

Polarity Tuning of Semiconducting Single-walled Carbon Nanotube by Dipole Field of Ferroelectric Polymer for Thermoelectric Conversion

Ryota Yamasaki¹, Shohei Horike^{1,2}, Yasuko Koshiba¹, Tatsuya Fukushima¹ and Kenji Ishida¹

¹ Department of Chemical Science & Engineering, Kobe University
1-1 Rokkodai-cho, Kobe, Hyogo 657-8501, Japan

Phone: +81-78-803-6150 E-mail: kishida@crystal.kobe-u.ac.jp

² National Institute of Advanced Industrial Science
1-1-1 Higashi, Tsukuba 305-8565, Japan

Abstract

Single-walled carbon nanotubes (SWCNTs) are important candidates for flexible thermoelectric (TE) devices. However since SWCNTs polarities spontaneously change to p-type in air, development of air-stable n-type is still challenging. Here, we demonstrate the modulations of the Seebeck coefficients of a semiconducting SWCNTs (s-SWCNTs) films using dipole fields of a ferroelectric polymer. The polarity was n-type under a down-poling dipole field, while p-type under an up-poling. The Seebeck coefficients we obtained were respectively about $-400 \mu\text{V K}^{-1}$ (n-type) and $+200 \mu\text{V K}^{-1}$ (p-type), both of which were higher than those of metallic ones or their mixtures, and showed a remarkable stability in air. Our findings enable simple and effective preparation of air-stable n-type SWCNTs and fine patterning of TE modules.

1. Introduction

Thermoelectric (TE) conversion, which generates electrical energy from temperature differences, is expected to be an important power generation technology because it can reuse waste heat which exists widely in the environment. Single-walled carbon nanotubes (SWCNTs) are attracting attention for TE energy harvesting because they have high electrical conductivity, mechanical robustness, and printability onto plastic films. They also have other good characteristics which inorganic materials don't have: flexible, non-toxic, and lightweight.

Every TE device needs to be connected to p-type and n-type materials electrically in series and thermally in parallel. This structure, so called π -type module, can convert temperature differences efficiently. Both p- and n-type materials are therefore required for practical TE devices. SWCNTs, in general, exhibit p-type in ambient air [1]. However, the developments of air-stable n-type components are still lagging.

SWCNTs show hole major charge carrier species, as electrons are withdrawn by oxygen impurities upon exposure to air [2]. Blocking this withdrawing and/or injecting electron have been tried using charge transfer interactions between SWCNTs and electron donors attached onto nanotube surfaces [3–5]. However, the SWCNTs modified by typical alkali metals and amine compounds are instable in air due to auto-oxidation [6]. In our previous study [7], we proposed a simple and effective technique to switch major charge carrier species of SWCNTs from holes to electrons using the devices

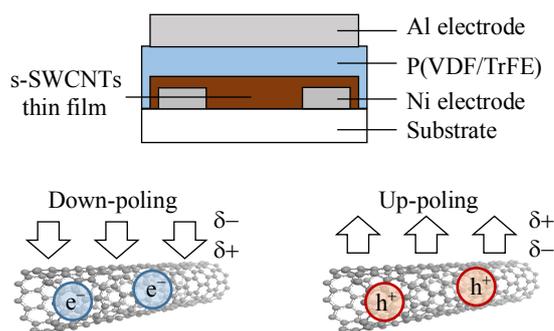


Fig. 1 Schematic of proposed FeFET structure and charge accumulation in nanotube at interface with P(VDF/TrFE).

shown in Fig. 1; like ferroelectric field effect transistors (FeFET). This controls and maintains the carrier species accumulated in SWCNTs by the applied electric fields, and then compensates the charges of the non-volatile dipoles.

On the other hand, it has been reported that SWCNTs are classified into semiconducting SWCNTs (s-SWCNTs) and metallic SWCNTs (m-SWCNTs), and s-SWCNTs can exhibit much higher Seebeck coefficients (voltage output per temperature difference) than m-SWCNTs or their mixtures [8]. In this study, we demonstrate charge carrier modulations of s-SWCNTs thin films to realize large Seebeck coefficients in both polarities as well as a remarkable stability.

2. Experimental methods

FeFET-like TE devices (Fig. 1) were fabricated according to our previous report using a ferroelectric polymer [7]. In brief, nickel source/drain electrodes were vapor deposited on a quartz glass substrate. The s-SWCNTs with a mean diameter of 1.4 nm (RS, Meijo Nano Carbon Co., Ltd) were ultrasonically dispersed in water using polyoxyethylene alkyl ether nonionic surfactant [9]. The s-SWCNTs thin film was inkjet-printed using this aqueous dispersion. Then we annealed it in vacuum to evaporate the residual surfactants. After that, a film of P(VDF/TrFE), a copolymer of vinylidene fluoride and trifluoroethylene, was stacked by spin coating. Finally, an aluminum gate electrode was vapor deposited.

The dipoles of P(VDF/TrFE) were set as “up-poling” or “down-poling” by applying the electric fields between the top

aluminum electrode and the s-SWCNTs thin film. The specimen was placed on a stage consisting of a ceramic heater and a heat sink. All Seebeck coefficient measurements were performed in vacuum by reading the voltage outputs (ΔV) between two nickel electrodes while giving the temperature differences (ΔT) in the in-plane direction. The low-temperature nickel electrode was kept at 300 K. The Seebeck coefficients were determined from the slope of the ΔV - ΔT plots.

