Measurement of the Seebeck coefficient and the thermal conductivity of SiC/Cu by AC method

交流法によるSiC/Cuのゼーベック係数及び熱伝導率の測定

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An AC method of simultaneous measurement for the Seebeck coefficient and the thermal conductivity is proposed. This method shortens measurement time compared with conventional methods. In this work, the thermoelectric properties of the SiC/Cu are measured by this method at room temperature. The Seebeck coefficient obtained by the AC method ($1.4 \sim 4.9 \times 10^{-4}$ V/K) is comparable to the data obtained by the DC method ($1.8 \sim 3.8 \times 10^{-4}$ V/K). The thermal conductivity obtained by the AC method ($78 \sim 86$ W/mK) is in good agreement with the data obtained by the photo pyro electric (PPE) method using the poly vinyliden difluoride (PVF₂) as the transducer ($53 \sim 80$ W/mK).

Keywords: AC method, Seebeck coefficient, Thermal conductivity, Thermoelectric semiconductor, SiC/Cu

I. INTRODUCTION

The electrical energy is the best form for us to use, so the effort to transform the various energies into the electrical one has been continued. Typical examples are the thermal power generation which uses the combustion energy and the nuclear power generation which uses the nuclear energy. These electric power generations face to the various problems including the shortage of petroleum resources in near future, the pollution by their exhaust especially CO₂ and the radioactive contamination. On the other hand, the thermoelectric semiconductor can transform the thermal energy into the electric one directly without such problems. Moreover, it can generate the electric power even when the temperature difference between the heat source and atmosphere is much smaller compared with the one needed in conventional thermal power generation.

The figure of merit Z , which characterizes the conversion coefficient of the thermal energy into the electric one, is defined as:

$$Z = \alpha^2 / \rho \kappa, \quad (1)$$

where α , ρ and κ are the Seebeck coefficient, the electrical resistivity and the thermal conductivity, respectively.¹ As the figure of merit over 10^{-3} K⁻¹ is required for practical use of the thermoelectric devices, it is necessary to measure the three parameters (Seebeck coefficient, electrical resistivity and thermal conductivity) to develop the effective thermoelectric semiconductor materials.

The Seebeck coefficient is generally measured by the DC method. But the DC method requires a bar-shaped sample. This method requires rather long time for the measurement. On the other hand the laser flash method is commonly used to measure the thermal conductivity. It requires the high power pulsed laser, which sometimes induces damages on the sample surface. To overcome these problems, some researchers have developed the AC methods. But it is focused to the estimation of the Seebeck coefficient by using very small temperature difference between two electrodes. Goto *et al.* have precisely measured the Seebeck coefficient of the thermoelectric semiconductor by using the fine thermocouples (25 μ m in diameter) with small heat

capacity.² Kawai *et al.* have already reported the Seebeck coefficient of p-Ge and n-TiO₂ by the AC measurement. Their method measured the instantaneous change of the electrical resistivity which was caused by the temperature variation in the sample.^{3,4}

This paper describes the extension of this AC Seebeck measurement method to the simultaneous measurement of the thermal conductivity. Though the figure of merit of Bi₂Te₃, which is known as a typical thermoelectric semiconductor, is large at room temperature,^{5,6} it decreases at higher temperatures.¹ SiC has the thermal stability and the large mechanical strength even in high temperature region,⁷ where very large temperature difference can be obtained. Moreover, the electrical resistivity of SiC is drastically reduced by adding Cu. In this paper, we study the thermoelectric properties of SiC/Cu systems to show the validity of the AC measurement.

II. AC METHOD

A. Measurement of the Seebeck coefficient

When the laser beam is focused on the semiconductor surface, the nonuniform temperature distribution is generated and induces the electro motive force inside the sample by the Seebeck effect. Let us consider two points (P, Q) in the disk-shaped sample, as shown in Fig. 1.

FIG. 1. The schematic of the disk-shaped sample.

When the laser beam is focused at P point of the sample, the local temperature difference ΔT between point P and Q generate as follows

$$\Delta T = \Delta T(\omega, P) - \Delta T(\omega, Q), \quad (2)$$

$$\Delta T(\omega) = \Delta T_0 / (1 + j\omega\tau), \quad (3)$$

where ω is the modulation frequency of the laser beam and τ is the thermal time constant. When the photovoltaic effect is negligible at the electrodes and the sample is not pyroelectric, the voltage difference between P and Q can be written as

$$|V|^{-2} = \{1/(S\Delta T)^2\} \times (1 + \omega^2\tau^2). \quad (4)$$

If $|V|^{-2}$ is a linear function of ω^2 and if ΔT_0 can be measured, the Seebeck coefficient S and thermal time constant τ can be determined by the gradient given by $1/(S\Delta T)^2$ and the intercept given by $\tau^2/(S\Delta T)^2$ in the $|V|^{-2}$ vs. ω^2 plots. (Fig.2)

FIG. 2. The modulation frequency dependence of the emf.

