Fabrication and Output Evaluation of Si-Ge Multilayered Thermoelectric Element

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p-n 多層型 Si-Ge 熱電素子の作製及び出力評価

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A $\text{Si}_{0.8}\text{Ge}_{0.2}$ multilayered thermoelectric element with ten pairs of p-n layers was fabricated by simultaneous sintering and joining of Si-Ge powders with a sandwiched alumina cloth. Every p-n joint of the element was firmly connected without any cracks and the alumina layer inserted here remained unchanged even after a pulse-current sintering process. The maximum output, P_{max} , of this element was determined in the temperature range of 473–1273 K, and then increased in proportion to the second order of the temperature difference between the hot and cold ends of the element. As a result, P_{max} was 120 mW when the temperature difference was 500 K.

[Received April 14, 2004; Accepted June 24, 2004]

Key-words : Silicon-germanium, Gas atomization, Pulse-current sintering, Thermoelectric element, Multilayer

1. Introduction

For the reduction in energy consumption and the realization of a sustainable global environment, research works on thermal-electrical energy conversion have increased resulting in the development of effective thermoelectric materials.^{1),2)} The thermoelectric element relevant to this work is usually fabricated by bridging each end of p- and n-type semiconductors with a metal plate, which generates electrical power by making use of the temperature difference between both ends of this bridged element.^{3),4)} Silicon-germanium (Si-Ge) is one of the thermoelectric materials used in a relatively high temperature range of 500–1000°C.⁵⁾ We reported the thermoelectric properties of p- and n-type Si-Ge dense bodies fabricated by pulse-current sintering (PCS) of Si-Ge gas-atomized powders,⁶⁾ where both figures of merit increased monotonically with temperature up to 1073 K and became 0.56 and 0.66, respectively, at this temperature. A thermoelectric element was also obtained by joining both types of semiconductor directly without a metal plate, where a slit was inserted between them except at the high-temperature part.⁷⁾ Thermoelectric elements using Si-Ge,⁸⁾ $\text{Li}_{0.025}\text{Ni}_{0.975}\text{O}-\text{Bi}_{0.4}\text{Sr}_{0.6}\text{PbO}_3$,⁹⁾ and $\beta\text{-FeSi}_2$ ¹⁰⁾ for the high-temperature application were fabricated by this process.

A p-n-joined $\text{Si}_{0.8}\text{Ge}_{0.2}$ thermoelectric element with a sandwiched alumina layer for strengthening was fabricated by simultaneous sintering and joining of Si-Ge gas-atomized powders and an alumina cloth, however, its output was shown to be insufficient.¹¹⁾ Thus, many elements should be connected electrically to increase the output for practical power supply. Multilayering of a p-n-joined element would be preferable for the enhancement of the output without the lowering of its strength. In this study, a multilayered element was fabricated by stacking p- and n-type semiconductors alternately for simplification of the process, as illustrated in Fig. 1, followed by the evaluation of its output.

Fig. 1. Multilayered element.

2. Experimental

2.1 Fabrication of multilayered element

Both p- and n-type Si-Ge powders were prepared by a gas atomization technique, as described in a previous paper.¹²⁾ The chemical composition of the p-type powder obtained was Si 79.7 mol%, Ge 20.1 mol%, and B 0.20 mol%; that of the n-type powder was Si 79.8 mol%, Ge 20.0 mol%, and P 0.20 mol%.

An alumina cloth of 30 mm diameter and 2 mm thickness (NICHIAS No.5475, Japan) as an insulator was sandwiched between the p- and n-type Si-Ge powders of 1 g each, which were charged ten times in a cylindrical carbon vessel with an inner diameter of 30 mm. Then it was uniaxially compressed

with a carbon punch at 49 MPa. The alumina cloth was cut off partly for the direct contact between the p- and n-type Si-Ge powders in advance. Simultaneous sintering and joining were carried out by heating at 1523 K for a soaking time of 180 s in vacuo using a PCS apparatus (Sumitomo Coal Mining SPS-1030). The as-sintered body of 30 mm diameter and 15 mm thickness was further processed into a rectangle using a cutting machine. Nickel plates were welded on p- and n-type surfaces of both ends of the multilayered element with silver solder prior to the output measurement.

2.2 Measurement of output

The output of a sample was determined using a measurement system equipped with a heating controller and electrical measurement devices.¹¹⁾ The hot end of the sample was heated at the prescribed temperatures ranging from 473 to 1273 K. Voltage and electric current generated from the sample were measured using data logger at each temperature. After a starting signal was sent from a trigger generator, voltage (V) and temperatures at both hot and cold ends (T_h and T_c) were monitored using the data logger while the current (I) was controlled from 0 to 1.0 A in 5 s by an electronic device for changing an external resistance.

