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Thermoelectric characteristics of nanocrystalline ZnO grown on fabrics for wearable power generator

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Abstract. The present paper reports the fabrication and characterization of low-cost and large-area flexible thermoelectric materials with nanocrystalline ZnO applicable for wearable power generator. The ZnO nanostructures were grown on cotton fabric (CF) and carbon fabric (CAF) by solvothermal synthesis. It was demonstrated that the polarity of Seebeck coefficient in ZnO-covered CF can be controlled by adding Sb and Ag. That is, for the Sb-ZnO/CF sample, the Seebeck coefficient was negative, indicating a n-type semiconductor. On the other hand, its value changed to positive for the Ag-ZnO/CF sample, indicating p-type one. For the ZnO/CAF sample, the Seebeck coefficient showed the same value as a CAF substrate. In this sample, ZnO hardly contributes to the thermoelectromotive force comparing with the CAF, which is due to a lack of the ZnO amount.

1. Introduction

The wearable thermoelectirc power generator, one of the energy harvesting devices, requires flexible thermoelectric materials. To achieve high power-generator efficiency using thermoelectric technology, it is necessary to increase the thermoelectric figure-of-merit (Z), denoted as $Z = S^2\sigma/\kappa$, 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 σ, 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 focus our attention on nanostructured ZnO as a thermoelectric material [5-7] while the ZnO nanostructures formed by solvothermal synthesis have been investigated for applying to gas sensor [8], dye-sensitized solar cell [9] and so forth. This is because ZnO is easily obtainable, inexpensive, stable for temperature and humidity, and nontoxic for human skin. Hence, ZnO-related flexible materials are available for clothing. In the present study, with the aim of applying the ZnO nanostructures to a flexible thermoelectric material, we constructed the fabrication method of ZnO nanostructre on cotton fabric (CF) and carbon fabric (CAF), and evaluated the Seebeck coefficient of the obtained ZnO-nanostructure/fabric samples.

2. Fabrication of nanocrystalline ZnO on fabrics

Figure 1 shows a schematic diagram of fabrication procedure of ZnO nanostructures on CF, substrate for flexible material, used in this study [6]. The two-step method was adopted for the fabrication, consisting of seed creation process and nanostructure growth process. Mixture of $Zn(NO_3)_2{\cdot}6H_2O$ and $(CH_2)_6N_4$ was used as precursor solution. A typical scanning electron microscope (SEM) image of ZnO/CF obtained from this fabrication condition is shown in Fig. 2. It is found that white ZnO nanosheet structures can be observed on the cotton fibers. We also confirmed that the UV-transmittance characteristics of the ZnO/CF sample does not change even after 10-times laundry treatment with water. This fact indicates that the nanocrystalline ZnO is chemically bonded to the cotton fiber.

With the aim of controlling the polarity of ZnO, we tried to add Sb and Ag to the ZnO/CF materials. The detailed process is described in Ref. 4. Moreover, instead of the insulator CF substrate, conductive CAF was used as a substrate for flexible thermoelectric materials. In this case, a simple solvothermal process was performed and the detail procedure will be described elsewhere.

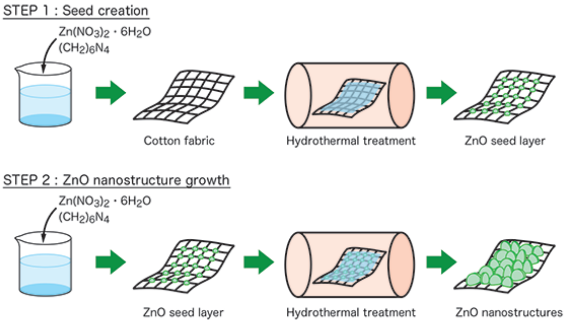

Figure 1. Schematic of fabrication process of ZnO nanostructures on a CF. The two-step method consists of seed creation process and nanostructure growth process.

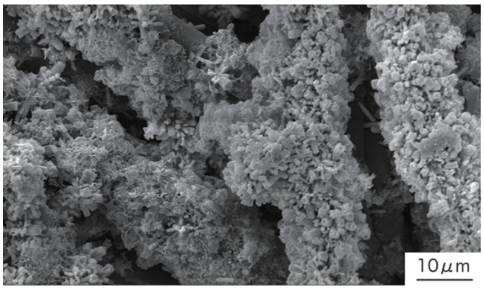

Figure 2. SEM image of ZnO nanostructures grown on a CF.

Our handmade measurement equipment used in this study is illustrated in Fig. 3. Two Peltier devices connected to heat sinks are placed side by side with a gap of 10 mm between them and can be heated individually. The flexible sample for measuring is placed across the gap, in contact with both of the Peltier devices. Two T-type thermocouples (TCs) buried within Cu electrodes are directly attached to the sample surface. The time evolution of the thermoelectromotive force (TEMF) was measured by a digital multimeter (Keithley 2700) equipped with a switching module (Keythley 7700), simultaneously with the temperatures at the high- and low-temperature regions. The Seebeck coefficient S was evaluated from the TEMF ($\Delta V \equiv V_L - V_H$) and the temperature difference ($\Delta T \equiv T_H - T_L$) by $S = \Delta V/\Delta T$ near room temperature.

