

Fabrication of Bismuth Telluride Thermoelectric Films Containing Conductive Polymers Using a Printing Method

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We prepared a mixture of thermoelectric bismuth telluride particles, a conductive polymer [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (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. $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ films fabricated by spin-coating the mixture showed a thermoelectric figure of merit (ZT) of 0.2 at 300 K when the $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particle diameter was 2.8 μm and its concentration in the elastic films was 95 wt.%.

Key words: Conductive polymer, bismuth telluride, microparticles, thermal conductivity

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 the 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 practical use 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 due to phonon scattering.^{2–7} Generally, thermoelectric devices are fabricated by vacuum processing, particularly for thin-film applications. There are many

deposition methods for obtaining high-quality thermoelectric thin films.^{8–10} Thermoelectric thin films with good thermoelectric properties can be prepared using the thin-film deposition processes mentioned above, but these processes are expensive because vacuum processing is a lengthy procedure. 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.^{11–17} 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

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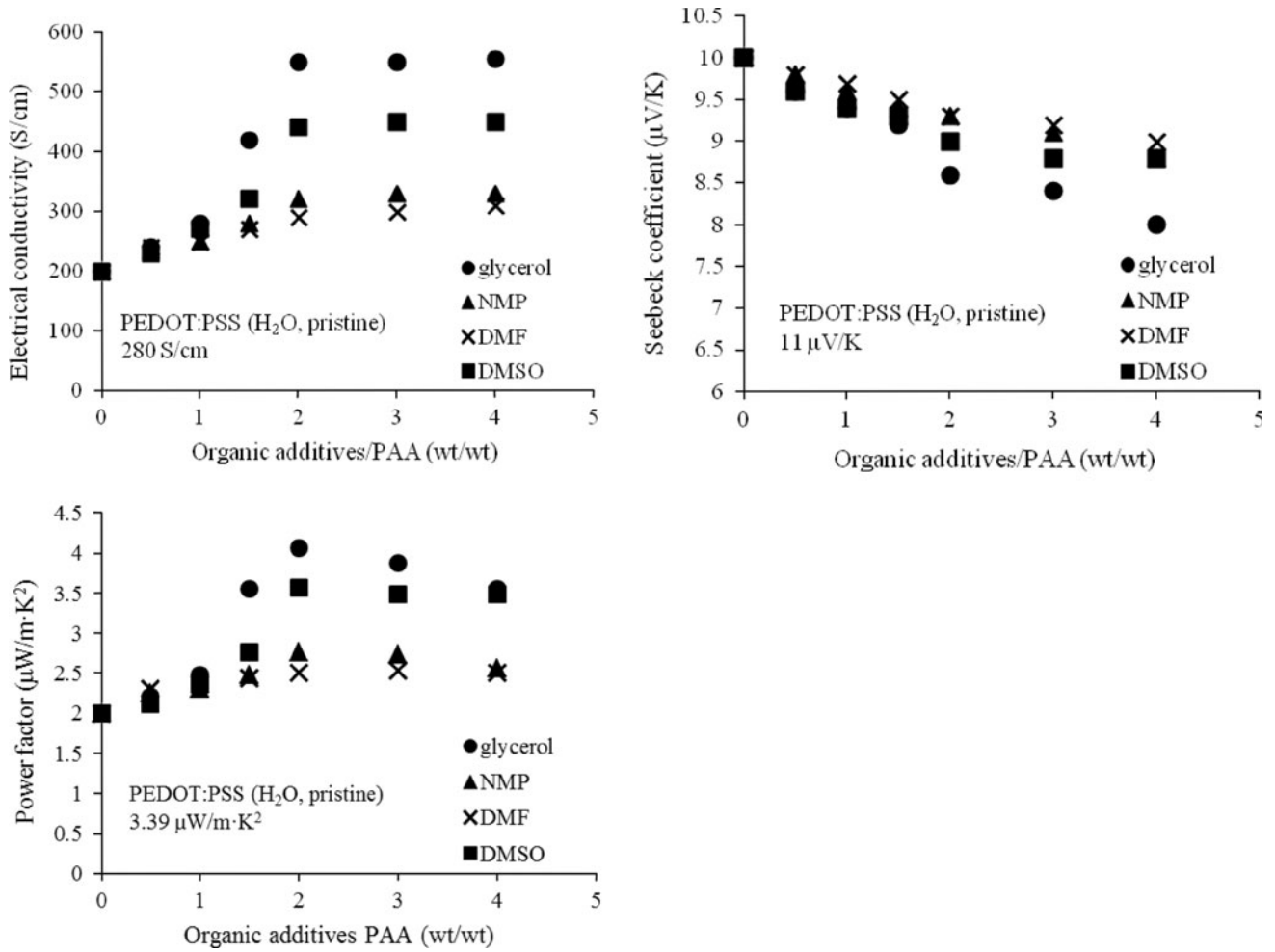


