Thermoelectric properties of WS$_2$ nanotube networks

Hideki Kawai, Mitsunari Sugahara, Ryotaro Okada, Yutaka Maniwa, Yohei Yomogida, and Kazuhiro Yanagi*

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
E-mail: yanagi-kazuhiro@tmu.ac.jp

Received October 21, 2016; accepted November 11, 2016; published online November 29, 2016

We report the thermoelectric properties of WS$_2$ nanotube networks. By using electrolyte-gating techniques, we turned on a conducting channel in the macroscopic networks of WS$_2$ nanotubes in both the hole and electron regions and evaluated the thermoelectric properties of the networks. We manipulated the P- and N-type Seebeck coefficients in the WS$_2$ nanotube networks by changing the shifts in the gate voltage potentials. The power factor of the WS$_2$ nanotube networks increased as the gate voltage shifted and exhibited a high thermoelectric performance approaching that of single-crystalline WS$_2$ flakes. © 2017 The Japan Society of Applied Physics

WS$_2$ nanotubes are cylindrical nanotubes with a rolled structure consisting of two-dimensional (2D) WS$_2$ sheets. Quantized conditions along the circumferential direction of the nanotubes—due to the chiral structure and van Hove singularities of the nanotubes, which reflect their one-dimensional (1D) nature—result in an electronic structure that is distinct from that of 2D sheets and exhibits unique physical properties. Thus, the physical properties of WS$_2$ nanotubes have attracted substantial attention. Since the discovery of WS$_2$ nanotubes in 1992, various physical properties—including electrical, optical, and mechanical properties—of these nanotubes in their single-rope form have been reported. However, the relatively strong van der Waals forces between WS$_2$ nanotubes make them bundle together, and consequently, WS$_2$ nanotubes tend to form macroscopic networks. Such networks provide strong advantages for the fabrication of devices with good scalability. Previous investigations of the electrical properties of WS$_2$ nanotubes have been limited to the single-rope state because of the insulating properties of WS$_2$ nanotube networks. However, in 2016, Sugahara et al. introduced carrier injections into thin films, specifically random networks of WS$_2$ nanotubes, and demonstrated the ambipolar field-effect transistor characteristics of the nanotubes by using the electrolyte-gating method. This technique paved the way for investigating the electrical properties of the macroscopic networks of WS$_2$ nanotubes.

This type of electrolyte-gating method was recently revealed to be applicable to the control of thermoelectric properties in macroscopic networks. For example, the continuous tuning of the Seebeck coefficient from P- to N-type carbon nanotubes was achieved using this approach. WS$_2$ nanotubes have also attracted theoretical research interest because of their thermoelectric properties and unique structural and electronic characteristics. In general, their 1D structure is advantageous for thermoelectric applications, as reported by Hicks and Dresselhaus. For example, the figure of merit, $ZT$, can be significantly enhanced as the diameter of a 1D system decreases. In addition, materials with a cylindrical structure are expected to have a superior $ZT$ because of the reduction of the thermal conductivity. WS$_2$ nanotubes have a suitable structure for such conditions; however, no experimental studies have revealed their thermoelectric characteristics. Therefore, we investigated the thermoelectric properties of WS$_2$ nanotubes by using electrolyte-gating approaches.

WS$_2$ nanotubes were purchased from Nanomaterials, Inc. Details regarding the preparation of the WS$_2$ nanotube film are provided in the online supplementary data. The mean diameter of the WS$_2$ nanotubes in the film was ~134 nm, and the mean number of layers was ~40 (see Fig. S1 in the online supplementary data at http://stacks.iop.org/APEX/10/10.7567/APEX.10.015001/mmedia). Figure 1 shows a schematic of the experimental setup for controlling the thermoelectric properties of the WS$_2$ nanotube film through electrolyte gating. For the thermal isolation of the film, a parylene layer (Parylene Japan parylene HT, ~10 µm thick) formed on a polyimide substrate was used. Au electrodes (100 nm thick) were thermally deposited, as illustrated in Fig. 1. The channel length was 400 µm, which was crucial for introducing a clear temperature gradient. The film thickness was ~1.2 µm in all the experiments. Thermocouples (alumel and chromel) were attached with silver paste to measure the temperature at both the ends of the film. A heater was attached to the back side of the substrate, as illustrated in Fig. 1, to create a temperature gradient. We used $N,N',N$-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)imide (TMA-TFSI; Kanto Kagaku) as the ionic liquid. To avoid electrochemical reactions between the silver paste and the ionic liquid, we coated the paste with an electric field-e
epoxy adhesive. The generated thermoelectric voltages were measured using source and drain electrodes. A gate voltage was applied to the channel from a gate electrode, and a reference electrode was used to measure the actual voltage applied to the channel (see Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/10/015001/mmedia). All of the experiments were performed in vacuum.

