Effect of metal electrode on thermoelectric power in bismuth telluride compounds

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The measurements of apparent effective Seebeck coefficients S_a, thermoelectric powers ΔE and *I-V* characteristics were made on a copper-semiconductor-metal contact junction, where the semiconductor is consisted of the *p*- and *n*-type bismuth telluride compounds. The S_a measured by heating either of copper and metal alternatively to produce the temperature differences of $\Delta T = \pm 6$ K changed slightly with the kind of metal electrodes, but it changed very little when the direction of the temperature gradient was reversed. The averaged $\langle S_a \rangle$ values over all kinds of metal electrodes agreed closely with the Seebeck coefficients S measured by the conventional technique using two alumel-chromel thermocouples as an electrode. The thermoelectric power ΔE generated by imposing the temperature differences of $\Delta T = \pm 6$ K on a thermoelement tended to increase with increase of S_a and reached large values in noble metal electrodes of Ag and Au. The ΔE was found to achieve enhancements of up to 10% or even more, when one end of a thermoelement contacts with Au electrode and the external electrical resistance is zero. Thus, the selection of the optimal metal electrode is necessary to make the thermoelectric conversion efficiency as high as possible.

1. 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]. There have been two approaches in improving the performance of thermoelectric devices. One approach is to increase the thermoelectric figure of merit ($ZT = S^2T/\rho\kappa$) of bulk thermoelectric materials by the conventional method, where S is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity and T the absolute temperature [1, 2]. 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 the ZT was not much more than 1 until recently. Recently, however, the as-grown p-type and annealed n-type bismuth telluride compounds exceeded large 1 as a bulk material [5, 6]. Another approach is to improve the performance by using multiple quantum wells of thermoelectrics [7–9]. It was reported recently that the superlattice structured thin film of p-type Bi_2Te_3/Sb_2Te_3 indeed reached an extremely high ZT of 2.4 [7].

Recently, Ju and Ghoshal [10] showed using a phenomenological model that when the thermoelectric devices are prepared, the boundary Seebeck effect at the interface between a thermoelectric material and a metal electrode has a marked influence on the performance of thermoelectric devices. However, there have been only a few experimental studies [11, 12] on the boundary effect; the effect of metal electrode on the Seebeck coefficient S has been reported by Nagao *et al.* [11] who showed that the S was enhanced significantly when Cr was deposited on PbTe semiconducting films as an electrode, so that it reached about twice as large as the minimum S obtained with Zn electrode. They interpreted that such an enhancement in the S is attributed to the Schottky barrier [13] at the interface, because the Cr-PbTe-Cr junction exhibited the Schottky type I-V characteristics, leading to an extremely high electrical resistance r of about 34 kΩ. Most recently, similar experiment has been made by one of authors on the bulk contact junction of brass-Si thermoelectrics-metal contact junctions with small r of 3 Ω or less, so that the *effective* Seebeck coefficient changed significantly with the kind of metal electrodes, although all of the contact junctions were the ohmic type [12]. It is the greatest interest to investigate whether the *effective* S changes with the kind of metal electrodes due to the boundary effect, even in bismuth telluride materials with lower electrical resistivities of 10^{-5} Ωm, resulting in lower electrical contact rsistance at the interface. It has not yet been clear whether such an additional enhancement in the S actually leads to an increase in the thermoelectric power.

To design and prepare a superior thermoelectric device, we do not only develop the ZT of the thermoelectric material, but also it is of importance to study the effect of the metal electrode on the Seebeck coefficient and the electrical resistance. The purpose of this study is to investigate whether the *effective* Seebeck coefficient S changes with the kind of metal electrodes even when the electrical resistance r of a contact junction reached a low value of 0.1 Ω or less, and whether the change in the S due to the different kinds of metal electrodes is indeed reflected on the change in the output of thermoelectric power.