3. Results and discussion

We first measured the Seebeck coefficients of the as-deposited s-SWCNTs thin film without P(VDF/TrFE) stacking as a control. The obtained maximum Seebeck coefficient was $-222 \mu\text{V K}^{-1}$, and it is higher than those of m-SWCNTs or their mixtures. Interestingly, the polarity is n-type. Considering that the carrier of SWCNTs is quite sensitive to oxygen [2], the n-type conduction can be attributed to the removal of oxygen impurity by vacuum annealing. However, after storing this film at room temperature in ambient air for 25 days, the polarity changed to p-type ($+145 \mu\text{V K}^{-1}$). Further strategy therefore is necessary for stable polarity tuning.

We next studied the TE properties of the s-SWCNTs under the dipole fields. Fig. 2 shows the remanent polarization (P_r) dependence of the Seebeck coefficients. The Seebeck coefficient of the s-SWCNTs stacked with P(VDF/TrFE) was negative ($-125 \mu\text{V K}^{-1}$) before poling treatment. The Seebeck coefficients increase the negative values (electron accumulation) with down-poling ($P_r < 0 \text{ mC m}^{-2}$), while increase the positive values (hole accumulation) with around up-poling ($P_r \geq +25 \text{ mC m}^{-2}$). These results clearly indicate that we can control the accumulating carrier species in s-SWCNTs film by the ferroelectric dipoles at the same interface, and in the same device.

Of particular interest is that the Seebeck coefficient takes the local maximum values at the specific P_r values for both polarities. This behavior is attributed to the one-dimensional van Hove singularity of the SWCNTs; the Fermi level of the s-SWCNTs would shift to the appropriate energy levels at these carrier densities, where the electron density of states of SWCNTs [10]. It is advantageous that the charge carrier densities and Fermi levels of the same material can be controlled in the same device. We expect higher Seebeck coefficient by controlling the P_r values more strictly, and then the polarity can be maintained even after stopping the gate voltage. This is one of the advantageous specification of ferroelectric materials beyond the other insulators such as silicon oxides and ionic liquids [10].

At last, we tested the stabilities of the Seebeck coefficients under the dipole fields for both polarities. The Seebeck coefficients obtained here were about $-400 \mu\text{V K}^{-1}$ for n-type and $+200 \mu\text{V K}^{-1}$ for p-type, respectively. These coefficients remain stable in ambient air for at least 3 weeks without any declines. We expect that the concept of the field-effect charge-type modulation, along with the demonstrated fabrication processes, can be extended to increase the practicality of thermal energy harvesting technologies.

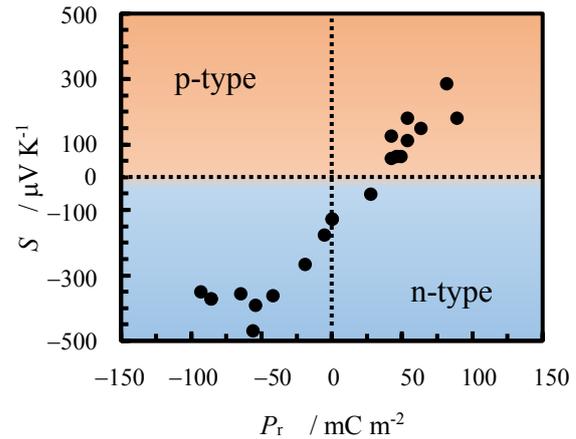


Fig. 2 Remanent polarization dependence of Seebeck coefficient of s-SWCNTs thin film

3. Conclusions

FET-like device stacked a ferroelectric polymer was explored as charge carrier modulation technique of s-SWCNTs at the same interface. Bistable p- and n-type s-SWCNTs with one of the largest Seebeck coefficients were achieved by optimizing the remanent polarization of the ferroelectric polymer. We expected that the demonstrated concept could be extended to the fast, cheap, and low-inwaste productions of TE modules.

Acknowledgements

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References

- [1] S. Horike, M. Misaki, Y. Koshiba, T. Saito, and K. Ishida, *Jpn. J. Appl. Phys.* **55**, 03DC01 (2016).
- [2] K. Bradley, S.-H. Jhi, P. G. Collins, J. Hone, M. L. Cohen, S. G. Louie, and A. Zettl, *Phys. Rev. Lett.* **85**, 4361 (2000).
- [3] S. Horike, T. Fukushima, T. Saito, T. Kuchimura, Y. Koshiba, M. Morimoto, and K. Ishida, *Mol. Syst. Des. Eng.* **2**, 616 (2017).
- [4] Y. Nonoguchi, M. Nakano, T. Murayama, H. Hagino, S. Hama, K. Miyazaki, R. Matsubara, M. Nakamura, and T. Kawai, *Adv. Funct. Mater.* **26**, 3021 (2016).
- [5] S. Horike, T. Fukushima, T. Saito, Y. Koshiba, and K. Ishida, *Chem. Phys. Lett.* **691**, 219 (2018).
- [6] T. Takenobu, T. Takano, M. Shiraiishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, and Y. Iwasa, *Nat. Mater.* **2**, 683 (2003).
- [7] S. Horike, M. Misaki, Y. Koshiba, M. Morimoto, T. Saito, and K. Ishida, *Appl. Phys. Express* **9**, 081301 (2016).
- [8] Y. Nakai, K. Honda, K. Yanagi, H. Kataura, T. Kato, T. Yamamoto, and Y. Maniwa, *Appl. Phys. Express* **7**, 025103 (2014).
- [9] S. Horike, T. Fukushima, T. Saito, Y. Koshiba, M. Morimoto, M. Misaki, and K. Ishida, *Flex. Print. Electron.* **3**, 025006 (2018).
- [10] K. Yanagi, S. Kanda, Y. Oshima, Y. Kitamura, H. Kawai, T. Yamamoto, T. Takenobu, Y. Nakai, and Y. Maniwa, *Nano Lett.* **14**, 6437 (2014).