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Enhancement of the generating power in Cu/Bi–Te/Cu composite thermoelectric devices

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Abstract The voltage ΔV and electric current ΔI of the p- and n-type Cu/Bi–Te/Cu composite thermoelectric devices were measured as a function of ΔT for four regions of the intrinsic Bi–Te compound, Cu/Bi–Te and Bi–Te/Cu interfaces and Cu/Bi–Te/Cu composite using thermocouples set at intervals of s = 2 and 6 mm, where the lengths of Bi–Te compound and copper are 4 and 5 mm, respectively. ΔV and ΔI of all regions tended to increase linearly with an increase of ΔT. The resultant α was obtained from the relation $\Delta V/\Delta T$. The resultant α values of regions including the interface are much higher in absolute value than those of the intrinsic Bi–Te compounds, so that the barrier thermo-emf is found to occur in the forward-bias direction. It indicates that the barrier thermo-emf appears even in the semiconductor-metal junction, as in the case of the p–n junctions. The resultant α of Cu(T_H)/Bi–Te interface rich in the heat flow increases with an increase of ΔT, while that of Bi–Te/Cu(T_C) interface poor in the heat flow decreases with an increase of ΔT. The ΔT-dependence of α of the interfaces is entirely opposite at the hot and cold sides. As a result, the resultant α of the p- and n-type Cu/Bi–Te/Cu composites remained little varied with changes of ΔT, so that the present composites have a thermal stability superior to the intrinsic Bi–Te compounds.The generating powers $\Delta W_{\text{Bi-Te}}$ and $\Delta W_{\text{Cu/Bi-Te/Cu}}$ for the p- and n-type intrinsic Bi–Te compounds and Cu/Bi–Te/Cu composites increased parabolalically with an increase of ΔT, and the ratios of $\Delta W_{\text{Cu/Bi–Te/Cu}}$ to $\Delta W_{\text{Bi–Te}}$ reached great values of 1.41 and 1.45 for the p- and n-type composites, respectively. It was thus found that the enhancement in the resultant α of the composite materials results in a significant improvement in the conversion efficiency for generators.

Introduction

The energy conversion system composed of thermoelectric devices has attracted much attention because it can convert directly thermal energy to electric energy without producing any harmful substance [1, 2]. The energy conversion efficiency increases with an increase of the thermoelectric dimensionless figure of merit ($ZT = \alpha^2 T/\rho\ \kappa$) of thermoelectric materials, where α is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity and T is the absolute temperature [1, 2]. For this reason, much effort has hitherto been made to raise the figure of merit mainly on high-Z materials such as tellurides and selenides of Bi, Sb, Pb, etc., and SiGe alloys [3, 4], but ZT was not much more than 1 till recently. However, it has been reported most recently that the superlattice structured thin film of the p-type Bi_2Te_3/Sb_2Te_3 reached an extremely high ZT of 2.4 [5] and the annealed bismuth-telluride compounds exceeded large 1 in both p- and n-type materials as a bulk material [6, 7].

Recently, it was reported by Bergman and Levy [8] that the resultant Z of a macroscopic composite device

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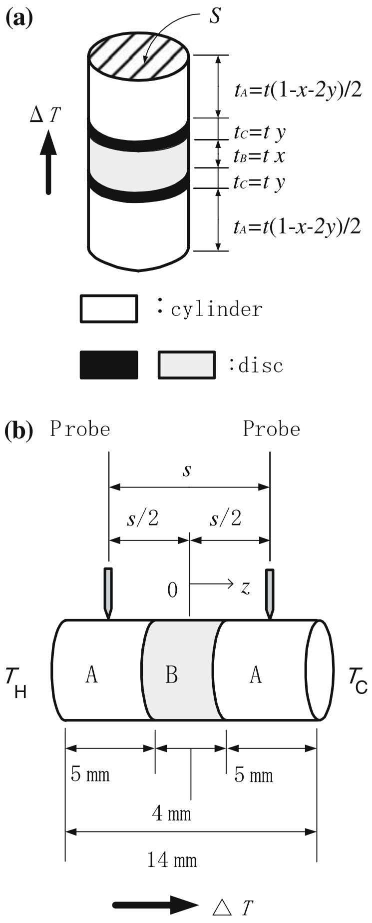

Fig. 1 (**a**) Composite thermoelectric device (CTD) with a sandwich structure (A/C/B/C/A) in which a disc of the thermoelectric material B is sandwiched directly between two thin discs of material C and further it is sandwiched between two cylinders of material A, and (**b**) a schematic diagram for the Seebeck coefficient and electrical resistivity measurements, where two thin discs of material C are omitted for simplicity