B. Measurement of the thermal conductivity

When the sample absorbs the energy of the laser beam, the heat is generated in the sample. In the conventional measurement of the photo pyro electric (PPE) method,⁸ the transducer converts the heat to the electric signal, and this electric signal is observed. But in the present AC method we need no transducer attached on the sample, because the electro motive force of the sample is directly detected as the signal. This signal depends on not only the thermal relaxation but also the thermal transmission in the sample.

According to the theory of the one dimensional model proposed by Rosencwaig, the phase lag $\Delta\theta$ for an optically thick and thermally thick sample can be written as

$$\Delta\theta = La = L(\omega/2\alpha)^{1/2}, \quad (5)$$

where L , a , ω and α are distance from heat source, thermal diffusion coefficient, modulation frequency and thermal diffusivity, respectively.⁹ The relation between $\Delta\theta$ and ω is expressed the equation as follows;

$$\Delta\theta = L/(2\alpha)^{1/2} \omega^{1/2} + D, \quad (6)$$

where D is a constant. Then α is determined from the $\Delta\theta$ vs. $\omega^{1/2}$ plots.

The thermal conductivity κ is given by

$$\kappa = \alpha \times \rho \times C, \quad (7)$$

where ρ is the density and C is the specific heat.

III. EXPERIMENT

The sample preparation¹⁰⁻¹³ is as follows. β -SiC and Cu (99 % in purity) were used as starting material. Slurries were made from mixed SiC, Cu (0.5, 1.0, 2.0 wt%) powders and PSS (Polysilastyrene) as in polyethylene jars with nylon coated iron balls as grinding media and xylene solution as the mixing agent. After mixing for 20 h and passing through 75 μ m mesh sieve, these slurries were dried. The dried mixture were granulated using 500 μ m mesh sieve and pressed into pellet. Then the pellets sealed into an evacuated rubber tube and then pressed isostatically at 2×10^8 N/m² (~ 2 ton/cm²). Next step they were pre-sintered for 1 hour at 1000 °C in Ar 1.0 atm atmosphere. After cooling they were sintered for 2 h at 2100 °C in Ar 1.3 atm atmosphere. The sample sizes are summarized in Table 1.

TABLE 1. The size of the samples.

Cu concentration (wt%)	0.5	1.0	2.0
diameter (mm)	18.40	18.10	18.50
thickness (mm)	3.55	3.40	4.15

Figure 2 shows the schematic diagram of the AC method equipment. One electrode is located at the center of the front surface, the other is located peripherally on the back surface, and the lead wires are attached by the Ag paste on the sample. The temperature at the electrodes were measured by the chromel-alumel thermocouples. To avoid the influence of the thermal convection, the sample was kept in the vacuum around 5 Torr. And to reduce the photovoltaic

FIG. 3. Schematic diagram of AC measurement equipment.

effect, the electrode is shaded from the direct laser irradiation on the front surface. When the laser beam is focused on the sample, the electro motive force and the phase lag between two electrodes were measured by the lock-in amplifier. Also the amplitude and phase shift of the temperature difference were measured simultaneously using two thermocouples. The modulation frequency was varied from 10 Hz to 100 Hz.

IV. RESULTS and DISCUSSION

Figure 4 shows $|V|^{-2}$ vs. ω^2 plots of the samples and Fig. 5 shows $|V|^{-2}$ vs. ω^2 plots at low frequency

FIG. 4. Modulation frequency dependence of the emf. The open squares represent Cu concentration 0.5 wt% data, closed circles represent 1.0 wt% data and open circles represent 2.0 wt% data.

FIG. 5. Modulation frequency dependence of the emf in the low frequency region (< 50 Hz). Notations are the same in Fig. 4.

TABLE 2. The result of the Seebeck coefficient S by AC method.

