Thermoelectric Properties of Printed Bismuth Telluride Films

Kunihisa Kato, Hisashi Iwata, and Koji Miyazaki
Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu, miyazaki@mech.kyutech.ac.jp

ABSTRACT

We prepared a mixture of thermoelectric bismuth telluride particles, a conductive polymer (PEDOT:PSS), poly(acrylic acid) (PAA), and several organic additives to fabricate thermoelectric films using printing or coating techniques. In the mixture, the organic components (PEDOT:PSS, PAA, and an additive) act as a binder to connect bismuth telluride particles mechanically and electrically. Among the organic additives used, glycerol significantly enhanced the electrical conductivity and bismuth telluride particle dispersibility in the mixture. $Bi_{0.4}Te_{3.0}Sb_{1.6}$ films fabricated by spin-coating the mixture showed a thermoelectric figure of merit (ZT) of 0.2 at 300 K when the $Bi_{0.4}Te_3Sb_{1.6}$ particle diameter was 2.8 μm and its concentration in the elastic films was 95 wt%.

Key words: $Bi_{0.4}Te_{3.0}Sb_{1.6}$,Thermoelectric, Printing, Conductive polymer

1. INTRODUCTION

Thermoelectric generators can convert low-grade waste heat into electricity, making it a key technology, contributing to sustainability through scavenging of waste heat or heat sources.[1] The performance of thermoelectric device is determined by the thermoelectric figure of merit, ZT, which is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature. For the practical uses of thermoelectric devices to spread, improvements in device performance and reductions in manufacturing costs are required. It has recently been reported that using nanostructured thermoelectric materials efficiently increases ZT as a result of reduced thermal conductivity by phonon scattering.[2-6] Generally, thermoelectric devices are fabricated by vacuum processing, particularly for thin film applications, but these processes are expensive. Printing or coating processes such as screen- and inkjet-printing are attractive methods for reducing the manufacturing costs of thermoelectric devices. In recent reports, a number of methods for obtaining thermoelectric materials by printing using polymer materials have been described.[7-9] The electrical conductivities and Seebeck coefficients of printed thermoelectric materials are lower than those of bulk materials. To improve the electrical conductivity and Seebeck coefficient of a thermoelectric compound, it is necessary to anneal the thermoelectric compound or fill the

grain boundaries with conductive materials. Polymer materials are very attractive as they have low thermal conductivity, good flexibility, and good printability. We fabricated flexible printed thermoelectric thin films containing thermoelectric particles, a conductive polymer, and various additives, and here we report the thermoelectric properties of the composite thermoelectric thin films.

2. EXPERIMENTS

The thin films of the thermoelectric compounds we produced consisted of thermoelectric particles, a conductive polymer, poly(acrylic acid) (PAA), and various organic additives. The films were prepared using two processes. As the starting material, we used p-type $Bi_{0.4}Te_{3.0}Sb_{1.6}$ particles (Kojundo Chemical Laboratory) with an average particle size of 180 μm. The particles were milled using a jet-milling apparatus for 30 min at 0.15, 0.30, and 0.95 MPa under a nitrogen atmosphere. The size distribution of each particle was measured using a laser diffraction particle size analyzer. The resulting average particle sizes after jet milling were approximately 0.66, 2.8, and 5.5 μm, respectively. We prepared a polymer compound from a conductive polymer (PEDOT:PSS), PAA, and various organic additives, namely glycerol, *N*-methylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The milled $Bi_{0.4}Te_{3.0}Sb_{1.6}$ particles were added to the polymer compound to make printable slurries. The thermoelectric thin films were prepared by spin-coating on a glass or alumina substrate and heated at 150 °C for 10 min under an argon atmosphere. The thicknesses of the thin films were determined using a stylus profilometer, and were approximately 0.1–10 μm. The surface and cross-section morphologies of the thermoelectric thin films were investigated using scanning electron microscopy (SEM). The in-plane electrical conductivities of the films were measured at room temperature using a four-point probe method, and the in-plane Seebeck coefficients S were measured at room temperature. One end of the thin film was connected to a heat sink and the other end to a heater. The Seebeck coefficient was determined as the ratio of the potential difference V along the film to the temperature difference T. The cross-plane thermal conductivity was determined at room temperature using a differential 3ω method with an accuracy of 10%.[10] The figure of merit ZT for each film was estimated from the results of the electrical conductivity, Seebeck coefficient, and the thermal conductivity.