can never exceed the largest Z among the component materials, unlike the superlattice systems, as long as the resultant α is not enhanced. When a semiconductor is kept in contact with a metal or a semiconductor with different types of conduction, a potential barrier generally occurs at their interfaces. Tauc [9] indicated theoretically about fifty years ago that when such a barrier was accompanied by a sufficiently great temperature drop, the additional barrier thermo-emf appears as a result of the separation of non-equilibrium carriers at the interface. The Seebeck coefficient corresponds to the differentiation of this thermo-emf with respect to ΔT, where ΔT is the temperature difference producing the thermo-emf. The appearance of the barrier thermo-emf was indeed observed in the p–n junctions by illuminating them with infrared light pulse from a laser [10]. Most recently, it was also observed as an enhancement in the resultant α even in the thermoelectric composites [11, 12] corresponding to the metal–semiconductor junction, in which a thermoelectric semiconductor is sandwiched between two metals. For example, the significant increase in the resultant α was observed by us in macroscopic n-type M/T/M (M = Cu or Ni and T = $Bi_{0.88}Sb_{0.12}$) composites welded with Bi–Sb alloy [11]. The maximum α of these composites was –110 μV/K, which is 29% higher in absolute value than –85 μV/K of Bi–Sb alloy. The maximum ZT of these M/T/M composites was a low value of 0.44 at 298 K, but the degree of increase in ZT reached a large value of 69%. Such a large increase in ZT of macroscopic composites was attributed to a significant enhancement in α. Similar phenomenon was also observed even in the n-type Cu/Bi/Cu composite in which the maximum α is 21% higher in absolute value than –70 μV/K of Bi [12]. In addition, the resultant α at 298 K of the p- and n-type Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn reached great values of 263 and –266 μV/K, respectively, at a relative thickness of 0.98 for a thermoelectric material, which are approximately 32% and 30% higher in absolute value than 202 and –205 μV/K of the intrinsic Bi–Te compounds [13]. As a result, surprisingly great ZT values of 1.53 and 1.66 were obtained for the p- and n-type Cu/Bi–Te/Cu composites, respectively, and they correspond to about twice as large as those of commercially utilized Bi–Te compounds [13]. It was clarified by us that the phenomenon of increase in α occurs not only in the p–n junctions, but also in the composites in which a thermoelectric semiconductor is sandwiched between two metals. The composite materials with a sandwich structure may thus be considered as useful means of further increase in ZT of bulk thermoelectrics.

However, it has not been observed whether the barrier thermo-emf generated by applying the thermal gradient to the composite is available as electric energy and the increase in the resultant ZT results really in the increase in the energy conversion efficiency. For this reason, the voltage ΔV and electrical current ΔI were measured as a function of ΔT for four regions of Bi–Te, Cu/Bi–Te, Bi–Te/Cu and Cu/Bi–Te/Cu of the p- and n-type Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn, and the generating power was estimated by the product of ΔV and ΔI for the intrinsic Bi–Te compound and Cu/Bi–Te/Cu component.

The purpose of this paper is to investigate whether the barrier thermo-emf generated near the interface of composites is available as electric energy and the increase in the resultant α leads directly to the increase in the energy conversion efficiency.

Calculation and experiments

Calculations of the resultant ρ, α, κ and ZT of a composite material

Let us consider a composite thermoelectric device (CTD) with a sandwich structure (A/C/B/C/A) in which a disc of the thermoelectric material B is sandwiched directly between two discs of material C and further it is sandwiched between two cylinders of material A, as shown in Fig. 1a. Here, we calculate the resultants ρ ,κ, α and ZT for CTD by treating it as an electrical and thermal circuit in which the direction of the temperature gradient is acting along the cylindrical axis. The materials A, B and C have the same cross-sectional area S and three different thicknesses t_A, t_B and t_C, respectively, where the thin disc C is dealt and regarded as the interface between two materials A and B. For this reason, it was assumed here that the scattering of carriers and phonons never occurs at the boundary between two materials A and B. When the electrical resistivities of the materials A, B and C are ρ_A, ρ_B and ρ_C and the total thickness is t, the total electrical resistivity ρ of CTD is expressed as

$$\rho = \frac{1}{t}(2\rho_A t_A + \rho_B t_B + 2\rho_C t_C). \tag{1}$$

Here if we suppose $t_A = t(1–x–2y)/2$, $t_B = tx$ and $t_C = ty$, Eq. 1 can be rewritten as

$$\rho = \rho_B\{x + b_1(1 - x - 2y) + 2b_2 y\}, \tag{2}$$

where $b_1 = \rho_A/\rho_B$ and $b_2 = \rho_C/\rho_B$. If the thermal conductivities of the materials A, B and C are κ_A, κ_B and κ_C, the total thermal conductivity κ of CTD is expressed as

$$\begin{aligned}\frac{1}{\kappa} &= \frac{(1 - x - 2y)}{\kappa_A} + \frac{x}{\kappa_B} + \frac{2y}{\kappa_C}\\ &= \frac{1}{\kappa_B}\{x + \frac{(1 - x - 2y)}{c_1} + \frac{2y}{c_2}\},\end{aligned} \tag{3}$$

where $c_1 = \kappa_A/\kappa_B$ and $c_2 = \kappa_C/\kappa_B$. For a given temperature difference ΔT, the temperature difference generated in each thermoelectric should be proportional to thickness but inversely proportional to thermal conductivity, at least for a thin CTD. Taking this into account, the ratios of ΔT_A and ΔT_C to ΔT_B are expressed as

$$\frac{\Delta T_A}{\Delta T_B} = \frac{t_A \kappa_B}{t_B \kappa_A} = \frac{(1 - x - 2y)}{2c_1 x} \tag{4}$$

and

$$\frac{\Delta T_C}{\Delta T_B} = \frac{t_A \kappa_B}{t_B \kappa_C} = \frac{y}{c_2 x} \tag{5}$$

