Organic-Inorganic Thermoelectric Material for a Printed Generator

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Abstract. We made a thermoelectric mini-generator by a screen printing method. The sub-milliwatt electric power was generated on a heated plate at 60°C. The composite of Bi₂Te₃ particles and polyimide with ionic-liquid was made as an ink for printing. The printed composite film was annealed at 400°C for 1 hour in Argon with hydrogen to improve the thermoelectric properties. The diameter of the Bi₂Te₃ particles was about 1-2 μm and polyimide with ionic-liquid was filled between the particles. The Seebeck coefficient of the film was measured by applying a temperature difference along the in-plane direction while measuring the Seebeck voltage. The electrical conductivity was measured by four-point probe method. The cross-plane thermal conductivity was measured by differential 3ω method. The measured Seebeck coefficient of p-type thermoelectric film was 245 μV/K, the electrical conductivity was 160 S/cm, and the thermal conductivity was 0.33 W/(m·K). The Seebeck coefficient, the electrical conductivity and thermal conductivity for n-type was -165 μV/K, 140 S/cm, and 0.23 W/(m·K), respectively. The non-dimensional figure of merit of the film is 0.87 for p-type, and 0.5 for n-type. Those thermoelectric properties were much improved than those of Bi₂Te₃ with PEDOT:PSS composite. The high thermoelectric properties are achieved by extremely low thermal conductivity of the composites. The thermal conductivities of both p-type and n-type films were lower than that of polyimide film.

1. Introduction
Thermoelectric generator is one of the important technologies for energy harvesting without any moving parts and fuels [1], [2]. In addition, electricity can be generated directly even at low-temperature by thermoelectricity. The thermoelectric micro-generators have been intensively developed by machining process [3], vacuum deposition [4],[5], electroplating [6], printing [7]-[13] and so on. Thermoelectric performance is evaluated non-dimensional figure of merit ZT, which is defined as ZT=(S²/σκ)×T, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The output power of the thermoelectric generator is increased as increasing ZT, and high-ZT materials have been reported by using nano-structures, such as nano-composite[14], nanowire[15], nano-crystalline[16], nano-porous[17], [18], superlattices[19], [20] etc. Recently, it has been pointed out that the production cost is also important for the practical use of thermoelectric generator as well as ZT[21][22]. New fabrication process with low cost must be developed. Here, we developed the organic-inorganic thermoelectric materials to make thermoelectric films with high ZT through the low cost processes. The developed materials can be applied to screen printing for making an in-plane
thermoelectric generator. The performance of the screen printed generator was evaluated by output power.

2. Experiment

We prepared for the several printed p-type Bismuth Telluride (Bi$_2$Te$_3$) to enhance the thermoelectric properties[7],[11], especially the improvement of the electrical conductivity. The electrical conductivity was measured by four-probe method, and the in-plane Seebeck coefficient of the films was measured at room temperature. One end of the film was heated by a temperature controlled hot plate and the other end was cooled by a heat sink. The temperature difference between the both ends was measured by two K-type thermocouples, and the generated voltage difference was measured simultaneously. The Seebeck coefficient was determined as the ratio of the potential difference along the film to the temperature difference. The cross-plane thermal conductivity was measured by differential 3ω method[23]. The effective thermal conductivity was calculated by the measured thermal resistance of the film in cross-plane. The film thickness was measured by using a stylus profilers (Dektak) to determine both electrical conductivity and thermal conductivity. The film thickness was double-checked from the cross-sectional view of SEM images.

2.1. P-type Bismuth Telluride nano-particles

The nano-particles of p-type Bi$_2$Te$_3$ were mixed with the toluene, and the nano-particle solution was dropped onto the Al$_2$O$_3$ substrate[7]. The film was sintered to remove the toluene, and to enhance the growth of nano-particles in hydrogen for 60 min at temperature ranging from 300 to 500°C. The samples were cooled down naturally to room temperature after sintering.