2. Experiments

The bismuth telluride compounds used here were purchased from Nihon Hatsujo Co., Ltd., in which they were prepared by the hot-pressing method. The main chemical components of p- and n-type thermoelectric materials were $(Bi_{0.25}Sb_{0.75})_2Te_3$ and $Bi_2(Te_{0.94}Se_{0.06})_3$ in molecular formula, respectively. These hot-pressed materials were consisted of fine grains with the cleavage c planes aligned partially perpendicular to the hot-pressed direction. The reason that the hot-pressed materials were employed in the present study is that these materials are much tougher in the mechanical strength than the ingots solidified by the Bridgman or Czochralski method, because the present experiment requires the strong mechanical strength, as will be mentioned later. All thermoelectric properties were measured along the direction perpendicular to the hot-pressed direction, because the thermoelectric properties of the hot-pressed bismuth telluride compounds are superior in the direction perpendicular to the hot-pressed direction.

In order to investigate the thermoelectric properties of the hot-pressed materials, they were cut into a parallelepiped of $5 \times 5 \times 15$ mm^3 and square plates of $10 \times 10 \times 3$ mm^3, where the length of 15 mm and thickness of 3 mm were cut perpendicular to the hot-pressed direction. The former sample was subjected to Seebeck coefficient and electrical resistivity measurements (Sinku-Riko, Inc., Model ZEM-1) and thermoelectric power measurements, and one of the latter samples, to Hall measurement (Toyotechnica, Model RESITEST 8300), as reported elsewhere [14]. Another square plate was cut into a disk of $\phi 10 \times 3$ mm in order to measure its thermal conductivity using a laser-flash instrument (Sinku-Riko, Inc., Model TC-3000).

The Seebeck coefficient S was measured with an accuracy of 2% by the conventional technique, using alumel-chromel thermocouples composed mainly of Ni as an electrode in the temperature range from 298 to 430 K with the temperature difference of about 6 K. The electrical resistivity ρ was measured concurrently by the four-probe method. The Hall coefficient was measured at 298 K with an accuracy of 5% under an applied magnetic field of 0.39 T. The thermal conductivity κ was measured at a temperature of 298 K. The thermoelectric properties of the p- and n-type specimens used here are listed in Table I.

Subsequently, the dependence of apparent *effective* Seebeck coefficient S_a on the work function of metal electrode was investigated using an apparatus schematically shown in Fig. 1. The reason that the copper was employed as a standard electrode is that most of the bismuth telluride materials are plated with copper as an electrode in assembling the thermoelectric devices. The metal electrode as a thermocouple is limited to only a few kinds of metals or alloys in commonly used Seebeck equipments, but the present apparatus in which the metal is used as a plate is available with any kind of metal electrode. The size of bismuth telluride specimens is $5 \times 5 \times 15$ mm^3, where the length of 15 mm is along the direction of the temperature gradient. The purity of metals used here equals or is higher than 99.99% and their sizes are a square plate of $50 \times 50 \times 1$ mm^3. The surface of metals was polished cleanly by the emery paper. The copper was employed at one end and various kinds of metals at another end, and either of both ends was heated alternatively to produce the temperature differences of $\Delta T = \pm 6$ K. One end was heated from 298 to 304 K by flowing the electrical current I_1 or I_2 through a thermoelectric module and another end was then maintained at 298 K, owing to a large heat capacity of a module with a volume of $50 \times 50 \times 5$ mm^3. The temperature difference ΔT of both ends was measured with an accuracy of 0.1 K by two thin copper-constantan thermocouples with a thickness of 0.1 mm. The S_a was estimated using the relation$S = \Delta V/\Delta T$ with an accuracy of 2% or less. The thermal voltage ΔV and the thermoelectric current ΔI induced by the ΔV were measured using a digital multimeter, in order to estimate the thermoelectric power $\Delta E = \Delta V \cdot \Delta I$ generated by imposing the temperature differences of $\Delta T = \pm 6$ K on a thermoelement. During these measurements, the specimen was put between two metal plates under a constant force of 29.4 N, so that the specimen contacts tightly with both copper and metal plates, leading to lower r. The tough hot-pressed specimens then have never been broken by such a compaction. The external electrical resistance R of the electrical circuit was then a constant value of 0.310 Ω.