The total temperature difference ΔT between both ends of CTD is given by

$$\Delta T = 2\Delta T_A + \Delta T_B + 2\Delta T_C. \tag{6}$$

By substituting Eqs. 4 and 5 into Eq. 6, the ratios of thermal difference ΔT_B and ΔT_C generated in sandwiched materials B and C to the total thermal difference ΔT are expressed as

$$\frac{\Delta T_B}{\Delta T} = \frac{c_1 c_2 x}{c_2(1 - x - 2y) + 2c_1 y + c_1 c_2 x} \tag{7}$$

and

$$\frac{\Delta T_C}{\Delta T} = \frac{c_1 y}{c_2(1 - x - 2y) + 2c_1 y + c_1 c_2 x} \tag{8}$$

respectively. When the Seebeck coefficients of the materials A, B and C are α_A, α_B and α_C, the total thermal voltage ΔV generated by ΔT_A, ΔT_B and ΔT_C is written as

$$\Delta V = 2\Delta T_A \alpha_A + \Delta T_B \alpha_B + 2\Delta T_C \alpha_C. \tag{9}$$

Therefore, the overall Seebeck coefficient α is expressed as

$$\alpha = \frac{\Delta V}{\Delta T} = \alpha_B \frac{a_1 c_2(1 - x - 2y) + 2a_2 c_1 y + c_1 c_2 x}{c_2(1 - x - 2y) + 2c_1 y + c_1 c_2 x} \tag{10}$$

using Eqs. 4–9, where $a_1 = \alpha_A/\alpha_B$ and $a_2 = \alpha_C/\alpha_B$. When the composites satisfy two conditions of $c_1 \gg 1$ and $y \ll 1$, the thermoelectric figure of merit $Z_{comp}T$ of CTD is expressed rather exactly as a function of x as

$$z_{comp}T = \frac{z_B T\{a_1 c_2(1 - x - 2y) + 2a_2 c_1 y + c_1 c_2 x\}^2}{c_1 c_2\{c_2(1 - x - 2y) + 2c_1 y + c_1 c_2 x\}\{x + b_1(1 - x - 2y) + 2b_2 y\}} \tag{11}$$

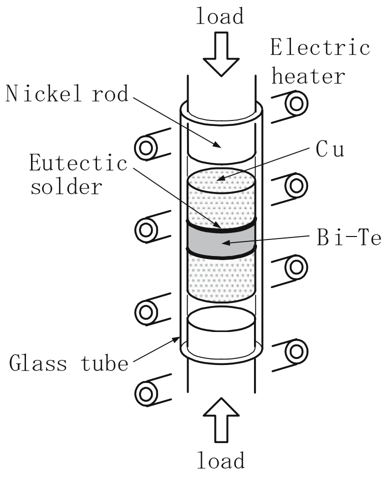

Fig. 2 Fabrication method of Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn

Of course, $Z_{\mathrm{comp}}T$ is also derived by substituting Eqs. 2, 3 and 10 into the relation $Z = \alpha^2/\rho\ \kappa$, but it is nothing but approximation, because Eq. 11 is derived theoretically only when $c_1 \gg 1$ and $y \ll 1$. These conditions for c_1 and y hold just for the present composites, because of $c_1 > 200$ and $y < 0.001$. As proved by Bergman and Levy [8], Z_{comp} has no local maximum at any relative thickness of a thermoelectric material, as long as the resultant α is not enhanced. As mentioned above, however, the experimental resultant ZT of the composite materials exceeded the largest ZT among the component materials [13].

Sample-preparation and measurements

The p-type $(Bi_{0.25}Sb_{0.75})_2Te_3$ doped with 12 wt% excess Te alone and n-type $Bi_2(Te_{0.94}Se_{0.06})_3$ codoped with 0.010 wt% CuBr, 0.102 wt% I and 0.026 wt% Te were prepared by the Bridgman method, using pure Bi granule of 99.999% and pure Sb, Te, Se, I and CuBr granules of 99.99% as starting materials [14, 15]. The materials were weighed out in appropriate atomic ratios, charged into a quartz tube and melted in an evacuated quartz tube by an induction heating to make a homogeneous ingot without segregation. After melting, the compounds were unidirectionally solidified by the Bridgman method at a fast rate of 6 cm/h, to produce intentionally scattered second-phase precipitates in the ingot. It is the same growth rate as that employed in preparing the previous specimens [14, 15] and is close to one of various growth conditions reported by Yim and Rosi [16]. Naturally, the resulting ingots consisted of relatively coarse grains with the cleavage planes aligned partially parallel to the freezing direction [7].

