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BRIEF PAPER *Special Section on Fundamentals and Applications of Advanced Semiconductor Devices*

Seebeck Coefficient of Flexible Carbon Fabric for Wearable Thermoelectric Device

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SUMMARY We have measured the Seebeck coefficient of a carbon fabric (CAF) using a homemade measurement system for flexible thermoelectric materials to evaluate Seebeck coefficient along the thickness direction. Our equipment consists of a thermocouple (TC) electrode contacted with a resistive heater and another TC electrode attached to a heat sink. A flexible sample is sandwiched with these TC electrodes and pressed by weights. The equipment is set on a weighing machine in order to confirm and hold the pressing force at the contact between the electrodes and the soft sample. Cu and Pb plates were measured as a reference material to calibrate and clarify the accuracy of our measurement system, and its validity was confirmed. The Seebeck coefficient of a single CAF layer ranged 4.3–5.1 μV/K, independent of extra weight. This fact indicates that the weight of heat sink is enough for stable contact at the TC-electrode/CAF interface. It was found that the Seebeck coefficient of layered CAF increases with an increase in the number of layers, which suggests the influence of the air between the CAF layers even though the heavy weight is used.

key words: *wearable power generator, flexible material, Seebeck coefficient, carbon fabric*

1. Introduction

As one of the energy-harvesting devices, the wearable thermoelectric power generator has attracted significant attention since it can reuse the waste heat as an electric power. For this device, flexible thermoelectric materials with appropriate thermoelectric properties are required to enhance the heat-electricity conversion efficiency. To achieve high power-generator efficiency using thermoelectric technology, it is necessary to increase the thermoelectric figure-of-merit Z, denoted as

$$Z = \frac{S^2\sigma}{\kappa}, \tag{1}$$

where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity of the thermoelectric material [1]. Therefore, it is necessary to achieve an increase in S and a decrease in κ, simultaneously. One method of overcoming this issue is the introduction of nanostructured semiconductors due to the confinement effect of carriers and phonons [2]–[4].

We have focused our attention on nanostructured ZnO as a thermoelectric material [5], [6], since ZnO is easily obtainable and inexpensive, and moreover, it is nontoxic for human skin. Hence, ZnO-related flexible materials are available for clothing. From point of thermoelectric view, however, characteristics of ZnO are not sufficient near room temperature. In our previous papers [5], [6], although we have measured the Seebeck coefficient of ZnO/cotton-fabric materials, it was obtained by applying the temperature gradient along the layer plane (in the horizontal direction). However, the temperature gradient must lie along the thickness direction of the layer (in the vertical direction) for a practical use of wearable devices. There are some reports related to the evaluation of the Seebeck coefficient in the vertical direction of the sample [7]–[9]. However, these Seebeck coefficient measurements were applied not to flexible layer materials but to bulk or rigid materials.

In addition, since the cotton fabric is insulator, less power in the vertical direction may be obtained due to its small electric current. Therefore, we have focused on conductive carbon fabric (CAF) as a flexible substrate. Many researchers worked on the Seebeck coefficient of flexible carbon materials such as carbon fiber [10]–[13]. However, none reported the Seebeck coefficient of CAF, especially in the vertical direction. In this study, we constructed a system for measuring the Seebeck coefficient of flexible layer material in the vertical direction and evaluated that of CAF. It will be demonstrated that the Seebeck coefficient of a CAF layer in the vertical direction is close to that evaluated in the horizontal direction. Moreover, the influence of air on the Seebeck coefficient in stacked CAF layers will be presented.

2. Experiment

Figure 1 shows a schematic diagram of a developed measurement system for Seebeck coefficient evaluation in the thickness direction of the sample. This has two T-type thermocouples (TCs) which are buried into Cu electrodes. One of the Cu electrodes with an area of 2×2 cm^2 is attached to a resistive heater and is set under the sample as a sample holder. The other with an area of 1×1 cm^2 is attached to a heat sink and is put on the sample. By flowing appropriate current to the heater, temperature gradient can be applied to the sample along the vertical direction. In electrically characterizing the flexible materials, it is important to remove the influence of contact resistance at the electrode/sample interface. Therefore, in order to confirm and control the

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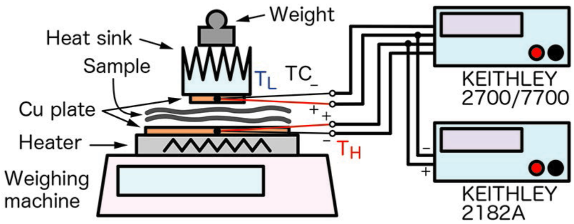

Fig. 1 Schematic diagram of developed Seebeck coefficient measurement system.

pressure between the electrode and the soft sample during the measurement, the above-mentioned equipment is constructed on a weighing machine, and some weights can be put on the heat sink, as drawn in Fig. 1. The weight of the heat sink was approximately 16 g. By using this system, stable and reproducible measurement can be performed in the same condition every time. Whole equipment is positioned in a shield box to avoid the environmental influences.