TABLE I Thermoelectric properties measured at 298 K for p- and n-type bismuth telluride compounds

		p-type	n-type
Electrical resistivity	ρ (Ωm)	1.17×10^{-5}	1.07×10^{-5}
Seebeck coefficient	S (μV/K)	223	−224
Thermal conductivity	κ (W/mK)	1.43	1.57
Hall mobility	μ (m^2/Vs)	1.87×10^{-2}	1.27×10^{-2}
Carrier density	n (1/m^3)	1.6×10^{25}	1.3×10^{25}
Figure of merit	ZT	0.87	0.89

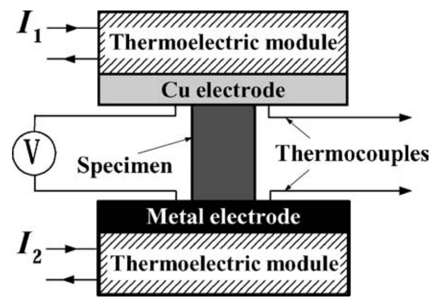

Figure 1 Schematic configuration for measurement of the thermal voltage ΔV generated by copper-semiconductor-metal contact junctions. One end was heated by flowing the electrical current I_1 or I_2 through a thermoelectric module to produce the temperature differences of $\Delta T = \pm 6$ K and another one was then maintained at room temperature. The thermocouples and leads on the metal electrode are about 1 mm distant from the top and bottom edges of the specimen.

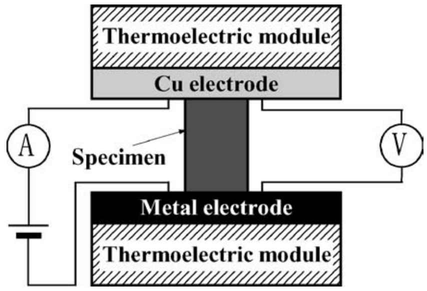

Figure 2 Schematic configuration for measurement of the I-V characteristics of a copper-semiconductor-metal contact junction. When the constant current I flows between the copper and metal electrode, the voltage drop V appeared on copper and metal electrode was measured.

The schematic configuration for measurement of the I-V characteristics is shown in Fig. 2. When the constant current I flows between the copper and metal electrode, the voltage drop V appeared on copper and metal electrodes was measured at 298 K under the same pressure as that compacted during the measurement of S_a. The measurement of the I-V characteristics was made to observe the electrical resistance r of copper-semiconductor-metal contact junctions and to investigate whether or not the contact junction is the ohmic type. In a series of experiments, the same specimen was used repeatedly, because there may be some differences in thermoelectric properties among the specimens. The metals used as an electrode were Ag, Al, Zn, Mo, Cu, Au, Ni and Pt whose work functions Φ_m are 4.26, 4.28, 4.33, 4.6, 4.65, 5.10, 5.15 and 5.65 eV, respectively [15].

3. Results and discussion

3.1. Apparent effective Seebeck coefficient and I-V characteristics

Fig. 3 shows the apparent effective Seebeck coefficient S_a as a function of work function Φ_m of the metal electrodes for copper-semiconductor-metal contact junctions, where the semiconductors composed of bismuth telluride contact tightly with both copper and various kinds of metal electrodes. As mentioned above, either of copper and metal was heated alternatively. Except for a copper-semiconductor-zinc contact junction, the S_a evaluated using the relation $S = \Delta V/\Delta T$ changed very little when the direction of the temperature gradient was reversed. Particularly, this small difference in the S_a of a copper-semiconductor-copper junction indicates clearly that the present apparatus itself has a substantial symmetry about a direction of the temperature gradient. The change in the S_a due to the different kinds of metal electrodes was very small compared to the previous brass-Si thermoelectrics-metal contact junction [12]. However, the dependence of S_a on Φ_m showed a remarkable similarity between the p- and n-type specimens, like the Si thermoelectrics [12]. The S_a values of the p- and n-type specimens show a saw-toothed change with increase of Φ_m, so that the S_a has nothing to do with Φ_m. This similarity between the p- and n-type specimens cannot be explained consistently by the difference alone in the Seebeck coefficients of metal electrodes, because the metal electrode does not create the same change in the positive and negative S_a of the p- and n-type ones. In a word, the S of metal electrode itself has little effect on the S_a. Such a change in the S_a, therefore, may be associated with the boundary effect at the interface, although the mechanism is not clear yet [10]. The p- and n-type specimens have a maximum S_a of $+230$ μV/K at 4.56 eV of Mo and -229 μV/K at 4.33 eV of Zn, respectively. However, the $\langle S_a \rangle$ values of $+224$ and -225 μV/K averaged over all kinds of metal electrodes for the p- and n-type specimens agreed closely with the S values of $+223$ and -224 μV/K (see Table I) obtained with the p- and n-type ones, by the conventional technique using two alumel-chromel thermocouples.