Cu concentration	0.5 wt%	1.0 wt%	2.0 wt%
$1/(S\Delta T)^2(V^{-2})$	3.1×10^{12}	2.0×10^{13}	8.6×10^{11}
$(\tau/S\Delta T)^2(V^2/S^2)$	2.4×10^9	1.5×10^9	2.5×10^6
$\Delta T_0(K)$	3.7×10^{-4}	9.8×10^{-4}	7.6×10^{-3}
$S(V/K)$	4.9×10^{-4}	2.1×10^{-4}	1.4×10^{-4}
$\tau(S)$	8.4×10^{-3}	8.6×10^{-3}	1.7×10^{-3}

FIG. 6. Cu concentration dependence of the Seebeck coefficient. Open circles represent the data obtained by the DC measurement and closed circle represents the data obtained by the AC measurement.

range. Table 2 summarizes the results obtained by the AC method.

Figure 6 shows the Seebeck coefficient S obtained by AC method. For comparison, the result obtained by the conventional DC method is also represented in Fig. 6. For the DC method, we use the bar shaped samples (3 mm×4 mm×8~12 mm) cut from disk shaped samples. The disk shaped samples may be inhomogeneous. In our study, however, it is not distinguished the position to take out the bar shaped samples from the disk shaped ones. Therefore there is a large difference among the samples which are the same Cu concentration in DC method, especially the data of the samples with Cu 1.0 wt%.

Figure 7 shows the $\Delta\theta$ vs. $\omega^{1/2}$ plots for the samples including Cu of 0.5 and 1.0 wt%. From eq.(5), the thermal diffusivity is obtained by the linear least squares method in the $\Delta\theta - \omega^{1/2}$ relation. Table 3 summarizes the experimental results of the thermal conductivity obtained by the AC method. Figure 8

FIG. 7. Modulation frequency dependence of the phase lag. Open squares represent the data obtained by PPE method and closed circles represent the data obtained by the AC method.

TABLE 3. The result of the thermal conductivity by the AC method.

Cu concentration	0.5 wt%	1.0 wt%
gradient (rad/s ^{1/2})	0.85	0.87
L(m)	9.86×10^{-3}	9.67×10^{-3}
α (m ² /s)	6.73×10^{-5}	6.18×10^{-5}
density (g/cm ³)	1.93	1.90
spec.heat(J/g K)	6.70×10^{-1}	6.68×10^{-1}
thermal conductivity (W/m K)	86.2	78.4

shows the thermal conductivity obtained by the AC method. To compare the data obtained the AC method, the data obtained by the θ -L characteristics of the PPE method which uses poly vinyliden difluoride (PVF₂) as the transducer are presented in Fig. 8.

We have estimated the Seebeck coefficient and the thermal conductivity at the same time. In this study, we focus the attention to the following;

- (1) the thermoelectric motive force $V(\omega)$ is generated by the temperature difference $\Delta T(\omega)$ between P and Q in Fig. 1.
- (2) the phase difference θ between $\Delta T(P, \omega)$ and $\Delta T(Q, \omega)$, which is the temperature rise at the point P or Q, is determinant by the time lag induced by the

FIG. 8. Cu concentration dependence of the thermal conductivity. Notations are the same as in Fig. 6.

thermal diffusion time τ .

So the Seebeck coefficient and the thermal conductivity can be determinant by measuring the modulation frequency dependence of ΔV , ΔT and θ . In the AC method, it is necessary for the evaluation of the Seebeck coefficient to extrapolate ω^2 - V^2 plot to $\omega=0$. Also the modulation frequency dependence of the phase difference θ is required to estimate the thermal diffusivity. In the lock in detection of the signal, one must be careful to restrict the phase difference below 360 degree, otherwise, detected signal may include other harmonic components which may lead to erroneous results. In our experiment, the Seebeck coefficient and the thermal conductivity are estimated by the data measured under the condition of $\omega^2 < 10^{-4} \text{ s}^{-1}$. One of the methods which overcome this problem is to select the optimum distance between the two electrodes. In addition, the photovoltaic effect caused by the non ohmic contact at electrodes may give the influence on this result.

V. CONCLUSION

The AC method proposed here allows simultaneous and versatile method of measurement for the Seebeck coefficient and the thermal conductivity. We have measured the Seebeck coefficient and the thermal conductivity of the SiC/Cu thermoelectric semiconductors at the same time by this method. The result of the Seebeck coefficient ($1.4 \sim 4.9 \times 10^{-4} \text{ V/K}$) is comparable to the value measured by the DC method ($1.8 \sim 3.8 \times 10^{-4} \text{ V/K}$). The result of the thermal conductivity measured by the AC method is in good

agreement with the value measured by the PPE method which uses the PVF_2 as the transducer.

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