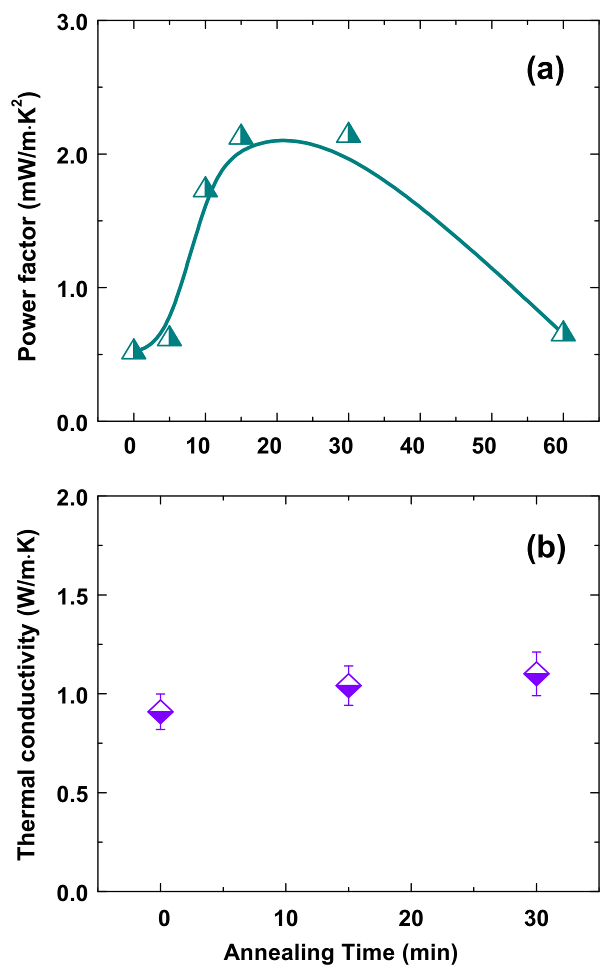


**Fig. 6.** (a) Power factor and (b) thermal conductivity of the screen-printed $Bi_2Te_3$ film as a function of annealing time. The annealing was done at 500 °C in Bi and Te powders ambient.

pensate the loss in ZT. The calculated ZT value of 0.61 at room temperature is comparable to that of bulk or thin-film $Bi_2Te_3$ [15,16]. The results above indicate that screen printing of $Bi_2Te_3$ is a good choice for low-cost thermoelectric device which operates at near room temperature.

## 4. Conclusion

$Bi_2Te_3$ film was successfully prepared by a screen-printing method for thermoelectric power generator application. It has been found that the annealing conditions after printing, such as the annealing temperature, time and ambient, are the important factors in determining the thermoelectric properties of the film. Through the optimal annealing process, a power factor of 2.1 mW/m $K^2$ and thermal conductivity of 1.0 W/m K was obtained. The ZT value of the screen printed $Bi_2Te_3$ film is 0.61 at room temperature. The results demonstrate that the screen-printed $Bi_2Te_3$ thick film is a good choice for low cost and large size thermoelectric device.

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