These as-grown p- and n-type Bi–Te ingots were employed to prepare the p-and n-type Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn. The as-grown Bi–Te ingots were cut into a length of 4 mm after grinding into a cylinder of Ø5 mm, where the cylindrical axis is parallel to the freezing direction. Cylindrical copper was prepared by cutting a copper rod with a diameter 5 mm into a length of 5 mm, where the purity of copper was 99.99%. Eutectic solder was melted into a thin disc of Ø5 × t mm, where t is smaller than 0.3 mm. The diameter of these cylinders and thin discs was made slightly smaller than 5 mm, to make it easy to put into a glass tube of an inner diameter Ø5 mm. Both end surfaces of cylindrical Bi–Te compounds and coppers were polished mechanically by the lapping method to make flat the welded surface. After one end of Bi–Te compounds was plated with Ni so that it has a thickness of several μm, a set of cylindrical coppers, eutectic solders and Bi–Te compound was put into a glass tube of an inner diameter Ø5 mm so that eutectic solders are sandwiched between copper and Bi–Te compounds and touched directly with the surface plated with Ni of Bi–Te compounds. Since eutectic solder has the lowest melting point of 456 K among them, eutectic solder is first melted in a glass tube by an electric heater. While eutectic solder is melted, Bi–Te compound was welded with two coppers

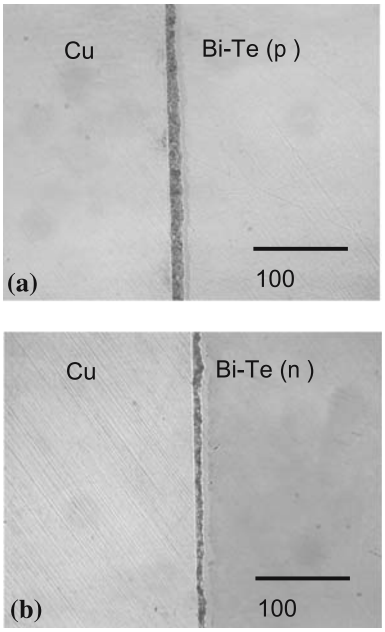

Fig. 3 Photographs of boundaries of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites welded with eutectic solder of Pb–Sn

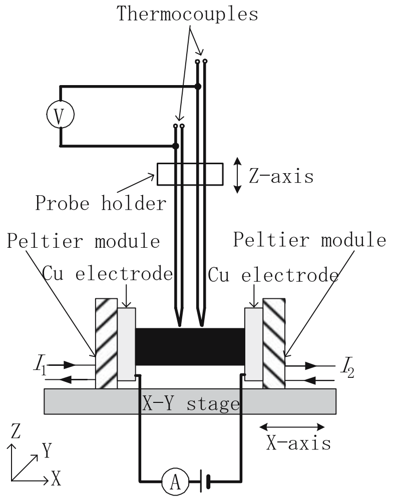

Fig. 4 Schematic configuration for measurements of the Seebeck coefficient α and electrical resistivity ρ. One end was heated by flowing the electrical current I_1 or I_2 through a Peltier module to produce the temperature differences and another one was then maintained at room temperature

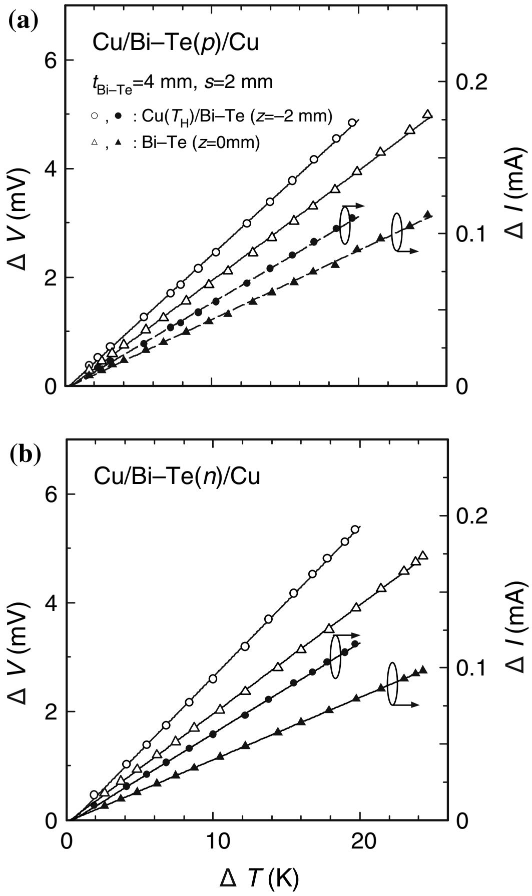

Fig. 5 ΔV and ΔI measured as a function of ΔT for Bi–Te and Bi–Te/Cu of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites using thermocouples set at an interval of s=2 mm

by compacting two cylindrical coppers of both ends at a constant force of 2 N using two nickel rods, as shown in Fig. 2. After a welded cylinder was naturally cooled to room temperature, it was ejected from a glass tube using a nickel rod. In order to investigate whether the composite materials are welded tightly, they were polished along the cylindrical axis of a welded device, so that no crack and no exfoliation were detected at the boundaries of all devices, as shown in Fig. 3. The thickness of solder was nearly equal to or less than 10 μm.

In order to investigate the thermoelectric properties of the as-grown ingots, a parallelepiped of $5 \times 5 \times 15$ mm^3 and a square plate of $10 \times 10 \times 3$ mm^3 was cut from the central part of ingots, where the length of 15 mm and thickness of 3 mm were cut parallel to the freezing direction. The former specimens were subjected to Seebeck coefficient α and electrical resistivity ρ measurements (Sinku-Riko Inc., Model ZEM-1), and the latter ones to thermal conductivity κ measurement (Sinku-Riko Inc., Model TC-3000) after grinding into a disk of Ø10×3 mm. The Seebeck coefficient α was measured by the conventional technique, using two alumel-chromel thermocouples set at an interval of 8 mm, in the temperature range from 293 to 303 K with the temperature difference of about 10 K. The electrical resistivity ρ was measured concurrently by the four-probe method. The thermoelectric properties of α, ρ and κ were measured at 298 K within an accuracy of 2%, 2% and 3%, respectively. The resultant accuracy was about 9% as a thermoelectric figure of merit.