Fig. 1. Dependences of electrical conductivity, Seebeck coefficient, and power factor on ratios of high-boiling-point materials added.

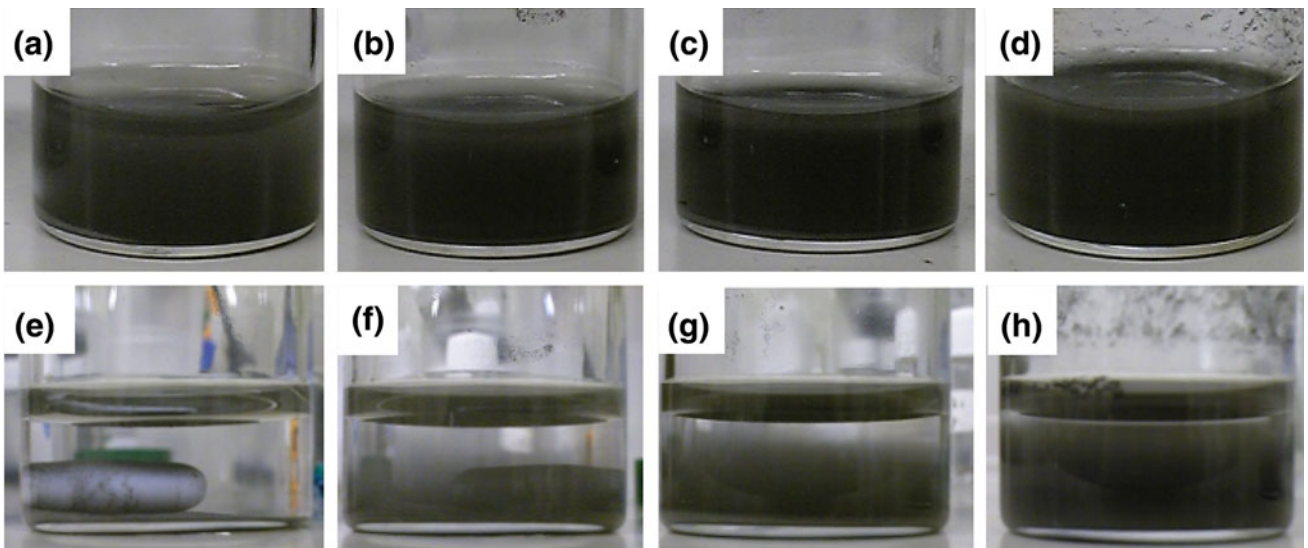


Fig. 2. Dispersibility test images of thermoelectric particles of various sizes. (a–d) Starting materials: (a) 180 μm , (b) 5.5 μm , (c) 2.8 μm , and (d) 0.66 μm ; (e–h) after 6 h: (e) 180 μm , (f) 5.5 μm , (g) 2.8 μm , and (h) 0.66 μm .