3. RESULTS AND DISCUSSION

The thermoelectric properties of the hybrid thermoelectric thin films were studied at room temperature. The electrical conductivities, Seebeck coefficients, and power factors of the thin films were investigated, as shown in Fig. 1. The electrical conductivities of the films were reduced when the particle diameter increased from 0.66 to 2.8 μm. The electrical conductivities of the thermoelectric particles were lower than that of the conductive polymer compound film itself, so the particles acted as electrical resistors. As the thermoelectric particle concentration increased, the Seebeck coefficients were significantly enhanced. The power factors of the thin films consisting of particles with diameters of 0.66 and 2.8 μm particles reached 74.1 and 237.2 $\mu W/(m \cdot K^2)$, respectively. The power factors of the thin films consisting of particles with diameters of 2.8 μm particles larger than previous report. [7] The thin films of the thermoelectric material by filling the particle boundaries by the addition of conductive polymer and organic additives. The cross-plane thermal conductivities of the p-$Bi_{0.4}Te_3Sb_{1.6}$ composite films with diameters of 0.66 and 2.8 μm particles were 0.24, 0.36W/(m·K), respectively. The measured thermal conductivities were close to the conductive polymer(0.32W/(m·K))and significantly less than those of standard p-type bulk bismuth telluride materials(1.5W/(m·K)). The reason for the low thermal conductivity is scattering of phonons at the grain boundaries and filling of the boundaries with materials of low thermal conductivity. The hybrid thermoelectric films were prepared by spin-coating on a PET substrate and heating at 150 °C for 10 min under an argon atmosphere. Figure 2 shows the visible appearance of the hybrid thermoelectric thin films on the polymer substrate. There were no cracks or defects in the material when the film was bent several times. The ZT values of the 0.66- and 2.8-μm p-$Bi_{0.4}Te_3Sb_{1.6}$ particle films were estimated to be 0.09 and 0.20, respectively. The reduction in the thermal conductivity effectively improved the ZT value. In order to further improve the thermoelectric performance, it is necessary to enhance the electrical properties.
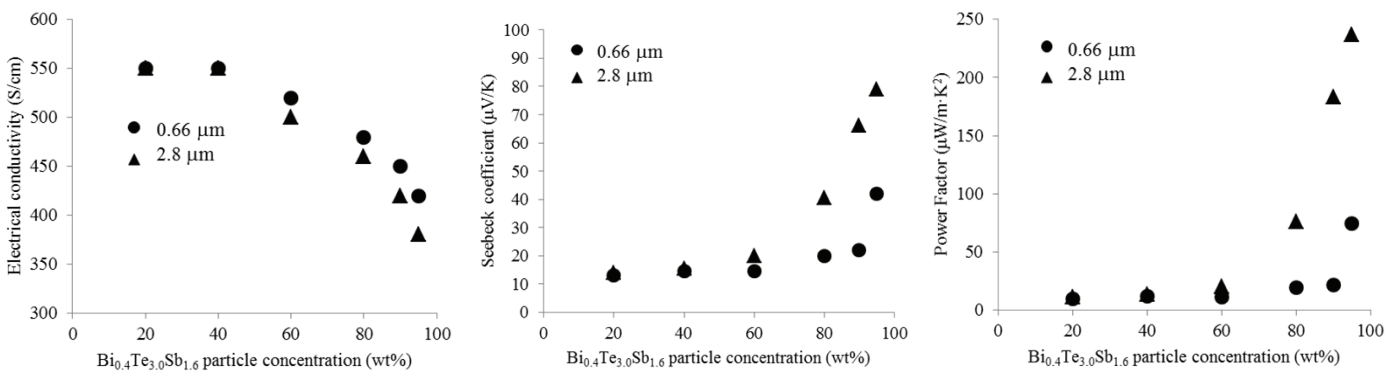