The temperature gradient was produced between both ends of a composite along the freezing direction of Bi–Te ingot. The voltage ΔV and electric current ΔI generated by the applied temperature gradient were measured as a function of ΔT for four regions of the intrinsic Bi–Te compound, Cu/Bi–Te and Bi–Te/Cu interfaces and Cu/Bi–Te/Cu composite using thermocouples set at intervals of s = 2 and 6 mm, where ΔT is the temperature difference between thermocouples. One end of a composite was then heated to 318 K and another was maintained at 293 K, so that the temperature of the central part of a composite reaches 298 K at ΔT = 10 K. These measurements were performed using an apparatus fabricated by us. Figure 4 shows a schematic of the apparatus. It has two alumel-chromel thermocouples (0.25 mm in diameter) to detect temperatures and a voltage on the surface of a composite. A composite is mounted on an X–Y stage and the temperature gradient was applied with two Peltier modules equipped to both ends of the specimen. The resultant α of each region was obtained from the

Table 1 Thermoelectric properties measured at 298 K for pure Cu and the p-and n-type Bi–Te compounds

		Cu	Bismuth-telluride	
			p-type	n-type
Electrical resistivity	ρ (μ Ω m)	0.0171	8.70	7.02
Seebeck coefficient	α (μV/K)	+1.9	202	–205
Thermal conductivity	κ (W/m K)	401 [a]	1.64	1.78
Power factor	P (mW/K^2 m)	0.21	4.60	5.99
Figure of merit	ZT	1.57×10^{-4}	0.85	1.00

[a] Ref. [17]

relation $\Delta V/\Delta T$ and the generating power ΔW of each region was estimated by the product of ΔV and ΔI. The external electrical resistance of a measuring circuit was about 40 Ω, which is about twenty thousand times as large as the intrinsic electrical resistance (~ 2 mΩ) measured with $s = 6$ mm for the p- and n-type composites.

Results and discussion

Dependences of ΔV, ΔI and α on ΔT for Bi–Te and Cu/Bi–Te of composites

The voltage ΔV and electrical current ΔI generated in the intrinsic Bi–Te compound and at the interfaces of Cu(T_H)/Bi–Te and Bi–Te/Cu(T_C) were measured at $z = 0$ and ± 2 mm as a function of ΔT using two thermocouples separated by $s = 2$ mm, where Cu(T_H) and Cu(T_C) denote Cu cylinders situated at the hot and cold sides, respectively, and z is the distance from the center of Bi–Te compound to the middle between two thermocouples. It is found from Fig. 1b that when $|z|$ = 0 mm, two probes are placed on Bi–Te compound, while when $|z|$ = 2 mm, one probe is placed on Bi–Te compound and another on copper. As shown in Fig. 5, ΔV and ΔI for the p- and n-type composites tend to increase linearly with an increase of ΔT, even in either region. ΔV and ΔI of the interface are much higher than those of the intrinsic Bi–Te compounds, irrespective to the type of conduction. It suggests that the barrier thermo-emf generated near the two interfaces of composites appears even in the semiconductor-metal junctions, as in the case of the p–n junctions, and occurs in the forward-bias direction (with a plus sign in the p-type region and a minus sign in the n-type region).

Figure 6 shows the dependence of α on ΔT, in which α was obtained from the relation $\Delta V/\Delta T$. The resultant α values at ΔT =10 K of the intrinsic p- and n-type Bi–Te compounds are 190 and –201 μV/K, respectively, which are approximately 6% and 2% lower in absolute value than those listed in Table I, where the temperature difference of 10 K is the same as that employed in measuring α by the conventional technique. The resultant α of the intrinsic Bi–Te compounds and Cu(T_H)/Bi–Te interfaces tend to increase monotonically in absolute value with an increase of ΔT, while those of Bi–Te/Cu(T_C) interfaces exhibit a tendency to decrease almost linearly in absolute value with an