2.2. P-type Bismuth Telluride – PEDOT:PSS

Thermoelectric films was prepared by using a mixture of p-type Bi$_2$Te$_3$ particles with conductive polymer (PEDOT:PSS), poly acrylic acid and glycerol[11]. The electrical conductivity of the films of Bi$_2$Te$_3$ particles was much improved by adding a conductive polymer. It is well known that the conductivity of a random porous material is much lower than that of a bulk material as the percolation effect. The pores between Bi$_2$Te$_3$ particles were filled by a conductive material to avoid the huge electrical conductivity reduction. The glycerol was added to the mixture for the effect of the high-boiling solvent for PEDOT:PSS. The growth of the PEDOT-rich particles was enhanced by adding high-boiling solvent to the mixture, and the electrical conductivity of PEDOT:PSS was increased.

2.3. P-type Bismuth Telluride – Polyimide

The composite films of Bi$_2$Te$_3$ and polyimide with ionic-liquid were prepared by printing method. Polyimide film was made by heating polyamic acid. Polyamic acid and ionic liquid is solved to NMP (N-methylpyrrolidone) with 2-Methoxyethanol. The Bi$_2$Te$_3$ particles were added to the solution of polyamic acid and ionic-liquid. The mixture was spin-coated on the Al$_2$O$_3$ substrate, and dried at 120°C for 10 min. The dried films were heated at 300 to 450°C for 60 min in Ar with hydrogen to enhance the thermoelectric properties. The fabricated thermoelectric films were evaluated by the measurements of Seebeck coefficient, electrical conductivity, and thermal conductivity.

3. Results and discussions

The thermoelectric properties of The Bi$_2$Te$_3$ nanoparticles films are shown in figure 1. The electrical conductivities were less than 130 S/cm even at high sintering temperature, although the electrical conductivity was improved by increasing sintering temperature. The crystal growth occurs at high temperature as shown in figure 2. The electrical conduction paths were increased by the crystal growth of Bi$_2$Te$_3$. The Seebeck coefficient was gradually decreased by increasing annealing temperature due to the Tellurium sublimation. Both high Seebeck coefficient and high electrical conductivity cannot be achieved at any sintering temperature. The highest power factor S$^2$$\sigma$ of the films was 1.3μW/(cm K$^2$) annealed at 350°C, and the highest non-dimensional figure of merit was 0.16 at 300K. Next, the
Conductive materials were filled between Bi$_2$Te$_3$ particles to avoid the huge reduction of electrical conductivity due to percolation effect. PEDOT:PSS was used as the conductive polymer. The measured thermoelectric properties are shown in figure 3. The effective properties of composite calculated the simple models were shown as the solid lines in the figures[9]. The series coupling model is as follows:

\[
\sigma = \frac{\sigma_{\text{Bi}_2\text{Te}_3} \sigma_{\text{Cond.}}}{x \sigma_{\text{Bi}_2\text{Te}_3} + (1-x) \sigma_{\text{Cond.}}} \quad S = \frac{S_{\text{Bi}_2\text{Te}_3} x/\kappa_{\text{Bi}_2\text{Te}_3} + S_{\text{Cond.}} (1-x)/\kappa_{\text{Cond.}}}{x/\kappa_{\text{Bi}_2\text{Te}_3} + (1-x)/\kappa_{\text{Cond.}}} 
\]

\(x\) is the volume fraction of Bi$_2$Te$_3$ in the composite. The parallel coupling model is as follows:

\[
\sigma = x \sigma_{\text{Bi}_2\text{Te}_3} + (1-x) \sigma_{\text{Cond.}} \quad S = \frac{S_{\text{Bi}_2\text{Te}_3} \sigma_{\text{Bi}_2\text{Te}_3} x + S_{\text{Cond.}} \sigma_{\text{Cond.}} (1-x)}{\sigma_{\text{Bi}_2\text{Te}_3} x + \sigma_{\text{Cond.}} (1-x)}
\]

