This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. This article appeared in Deepa Madan, Alic Chen, Paul K. Wright, and James W. Evans, "Dispenser printed composite thermoelectric thick films for thermoelectric generator applications", Journal of Applied Physics 109, 034904 (2011) https://doi.org/10.1063/1.3544501. and may be found at https://aip.scitation.org/doi/full/10.1063/1.3544501.

Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing scholarworks-group@umbc.edu and telling us what having access to this work means to you and why it’s important to you. Thank you.
Dispenser printed composite thermoelectric thick films for thermoelectric generator applications

Deepa Madan, Alic Chen, Paul K. Wright, et al.

ARTICLES YOU MAY BE INTERESTED IN

Dispenser printed circular thermoelectric devices using Bi and Bi$_{0.5}$Sb$_{1.5}$Te$_3$

Flexible and lightweight thermoelectric generators composed of carbon nanotube-polystyrene composites printed on film substrate

Low-cost flexible thin film thermoelectric generator on zinc based thermoelectric materials
Dispenser printed composite thermoelectric thick films for thermoelectric generator applications

Deepa Madan,1,a) Alic Chen,1 Paul K. Wright,1 and James W. Evans2
1Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California 94720, USA
2Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California 94720, USA

(Received 14 August 2010; accepted 13 December 2010; published online 4 February 2011)

This paper describes novel processes for preparing thermoelectric composite materials compatible with thick film dispenser printing fabrication processes. Optimization of process parameters to improve thermoelectric properties is introduced. We explore the use of n-type Bi2Te3 and p-type Sb2Te3 materials to achieve properties suitable for use in low cost high aspect ratio microscale thermoelectric generators. Printable thermoelectric inks consisted of dispersed semiconductor powders in an epoxy resin system. Thick films were printed on glass substrates and cured at temperatures ranging from 150 to 350 °C. The best achievable power factors for n-type Bi2Te3-epoxy and p-type Sb2Te3-epoxy composite films were 1.5 × 10−4 W/m K2 and 8.4 × 10−4 W/m K2, respectively. Figure of merit (ZT) values for n-type Bi2Te3-epoxy and p-type Sb2Te3-epoxy composites were 0.16 and 0.41, respectively, which are much higher than previously reported ZT values for composite thermoelectric materials. © 2011 American Institute of Physics. [doi:10.1063/1.3544501]

I. INTRODUCTION

The growth of autonomous residential, industrial, and medical monitoring applications utilizing wireless sensor networks (WSNs) has spurred new research into “perpetually available” ambient energy harvesting power sources.1 Batteries have traditionally been used to meet the low power requirements of these WSN devices. However, they have finite lifetimes that are often less than the programmed life of the WSN.2 Battery replacement is thus undesirable, costly, and inefficient for large-scale deployments of WSN’s. Thermoelectric devices are attractive potential power sources because they directly convert thermal gradients into electrical power, providing power while temperature gradients are present.3 However, for thermoelectric devices to be suitable for use in WSN’s, they must provide a minimum potential of 0.5 V and element leg lengths should range between 100 and 200 μm to maximize power output.4–6 The element length optimization is due to a balance between increasing electrical resistance with longer elements and the non-negligible thermal resistance of the substrates for short elements. These requirements are challenging for existing mass production manufacturing techniques. Traditional bulk thermoelectric elements prepared by dicing and extrusion are limited by the resolution of the dicing step to >300 μm thermoelectric leg lengths.7 Alternatively, conventional microfabrication processes involving lithography and thin-film deposition are limited to <60 μm leg lengths.8,9 There exists a gap in the available manufacturing technologies for producing optimized elements in the range of 100–200 μm. Therefore, a direct-write method has been investigated to fabricate elements in the desired thickness ranges. Direct-write process-
ing. We also report the thermoelectric properties and ZT values of such composite thermoelectric thick films.

II. EXPERIMENTAL

A. Polymer matrix: Filler particles and polymer

To achieve the 100–200 μm feature sizes, 50–100 μm printer tips are required to dispense materials. The printer tip size thus limits the maximum particle size of the active materials. Empirical testing suggests that the particle size of the active materials needs to be less than 10–20 μm to allow for continuous dispensing without clogging the tip. To produce 10 μm average particles, bulk 80–100 mesh Bi₂Te₃ (n-type) and Sb₂Te₃ (p-type) powders purchased from SCM, Inc. were processed using a high-energy planetary ball-mill (Torrey Hills ND 0.4L). The starting powders were placed in 100 ml stainless steel jars with 3 mm stainless steel balls at a ball-to-powder mass ratio of 10:1. Isopropanol was used as a wet-grinding agent with a 1:1 solvent-to-powder weight ratio. The jars were then placed in the planetary ball mill and run at 180 rpm for 30 min. All materials preparation and extraction were performed under a dry argon environment to prevent oxidation of materials. The particle size distribution of the powders was measured using a Coulter LS-100 laser diffraction particle size analyzer. The resulting average particle size after ball milling is approximately 10 μm while the bulk of the particles range between 3 and 30 μm.