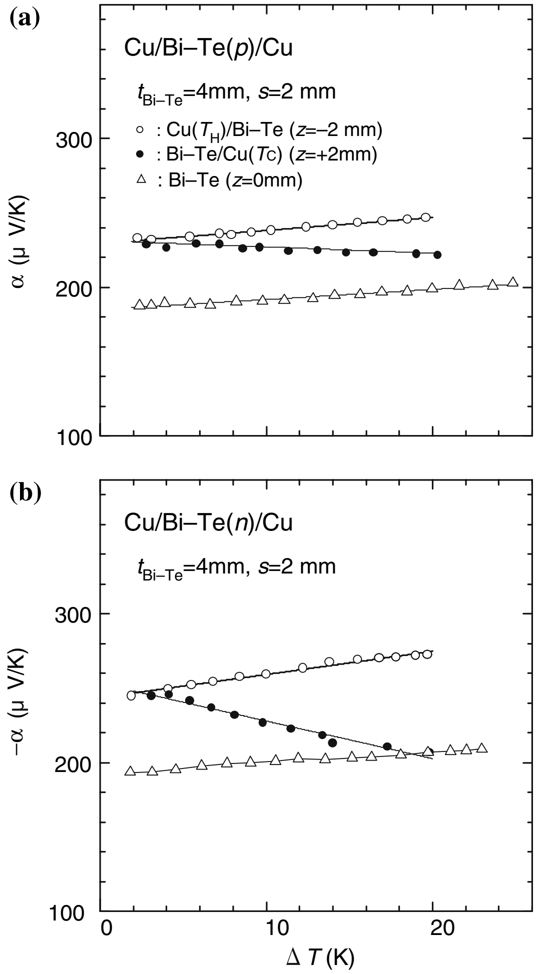

Fig. 6 α measured as a function of ΔT for Bi–Te, Cu(T_H)/Bi–Te and Bi–Te/Cu(T_C) of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites using thermocouples set at an interval of s = 2 mm

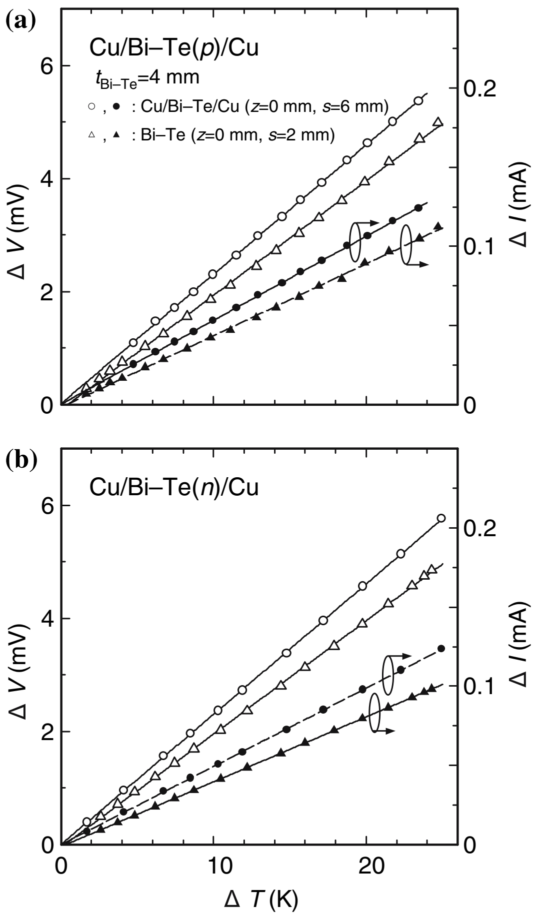

Fig. 7 ΔV and ΔI measured as a function of ΔT for Bi–Te and Cu/Bi–Te/Cu of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites using thermocouples set at an interval of $s = 6$ mm

increase of ΔT. The increase in α with increase of ΔT for the intrinsic Bi–Te compounds may be considered to result from the rise in specimen temperature, because α of the present compounds tends to increase linearly with temperature [6]. However, it is found that the barrier thermo-emf of two interfaces occurs in the forward-bias direction, although the ΔT-dependence of α of interfaces varies depending on the direction of the heat flow at the interface. In other words, the resultant α of the interface rich in the heat flow increases with an increase of ΔT, while that of the interface poor in the heat flow decreases with an increase of ΔT. The ΔT-dependence of α of the interfaces is found to be entirely opposite at the hot and cold sides.

Dependences of ΔV, ΔI and α on ΔT for Bi–Te and Cu/Bi–Te/Cu

The voltage ΔV and electrical current ΔI for the intrinsic Bi–Te compound and Cu(T_H)/Bi–Te/Cu(T_C)

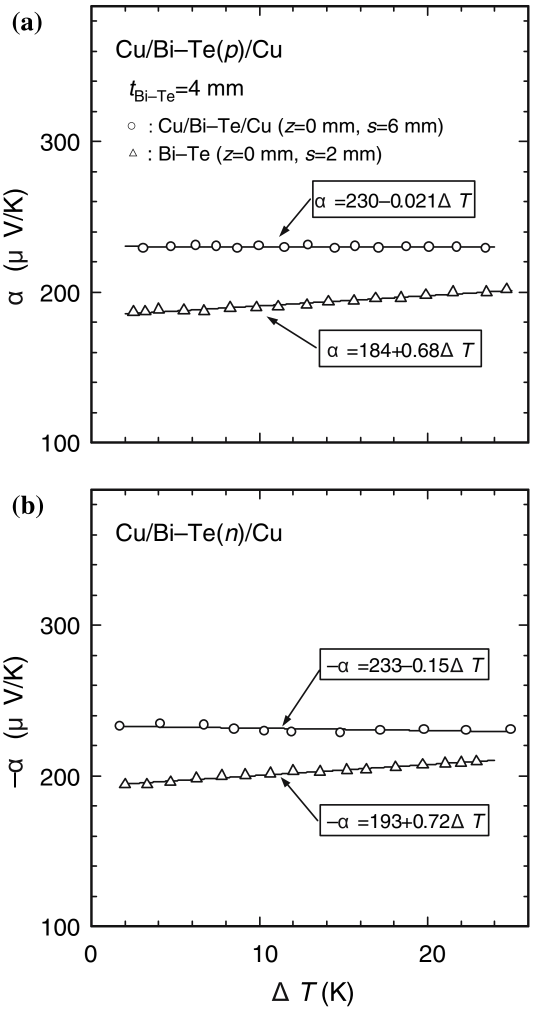

Fig. 8 α measured as a function of ΔT for Bi–Te and Cu(T_H)/Bi–Te/Cu(T_C) of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites using thermocouples set at intervals of $s = 2$ and 6 mm