Figure 2(a) shows the transport characteristics of the film. The conductivities of the film, \( \sigma \), are plotted with respect to the gate voltage, \( V_G \). The data clearly indicate ambipolar behavior similar to that previously reported\(^{12} \) and suggest that the electrons and holes were injected via the formation of an electric double layer by electrolyte gating. The on-state conductivities for holes and electrons reached 22 and 3.3 S·m\(^{-1} \), respectively. The reported value for the on-state conductivity of the individual WS\(_2\) nanotubes was 1.0 \( \times \) 10\(^3\) S·m\(^{-1} \), \(^{6,10}\) which is two orders of magnitude higher than that presented in our results. The tube–tube junctions may have been the cause of the decreased conductivity in the WS\(_2\) nanotube film compared with the single-rope state.

To discuss the electronic characteristics of the WS\(_2\) nanotubes, we plotted the conductivity of the film with respect to the reference voltage \( V_R \), as shown in the inset of Fig. 2(a). We evaluated the width of \( V_R \) in the off-state (see Fig. S3 in the online supplementary data at http://stacks.iop.org/APEX/10/015001/mmedia) as 2.57 \( \pm \) 0.07 V. We also measured the capacitance of the WS\(_2\) nanotube networks with respect to the reference voltage (see Fig. S4 in the online supplementary data at http://stacks.iop.org/APEX/10/015001/mmedia). There was a dip in the capacitance, as shown in Fig. S4(c), reflecting the presence of the semiconducting bandgap.\(^{19-21}\) The dip width was evaluated to be \( \sim 2.5 \) V, which is similar to the off-state width estimated according to the transfer characteristics.\(^{22}\) The value well coincides with the bandgap of WS\(_2\) bulk crystals (1.3–1.35 eV). The number of layers in our sample is similar to that reported for the thin WS\(_2\) flakes (~50 layers); thus, the bandgap of the WS\(_2\) nanotube networks should be similar to that of a WS\(_2\) bulk crystal. However, the observed width of the off-state and the capacitance dip was rather large: \( \sim 2.5 \) V. Such an increase of the width is often caused by trap states within the bandgap of the semiconductor.\(^{23,24}\) In the case of transition-metal dichalcogenides, trap states are generated within the bandgap because of structural defects, such as absence of chalcogen or metal atoms and dislocations of these atoms.\(^{25}\) The rather large off-state width indicates the presence of numerous trap states in our WS\(_2\) nanotube networks.

Figure 2(b) plots the Seebeck coefficient with respect to the gate voltage. Before the gate-controlled thermoelectric measurement, we confirmed the linear relationship between the thermoelectric voltage and the temperature gradient (see Fig. S5 in the online supplementary data at http://stacks.iop.org/APEX/10/015001/mmedia). Both the positive and negative Seebeck coefficients clearly reflect the ambipolar behavior of the WS\(_2\) nanotube networks. In the \( V_G \) region of \(-1.6 \) to \( 1.9 \) V, the Seebeck coefficient could not be correctly evaluated because of the limitations of our measurement setup. However, in the \( V_G \) regions above \( 1.9 \) V and below \(-1.6 \) V, the Seebeck coefficient could be evaluated. The Seebeck coefficients tended to decrease as \( |V_G| \) increased. This behavior is consistent with results for polycrystals of thin WS\(_2\) flakes,\(^{26}\) whose Seebeck coefficients were controlled by indium intercalation. We calculated the power factor \( S^2\sigma \) as shown in Fig. 2(c). In both the P- and N-type regions, the power factor increased with \( |V_G| \), indicating the importance of carrier injections for improving the thermoelectric performance.