The heater current was supplied from a DC power supply (MATSUSADA PK160-2.5). The temperatures at the top (T_L) and bottom (T_H) of sample were measured by a digital multimeter (Keithley 2700), and the thermoelectromotive force (TEMF) of the sample was measured by a nanovoltmeter (Keithley 2182A) through the Cu wires in the T-type TCs. The power supply and voltmeters were automatically controlled by a computer. After putting a sample between the Cu electrodes, the temperature gradient was applied along the sample in the thickness direction by heating. Time evolution of temperatures T_L and T_H were measured simultaneously with the TEMF. Then, the Seebeck coefficient was evaluated from the gradient of the linear relationship between the TEMF and the temperature difference, $\Delta T = T_H - T_L$.

3. Result and Discussions

3.1 Calibration and Precision

In general, the Seebeck coefficient is a relative value, that is, there is a criterion. Hence, the TEMF (ΔV) is expressed by [14], [15]

$$\Delta V = -\int_{T_L}^{T_H} [S_X - S_{cr}] dT, \tag{2}$$

where T is the temperature, S_X and S_{cr} are the Seebeck coefficient of the sample X and the criterion material, respectively. T_H and T_L are the temperature at the hot and cold junctions, respectively. The criterion material is Cu in our equipment because Cu wires in the T-type TC are used for measuring the TEMF.

For calibration of our system, we measured the Seebeck coefficient of a 2-mm-thick Cu plate (purity: 99.9%). According to Eq. (2), the TEMF obtained in measuring the Cu plate is ideally $\Delta V = 0$ V [16]. However, finite TEMF values were measured under temperature gradient and the evaluated Seebeck coefficient was $S_{Cu} =$ -0.6 μV/K. We performed the measurement 7 times and the obtained S_{Cu} values were barely scattered with a standard deviation of 0.1 μV/K, which indicates the good reproducibility. In addition, this fact suggests that our system has a parasitic component $S_{para} = -0.6$ μV/K which is likely to come from the measurement environment. Therefore, when evaluating the Seebeck coefficient for a material X, S_X, by using the developed system, the true value of the material, S_X^*, should be calibrated by

$$S_X^* = S_X - S_{para}. \tag{3}$$

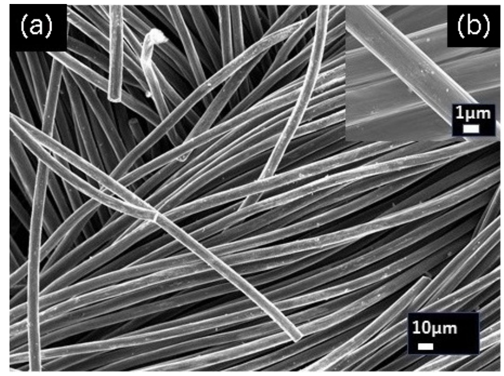

Fig. 2 (a) SEM image of CAF and (b) its magnified image.

Since the Seebeck coefficient of bulk Pb is well known [17], [18], a 0.5-mm-thick Pb plate (99.9%) was measured 7 times with the aim of confirming the precision of the developed system. The calibrated Seebeck coefficient for the Pb plate was $S_{Pb}^* = -1.9$ μV/K, with a standard deviation of 0.1 μV/K. The absolute Seebeck coefficient is 1.2 μV/K smaller than the reported value -3.1 μV/K with respect to Cu [19]. Accordingly, it can be concluded that our constructed system is valid for evaluating the Seebeck coefficient in the thickness direction with an error of about 1 μV/K.

3.2 Characterization of Flexible CAF

We use a CAF produced by Fibre Glast Development Corporation (# 2363), which is considered as one of the fabric substrates for ZnO nanostructures. Figure 2 shows the scanning electron microscope (SEM) images of the CAF. It is found that the fibers with a diameter of several micrometers are intertwined in the fabric. The CAF was characterized by our system for confirming and optimizing measurement conditions such as the TC-electrode/flexible-material contact. An example of the time evolutions of TEMF, T_L and T_H for the CAF is shown in Fig. 3. It is clearly observed that the TEMF negatively increases with an increase in the temperature difference ΔT.