composite were measured at $z = 0$ mm as a function of ΔT using two thermocouples separated by s=6 mm. When $z = 0$ mm, two probes are placed on two separate copper cylinders sandwiching the Bi–Te compound. The relative thickness of a thermoelectric material for the composite of Cu/Bi–Te/Cu corresponds to $x = 0.67$ from the definition of $x = t_B/s$. As shown in Fig. 7, ΔV and ΔI for the p- and n-type composites also increase linearly with an increase of ΔT, independently of measuring regions. ΔV and ΔI of the p-type Cu/Bi–Te/Cu are approximately 13% and 17% higher those of the intrinsic p-type Bi–Te compound, respectively, and ΔV and ΔI of the n-type composite are approximately 21% and 15% higher than those of the intrinsic n-type one, respectively. It was thus observed that the additional barrier thermo-emf generated near the two interfaces occurs in the forward-bias direction.

Figure 8 shows the ΔT-dependence of α for the intrinsic Bi–Te compounds and Cu/Bi–Te/Cu composites. The resultant α values at $\Delta T = 10$ K of the p- and n-type Cu/Bi–Te/Cu composites are 231 and –230 μV/K, respectively, which are approximately 22% and 14% higher in absolute value than 190 and –201 μV/K of the intrinsic p- and n-type Bi–Te compounds obtained above. The reason that the present α values were approximately 13% lower in absolute value than those obtained at $x = 0.98$ comes from the fact that they were measured at small x of 0.67, because the resultant α tends to increase almost linearly with an increase of x [13]. Interestingly, the resultant α of Cu/Bi–Te/Cu composites remained almost unchanged with ΔT, although those of the intrinsic p-and n-type Bi–Te compounds tend to increase slightly linearly with an increase of ΔT. The resultant α of Cu/Bi–Te/Cu are thus found to exhibit a thermal stability superior to those of the intrinsic Bi–Te compounds, as shown in Fig. 7; the ΔT-dependence of α for the p- and n-type composites is expressed in terms of $\alpha = 230–0.021\Delta T$ and $-\alpha = 233–0.15\Delta T$, respectively. The reason that the ΔT-dependence of the resultant α is very small is that the increase in α with increase of ΔT for both the intrinsic Bi–Te compound and interface of Cu(T_H)/Bi–Te may be canceled by the decrease in α with increase of ΔT for the interface of Bi–Te/Cu(T_C), so that the resultant α of composites is little changed with ΔT.

The place producing a large barrier thermo-emf is expected to be within Bi–Te compound adjacent to plated Ni, because Cu, Pb–Sn and Ni are metallic and have Seebeck coefficients much smaller than Bi–Te compounds. If so, the depth of interface layers giving the large barrier thermo-emf is guessed to be within 4–6% of the thickness of bulk Bi–Te compounds [13]. Therefore, the present barrier thermo-emf is considered to be generated in the region adjacent to the interface inside the thermoelectric material, not at the interface. When there are both a potential barrier and a sharp temperature drop at the interface between a metal and a thermoelectric semiconductor, therefore, the mechanism for the generation of the barrier thermo-emf may be different from that of the p–n junction. That is, the barrier thermo-emf may appear as a result of the separation of non-equilibrium carriers in the region adjacent to the interface inside the Bi–Te compound. In the present case, thus, a potential barrier may correspond to the energy gap between the acceptor level and the top of the valence band for the p-type compound or between the donor level and the bottom of the conduction band for the n-type Bi–Te one.

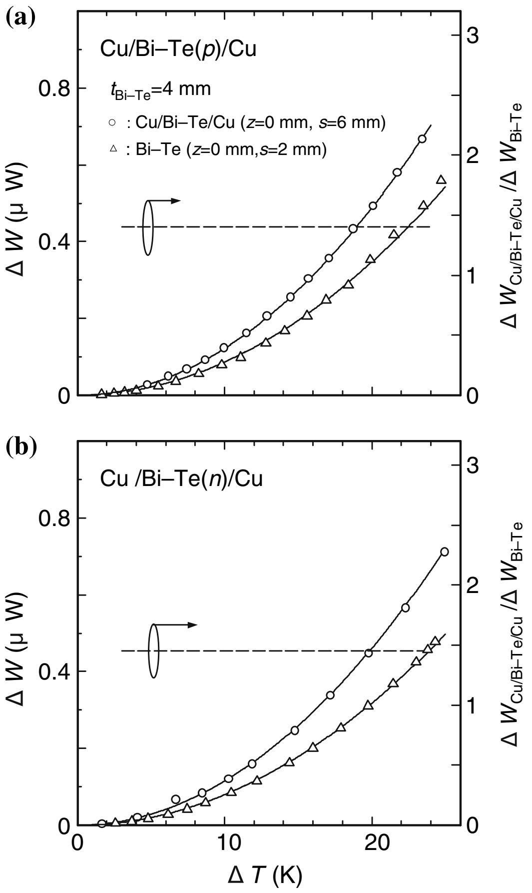

Fig. 9 Generating power ΔW measured as a function of ΔT for Bi–Te and Cu/Bi–Te/Cu of the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites using thermocouples set at intervals of s=2 and 6 mm. The dashed lines denote the ratios of $\Delta W_{\mathrm{Cu/Bi–Te/Cu}}$ to $\Delta W_{\mathrm{Bi\text{-}Te}}$ for the p- and n-type composites