The electrolyte-gating approach was crucial for revealing the thermoelectric properties of the WS\(_2\) nanotube networks. Here, we discuss the results of a back-gating technique in which SiO\(_2\) (100 nm) was used as a gate dielectric. Figure 3 shows the relationships between the Seebeck coefficients and the conductivities of the WS\(_2\) nanotube networks with respect to \( V_G \) for the electrolyte-gating technique, as well as the conductivities for the back-gating technique. The electrolyte-gating results indicate that the Seebeck coefficients became measurable in the region where the conductivity was in the on-state. However, in the case of the back-gating technique, the conductivity did not enter the on-state, and the thermoelectric properties could not be correctly evaluated. Levi et al. caused a single rope of WS\(_2\) nanotubes to enter the on-state using the back-gating approach.\(^6\) However, in our \( \sim 1\)-µm-thick film sample, the WS\(_2\) nanotube networks could not be induced to enter the on-state using the back-gating approach. We assume the following background. In the case of the back-gating technique, the surface roughness and thickness of the thick film prevented uniform carrier injection into the nanotubes comprising the networks, and consequently, a conducting channel could not be formed between the source and drain electrodes. However, in the case of the electrolyte gating, electrical double layers were formed on the surface of all the nanotubes in the film, and carriers were properly injected into them. As a result, the channel entered the on-state, and the thermoelectric properties were measurable.

Figure 4 compares the power factors of the WS\(_2\) nanotubes with the reported values for polycrystalline and single-crystalline WS\(_2\) flakes.\(^{26-29}\) The power factors of the samples
are plotted with respect to the conductivity. As shown here, the power factors of the WS2 nanotube networks were similar to those of polycrystalline WS2. The power factors of the nanotubes improved as the amount of injected carriers increased. The maximum power factor of the WS2 nanotubes approached that of single-crystalline WS2 flakes, suggesting the good potential of the WS2 nanotubes for thermoelectric applications. It was reported that the on-state conductivity of single-rope WS2 nanotubes is two orders of magnitude larger than that of single-crystalline WS2. However, in this study, the maximum conductivity of the WS2 nanotube networks was comparable to that of single-crystalline WS2. The tube–tube junctions became the scattering center of the carriers and degraded the conductivity. Therefore, improving the conductivity is the most important factor for enhancing the thermoelectric performance of WS2 nanotube networks.

In summary, we revealed the thermoelectric properties of WS2 nanotube networks. By using an electrolyte-gating approach, we achieved ambipolar transfer characteristics in a WS2 nanotube network channel. We evaluated the thermoelectric properties of the WS2 nanotube networks and found that the power factor of the WS2 nanotubes was significantly improved by carrier injections, approaching that of single-crystalline WS2 flakes.

Acknowledgment This work was supported by JSPS KAKENHI Grant Numbers JP16H00919, JP16H07103, and JP25246006.

Fig. 3. (a) Comparison of the back-gating and electrolyte-gating methods for the WS2 nanotube networks. Red (N-type) and blue (P-type) circles represent the $|V_{G}|$ dependence of the electron and hole conductivities, respectively, for the electrolyte-gating technique. Black circles represent the $|V_{G}|$ dependence of the electron conductivity for the back-gating technique. (b) Details regarding the conductivity and Seebeck coefficients in the low-$|V_{G}|$ region of (a). Red and blue indicate N- and P-type, respectively. Red and blue vertical lines indicate the $|V_{G}|$ values at which the Seebeck coefficients became measurable in the N- and P-type regions, respectively.

Fig. 4. $S^{\sigma}$ values of WS2 nanotubes and single-crystalline and polycrystalline flakes with respect to $\sigma$. Red (N-type) and blue (P-type) symbols represent the values for the WS2 nanotubes. Black squares and circles represent the reported values for polycrystalline$^{26,28}$ and single-crystalline$^{27,28}$ WS2 flakes, respectively.