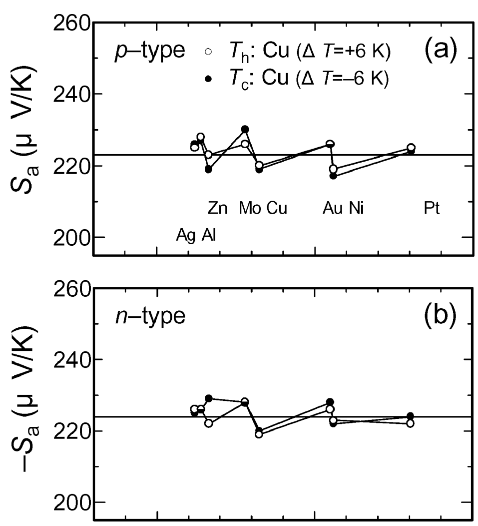

Figure 3 Apparent Seebeck coefficient S_a as a function of work function of the metal electrodes for copper-semiconductor-metal contact junctions, when either of copper and metal was heated alternatively.

Fig. 4 shows the representative I-V characteristics for copper-semiconductor-metal contact junctions. In all junctions, the voltage drop V changed linearly in proportion to the electrical current I. All of the electrical contacts of the specimens with metals, therefore, are the ohmic type from the linearity of the I-V characteristics. The electrical resistance r was calculated from the I-V characteristics by the linear square method using the linear function, where the resistance r is the sum of the contact resistance r_c at both ends of a thermoelement and the intrinsic resistance r_i of the thermoelement itself. The r values were plotted as a function of work function Φ_m of the metal electrode in Fig. 5. Interestingly, the dependence of r on Φ_m also showed a remarkable similarity between the p- and n-type specimens, like the S_a. Probably this similarity may be derived mainly from the physical properties peculiar to the metal such as ductility and malleability, which control the degree of electrical contact at the interface. The electrical resistances r of copper-semiconductor-metal contact junctions are less than 0.07 Ω which is lower by the order of 10^2 and 10^6 than those of contact junctions of the brass-Si thermoelectrics-metal [12] and Cr-PbTe-Cr [11], respectively. Such low r values are attributed to

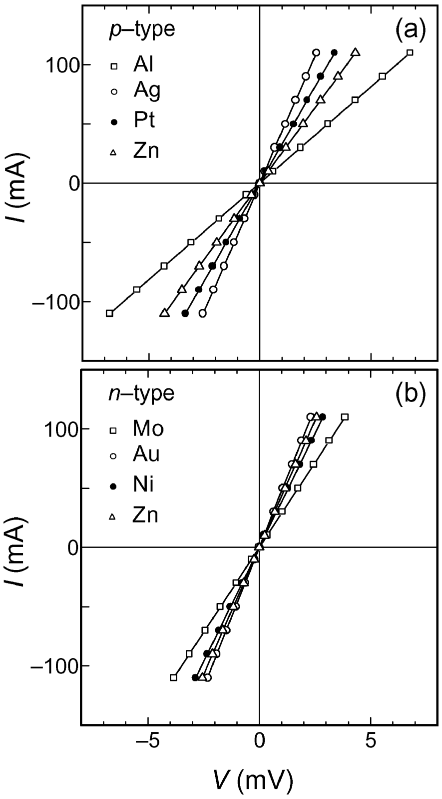

Figure 4 Representative I-V characteristics of a copper-semiconductor-metal contact junction at 298 K for the p- (a) and n-type (b) specimens.