Dependence of ΔW on ΔT for Bi–Te and Cu/Bi–Te/Cu

In order to investigate whether the additional barrier thermo-emf generated near the interface of composites is available as electrical energy, the generating power $\Delta W(= \Delta V \Delta I)$ was estimated as a function of ΔT using ΔV and ΔI measured for the p- and n-type intrinsic Bi–Te compounds and Cu/Bi–Te/Cu composites. Figure 9 shows the ΔT-dependences of $\Delta W_{\mathrm{Bi\text{-}Te}}$ and $\Delta W_{\mathrm{Cu/Bi–Te/Cu}}$ for the intrinsic p- and n-type Bi–Te compounds and Cu/Bi–Te/Cu composites. The observed generating power $\Delta W_{Bi–Te}$ and $\Delta W_{\mathrm{Cu/Bi–Te/Cu}}$ fall closely on the solid curves obtained by the least square fitting of a quadratic function of ΔT to the experimental values. The ratios of $\Delta W_{\mathrm{Cu/Bi–Te/Cu}}$ to $\Delta W_{Bi–Te}$ which were obtained by the least square fitting are denoted by the dashed lines in the figure, so that their ratios reached great values of 1.41 and 1.45 for the p- and n-type composites, respectively, independently of the magnitude of ΔT. The difference (ΔR) between the total electrical resistances $R = (\Delta V/\Delta I)$ of Bi–Te compound and Cu/Bi–Te/Cu composite is little reflected in the ratio, because $\Delta R/R$ is less than 5%. Of course, this ratio should be little changed theoretically even when the external electrical resistance was reduced extremely. It indicates that the additional barrier thermo-emf generated near two interfaces is available as generating powers, as well as the bulk thermo-emf of the intrinsic thermoelectric material, because it is not a mere polarization of non-equilibrium carriers caused by the temperature gradient. Therefore, the enhancement in the resultant α of the present composites is found to result in a significant improvement in the conversion efficiency for generators, but it would have little effect on a Peltier module. Combining with the previous result [13] that great ZT values of 1.53 and 1.66 were obtained for the p- and n-type Cu/Bi–Te/Cu composites, the increase in the energy conversion efficiency of composites may be related to the enhancement in the resultant ZT of composites.

Summary and conclusion

The voltage ΔV and electric current ΔI of the p- and n-type Cu/Bi–Te/Cu composites were measured as a function of ΔT for four regions of the intrinsic Bi–Te compound, Cu/Bi–Te and Bi–Te/Cu interfaces and Cu/Bi–Te/Cu composite using thermocouples set at intervals of $s = 2$ and 6 mm. ΔV and ΔI of these regions tend to increase linearly with an increase of ΔT. The resultant α was obtained from the relation $\Delta V/\Delta T$. The resultant α values of regions including the interface are much higher than those of the intrinsic Bi–Te compounds, irrespective to the type of conduction. It suggests that the barrier thermo-emf appears even in the interface between copper and Bi–Te compounds, as in the case of the p–n junction, and occurs in the forward-bias direction. The resultant α of Cu(T_H)/Bi–Te interface rich in the heat flow increases with an increase of ΔT, while that of Bi–Te/Cu(T_C) interface poor in the heat flow decreases with an increase of ΔT. The ΔT-dependence of α of the interfaces is entirely opposite at the hot and cold sides. As a result, the resultant α of Cu/Bi–Te/Cu composites was found to exhibit a thermal stability superior to those of the intrinsic Bi–Te compounds.

The generating powers $\Delta W_{\text{Bi-Te}}$ and $\Delta W_{\text{Cu/Bi–Te/Cu}}$ of the p- and n-type intrinsic Bi–Te compounds and Cu/Bi–Te/Cu composites increased parabolalically with an increase of ΔT. The ratios of $\Delta W_{\text{Cu/Bi-Te/Cu}}$ to $\Delta W_{\text{Bi-Te}}$ which were obtained by the least square fitting reached great values of 1.41 and 1.45 for the p- and n-type composites, respectively, independently of the magnitude of ΔT. It was thus found that the additional barrier thermo-emf generated in the region adjacent to the interface inside Bi–Te compound is available for the improvement of generating power, like the bulk thermo-emf of the intrinsic thermoelectric material. The enhancement in the resultant α of the present composites is thus considered to result in a significant improvement in the conversion efficiency for generators. Finally, it is desired that the mechanism for the generation of the barrier thermo-emf would also be established for the semiconductor-metal junction, not for the p–n junction alone.

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