The higher curve was calculated by a parallel model and the lower curve was calculated by a series model. The measured properties were used for PEDOT:PSS at \(x=0\) in figure 3. The measurements results were expected between two models, but all thermoelectric properties were measured to be lower than the minimum value. The only effective Seebeck coefficient was roughly explained by series connection model. The measured electrical conductivity was well improved to be 400 to 600 S/cm, although the measured electrical conductivity was lower than the expected values. The decrease of thermal conductivity was also huge, therefore the non-dimensional figure of merit is slightly improved.
to be 0.2. Finally, we used polyimide with ionic-liquid for filling materials into the porous Bi$_2$Te$_3$ film. The sintering temperature can be increased because both polyimide and ionic-liquid are heat resisting materials. The SEM images of the sintered Bi$_2$Te$_3$ films were shown in figure 4. The polyimide with ionic-liquid was filled in pores between Bi$_2$Te$_3$ particles. The Seebeck coefficient of the composite film were increased as increasing sintering temperature up to 450°C. The maximum power factor was

### Table 1. Thermoelectric properties of printed films

| Materials                                | Particle Diameter, µm | $\sigma$, S/cm | $S$, $\mu$V/K | $\kappa$, W/(m·K) | ZT at 300K |
|------------------------------------------|-----------------------|----------------|---------------|-------------------|-------------|
| P-type Bi$_2$Te$_3$ nano particles[7]    | 0.05                  | 72             | 135           | 0.25              | 0.16        |
| P-type Bi$_2$Te$_3$ and PEDOT:PSS [11]   | 0.66                  | 420            | 42            | 0.24              | 0.09        |
| P-type Bi$_2$Te$_3$ and PEDOT:PSS [11]   | 208                   | 380            | 79            | 0.36              | 0.20        |
| P-type Bi$_2$Te$_3$ and Polyimide        | 1.2                   | 160            | 245           | 0.33              | 0.87        |
| N-type Bi$_2$Te$_3$ and Polyimide        | 1.2                   | 140            | -165          | 0.23              | 0.5         |
| Single Crystal Bulk p- Bi$_2$Te$_3$ [24] | -                     | 780            | 225           | 1.37              | 0.87        |
| Thin film p-Bi$_2$Te$_3$[25]             | -                     | 640            | 236           | 1.05              | 1.0         |
measured to be 9.6 \mu W/(cm·K²) in the p-type film, and 3.5 \mu W/(cm·K²) in n-type films sintered at 415°C. The thermal conductivity of the film was 0.33 W/(m·K). The thermal conductivity of the polyimide film was measured to be 0.39 W/(m·K) by 3ω method. The effective thermal conductivity was lower than thermal conductivities of both polyimide and Bi₂Te₃. The measured thermoelectric properties of the composite films are summarized in table 1. The measured extremely low thermal conductivity resulted in high ZT of the films. The thermal transport can be suppressed due to strong phonon scattering at the interfaces between inorganic and organic materials. The evaluated number of interfaces with 10⁻⁷ (m²·K)/W interfacial thermal resistance well explained the measured low effective thermal conductivity of the composite films in the present study.

4. Thermoelectric module
The thermoelectric mini-modules were made by screen printing method as shown in figure 5. The output power of the module was measured during heating up to 60°C of the bottom of the sheet module temperature as well as keeping 17°C of the top surface temperature of the sheet module. The measured open circuit voltage and output power were plotted in Fig. 6. The maximum output power was measured to be 200\mu W generated by a 5cm×5cm module. The sub-milli-watt output power was generated at 60°C by a printed low cost thermoelectric module.

5. Conclusions
The composite of Bi₂Te₃ and conductive polymer were printed on the flexible substrate by a printing method to reduce the production cost as well as keeping the high thermoelectric properties. The maximum ZT was 0.87 for p-type and 0.5 for n-type by using polyimide with ionic-liquid as the
conductive polymer. Thermoelectric performance was improved by high temperature sintering using heat-resisting materials. The high ZT was measured due to low thermal conductivity in the present study. The mechanisms of the thermal conductivity reduction should be investigated for the future work. Finally, the thermoelectric mini-generator was made by screen printing, and the performance was measured at near room temperature. The generated power was 200 µW by a 5cm×5cm module at 60°C. We demonstrated the high performance of thermoelectric module prepared by low cost processes.

6. References

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