Observation of Interface between Thermoelectric Material Zn_4Sb_3 and Electrodes by Resistance Scanning and Seebeck Coefficient Mapping Techniques

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A ready-for-soldering thermoelectric element composed of Zn_4Sb_3 with Ni–Al diffusion barrier layer and Cu electrode was fabricated by means of a hot-press method. Batch-to-batch variation of the resistance of the element was within 7%, the average resistance was 3.23 m Ω and the standard deviation 0.25 m Ω . Annealing effects on the interface structure between the electrodes and Zn_4Sb_3 were investigated using microprobe techniques such as Seebeck coefficient mapping and resistance scanning. The element showed lower Seebeck coefficient and resistivity than those of the pristine Zn_4Sb_3 without the electrodes. After annealing for 3.6 ks, the Seebeck coefficient and resistivity returned to the intrinsic values of Zn_4Sb_3 . Increased resistivity was clearly observed near electrode/ Zn_4Sb_3 interfaces of all annealed samples. Seebeck coefficient maps also indicated variation near the interfaces, showing good consistency with the resistance variation.

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1. Introduction

The movement to minimize energy consumption is spreading worldwide. Using waste heat effectively is one of the solutions to conserve the world's energy resources. Thermoelectric (TE) technology has been actively researched for recycling waste heat.

The performance of a TE material can be quantified using the dimensionless figure of merit ZT that can be expressed as $ZT = S^2T/\kappa\rho$, where S is the Seebeck coefficient, ρ electric resistivity, κ thermal conductivity, and T the absolute temperature. Zn_4Sb_3 has a high figure of merit ($ZT = 1.3$ at 673 K¹⁾) because of its unusually low thermal conductivity of $\kappa = 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, which is much lower than that of glass. Electrode fabrication is an important step to put Zn_4Sb_3 to practical use. The electrode has a key role in drawing the electricity, and transferring heat from the heat source to the TE material efficiently. The reliability of the interface between the electrode and TE material is significant for TE devices in case of long-term operation. TE materials with metallic electrodes—called “TE elements”—form unfavorable intermetallic compound layers just after fabrication of the sample, which is caused by inter-diffusion between the electrode and the TE material.^{2–5)} Inter-diffusion has a role for good mechanical connection, however this phenomenon leads to disadvantages such as a high contact resistance and breakage of TE material in case the electrode is not suitable for TE material. Diffusion barrier layer is necessary in such a case for preventing TE material and the electrode from the inter-diffusion.

Previous papers have reported that Zn_4Sb_3 is unstable above 500 K, because it readily decomposes to $\text{Zn} + \text{ZnSb} + \text{Sb}$.^{6–9)} This decomposition has a possibility affecting the diffusion barrier layer with Zn_4Sb_3 and forming the inter-diffusion layer. It is necessary to quantitatively evaluate the properties at the interface with microscale spatial resolution

to verify if the interface is completely fabricated as per the required design.

Resistance scanning along the TE element length is frequently used to determine the contact resistance R_c between the electrode and TE material. This method also allows the quantification of the distribution of the local resistivity inside the TE material, which is an important parameter for calculating the figure of merit ZT and device performance. The other thermoelectric parameters such as Seebeck coefficient and thermal conductivity which are phenomena related to heat, also need to be verified with spatial resolution. Seebeck coefficient mapping by the thermal probe method is useful for this purpose and has been successfully applied to investigate the homogeneities of materials.^{10–12)} de Boer reported the combined use of resistance scanning and Seebeck coefficient mapping,¹³⁾ which permits the estimation of interface properties such as the contact resistance and interface Seebeck coefficient. This is a good methodology to verify interfacial structure in a non-destructive way.

It is necessary to investigate the annealing effect on the interfacial structure since TE elements such as those composed of Zn_4Sb_3 —which are subjected above 573 K and show inter-diffusion at the interface—are expected to be under operation for a long time. The inter-diffusion between the electrode and Zn_4Sb_3 affects the resistivity of TE material and the Seebeck coefficient. There are several papers evaluating the influence of annealing on the reliability of the electrode interface, based on electric resistance and thickness of the diffusion layer.^{14,15)} However, there is no article investigating the interface structure from the viewpoint of the Seebeck coefficient.

