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Thermoelectric characteristics in out-of plane direction of thick carbon nanotube-polystyrene composites fabricated by the solution process

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ABSTRACT

When sheet-like flexible devices are placed on heat sources, a thermal flow is induced along the out-of-plane direction in regards to the device surface. To obtain carbon nanotube-based (CNT-based) thermoelectric devices that work under thermal flows along the out-of-plane direction, it is indispensable to fabricate sufficiently thick CNT-based materials that will allow for an out-of-plane temperature difference to occur. Therefore, we investigated the out-of-plane thermoelectric characteristics of thick CNT-polymer composites (thickness = 0.74–0.84 mm), which were fabricated by overcoating a dense CNT-dispersed solution, and found that the electrical and thermal conductivities of the composites in the out-of-plane direction were significantly lower than those in the in-plane direction, respectively. We observed that the composites' figure of merit values in the out-of plane direction was approximately one order of magnitude lower than those in the in-plane direction. This anisotropy in the characteristics of thick CNT-polystyrene composites may be caused by the orientation of the CNTs along the in-plane direction. Therefore, the results indicate that controlling the orientation of CNTs in thick composites is a key factor to improve the performance of devices that work on the basis of temperature differences along the out-of plane direction.

1. Introduction

Carbon nanotube-based (CNT-based) thermoelectric materials have been extensively researched because of their many desirable properties for the fabrication of flexible and light-weight devices using printing processes [1–11]. Hereof, composite materials consisting of single-walled carbon nanotubes (SWCNT) and polymers are promising candidates for high performance CNT-based thermoelectric materials because CNTs have a very high electrical conductivity [12], SWCNTs possess relatively high Seebeck coefficients [13], and polymer materials generally have a low thermal conductivity. Considerable research efforts have been devoted to improve the thermoelectric performance of CNT/polymer-based composites, and high-performance composites with high power factors, of the order of several hundred to a thousand $\mu W/K^2m$, have been reported [1,3,10].

Most papers related to CNT-based thermoelectric materials have reported the in-plane thermoelectric characteristics of thin film-shaped materials. However, when CNT-based devices are placed on a heat source, temperature differences are generated along the out-of-plane direction in regards to the device surface. Thus, studies on the out-of plane characteristics of CNT-based materials and devices are important from an operational point of view. We have previously reported CNT-based thermoelectric devices with a uni-leg structure, which is suitable for generating electric power using temperature differences along the out-of-plane direction [11]. In order to construct such devices it is indispensable to fabricate CNT-based materials that are thick enough to ensure a temperature difference in the out-of plane direction. Additionally, solution processability is recognized as one of the most important merits of CNT-based thermoelectric materials, thus, it is important to evaluate the out-of plane thermoelectric characteristics of thick CNT-based materials fabricated by solution processes. However, because the thickness of CNT-based materials formed by solution processes is small, typically of the order of several micrometers [3,9,10]. Thus, it is difficult to fabricate films that are thick enough to ensure a temperature difference along the out-of plane direction by using simply printing CNT-dispersed polymer solutions. Additionally, although there are few papers reported thermoelectric characteristics in the out-of plane direction of organic and CNT-based materials [14], a good measurement method for the out-of plane

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characteristics of thick printed CNT-based materials has not been well established.

In this paper, we investigated and compared the out-of-plane and in-plane thermoelectric characteristics of thick SWCNT-polymer composites fabricated by over coating a dense SWCNT-dispersed solution. Polystyrene was chosen as the binder polymer because we previously reported that SWCNTs/polystyrene composites have a high thermoelectric power factor of 413 μW/m K^2 [10]. We observed that the ZT values in the out-of plane direction of the composites were significantly lower than those in the in-plane direction, which indicate that controlling the orientation of CNTs in thick composites is a key factor to improve the performance of devices whose working principle is based on temperature difference along the out-of plane direction.

2. Experimental

To fabricate the SWCNTs-polystyrene composites, we used SWCNTs with an average diameter of 2.0 nm, and atactic polystyrene (average molecular weight of ~280000). First, the SWCNTs and polystyrene were mixed through planetary ball milling at 500 rpm in toluene (10 mL) as a solvent. The total weight of SWCNTs and polystyrene in the mixed solution was kept at 50 mg. Subsequently, the mixed solution was heated on a hot plate (50 °C) to evaporate the toluene, until it was condensed to 1/5 of its weight. Thereafter, the thick SWCNT/polystyrene composites were fabricated by over coating the condensed solution onto a fluorine-based film substrate at 50 °C, using a printing plate with a rectangular-shaped opening of 5 × 4 mm. Then, the composites were annealed at 70 °C for 5 h to remove the remaining solvent. We confirmed that the Seebeck coefficient and electrical conductivity were not significantly affected by further annealing. This indicates that the residual solvent in the composites was sufficiently removed under this annealing condition. Finally, the thick SWCNT-polystyrene composites were removed from the substrate.

To measure the thermoelectric characteristics in the in-plane and out-of plane directions of the composites, we cut the composites in half using a cutter, and shaved the cutting surface using a microtome (Fig. 1). One half of the cut composite piece was used for the in-plane direction measurements, while the other half was used for the out-of plane direction measurements. Thus, the in-plane and out-of plane characteristics were measured using the same sample.

