## 異なる半導体性純度のカーボンナノチューブシートの熱電特性

## Thermoelectric Properties of SWNT Sheets with Different Semiconducting SWNT Ratio 九大院工<sup>1</sup>, WPI-I<sup>2</sup>CNER<sup>2</sup>, 九大 IMS<sup>3</sup>, JST-さきがけ<sup>4</sup> <sup>O</sup>(D) 黄 文シン<sup>1</sup>, 藤ヶ谷 剛彦<sup>1,2,3,4</sup> Kyushu Univ.<sup>1</sup>, WPI-I<sup>2</sup>CNER<sup>2</sup>, IMS<sup>3</sup>, JST-PRESTO<sup>4</sup> °(D) Wenxin Huang<sup>1</sup>, Tsuyohiko Fujigaya<sup>1,2,3,4</sup> E-mail: huang.wenxin.619@s.kyushu-u.ac.jp

<u>Abstract</u> Figure of merit (*ZT*) values of semiconducting (s-), metallic (m-) and their mixture of single-walled carbon nanotube (SWNT) together with unsorted SWNT were evaluated by measuring their electrical conductivity ( $\sigma$ ), Seebeck coefficient (*S*) and thermal conductivity ( $\kappa$ ).

**Introduction** SWNTs have attracted strong attentions as thermoelectric (TE) material due to their extremely high electrical conductivity ( $\sigma$ ), light weight, mechanical toughness and flexibility. Especially, s-SWNT sheet is proved to have large *S* theoretically and experimentally [1, 2]. However, the improvement of *ZT* value by separating s-SWNT from the as-produced SWNT mixture is still uncertain. In this study, we characterized the TE properties of s-SWNT sheets with different s-SWNT ratio and compared their *ZT* values with that of the unsorted SWNT sheet.

**Experiment** s-SWNTs 2.4 mg (98% Nanointegris) and m-SWNT 0.6 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=4:1 sheet was obtained (80% s-SWNT). 98% s-SWNT sheet, s:m-SWNT=2:1 sheet (67% s-SWNT), s:m-SWNT=1:2 sheet (33% s-SWNT), and 2% s-SWNT sheets were made in the same fashion. In-plane  $\sigma$  and *S* of the sheets were measured by ZEM-3 (ADVANCE RIKO) from 30 to 100 °C. 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<sup>-1</sup>. In-plane thermal diffusivity ( $\alpha$ ) were evaluated using a Thermowave Analyzer TA (Bethel Co., Ltd.,). Density ( $\rho$ ) was calculated from the weight and volume of the sheets.

**<u>Results and discussion</u>** Table 1 summarized the in plane  $\sigma$ , *S*, power factor (*PF*),  $\kappa$  and *ZT* of the unsorted SWNT, 2%, 33%, 67%, 80% and 98% s-SWNT sheets at 30 °C. Unsorted SWNT sheet exhibited nearly 1.7 times higher  $\sigma$  than the 2% s-SWNT sheet. This was due to the defects induced during the separation process of the m-SWNTs, which was confirmed by the larger D band of m-SWNTs than that of unsorted SWNT in Raman spectra (data not shown). As s-SWNT ratio increased, *S* increased leading to higher *PF*, which was the same as previous report [3]. No significant difference was observed in the average  $\kappa$  values as the s-SWNT ratio increased, which was in accordance with the literature [4,5]. Mixed SWNT sheets showed lower  $\kappa$  than unsorted SWNT probably due to the higher defect of m- and s-SWNTs [6]. In conclusion, as s-SWNT ratio increased, *PF* increased while  $\kappa$  stayed the same, leading to an increasing *ZT*. The result was practically quite informative when considering the advantage of the s-SWNTs for TE applications.

| fuble 1. 12 properties of various 5 with sheet |                                  |                                  |                                  | (values inside the () is the error bar) |                                  |                                  |
|--|----------------------------------|----------------------------------|----------------------------------|---|----------------------------------|----------------------------------|
|  | Unsorted                         | 2%                               | 33%                              | 67%                                     | 80%                              | 98%                              |
|  | SWNT                             | s-SWNT                           | s-SWNT                           | s-SWNT                                  | s-SWNT                           | s-SWNT                           |
| $\sigma$ (S m <sup>-1</sup> )                  | 5.03×10 <sup>4</sup>             | 2.89×10 <sup>4</sup>             | $1.54 \times 10^{4}$             | $2.12 \times 10^{4}$                    | $1.24 \times 10^{4}$             | $1.04 \times 10^{4}$             |
| S (μV K <sup>-1</sup> )                        | 35.0                             | 11.9                             | 26.1                             | 47.9                                    | 58.6                             | 76.0                             |
| $PF (\mu W m^{-1} K^{-2})$                     | 61.62                            | 4.090                            | 10.47                            | 48.49                                   | 42.64                            | 60.28                            |
| $\kappa ({ m W}{ m m}^{-1}{ m K}^{-1})$        | 17.90 (1.88)                     | 9.16 (0.95)                      | 9.34 (0.98)                      | 10.16 (2.17)                            | 11.41 (2.14)                     | 9.57 (0.63)                      |
| ZT   | 1.04 (0.12)<br>×10 <sup>-3</sup> | 1.36 (0.16)<br>×10 <sup>-4</sup> | 3.40 (0.39)<br>×10 <sup>-4</sup> | 1.45 (0.34)<br>×10 <sup>-3</sup>        | 1.13 (0.27)<br>×10 <sup>-3</sup> | 1.91 (0.18)<br>×10 <sup>-3</sup> |

 Table 1. TE properties of various SWNT sheet
 (Values inside the () is the error bar)

[1] Ferguson, A. J. et al, *Nature Energy*, **1**, 16033 (2016) [2] Maniwa, Y. et al, *Appl. Phys. Express*, **7**, 025103 (2014) [3] Kim, G. et al, *J. Phys. Chem. C*, **118** (**46**), 26454 (2014) [4] Lian, F. et al, *Appl. Phys. Lett.*, **108**, 103101 (2016) [5] Yamamoto, T. et al, *Phys. Rev. Lett.*, **92** 075502 (2004) [6] Yamamoto, T. et al, *e-J. Surf. Sci. Nanotech.*, **4**, 239 (2006)