The preparation of thermoelectric composite inks requires active particles mixed in a polymer binder with some solvents. The ball-milled Bi₂Te₃ and Sb₂Te₃ were used as filler particles for n-type and p-type inks respectively. Epoxy resin systems are proven polymer systems and are commonly used in commercially available electrically conductive composites. Epoxy resin systems as a binder. 24 The epoxy resin system was formulated using diglycidyl ether of bisphenol f epoxy resin (EPON 862, Hexion Specialty Chemicals, Inc.) and methylhexahydrophthalic anhydride (MHHPA, Dixie Chemicals, Inc.) as the hardener. The ratio of epoxy-to-hardener was 1:0.85 based on the epoxy equivalent weight of the resin and the hydroxyl equivalent weight of the hardener. 1-cyanoethyl-2-ethyl-4-methyimidazole (2E4MZCN, Sigma-Aldrich, Inc.) was used as the catalyst. 10–20 wt % of butyl glycidyl ether (Heloxy 61, Hexion Specialty Chemicals, Inc.) was employed in the resin blend as a reactive diluent to adjust the viscosity of the slurry to the desired properties. The epoxy resin system as a polymer binder resulted in compact films with high mass loading and overall good thermoelectric properties with minimal cure shrinkage. We therefore chose to use the epoxy resin system as a binder.

The ball-milled Bi₂Te₃ powder was then added to the epoxy resin system to make printable slurries. 5 wt % toluene was used as a solvent to mix the epoxy resin system together with active filler particles. The choice of toluene as a solvent was due to its low boiling point and low viscosity. Empirical testing has shown that 80 wt % of filler particles provide the best film properties. The slurry was mixed using a vortex mixer for about 1–3 h with regular pause intervals and ultrasonic bath for 15 min to disperse the particles. The thermoelectric inks were then printed on a glass substrate to form 100–200 μm thick films using the dispenser printer and were cured at various temperatures to form solid thick films.

B. Measurements

To study the curing profile of the polymer matrix, a modulated differential scanning calorimeter (DSC, Model 2920, TA Instruments) was used. The onset peak and integration temperatures from the exothermic and endothermic diagrams were recorded and analyzed. The morphology of grains and grain boundaries were observed using a scanning electron microscope (SEM) JSM-6490 LV. Crystalline Sb₂Te₃ and Bi₂Te₃ are known to exhibit strong anisotropic thermoelectric properties. However, in polycrystalline powder form they exhibit isotropic behavior. This isotropic behavior in the powder form results due to the random orientation of the crystallites. 25 Polycrystalline grains of the active filler particles are also randomly oriented in the epoxy matrix and result in isotropic thermoelectric properties of composites. Thermoelectric properties are therefore reported in one direction only. Electrical resistivity measurements of the printed thermoelectric films were carried out using a standard four-point probe method to determine the sheet resistance of the material. Seebeck measurements were performed using a custom Seebeck testing device to determine the voltage output of the material for a given temperature difference. The thermal conductivity of composite samples was measured by the guarded heat flow meter method at a steady state with a bulk thermal conductivity analyzer (Anter corp Model 2021). Relatively larger samples (20 × 20 × 3 mm³) were used for thermal conductivity measurements. The Hall coefficients, carrier concentration, and carrier mobility of the samples were measured at room temperature using an Ecopia HMS-3000 Hall effect measurement system; a magnetic field of 0.6 T and electrical current of 10 mA were applied.