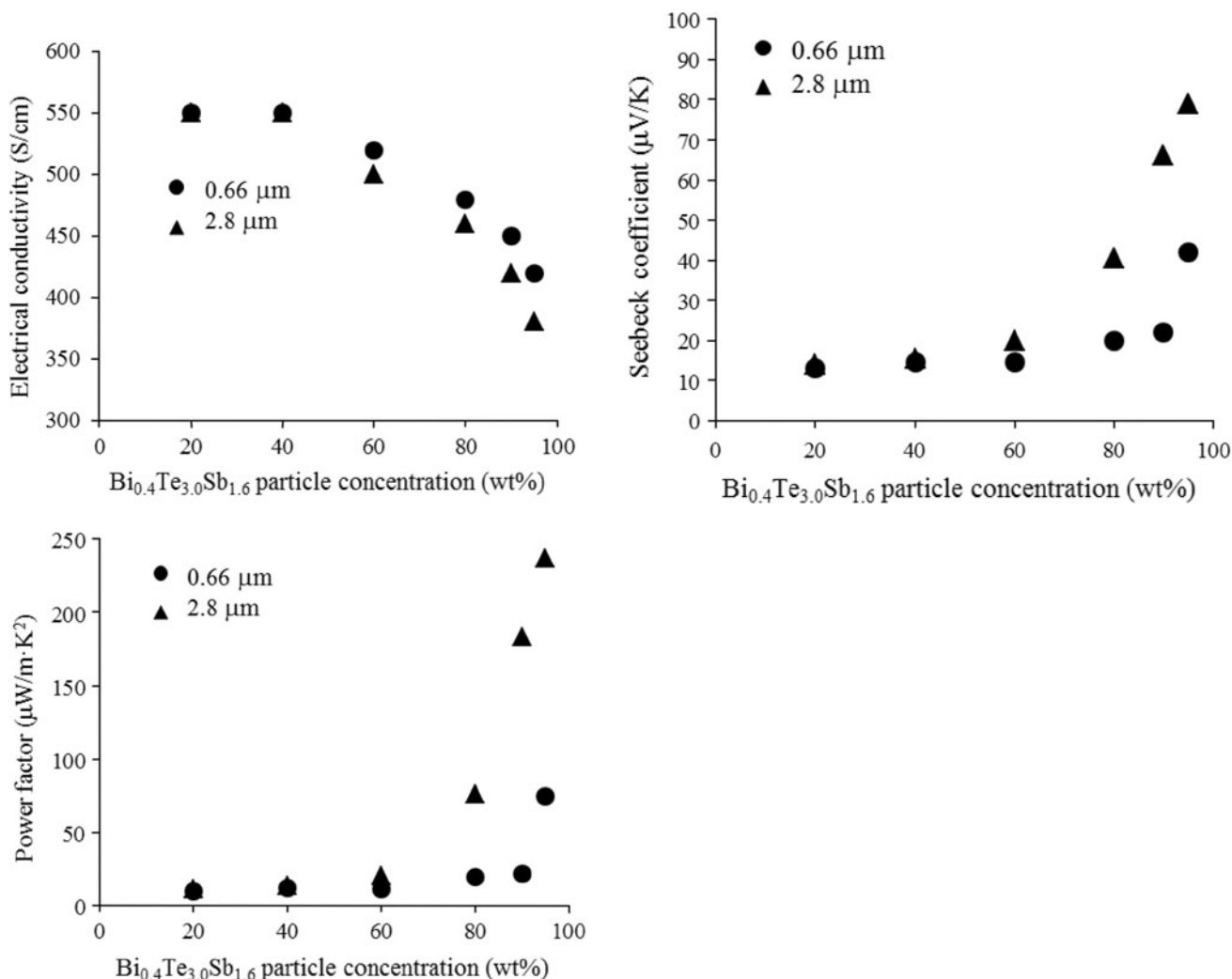


Fig. 3. Dependences of electrical conductivity, Seebeck coefficient, and power factor on the weight ratio of $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particles.

thermoelectric properties of the composite thermoelectric thin films.

EXPERIMENTAL PROCEDURES

The thin films of thermoelectric compounds that 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 $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particles (Kojundo Chemical Laboratory) with average particle size of 180 μm . The particles were milled using a jet-milling apparatus for 30 min at 0.15 MPa, 0.30 MPa, and 0.95 MPa under nitrogen atmosphere. The size distribution of each particle type was measured using a laser diffraction particle size analyzer. The resulting average particle sizes after jet milling were approximately 0.66 μm , 2.8 μm , 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 $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ 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 argon atmosphere. The thicknesses of the thin films were determined using a stylus profilometer, and were approximately 0.1 μm to 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.¹⁸ One end of the thin film was connected to a heat sink and the other end to a heater. The Seebeck coefficient was

Table I. Thermoelectric properties of the thermoelectric thin films

Sample	Particle Diameter (μm)	Particle Concentration (wt.%)	σ (s/cm)	S ($\mu\text{V/K}$)	κ [$\text{W}/(\text{m K})$]	ZT (300 K)
$\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particle	0.66	95	420	42	0.24	0.09
$\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particle	208	95	380	79	0.36	0.20
Conductive polymer compound	—	—	280	11	0.2	0.005
$\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particle ¹¹	0.05	100	72	135	—	—
$p\text{-Bi}_{1/2}\text{Te}_3$ particle ¹⁷	2–5	90	60–70	140–150	0.52	0.08
Bulk $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$	—	—	840	212	1.5	0.8
$\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ thin film (as deposited)*	—	—	165	191	0.8	0.23

* Sample fabricated by flash evaporation method.