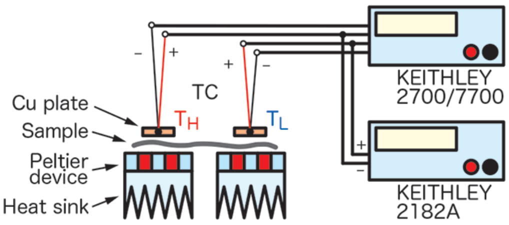

Figure 3. Schematic diagram of the apparatus for Seebeck coefficient measurement.

3. Results and discussion

3.1. Seebeck coefficient of ZnO/CF

Figure 4 shows the Seebeck coefficient evaluated for ZnO/CF, Sb-ZnO/CF, and Ag-ZnO/CF. From the SEM observation, the Sb- and Ag-ZnO/CF samples were confirmed to have composite structure rather than impurity doping [7]. However, it is clearly found that both two Sb-ZnO/CF samples synthesized for different conditions show negative Seebeck coefficient, or n-type semiconductor. As for the difference between these samples, it is worth noting that the Sb-ZnO network on the cotton fiber surface is formed as a freestanding composite, which should be attributed to the Sb incorporation into the Zn sites and O vacancies, resulting in n-type behavior [10-12]. On the contrary, both two Ag-ZnO/CF samples show positive Seebeck coefficient, or p-type semiconductor. In the case of Ag-ZnO composites, the growth process of ZnO is disrupted when the Ag composites are introduced, and the growth process is again favored when enough Ag have recombined with the Zn material which may cause the positive effect on the charge separation efficiency [13,14]. Consequently, the polarity in Seebeck coefficient of ZnO can be controlled by adding Sb and Ag.

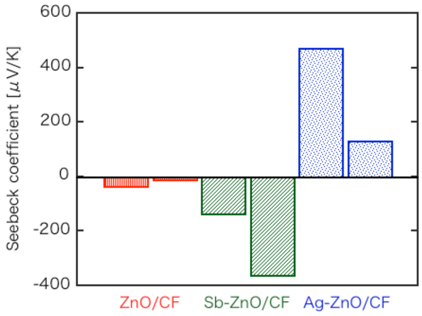

Figure 4. Seebeck coefficients evaluated for ZnO/CF, Sb-ZnO/CF, and Ag-ZnO/CF.

3.2. Nanocrystalline ZnO grown on CAF

Figure 5 shows the measured TEMF as a function of temperature difference for ZnO/CAF and CAF itself. Both graphs make a linear relation, indicating that the Seebeck coefficient is nearly constant in the measured temperature range. The Seebeck coefficient of CAF evaluated from the gradient was 5.0 μV/K. The value is positive, so the CAF used is a p-type material, which was confirmed also by Hall measurement. On the other hand, the Seebeck coefficient of ZnO/CAF sample was evaluated also to be 5.0 μV/K. This fact suggests that the TEMF in the ZnO/CAF sample is produced at CAF since the obtained value is not influenced by the formation of ZnO nanostructures on CAF. Insignificant influence of ZnO nanostructures is considered to be due to a lack of its amount.

4. Conclusions

We investigated the thermoelectric characteristics of ZnO nanostructures formed on CF and CAF by a solvothermal method for the application of wearable power generator device. The ZnO nanosheet structure formed on the cotton fiber. The Seebeck coefficient of nanocrystalline-ZnO/CF was negatively increased by forming the Sb-ZnO composites. In addition, it changed to positive values by forming the Ag-ZnO composites. Therefore, it is found that the ZnO/CF material can be available for n- and p-type thermoelectric materials by adding Sb and Ag. The Seebeck coefficient of ZnO/CAF is about 5 μ V/K and equal to that of CAF itself. The ZnO nanostructures on CAF hardly contributes to TEMF under a given temperature gradient.

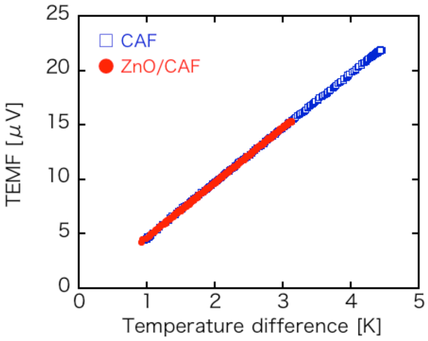

Figure 5. Relation between TEMF and temperature difference for CAF and ZnO/CAF samples. The Seebeck coefficients evaluated from the gradient were 5.0μV/K both for CAF and ZnO/CAF samples.

Acknowledgments
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