III. RESULTS AND DISCUSSION

A. Phase change and microstructure

As with any composite material system, the effective property of the composite is a function of all the properties of the individual material properties. 26 It is ultimately desirable to achieve composite properties similar to or exceeding those of the bulk properties of individual materials. However, given that the electrical conductivity and the Seebeck coefficient of the polymer binder are significantly lower than that of the active filler thermoelectric material, the effective properties of the composite system are expected to be less than desirable. To achieve the preferred conductivity of the thermoelectric composite films, curing temperatures need to be optimized. The shrinkage of the polymer matrix upon curing effectively packs the fillers involved. 24 The curing profiles for the epoxy polymer matrix and the electrically conductive composites measured by the DSC method is displayed in Fig. 1(a). Exothermic peaks are observed at about 150 °C for the epoxy polymer as well as for the composites. The peaks are shorter for composites compared to pure epoxy due to the smaller weight percent of epoxy in composite slurries. The peak at about 150 °C is typical for imidazole
derivative catalyzed curing reaction of an epoxy resin with an anhydride hardener. We also observed an endothermic peak at approximately 400 °C for the epoxy resin suggesting the pyrolysis of the epoxy. Similar peaks were not pronounced for the composite systems as their profiles were dominated by the larger weight percent of active filler particles. DSC of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ ball milled powders is shown in Fig. 1 for comparison and study of the phase change. A sharp endothermic peak for Sb$_2$Te$_3$ is observed at about 425 °C which corresponds to the melting point of Te or a Te rich phase. No endothermic sharp peaks were observed in the DSC curve for Bi$_2$Te$_3$ ball milled powder in the studied temperature range Fig. 1.

X-ray powder diffraction (XRD) studies were performed on the as received Sb$_2$Te$_3$ and Bi$_2$Te$_3$ as shown in Fig. 2. Extra peaks of Te were found in the Sb$_2$Te$_3$ suggesting the presence of excess Te in the as received powder. It substantiates the lower melting point of Sb$_2$Te$_3$ as shown in DSC of Sb$_2$Te$_3$, Fig. 1(b). To understand if the excess Te in the as received powder from the manufacturer was present in the form of pure Te or Te rich Sb$_2$Te$_3$ phase, we performed electron probe microanalysis (EPMA). EPMA studies, as shown in Fig. 3, indicate the presence of a Te rich Sb$_2$Te$_3$ phase (bright areas) as well as stoichiometric Sb$_2$Te$_3$ (main area). The elemental ratio of Sb to Te was approximately 1:3.4 in the bright area whereas it was approximately 2:3 in the main area.

Figure 4 shows the SEM micrographs of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ DSC samples. Figure 4(a) shows the nonuniform distribution of micron and submicron particles of Sb$_2$Te$_3$ ball milled powder. Figures 4(b) and 4(c) show SEM images of Sb$_2$Te$_3$ ball milled powders heated to 350 °C and 475 °C, respectively. There is evidence of grain coalescence at 350 °C and formation of large grains at 475 °C. Figure 4(d) shows the SEM image of Bi$_2$Te$_3$ powder heated to 475 °C. No evidence of sintering is observed. Figure 5 shows the SEM image of p-type Sb$_2$Te$_3$ and epoxy resin composite film cured at 350 °C. The image of p-type composite film shows a similar clustering of particles as observed in SEM images of Sb$_2$Te$_3$ DSC powders.

### B. Thermoelectric properties

The thermoelectric and thermal transport properties of n-type Bi$_2$Te$_3$ and p-type Sb$_2$Te$_3$ thermoelectric composites films, cured in the temperature range of 150–350 °C, were studied at room temperature. This temperature range was chosen based on the DSC curves of the epoxy and ball milled thermoelectric powders. The effect of curing time was studied on composite films cured at 350 °C. Curing time was varied in the range of 6–48 h.

Figure 6 shows the thermoelectric properties of p-type Sb$_2$Te$_3$ and n-type Bi$_2$Te$_3$ composite films as a function of curing temperature. While the electrical conductivity (σ) of n-type Bi$_2$Te$_3$ show little change, the conductivity of p-type Sb$_2$Te$_3$ composite films increase by orders of magnitude with increasing curing temperature as shown in Fig. 6(a).

At a curing temperature of 150 °C, the conductivity was low (1.80 S/cm) as charge carriers were limited by grain boundary scattering. However, as the curing temperature increased, sintering took place resulting in larger grains and reduction in grain boundary scattering. This resulted in higher conductivity of the samples cured at higher temperature (450 S/cm for sample cured at 350 °C). The DSC curve of Sb$_2$Te$_3$ submicron particles showed in Fig. 1(b) and SEM micrograph shown in Fig. 4(b) support the described mechanism. The insensitivity of the conductivity of Bi$_2$Te$_3$ composite film curing temperature can be explained by the
absence of sintering. The DSC curve for Bi$_2$Te$_3$ powder in Fig. 1(b) and the SEM micrograph in Fig. 4(d) imply that sintering is unlikely in the case of Bi$_2$Te$_3$ films.