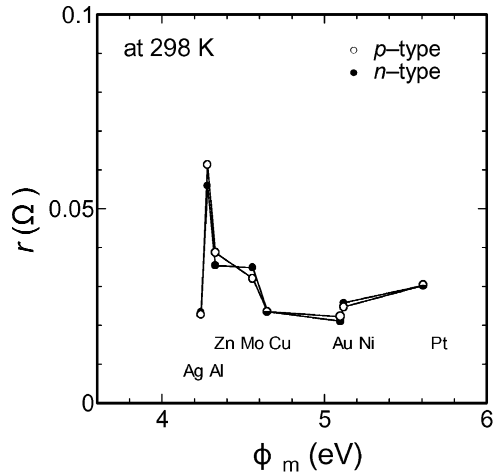

Figure 5 Electrical resistance r as a function of work function Φ_m of the metal electrode used for the p- and n-type specimens.

the low electrical resistivity peculiar to the bismuth telluride material. For this reason, the electrical contact at the interface is considered to be close to a metal-metal contact junction rather than a metal-semiconductor one. Even in the ohmic contact, therefore, the apparent effective S_a is found to change with the kind of metal electrodes. The r_i calculated using the ρ listed in Table I is 7.0 mΩ for the p-type specimen and 6.4 mΩ for the n-type, both of which are about one third of the minima of the r. The major part of r, therefore, is found to arise from the r_c.

Fig. 6a shows the absolute value of S_a plotted as a function of electrical resistance r for the p- and n-type specimens. As a whole, the S_a tends to increase slightly with increase of r, where the correlation coefficient γ

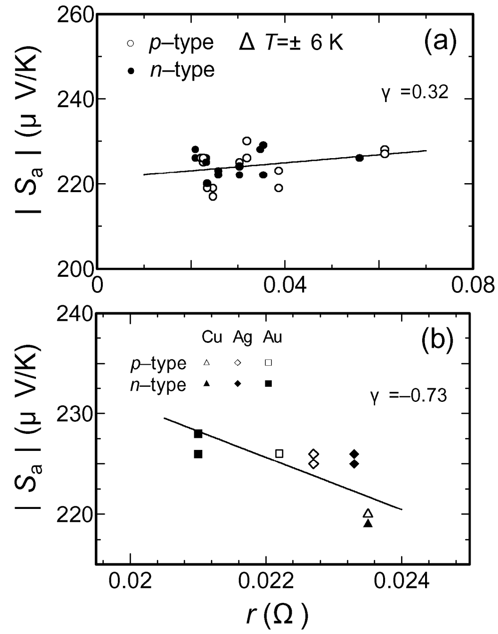

Figure 6 Apparent Seebeck coefficient $|S_a|$ in absolute value as a function of electrical resistance r for all metal electrodes (a) and Cu, Ag and Au electrodes (b) of the p- and n-type specimens.

is 0.32. Similar phenomenon has often been observed in the Schottky type contact junctions [11], but it was observed even in the ohmic contact junctions with low r of 0.06 Ω or less. Interestingly, however, the S_a tended to decrease with increase of r for the contact junctions with lower r below 0.024 Ω in which the metals of Cu, Ag and Au were used as an electrode. The dependence of the S_a on the electrical resistance r may vary entirely according to the magnitude of the r, even in such low r region.

3.2. Thermoelectric power

The thermoelectric power ΔE generated by imposing the temperature differences of $\Delta T = \pm 6$ K on a thermoelement was plotted as a function of $|S_a|$ in Fig. 7, in order to investigate whether an additional increase in the $|S_a|$ actually leads to an enhancement in the ΔE. As shown in Fig. 7a, it was found that the ΔE has a tendency to increase with increase of $|S_a|$ for all contact junctions, where the correlation coefficient γ is 0.56. As shown in Fig. 7b, the correlation between ΔE and $|S_a|$ became stronger in contact junctions with lower r whose electrodes are composed of Cu, Ag and Au and then the correlation coefficient γ reached 0.92. This indicates that an additional enhancement in the S_a due to the boundary effect leads directly to an increase in the thermoelectric power; the output of the thermoelectric power ΔE varies depending on the kind of metal electrodes. The ΔE generated by pairs of Au-Cu and Ag-Cu were 5–7% higher than that produced by a pair of Cu-Cu. The selection of the optimal metal electrode, therefore, is necessary to enhance the thermoelectric power, even when the electrical contact of the metal-semiconductor is the ohmic type.

