半導体性単層カーボンナノチューブシートの熱電特性

Thermoelectric Properties of Semiconducting Single-walled Carbon Nanotube Sheets

九大院工 [1], WPI-I^{2}CNER [2], JST-さきがけ [3] ○(DC)黄　文シン [1], 徳永　恵梨子 [1], 中島　祐樹 [1], 藤ヶ谷　剛彦 [1,2,3]

Kyushu Univ. [1], WPI-I^{2}CNER [2], JST-PRESTO [3] ○(DC)Wenxin Huang[1], Eriko Tokunaga[1], Yuki Nakashima[1] and Tsuyohiko Fujigaya[1,2,3]

E-mail: huang.wenxin.619@s.kyushu-u.ac.jp

Abstract Single-walled carbon nanotubes (SWNTs) have attracted strong attention as thermoelectric (TE) material due to their extremely high electrical conductivity (σ), light weight, mechanical toughness and flexibility. However, SWNTs are produced as a mixture of metallic (m-) and semiconducting SWNTs (s-SWNTs). s-SWNT sheet is proved to have large Seebeck coefficient (S) theoretically and experimentally [1, 2], however, its improvement in ZT value is still uncertain compared with the unsorted SWNT sheet. In this study, we systematically characterized the TE properties of s-SWNT sheets with different ratio of m-SWNTs as well as the unsorted SWNT sheet to evaluate the necessity of s-SWNT extraction from its SWNT mixture.

Introduction Density gradient ultracentrifugation (DGU) is used as the extraction method of commercial s- and m-SWNT [3]. However, DGU method may induce defects in s- and m-SWNTs. To cancel this factor, we mixed the extracted s- and m-SWNT in the ratio of 4:1, 2:1 and compared their ZT value with pure s- and m-SWNT. Raman and UV spectra were used to characterize the defect of the extracted SWNTs and the ratio to s- and m-SWNTs, respectively.

Experiment s-SWNTs 2.0 mg (98% Nanointegris) and m-SWNT 1.0 mg (98% Nanointegris) were added to 0.5% SDBS solution and dispersed by bath sonicator (BRANSON, 1 hr) and probe sonicator (TOMY UD-200). The dispersion were filtrated and the free-standing s-:m-SWNT=2:1 sheet was obtained (2:1 mix). s:m-SWNT=4:1 sheet (4:1 mix), s- and m-SWNT sheets were made in the same fashion, using 2.4 mg s-SWNT and 0.6 mg s-SWNT, 3.0 mg s-SWNT and 3.0 mg m-SWNT respectively. In-plane electrical conductivity and Seebeck coefficient of were measured by ZEM-3 (ADVANCE RIKO) from 30 to 100 ºC. The specific heat capacity (C_p) was measured by differential scanning calorimetry (DSC) method using EXSTAR DSC 6200 (SII Nanotechnology) at the heating rate of 10 K min^{-1}. In-plane thermal diffusivities (α) were evaluated using a Thermowave Analyzer TA (Bethel Co., Ltd.,). The density of the sheets (ρ) was calculated from the weight and volume of the sheets.

Results and discussion Table 1 summarized the in plane σ, S and power factor (PF) of the Unsorted SWNT, s-SWNT, m-SWNT and 2:1 mix sheets at 30 ºC. Unsorted SWNT sheet exhibits nearly 1.9 times higher electrical conductivity than the m-SWNT sheet. This is due to the defects induced during the DGU extraction of the m-SWNT, which was confirmed by the larger D band of m-SWNT than that of unsorted SWNT in Raman spectra (data not shown). s-SWNT sheet illustrated higher Seebeck coefficient, however, its PF was the same as the unsorted SWNT sheet due to the large decrease of electrical conductivity. According to UV spectra, the unsorted SWNT and the 2:1 mix sheet have the same s- and m-SWNT ratio, however, 2:1 mix sheet showed higher Seebeck coefficient, which was probably due to its the lower chirality distribution.

Table 1. TE properties of SWNT and s-SWNT sheet

	Unsorted	s-SWNT	m-SWNT	2:1 mix
σ (S m^{-1})	5.49×10^4	1.04×10^4	2.89×10^4	2.12×10^4
S (μV K^{-1})	34.4	76.0	11.9	47.9
PF (μW m^{-1}K^{-2})	64.98	60.34	4.090	48.56
κ (W m^{-1} K^{-1})	16.4	17.4	9.52	14.6
ZT	1.20×10^{-3}	1.05×10^{-3}	1.30×10^{-4}	1.01×10^{-3}

[1] Ferguson, A. J. et al. *Nature Energy,* **1**, 16033 (2016) [2] Maniwa, Y. et al, *Appl. Phys. Express*, **7**, 025103 (2014) [3] Liu, Y. et al, *Chem. Soc. Rev.*, **40**, 1324 (2011)