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 accuracy of 10%.¹⁸ Details of the thermal conductivity measurements and sample fabrication have been described elsewhere.^{19,20} The figure of merit ZT for each film was estimated from the results of the electrical conductivity, Seebeck coefficient, and thermal conductivity.

RESULTS AND DISCUSSION

Conducting Polymer Optimization

The dependences of the electrical conductivities, Seebeck coefficients, and power factors of the thin films on the organic additives and matrix polymer PAA were investigated, as shown in Fig. 1. The electrical conductivities of the thin films were reduced by an insulating binder polymer without any organic additives. It is known that the electrical conductivity of PEDOT:PSS is improved by the addition of organic molecules.^{21–23} The highest electrical conductivity of the films with added glycerol, NMP, DMF, and DMSO were 555 S/cm, 330 S/cm, 310 S/cm, and 450 S/cm, respectively. The Seebeck coefficients decreased on addition of organic additives. The power factors of the thin films were higher than that of PEDOT:PSS as a result of the improved electrical conductivities. The highest power factors of the films with added glycerol, NMP, DMF, and DMSO were $4.07 \mu\text{W}/(\text{m K}^2)$, $2.77 \mu\text{W}/(\text{m K}^2)$, $2.50 \mu\text{W}/(\text{m K}^2)$, and $3.56 \mu\text{W}/(\text{m K}^2)$, respectively. The electrical conductivities of the thermoelectric materials increased significantly as a result of the addition of organic additives, and the Seebeck coefficients were only slightly reduced. The electrical conductivity (σ) can be expressed as

$$\sigma = ne\mu,$$

where n is the carrier concentration, e is the electronic charge, and μ is the carrier mobility.

The electrical conductivity of the thin films is enhanced because the carrier mobility increases more than the carrier concentration decreases; this occurs because of the increase of the carrier hopping length due to the growth of the PEDOT-rich particles resulting from the effect of the high-boiling solvent.²⁴ The dispersibilities of thermoelectric particles of various sizes were evaluated after stirring, as shown in Fig. 2. The particles with diameters of 180 μm and 5.5 μm had poor dispersibilities. The smaller particles exhibited better dispersibilities, and the particles with diameters of 0.66 μm and 2.8 μm maintained full dispersion after 6 h (Fig. 2g, h). The dispersibility was improved by using high-viscosity materials with milled particles. Accordingly, we fabricated hybrid-type thermoelectric thin films using particles with diameters of 2.8 μm and 0.66 μm .

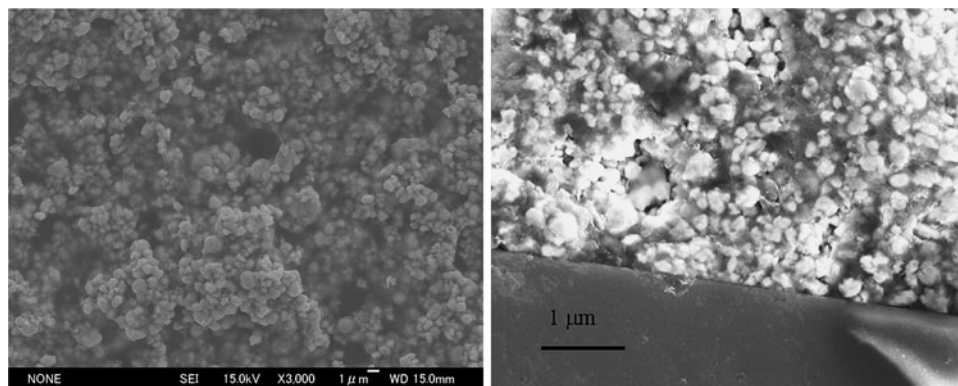


Fig. 4. In-plane and cross-plane images of thermoelectric compound thin films.