Figure 6(b) shows the trend of Seebeck coefficients ($\alpha$) for n-type and p-type printed composite films with curing temperature. Table I shows the comparison of composite material properties under various processing conditions, along with bulk material properties of pellets made from the n-type Bi$_2$Te$_3$ and p-type Sb$_2$Te$_3$ powders using cold-pressed methods. On increasing the curing temperature above 200 °C, $\alpha$ decreases for p-type Sb$_2$Te$_3$ thermoelectric composite films as shown in Fig. 6(b) as well as in Table I. As the curing temperature approached the sintering temperature (350 °C), more antisite defects were generated and therefore carrier (holes) concentration increased.\(^{31}\) According to Ioffe, the Seebeck coefficient is a function of the carrier concentration.\(^3\) Hall effect measurements have confirmed that carrier concentration was much higher for samples cured at 350 °C as compared to samples cured at 200 °C and bulk
The effects of annealing time (t) on thermoelectric properties of printed composite thick films were also examined. Figure 7(a) shows that the electrical conductivity of p-type Sb$_2$Te$_3$ composite films increased with increased annealing time at 350 °C. This is likely due to an increase in grain sizes with increasing annealing time, which reduces the scattering by grain boundaries and increases the conductivity. No improvement in n-type Bi$_2$Te$_3$ has been observed with increased annealing time.

Figure 7(b) shows the effect of annealing time on the Seebeck coefficient for both p-type Sb$_2$Te$_3$ composites and n-type Bi$_2$Te$_3$ composites. For p-type composites, the Seebeck coefficient decreased due to increased carrier concentration as previously explained. For n-type Bi$_2$Te$_3$ composite thick films, Seebeck coefficient increased with increased annealing time. The carrier concentrations for various samples annealed at 350 °C for different hours were measured and were found to continuously decrease with increased annealing time as previously explained.

Figure 7(c) shows the power factor ($\alpha^2\sigma$) as a function of curing time at 350 °C. The power factor for Bi$_2$Te$_3$ sample increased when the curing time increased from 6 to 12 h but remained unchanged afterwards. While the Seebeck coefficient increased, the electrical conductivity decreased.
with increasing curing temperatures, thus reducing the power factor. The power factor (\(\alpha^2/\sigma\)) for p-type Sb2Te3 composite films increased with increasing curing time from 6 to 12 h but also showed no improvement with additional annealing time. These graphs indicate that a 12 h curing and annealing at 350 °C provide optimized thermoelectric properties for p-type Sb2Te3 composite films.

The thermal conductivity (k) of the composite material is reduced significantly as compared to bulk thermoelectric materials due to the insulating epoxy (thermal conductivity 0.2 W/m K) and the fine grains of the active filler particles present.\(^{35}\) The thermal conductivity of the n-type Bi2Te3 and p-type Sb2Te3 composites are 0.24 W/m K when cured at 200 °C, and results are comparable to that of silver based electrically conductive adhesives.\(^{24}\) At 350 °C curing temperatures, the thermal conductivity of Bi2Te3 composite sample remains unchanged while the thermal conductivity of Sb2Te3 composite sample increased to 0.54 W/m K.

This is likely due to larger grain formation from sintering, resulting in increase in the thermal conductivity.\(^{35}\) While precautions were taken during sample preparation to form dense samples, the larger samples exhibited some porosity. Therefore, further work needs to be performed to measure the thermal conductivity of films.

**IV. CONCLUSIONS**

N-type Bi2Te3 and p-type Sb2Te3 composite materials were successfully developed for fabricating thermoelectric devices using a dispenser printer. Processing parameters to optimize thermoelectric performance of the composite materials were also explored. The Seebeck coefficients of the composite materials were similar to the bulk material properties and the fine grains of the active filler particles present.\(^{35}\) The thermal conductivity of the n-type Bi2Te3 and p-type Sb2Te3 composites are 0.24 W/m K when cured at 200 °C, and results are comparable to that of silver based electrically conductive adhesives.\(^{24}\) At 350 °C curing temperatures, the thermal conductivity of Bi2Te3 composite sample remains unchanged while the thermal conductivity of Sb2Te3 composite sample increased to 0.54 W/m K.

This is likely due to larger grain formation from sintering, resulting in an increase in the thermal conductivity.\(^{35}\) While precautions were taken during sample preparation to form dense samples, the larger samples exhibited some porosity. Therefore, further work needs to be performed to measure the thermal conductivity of films.

**ACKNOWLEDGMENTS**

The authors thank the California Energy Commission for supporting this research under Award No. DR-03-01. We would also like to thank Mike Koplow, Brian Mahlstedt, Christine Ho, and Jay Keist for their contributions.