We investigated the interface structure between the electrode and the TE material by using a resistance scanning system and Seebeck coefficient mapping system for Zn_4Sb_3 , before and after annealing.

2. Experimental

2.1 Sample preparation

The starting Zn_4Sb_3 powder (Toshiba Manufacturing Co., Ltd., mesh#200) was placed in a graphite die and sintered at 753 K for 18 ks in an Ar atmosphere using the hot-press method. After sintering, Zn_4Sb_3 was cut to about $3\text{ mm} \times 3\text{ mm} \times 15\text{ mm}$. The electric resistivity and Seebeck coefficient were then evaluated by the DC four-probe method using ZEM-3 (Advance-Riko Inc.) in the temperature range of 323 K to 674 K under 0.5 atm He.

The TE element examined in this study was prepared by powder metallurgy processes. The aforementioned Zn_4Sb_3 powder was placed in a graphite die together with powders of electrode materials required to form the electrode/TE material/electrode structure inside the die. The electrode used in this study consisted of two stacked layers: a Cu layer and a Ni–Al composite layer (diffusion barrier layer). A series of experimental tests had performed to select appropriate barrier layer materials prior to this study and the combination of coarse mixture of Ni and Al fine powders showed the best performance from a view point of interfacial resistance and adhesion strength. The designed thickness of each layer was 0.3 mm, and the thickness of the Zn_4Sb_3 layer was 4.0 mm. Alternately stacked powders of the electrode and Zn_4Sb_3 , as well as (Cu)/(Ni–Al composite)/(Zn_4Sb_3)/(Ni–Al composite)/(Cu) were then sintered by the hot-press method under the same conditions as that in the preparation of Zn_4Sb_3 pellet. A starting powder of “Ni–Al composite” was prepared by hand-mixing with relatively coarse Al powder (Furuuchi Chemical. Inc. 99.99%, Mesh#100) and fine Ni powder (Furuuchi Chemical Inc., 99.99%, Mesh#300). The molar ratio of Ni to Al was 1:3. Cu powder (Furuuchi Chemical Inc., 99.99%, Mesh#200) was used to form dense Cu electrodes for post-processing such as soldering.

The resultant pellet after sintering had a 15 mm diameter, and was cut into rectangular shapes to form the “TE element”. The area of the electrode was roughly $3\text{ mm} \times 6\text{ mm}$ and the height was 5.2 mm.

2.2 Microprobe analysis of samples

An optical microscope (OM) and scanning electron microscope (SEM, TM3030 Plus, Hitachi High Technologies Inc. equipped with energy dispersive spectroscopy, Burker Quantax 70) were used to investigate the micro-structure and the chemical composition at the interface between the electrode and Zn_4Sb_3 . The resistance of the individual element was measured at room temperature (298 K), using an AC resistance meter (BATTERY HITESTER BT3562, HIOKI E.E. Corporation), to check the statistical variation of the resistance using 34 samples from nine different batches, but under the same process conditions. The distribution of resistance variation along the sample length was evaluated using a resistance scanning system equipped with a moving probe, as shown in Fig. 1(a). Measurements of the distribution of local Seebeck coefficient—mapping of Seebeck coefficient—using the thermal probe method were conducted to analyze the interfacial structure between the electrode and Zn_4Sb_3 . A schematic diagram of the measurement system used in this study is shown in Fig. 1(b) and detailed

Fig. 1 Schematic diagram of the measurement system. (a) Resistance scanning system, (b) Distribution of local Seebeck coefficient.

explanation of the principles are in earlier papers.^{12,16,17)} The probe temperature was kept at $\sim 320\text{ K}$, almost 25 K higher than the isothermal copper baseplate during the measurement, and the Seebeck coefficient determined by $S = V/\Delta T$ where V is electromotive force from the sample surface and ΔT the temperature difference between the probe and the reverse side of the sample. To have good thermal and electrical contact with the copper baseplate and samples, In–Ga eutectic liquid metal was used to mount the sample.