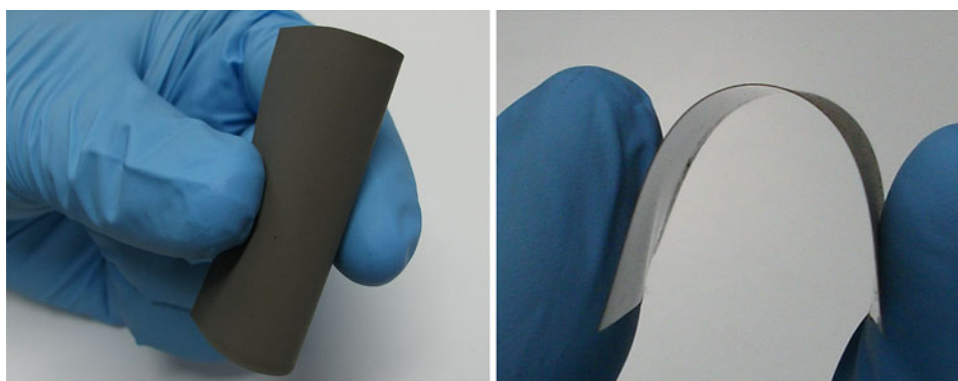


Fig. 5. Photographs of fabricated flexible thermoelectric thin films.

Thermoelectric Properties of Hybrid Thermoelectric Thin Films

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. 3. The electrical conductivities of the films were reduced from 550 S/cm to 420 S/cm and 550 S/cm to 380 S/cm when the particle diameter increased from 0.66 μm 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 of the 0.66- μm and 2.8- μm particle films were significantly enhanced to 42 $\mu\text{V/K}$ and 79 $\mu\text{V/K}$, respectively. This is explained by the carrier concentration of the thermoelectric particles being lower than that of the conductive polymer composite. Increasing the fraction of added particles reduced the carrier concentration of the thin film. Then the Seebeck coefficients of the thin films improved, and, as a result, the power factors of the thin films consisting of particles with diameters of 0.66 μm and 2.8 μm reached 74.1 $\mu\text{W}/(\text{m K}^2)$ and

237.2 $\mu\text{W}/(\text{m K}^2)$, respectively. The power factors of the thin films consisting of particles with diameter of 2.8 μm were larger than previously reported.¹¹ 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 $p\text{-Bi}_{0.4}\text{Te}_3\text{Sb}_{1.6}$ composite films are presented in Table I. The cross-plane thermal conductivities of the 0.66- μm and 2.8- μm particle films were 0.24 W/(m K) and 0.36 W/(m K), respectively. The measured thermal conductivities were close to that of the conductive polymer and significantly less than those of standard p -type bulk bismuth telluride materials. There are two reasons for the reduction in thermal conductivity. First, the thermal conductivity of the thermoelectric composite thin film decreased as the average grain size decreased. The number of grain boundaries in the thin film is larger for a smaller grain size, thus reducing the thermal conductivity through increased scattering of phonons at the grain boundaries. Secondly, as seen from the SEM image of the thermoelectric thin films shown in Fig. 4, the thermoelectric particle boundaries were filled with the conductive polymer compound. The thermal conductivity of the conductive polymer

compound was 0.20 W/(m K), comparable to that of the p -type $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particles. 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 polyethylene terephthalate (PET) substrate and heating at 150°C for 10 min under argon atmosphere. Figure 5 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. As can be seen from the SEM results, flexibility could be imparted to the thermoelectric material by filling the particle boundaries by the addition of a small amount of conductive polymer and organic additives. The ZT values of the 0.66- μm and 2.8- μm p - $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ 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.

CONCLUSIONS

We have proposed a method for fabricating flexible printing-type thermoelectric thin films containing p -type $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ particles, a conductive polymer, and various additives. The dispersibilities of the thermoelectric particles in ink were improved by milling the particles. We used submicron thermoelectric particles, and the cross-plane thermal conductivities of p -type $\text{Bi}_{0.4}\text{Te}_{3.0}\text{Sb}_{1.6}$ thin films were significantly reduced by phonon scattering at the grain boundaries. Flexibility could be imparted to the thin films of 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.

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