Figure 4 shows the relationship between TEMF and temperature difference replotted from Fig. 3. In this figure, “Increase” means the data collected from the range where the temperature difference is increasing, and “Decrease” corresponds to the data under decreasing the temper-

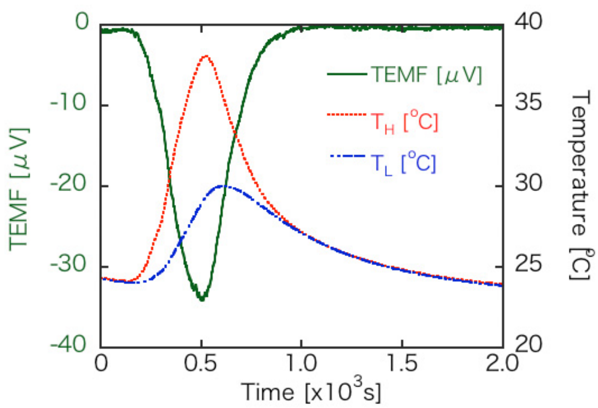

Fig. 3 Time evolutions of TEMF and temperatures at hot T_H and cold T_L junctions for single CAF layer.

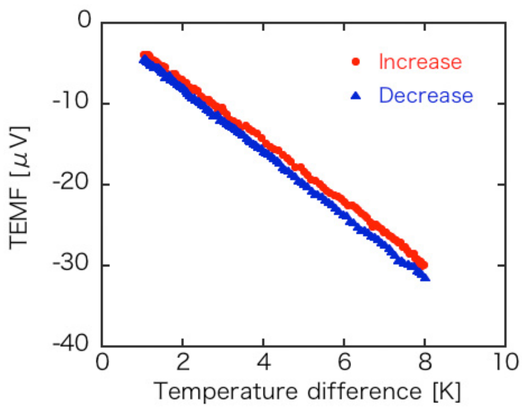

Fig. 4 Relationship between TEMF and temperature difference for single CAF layer. "Increase" and "Decrease" correspond to the data collected from the range where the temperature difference is increasing and decreasing, respectively, in Fig. 3.

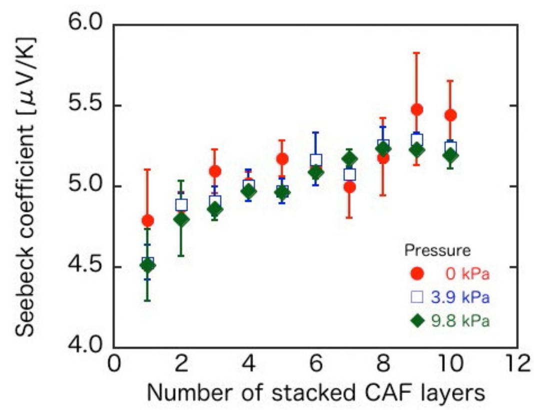

Fig. 5 Relationship between Seebeck coefficient and the number of stacked CAF layers, as a parameter of extra pressure by weight. In the horizontal axis, 0 kPa corresponds to the pressure of heat sink only, 1.6 kPa.

ature difference in Fig. 3. Both "Increase" and "Decrease" data are nearly identical. This fact means that the measured data are reliable even for flexible materials. In addition, both data make a linear relation, indicating that the Seebeck coefficient is nearly constant in the measured temperature range. Therefore, the average Seebeck coefficient of CAF is evaluated from the gradient of the linear graph to be $S^*_{\mathrm{CAF}} \sim 4.5\,\mu$V/K, which is close to that of the same CAF obtained in the horizontal direction, 5.0 μV/K. The Seebeck coefficient is positive, indicating that the CAF used is a p-type material, which was also confirmed by Hall measurement.

Figure 5 shows the relationship between Seebeck coefficient and the number of stacked CAF layers, as a parameter of extra pressure by weights, where 0 kPa corresponds to the pressure of heat sink only, 1.6 kPa. It is found from the weight dependency that the weight hardly influences the Seebeck coefficient. This means that the weight of heat sink over the upper TC electrode is enough for realizing a stable measurement condition at the contact between the TC electrode and a soft sample.

As for the influence of stacking, the Seebeck coefficient tends to increase with increasing the number of stacked layers. The increment in Seebeck coefficient by stacking is likely to originate from the influence of air between layers, and the number of air layers increases with an increase in that of stacked CAF layers. However, further investigation is required to clarify the details.

4. Conclusions

We have successfully constructed a measurement system of Seebeck coefficient in the vertical direction available for flexible thermoelectric materials. By measuring a Cu plate, the parasitic component from the experimental environment was estimated to be $-0.6\,\mu$V/K. Therefore, the Seebeck coefficient obtained directly from the gradient in the relationship between TEMF and temperature difference should be calibrated by a factor of $-0.6\,\mu$V/K. Through the measurement of a Pb plate, the characterized Seebeck coefficient has an error about 1 μV/K. The Seebeck coefficient of a CAF material was evaluated to be 4.5 μV/K, which is close to that in the horizontal direction. Moreover, it was found that the multi-layered CAF has a Seebeck coefficient slightly larger than the single layer and that as the number of stacked CAF layers increases, the Seebeck coefficient increases. This phenomenon may be due to the influence of air between the stacked CAF layers.

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