1) R. Tenne, L. Margulis, M. Genut, and G. Hodes, Nature 360, 444 (1992).
2) I. Milostević, B. Nikolić, E. Dobardžić, M. Damnjanović, I. Popov, and G. Seifert, Phys. Rev. B 76, 233414 (2007).
3) N. Zibouche, A. Kuc, and T. Heine, Eur. Phys. J. B 85, 49 (2012).
4) K. X. Chen, X. M. Wang, D. C. Mo, and S. S. Lu, J. Phys. Chem. C 119, 26706 (2015).
5) C. Y. Zhang, Z. Y. Ning, Y. Liu, T. T. Xu, Y. Guo, A. Zak, Z. Y. Zhang, S. Wang, R. Tenne, and Q. Chen, Appl. Phys. Lett. 101, 113112 (2012).
6) R. Levi, O. Bitton, G. Leitus, R. Tenne, and E. Joselevich, Nano Lett. 13, 3736 (2013).
7) C. Y. Zhang, S. Wang, L. Yang, Y. Liu, T. T. Xu, Z. Y. Ning, A. Zak, Z. Y. Zhang, R. Tenne, and Q. Chen, Appl. Phys. Lett. 100, 243101 (2012).
8) Y. Q. Zhu, T. Sekine, Y. H. Li, M. W. Fay, Y. M. Zhao, C. H. P. Poo, W. X. Wang, M. J. Roe, P. D. Brown, N. Fleischer, and R. Tenne, J. Am. Chem. Soc. 127, 16263 (2005).
9) E. Kallon-Cohen, O. Goldbart, R. Schreiber, S. R. Cohen, D. Barlam, T. Lorenz, J. O. Joswig, and G. Seifert, Appl. Phys. Lett. 98, 081908 (2011).
10) R. Rosentsveig, A. Margolin, Y. Feldman, R. Popovitz-Biro, and R. Tenne, Appl. Phys. A 74, 367 (2002).
11) R. Rosentsveig, A. Margolin, Y. Feldman, R. Popovitz-Biro, and R. Tenne, Chem. Mater. 14, 471 (2002).
12) M. Sugahara, H. Kawai, Y. Yomogida, Y. Maniwa, S. Okada, and K. Yanagi, Appl. Phys. Express 6, 075001 (2016).
13) K. Yanagi, S. Kanda, Y. Oshima, Y. Kitamura, H. Kawai, T. Yamamoto, T. Takenobu, Y. Nakay, and Y. Maniwa, Nano Lett. 14, 6437 (2014).
14) Y. Oshima, Y. Kitamura, Y. Maniwa, and K. Yanagi, Appl. Phys. Lett. 107, 043106 (2015).
15) S. Shimizu, T. Izuka, K. Kanahashi, J. Pu, K. Yanagi, T. Takenobu, and Y. Iwasa, Small 12, 3388 (2016).
16) L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 16631 (1993).
17) R. G. Yang, G. Chen, and M. S. Dresselhaus, Phys. Rev. B 72, 125418 (2005).
18) R. G. Yang, G. Chen, and M. S. Dresselhaus, Nano Lett. 5, 1111 (2005).
19) S. Ilani, L. A. K. Donev, M. Kindermann, and P. L. McEuen, Nat. Phys. 2, 687 (2006).
20) T. Igarashi, H. Kawai, K. Yanagi, N. T. Cuong, S. Okada, and T. Pichler, Phys. Rev. Lett. 114, 176807 (2015).
21) J. Pu, K. Kanahashi, N. T. Cuong, C. H. Chen, L. J. Li, S. Okada, H. Ohta, and T. Takenobu, Phys. Rev. B 94, 014312 (2016).
22) D. Braga, I. G. Lezama, H. Berger, and A. F. Morpurgo, Nano Lett. 12, 5218 (2012).
23) K. P. Fromstich, S. Haas, D. Oberhofer, C. Goldmann, D. J. Gundlach, B. Ballhog, A. N. Rashul, and G. Schüter, J. Appl. Phys. 96, 6431 (2004).
24) C. S. S. Sangeeth, P. Stadler, S. Schaur, N. S. Sariciftci, and R. Menon, J. Appl. Phys. 108, 113703 (2010).
25) W. Zhou, X. L. Zou, S. Najmani, Z. Liu, Y. M. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, and J. C. Idrobo, Nano Lett. 13, 2615 (2013).
26) S. K. Srivastava and B. N. Avasthi, Synth. Met. 160, 213 (1985).
27) G. K. Sorensi, D. N. Gujarathi, M. P. Dehpande, D. Lakshminarayana, and M. K. Agarwal, Cryst. Res. Technol. 43, 179 (2008).
28) J. Y. Kim, S. M. Choi, W. S. Seo, and W. S. Cho, Bull. Korean Chem. Soc. 31, 3225 (2010).
29) A. Pisoni, J. Jucimovic, R. Gaal, B. Nafradi, H. Berger, Z. Revay, and L. Forro, Scr. Mater. 114, 48 (2016).