To measure the Seebeck coefficient, the SWCNT-polystyrene composites were sandwiched between hot and cold copper plates, and the Seebeck coefficient was obtained from the voltage generated between the copper plates as result of temperature differences in the composites. The electrical conductivity was obtained using the 4-probe method. The thermal diffusivity (α) was measured using the temperature wave analysis method [15] (ai-Phase Mobile 1u, ai-Phase Co. Ltd.) The thermal conductivity (κ) was calculated from the relationship $\kappa = C\cdot\alpha\cdot\rho$, where C and ρ are the heat capacity and density, respectively. The C values were obtained through differential scanning calorimetry (DSC-7020, Hitachi High-Tech Science Corp.).

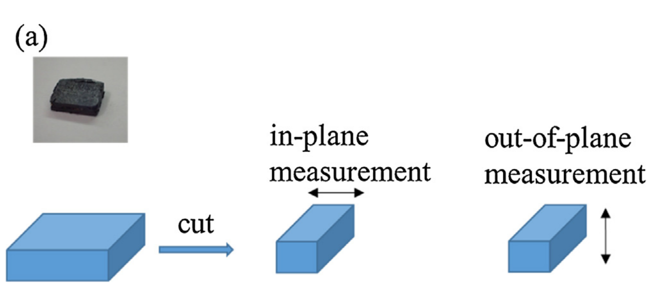

Fig. 1. Preparation method of measurement samples of a thick and printed SWCNT-polystyrene composite.

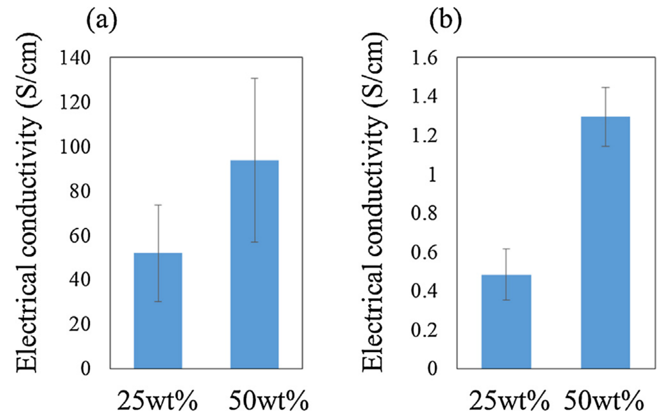

Fig. 2. In-plane (a) and out-of plane (b) electrical conductivity of SWCNT-polystyrene composites with 25 and 50 wt% SWCNT concentrations. Mean values obtained from 3 samples are plotted with error bars representing the standard deviation.

3. Results and discussion

The inset in Fig. 1 shows a photograph of the thick SWCNT-polystyrene composites. The densities of composites with 25 and 50 wt% SWCNTs were 1.07 and 1.08 g/cm^3, respectively. The thicknesses of the composites used in this study were 0.74–0.84 mm. These thickness values are several orders of magnitude higher than those commonly reported for CNT-polymer composites fabricated by the solution process [3,9,10].

Fig. 2 shows the electrical conductivity (σ) along the in-plane and out-of-plane directions of SWCNT-polystyrene composites with 25 and 50 wt% SWCNT concentrations. In both concentrations, the electrical conductivity in the in-plane direction was approximately two orders of magnitude higher than in the out-of-plane direction. On the other hand, the Seebeck coefficients (S) were almost identical between the in-plane and out-of-plane directions for both SWCNT concentrations (Fig. 3).

Fig. 4 shows the thermal conductivity (κ) along the in-plane and out-of-plane directions of the SWCNT-polystyrene composites. It is recognized that the precisely measurement of in-plane thermal conductivity of thin film is difficult by using well-established measurement method, and this is an obstacle to

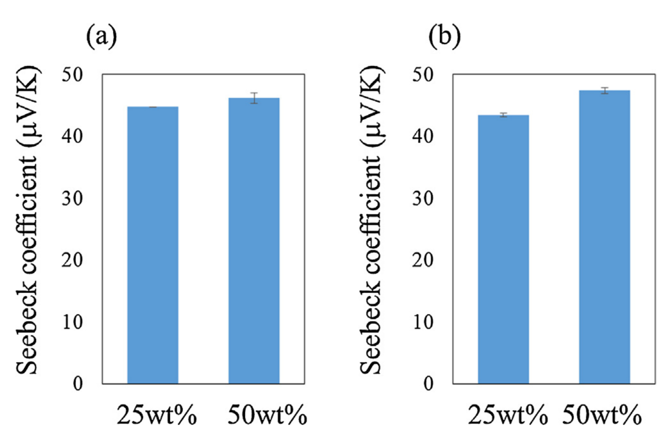

Fig. 3. In-plane (a) and out-of plane (b) Seebeck coefficients of the SWCNT-polystyrene composites with 25 and 50 wt% SWCNT concentrations. Mean values obtained from 3 samples are plotted with error bars representing the standard deviation.