To examine the annealing effect, the TE element was sealed in a quartz ampoule under vacuum and annealed for 3.6 ks (1 h) at 473, 573, and 673 K. The cross-section of the interface between the electrode and Zn_4Sb_3 was polished and observation conducted by SEM, Seebeck coefficient mapping, and resistance scanning, as mentioned before.

3. Results and Discussion

3.1 TE properties of Zn_4Sb_3 and resistance of the TE element

Original TE properties of Zn_4Sb_3 used in this study are shown in Fig. 2. The graphs plot two heating/cooling cycles between 323 K and 673 K. Initial data of Seebeck coefficient and resistivity start from relatively low values, $10\text{ }\mu\Omega\text{ m}$ and $80\text{ }\mu\text{V K}^{-1}$, and then exhibit sharp increases at around 500 K. After the first heating, both Seebeck coefficient and resistivity traced the same temperature dependence, while heating and cooling. Hysteresis of thermoelectric properties observed presumably attributed to instability of zinc atom position in the Zn_4Sb_3 crystal structure which causes the change of the electronic structure. A similar low Seebeck coefficient and electric resistivity have been reported, and the instability observed in the Zn_4Sb_3 system seemed to be typical.^{18,19)} A relatively high pressure (100 MPa) was applied to the material during the hot-pressing process and this probably is one of the reasons for the irregular trend in the first heating cycle. Figure 3 shows the AC resistance variation of 34 TE elements prepared under the same hot-pressing conditions from nine different batches. The overall average AC resistance was $3.23\text{ m}\Omega$ and the standard deviation was $0.25\text{ m}\Omega$. These data showing relatively good reproducibility suggest a reliable sample preparation procedure for the (Cu)/(Ni–Al composite)/(Zn_4Sb_3)/(Ni–Al composite)/(Cu) layered structure adopted in this study.

3.2 Investigation of interface structure

Figure 4 shows cross-sectional OM and SEM/EDX images. EDX results revealed that no clear intermetallic

Fig. 2 TE properties of Zn_4Sb_3 . (a) Electric resistivity versus temperature. (b) Seebeck coefficient versus temperature.

Fig. 3 AC resistance variation measured using 34 TE elements.

compound layer existed between Zn_4Sb_3 and Ni–Al composite electrode material. In the electrode layer, Ni and Al showed slight inter-diffusion at the boundary, forming intermetallic NiAl_3 . The diffusion of some Zn and Sb atoms into Ni–Al composites was confirmed by detailed analysis with a magnified view. No cracks were visible in the (Cu)/(Ni–Al composite)/(Zn_4Sb_3) interface structure, which implied good electrical and thermal connections. Figure 5 shows resistance scanning along the entire sample length (blue plot) and the average of Seebeck coefficient measured near the electrode/ Zn_4Sb_3 interface (red plot). The gradient of the resistance plot rapidly changed at the interface position. Since the gradient of the plot meant local resistivity at relevant positions, a sharp change meant a big difference in resistivity between the (Cu)/(Ni–Al composite) electrode region and Zn_4Sb_3 region. The average Seebeck coefficient profile also showed a large difference from the value of $4 \mu\text{V K}^{-1}$ in the metal electrode region to $70 \mu\text{V K}^{-1}$ in the Zn_4Sb_3 region. In the Zn_4Sb_3 region, the difference in resistance was not big, which could be regarded as contact resistance R_c . The gradient

Fig. 4 Interface observation. (a) Cross-section view by OM and SEM/EDX, (b) EDX mapping of Al, Ni, Zn, Sb atoms.

Fig. 5 Resistance scanning profile (blue plot) and average Seebeck coefficient profile (red plot) for as-hot-pressed element. The average Seebeck coefficient was calculated from raw mapping data (10×50 points) by averaging 10 data with the same distance.

of the resistance plot changed slightly near the electrode interface showing deviation from the linear relationship between resistance and distance (Fig. 5).