Next, the observed thermoelectric power ΔE was compared with the $\Delta E_{calc.}$ calculated for the p- and

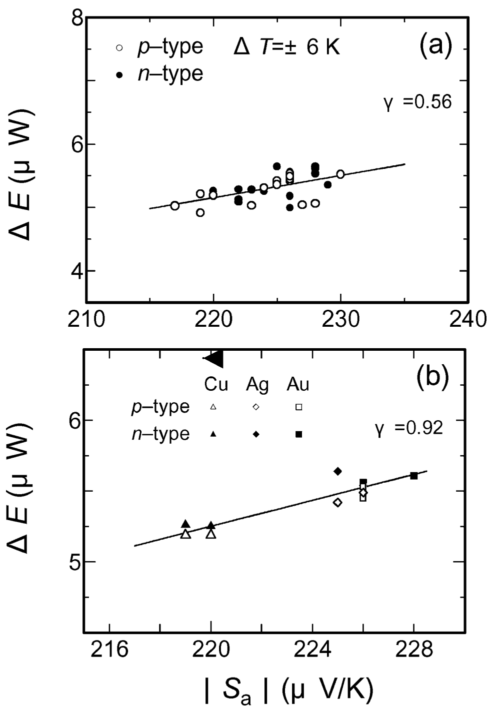

Figure 7 Thermoelectric power $\Delta E (=\Delta V \cdot \Delta I)$ as a function of apparent Seebeck coefficient $|S_a|$ in absolute value for all metal electrodes (a) and Cu, Ag and Au electrodes (b) of the *p*- and *n*-type specimens, where the absolute temperature difference is 6 K.

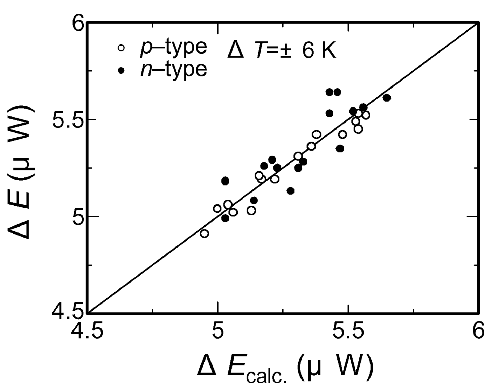

Figure 8 Comparison between the observed thermoelectric power ΔE and calculated one $\Delta E_{\text{calc.}}$ for the *p*- and *n*-type specimens, where $E_{\text{calc.}}$ was calculated from the relation $E_{\text{calc.}} = (S_a \Delta T)^2/(r + R)$ using the apparent Seebeck coefficient S_a, a temperature difference of $|\Delta T| = 6$ K and an external electrical resistance R of 0.310 Ω.

n-type specimens, as shown in Fig. 8, where $\Delta E_{\text{calc.}}$ was calculated from the relation $\Delta E_{\text{calc.}} = (S_a \Delta T)^2/(r + R)$ using each S_a, a temperature difference of $|\Delta T| = 6$ K and an external electrical resistance R of 0.310 Ω. As expected, the ΔE plotted as a function of $\Delta E_{\text{calc.}}$ fell roughly on the straight line of $\Delta E = \Delta E_{\text{calc.}}$, where the deviations from the straight line arise mainly from the experimental errors of the S_a.