3. Results and discussion

Figure 2 shows the appearance of the multilayered element with 10 pairs of p- and n-type Si-Ge semiconductors $15\text{ mm} \times 25\text{ mm} \times 14\text{ mm}$ and weighing 14.7 g. These p-n joints were firmly connected to each other without any cracks. The alumina layers became thinner and blackish via the PCS process. Both thicknesses of Si-Ge and alumina layers were approximately 600 and $80\text{ }\mu\text{m}$, respectively. The alumina layers existed without a significant reaction with the Si-Ge layers even after the sintering process, which may be attributed to the short sintering time of 300 s of the PCS process.

Figure 3 shows that both high open voltage and short-circuit current were obtained at a high heating temperature due to a large temperature difference. The slope of the straight line indicates the internal resistance including the contact resistance between the element and the conductor. This slope gradually decreased as the heating temperature increased, presumably resulting from the lowering of the contact resistance at relatively high temperatures. The internal resistance of this element was $1.95\text{ }\Omega$ on average in the temperature range of 478–1277 K. Furthermore, the maximum output (P_{max}), which was the maximum value of the product of voltage and electric current, was calculated at each heating temperature

Fig. 2. Multilayered element with alumina layers.

for the evaluation of the element. The maximum output was compared with that of the p-n-joined Si-Ge thermoelectric element with a sandwiched alumina layer (joined element) reported in a previous paper,¹¹⁾ as shown in **Fig. 4**. Here, the P_{max} of the element was proportional to the second order of the temperature difference, as expected from the theoretical consideration.¹³⁾ The difference in P_{max} between these two elements increased as the temperature difference increased, indicating the effectiveness of the integration here for the enhancement of the output. The P_{max} of the multilayered element was 120 mW, which was approximately 3.5 times higher than that of the joined element when the temperature difference was 500 K.

The internal resistance r , temperature difference ΔT , and the output at 1273 K of the joined and multilayered elements are summarized in **Table 1**. The small ΔT of the multilayered element occurred due to its large cross-sectional area caused by the integration, which may be improved by the use of cooling water or heat-radiation fins. This integration technique

Fig. 3. Relationship between output voltage and electric current of multilayered element with nine heating temperatures.

Fig. 4. Maximum outputs, P_{max} , of multilayered and joined elements.

Table 1. Comparison of Joined and Multilayered Elements (Heated at 1273 K)

	Internal Resistance	Temperature Difference	Output	
			Total	One pair
	r / Ω	$\Delta T / K$	P / mW	P / mW
Joined element	0.9	647	48	48
Multilayered element	1.7	495	120	12

would be applicable for the fabrication of the thermoelectric power generator because of many advantages such as supply of higher voltage, simplification of assemblies, and reduction in weight.

4. Conclusion

A Si-Ge multilayered thermoelectric element with 10 pairs of joined p- and n-type Si-Ge layers was fabricated by pulse-current sintering of p- and n-type gas-atomized powders. The maximum output of the element was 120 mW when the temperature difference between the hot and cold ends of the element was 500 K. The integration of the elements here was effective for the miniaturization and process simplification as well as the output enhancement.

References

- 1) Rowe, D. M., "CRC Handbook of Thermoelectrics," Ed. by Rowe, D. M., CRC Press, London, U. K. (1995) pp. 1-5.
- 2) Rowe, D. M., *J. Power Sources*, Vol. **19**, pp. 247-259 (1987).
- 3) Wood, C., *Rep. Prog. Phys.*, Vol. **51**, pp. 459-539 (1988).
- 4) Kibayashi, Y., "Thermoelectrics, Principals and Applications," Ed. by Sakata, R., Realize, Tokyo (2001) pp. 329-348 [in Japanese].
- 5) Vining, C. and Fleurial, J. P., "Silicon Germanium, An Overview of Recent Developments," Ed. by Rowe, D. M., Babrow Press, Cardiff, U. K. (1991) pp. 1-14.
- 6) Otake, M., Sato, K., Sugiyama, O. and Kaneko, S., *J. Ceram. Soc. Japan*, Vol. **111**, pp. 907-911 (2003).
- 7) Stohrer, U., Voggesverger, R. Wagner, G. and Birkholz, U., Proc. 8th Int. Conf. Thermoelectric Energy Conversion, pp. 130-132 (1989).
- 8) Noguchi, T., Proc. 16th Int. Conf. Thermoelectrics, pp. 207-214 (1997).
- 9) Shin, W., Murayama, N., Ikeda, K. and Sago, S., *Jpn. J. Appl. Phys.*, Vol. **39**, pp. 1254-1255 (2000).
- 10) Gross, E., Powalla, M., Stohrer, U. and Birkholz, U., Proc. 9th Int. Conf. Thermoelectrics, pp. 336-342 (1990).
- 11) Otake, M., Sato, K., Sugiyama, O. and Kaneko, S., *J. Electrochem. Soc.*, in submission.
- 12) Otake, M., Sato, K., Sugiyama, O. and Kaneko, S., *J. Ceram. Soc. Japan*, Vol. **111**, pp. 749-754 (2003).
- 13) Goldsmid, H. G., "CRC Handbook of Thermoelectrics," Ed. by Rowe, D. M., CRC Press, London, U. K. (1995) pp. 19-25.