The reason for this deviation from linear relationship was due to change in composition near the electrode interface. As pointed out in the explanation of Fig. 4, zinc atoms near the interface in Zn_4Sb_3 region diffused into the Ni–Al composite electrode region and this caused a Zn-poor region in Zn_4Sb_3 . Zn_4Sb_3 was unstable at elevated temperatures. Previous reports suggest that the Zn_4Sb_3 phase decomposed to ZnSb and Zn while annealing above 500 K.^{6–9)} The sintering temperature was 753 K. While sintering, the Zn_4Sb_3 phase decomposed to ZnSb and Zn , and Zn moved to the Ni–Al composite electrode and a Zn-poor region was formed. The Zn-poor region was a mixture of the Zn_4Sb_3 phase and high-resistivity ZnSb phase.

To estimate the region from the interface where the resistance profile was non-linear, we used a simple algebraic equation to reproduce the resistance scanning profile. The equation used in the analysis was as follows:

$$\begin{aligned} y &= m_1 + m_2x + m_3(x - m_5)^2 \quad (x \leq m_5) \\ y &= m_1 + m_2x \quad (m_5 \leq x \leq m_6) \\ y &= m_1 + m_2x + m_4(x - m_6)^2 \quad (x \geq m_6) \end{aligned} \quad (1)$$

where y and x are the resistance and distance, and m_1 , m_2 , m_3 , m_4 , m_5 , and m_6 are fitting coefficients. The non-linear region was expressed by a second regression characterized by m_3 and m_4 , while the linear region was expressed by linear fitting with coefficients m_1 and m_2 . Since m_2 was a slope of the resistance scanning profile, one could obtain the resistivity of Zn_4Sb_3 from the equation below.

$$\rho = m_2 \times A \quad (2)$$

where A is the cross-section of the TE element. The coefficients m_5 and m_6 represent the border between the non-linear region and the linear region near the interface. The

Fig. 6 SEM image of TE element annealed at (a) 573 K, (b) 673 K.

length of non-linear regions 1 and 2 are estimated as the distance from the interface between Zn_4Sb_3 and the electrode to the border position m_5 and m_6 , respectively.

Equations (1) and (2) were applied to the resistance data shown in Fig. 5 to determine resistivity $\rho = 12.8 \mu\Omega \text{ m}$. The resistivity value of Zn_4Sb_3 was lower than the typical values in the literature and consistent with the values shown in Fig. 2(a).²⁰⁾ The average Seebeck coefficient S_{av} , $70 \mu\text{V K}^{-1}$ also agreed with the values in Fig. 2(b).

3.3 Annealing effect

SEM images of the interface after annealing are shown in Fig. 6. There was no obvious inter-diffusion regions or newly created intermetallic layer between Zn_4Sb_3 and the electrodes.

Resistance scanning results for as-hot-pressed element and elements annealed at 473 K, 573 K, and 673 K are shown in Fig. 7(a). Local resistivity distribution—which was calculated using the gradient averaged over three data points from resistance scanning—is also shown in Fig. 7(b).

The total resistance of the TE element increased with increasing annealing temperature. The resistivity of Zn_4Sb_3 near the electrode was higher than the typical value of Zn_4Sb_3 , which was $28 \mu\Omega \text{ m}$. Two-dimensional mapping images of Seebeck coefficients for annealed Zn_4Sb_3 elements are shown in Fig. 8. Two different regions in the element —(Cu)/(Ni–Al composite) electrode region showing $\sim 4 \mu\text{V K}^{-1}$ and p-type Zn_4Sb_3 region showing $70 \mu\text{V K}^{-1}$ —are clearly distinguished by mapping. Variation of Seebeck coefficient near the interface was very sharp while the color in the other area of the Zn_4Sb_3 region was almost the same, indicating that the material was homogeneous.

The fitting coefficients, and correlation coefficient r , calculated from fitting equation (1) are shown in Table 1. Obtained properties of the as-hot-pressed and annealed TE elements are summarized in Table 2. Length of the non-linear region in resistance scanning was determined using eq. (1), as mentioned before. The non-linear regions 1 (left side) and 2 (right side) are the Zn_4Sb_3 region near the Ni–Al composite where the resistance profile was non-linear, as shown in Fig. 7.