In order to make clearer the effect of the metal electrodes, the thermoelectric power was calculated form the relation $\Delta E_{\text{calc.}} = (S_a \Delta T)^2/r$ for the *p*- and *n*-type specimens themselves. As shown in Fig. 9, the calculated values fell almost exactly on a hyperbola calculated using an averaged value $\langle S_a \rangle$ of 225 μV/K. As a result, pairs of Au-Cu and Ag-Cu as electrodes were found to generate larger thermoelectric powers

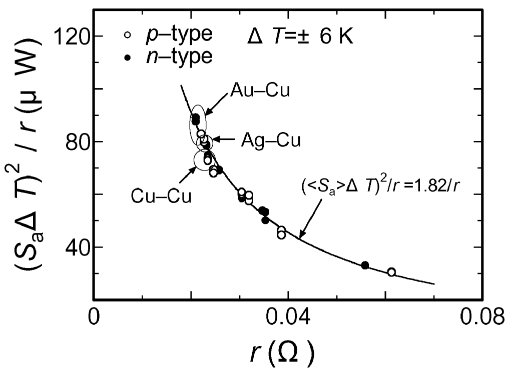

Figure 9 Thermoelectric power $\Delta E_{\text{calc.}} (=(S_a \Delta T)^2/r)$ calculated as a function of electrical resistance r for the *p*- and *n*-type specimens, where the absolute temperature difference is 6 K and the external resistance R is assumed to be zero. The solid line represents the thermoelectric power calculated using an averaged value $\langle S_a \rangle$ of 225 μV/K.

than a pair of Cu-Cu. In the case of the *p*-type specimen, the thermoelectric powers generated by pairs of Au-Cu and Ag-Cu were 13.2 and 9.1% higher than that by a pair of Cu-Cu, respectively, at least when the external electrical resistance R is zero. When the external resistance is zero, the thermoelectric power calculated for a pair of Au-Cu became higher than that for a pair of Ag-Cu, although there was no significant difference in the ΔE values of both pairs in the presence of the external resistance ($R = 0.310$ Ω). The justification of this calculation would be supported by the good agreement between ΔE and $\Delta E_{\text{calc.}}$, as shown in Fig. 8.

In general, most of the thermoelements composed of bismuth telluride materials are plated with copper. Therefore, it is expected from the present result that the thermoelectric conversion efficiency can achieve enhancements of up to 10% or even more, when one end of a thermoelement was plated with gold instead of copper and the external electrical resistance R is zero.

4. Summary

The present experimental results can be summarized as follows:

(1) The measurements of the apparent *effective* Seebeck coefficient S_a and thermoelectric power ΔE were made on a copper-semiconductor-metal contact junction by heating either of copper and metal alternatively to produce the temperature differences of $\Delta T = \pm 6$ K, where the semiconductor is the *p*- and *n*-type bismuth telluride materials prepared by the hot-pressed method. With the present contact junctions with low r below 0.06 Ω, the S_a exhibited a remarkable similarity between the *p*- and *n*-type specimens but changed slightly with the kind of metal electrode. The S_a tended to increase slightly with increase of r when r ranges from 0.02 to 0.06 Ω, while it reversely decreased with increase of r in the contact junctions with lower r below 0.024 whose electrodes are composed of Cu, Ag and Au. However, the averaged values $\langle S_a \rangle$ agreed closely with the Seebeck coefficients S measured by the conventional technique using two alumel-chromel thermocouples as an electrode.

(2) The ΔE tended to increase with increase of S_a and reached maximum values in the contact junctions with lower r below 0.024 whose electrodes are composed of Ag and Au, owing to the low electrical resistance. An additional increase in the S_a due to the boundary effect led directly to an enhancement in the thermoelectric power ΔE. When the p- and n-type bismuth telluride materials are connected as a copper-semiconductor-metal contact junction, the thermoelectric power was found to achieve enhancements of up to 10% or even more, when one end of a thermoelement is in contact with Au electrode and the external electrical resistance R is zero. The selection of the optimal metal electrode is necessary to make the thermoelectric conversion efficiency as high as possible.

Acknowledgements
This work was supported financially by the Cooperation of Innovative Technology and Advanced Research in Evolutional Area (CITY AREA) which was projected by the Ministry of Education, Culture, Science and Technology of Japan.

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Received 8 December 2003
and accepted 2 April 2004