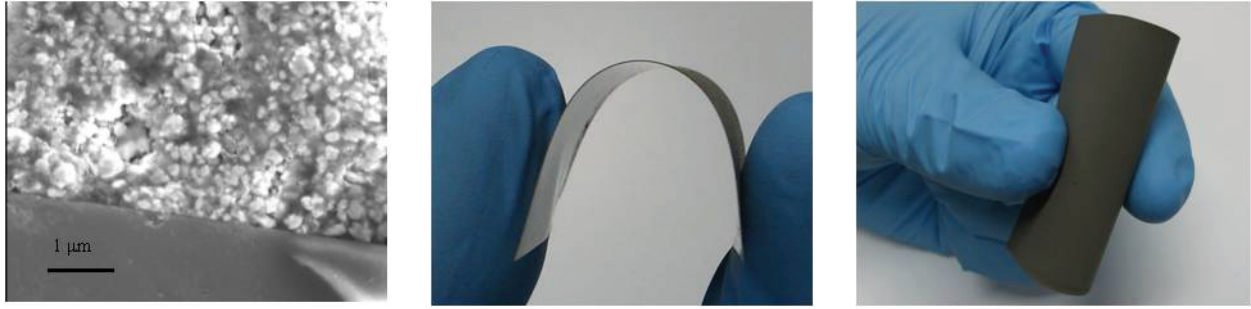Fig.1 Electrical properties of hybrid thermoelectric films

Fig.2 Fabricated printed flexible thermoelectric thin films

4. CONCLUSION

In summary, we have proposed a method for fabricating flexible printing-type thermoelectric thin films containing p-type $Bi_{0.4}Te_{3.0}Sb_{1.6}$ particles, a conductive polymer, and various additives. The dispersibilities of the thermoelectric particles in ink were improved by milling the particles. We used sub-micron thermoelectric particles, and the cross-plane thermal conductivities of p-type $Bi_{0.4}Te_{3.0}Sb_{1.6}$ thin films were significantly reduced by phonon scattering at the grain boundaries. Flexibility could be imparted to the thin films of the thermoelectric material by filling the particle boundaries by the addition of small amounts of conductive polymer and organic additives. When the particle concentration was 95 wt%, we achieved the highest *ZT* value, estimated to be 0.2.

REFERENCES

1. G.J. Snyder, E.S. Toberer, *Nat. Mater.* 7, 105 (2008)

2. R. Venkatasubramanian, E. Siivola, T. Colpitts, B. O'Quinn, *Nature (London, U. K.)* 413, 597 (2001)

3. T.C. Harman, P.J. Taylor, M.P. Walsh, B.E. LaForge, T.C. Harman, *Science* 297, 2229 (2002)

4. M. Takashiri, K. Miyazaki, S. Tanaka, J. Kurosaki, D. Nagai, H. Tsukamoto, *J. Appl. Phys.* 104, 084302 (2008)

5. A.I. Hochbaum, R. Chen, R.D. Delgado, W. Liang, E. Garnett, M. Najarian, . Majumdar, P. Yang, *Nature* 451, 163 (2008)

6. M. Kashiwagi, S. Hirata, K. Harada, Y. Zheng, K. Miyazaki, M. Yahiro, C. Adachi, *Appl. Phys. Lett.* 98, 023114 (2011)

7. M. Takashiri, S. Tanaka, M. Takiishi, M. Kihara, K. Miyazaki, H. Tsukamoto, *J. Alloys Compd.* 462, 351 (2008)

8. D. Madan, A. Chen, P.K. Wright, J.W. Evans, *J. Appl. Phys.* 109, 034904 (2011)

9. B. Zhang, J. Sun, H. E. Katz, F. Fang, R. L. Oplia, *Applied Materials & Interfaces*, 2, 3170 (2010)

10. M. Takashiri, M. Takiishi, S. Tanaka, K. Miyazaki, H. Tsukamoto, J. Appl. Phys., 101, 074301 (2007)