Average Seebeck coefficient S_{av} of the Zn_4Sb_3 region was calculated from the entire Zn_4Sb_3 region. S_{av} of the hot-pressed element was lower than that of the original material, whose value was $70 \mu\text{V K}^{-1}$ at around 320 K. The resistivity ρ was lower ($13 \mu\Omega \text{ m}$) than that of the original Zn_4Sb_3 ($17 \mu\Omega \text{ m}$). ρ and S_{av} of the annealed TE element were higher than those of the as-hot-pressed TE element and the values were almost identical to the intrinsic values reported

Fig. 7 Resistance scanning of each TE element. (a) Resistance scanning profile (b) Resistivity distribution.

Fig. 8 Seebeck coefficient mapping of each TE element.

elsewhere and shown in Fig. 1. The length of the non-linear region showed an increasing trend with increase in annealing temperature, from 0.24 mm to 1.07 mm. It was clear from non-linear regions 1 and 2 that the interfacial characters of the upper and bottom sides of the TE element were not the same. This might be because the pressure was not homogeneous at the bottom and top sides during sintering. From non-linear region 1, the length increased with an increase in annealing temperature. A similar tendency was not seen in non-linear region 2 because the interfacial character was not the same as in non-linear region 1.

Table 1 The fitting coefficients and correlation coefficient r .

Annealing Temperature / K	m_1 (Ω)	m_2 (Ωm^{-1})	m_3 (Ωm^{-2})	m_4 (Ωm^{-2})	m_5 (mm)	m_6 (mm)	r
-	-	0.78 ± 0.0008	-	0.37	1.52 ± 0.014	4.52 ± 0.022	0.99995
473	-	1.07 ± 0.0008	-	1.27	1.83 ± 0.014	4.91 ± 0.018	0.99997
573	-	1.04 ± 0.0009	-	0.43	1.48 ± 0.017	4.31 ± 0.018	0.99997
673	-	1.06 ± 0.002	-	4.67	2.49 ± 0.020	5.03 ± 0.023	0.9999

Table 2 The resistivity, non-linear region length, and average Seebeck coefficient for each TE element. Non-linear region length is calculated by Eq. (1).

Annealing Temperature / K	Non-linear region 1 / mm	Non-linear region 2 / mm	Resistivity / $\mu\Omega\text{m}$	S_{av} / μVK^{-1}
-	0.24	0.31	12.8	69.1
473	0.55	0.33	16.3	82.9
573	0.77	0.25	17.4	81.9
673	1.07	0.27	17.0	83.5

Although minor changes in resistivity at the interface were observed, the Seebeck coefficient was not influenced seriously in the region. After the evaluation using resistance scanning and Seebeck mapping techniques shown above, the annealed TE elements still held the ability to generate electric power under a temperature gradient.

4. Conclusions

TE elements consisting of Zn_4Sb_3 , Ni–Al composite barrier layer, and Cu electrode layer were prepared by the hot-press method. The interface showed no visible cracks, which implied good electrical and thermal connection. Good reproducibility was confirmed by showing, average AC resistance was 3.23 m Ω and the standard deviation was 0.25 m Ω . The structure of the interface between TE materials and the electrode was carefully investigated by combined use of EDX, resistance scanning, and Seebeck coefficient mapping. From EDX results, Zn-diffusion into NiAl₃ was confirmed at the interface of Zn_4Sb_3 /Ni–Al composite electrode.

Resistivity distribution along the TE element calculated using resistance scanning revealed that regions with slightly higher resistivity were formed near the interface. The length of high resistivity part in the resistance scanning plots of all TE elements annealed for 3.6 ks increased with an increase in the annealing temperature from 0.24 mm to 1.07 mm. Seebeck mapping measurement over the interface structure confirmed that the values were not affected significantly by annealing. The combined techniques of resistance scanning and Seebeck coefficient mapping used in this study could be an optimal verification method for analyzing the interfacial structures of TE elements.

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