様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

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研究課題名（和文） 形状制御による２次元熱輸送及び熱電変換の実験的チューニング

研究課題名（英文） Experimental tuning of 2D heat conduction and thermoelectric conversion based on shape control

研究代表者
李　秦宜（Li, Qin-Yi）

九州大学・工学研究院・助教

研究者番号：６０７９２０４１

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研究成果の概要（和文）：本研究では、グラフェンの形状を精密かつ自由自在に変化させる実験手法を構築し、ナノ構造を有する２次元材料の熱伝導率・導電率・ゼーベック係数の同時計測技術を開発した。これらの技術により、グラフェンの幅と長さを制御することで、高い導電率を維持したまま、熱伝導率が大幅に低減できて、ゼーベック係数も数倍に向上できた。結局、グラフェンの熱電性能指数を文献の報告より2～4桁向上させた。更に、形状制御による物性チューニングの物理機構を準粒子輸送のシミュレーションで解明出来た。

研究成果の学術的意義や社会的意義
非毒性かつ柔軟な2次元熱電材料は超スマートIoT社会のフレキシブルデバイスの電力供給源として注目されているが、熱電変換の効率はまだ非常に低いため大規模な展開は厳しく制限されている。本研究ではグラフェンの熱電性能指数を2～4桁向上させて、グラフェンが有望な柔軟熱電材料であることを示した。更に、２次元材料の熱と電気特性を前例のないレベルの別々にチューニングすることを実現して、熱科学の基礎研究に貢献できた。

研究成果の概要（英文）：In this project, we designed a one-process approach for fabricating shape-tunable, high-quality graphene along with a new test device, which allows for simultaneous precise measurements of the thermal conductivity, electrical conductivity, and Seebeck coefficient. By adjusting the sample length and width, we measured largely reduced thermal conductivity and enhanced Seebeck coefficient while keeping high electrical conductivity. As a result, we obtained record-high thermoelectric figure of merit of graphene that is 2-4 orders of magnitude higher as compared to literature reports. The mechanisms behind the shape-tunable properties were clearly revealed by our physical simulations of quasi-particles.

研究分野： 熱工学

キーワード： ナノスケール伝熱　グラフェン　熱伝導率　導電率　ゼーベック係数　熱電性能指数　形状制御　ナノ構造

１．研究開始当初の背景

2D materials represented by graphene possess unique thermal and thermoelectric properties that are totally different from the bulk counterpart. Especially, it has been predicted that the thermal and thermoelectric properties of graphene are dependent on the lateral sizes and nanostructures. For example, because of phonon-edge scattering or ballistic effects, the thermal conductivity of a graphene nanoribbon is expected to be significantly suppressed if the characteristic in-plane sizes are comparable to the phonon mean free path. Further, because of the disparate phonon and electron mean free paths, the effects of the nanostructure can be remarkably different on electrical and thermal conductivities, and thus we could independently tune electrical and thermal properties by controlling nanoscale sample shapes. Moreover, the Seebeck coefficient can also be tuned by controlling the nanostructure to adjust the band gap. Despite many theoretical studies on the tunable properties of graphene via nanostructuring, very few experiments had been carried out at the beginning of the project, mainly due to the challenges of reliable thermal and thermoelectric measurements for the fragile, nanoscale materials, and also due to the lack of high-quality nanostructured samples.

２．研究の目的

Based on the above background, the project aims to realize simultaneous measurements of thermal and electrical conductivies and Seebeck coefficient of defect-free, shape-tunable graphene samples, to manipulate phonon and electron transports by controlling the sample shapes and to reveal the physical mechanisms. By comprehensively manipulating the thermal and electrical properties, we can hopefully enhance the thermoelectric performance of graphene and thus contribute to the development of energy harvesting technologies.

３．研究の方法

(1) Sample fabrication. We designed a one-process approach to fabricate suspended defect-free and shape-tunable graphene nanostructures along with the test device (Fig. 1) by collaborating with the chemical synthesis scientists at Tohoku University. Firstly, using the electron-beam lithography followed by Ni deposition, we patterned Ni nanobar catalyst along with Ni heater, sensor and electrodes on a SiO2/Si wafer. Then the wafer was put in the electric furnace for the rapid-heating plasma CVD synthesis that was developed at Tohoku, during which the Ni nanobar catalyst melted and dewetted to the electrodes, leaving the above graphene sheet free-standing and ready for the measurements. There is no post process after the CVD, so the as-grown suspended samples are free of polymer residue that is usually inevitable in other experiments involving graphene transfer and post electrode fabrication.

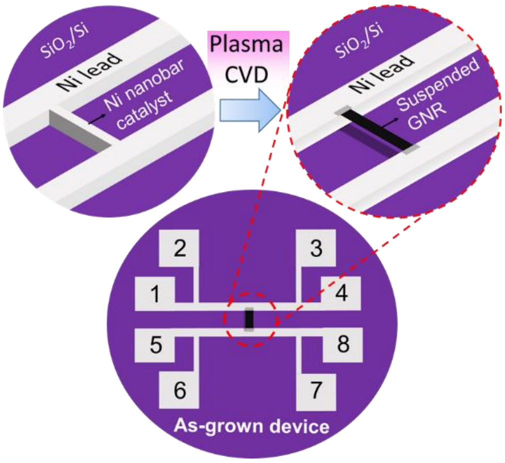

Fig. 1 The as-grown test structure for the thermal and thermoelectric measurements using an 8-terminal device.

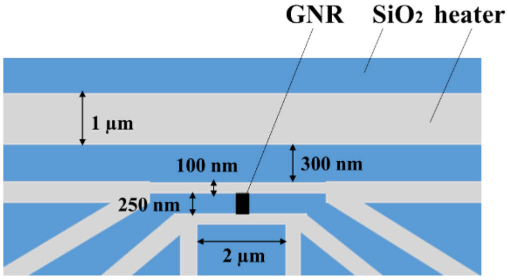

Fig. 2 The optimized 10-terminal device.

(2) Measurement methods. We developed two methods to measure the thermal and thermoelectric properties of graphene nanostructures. One is the 8-terminal method as illustrated in Fig. 1, where the graphene nanoribbon (GNR) bridges two long Ni films that act as both electrical leads and the resistive heater or sensor. The electrical resistance of the GNR was measured at varying electrical power using the four-probe scheme, and the thermal conductivity was extracted from the Joule-heating induced temperature rise that is determined from the resistance-temperature relationship. During the thermopower measurement, one of the long Ni films serves as the heater and a temperature gradient is established along the GNR. The temperatures of both the heater and sensor were measured from their resistance using the four-terminal scheme, while the Seebeck voltage was measured across the GNR after cancelling out the voltage drop in the Ni heater. In FY2019 we improved the measurement accuracy and established an optimized 10-terminal approach as illustrated in Fig. 2. Here, a separate heater is patterned beside the 8-terminal device so that we can avoid the uncertainty from the cancelling out of the voltage drop in the heater. The 10-terminal structure was optimized by 3D finite-element heat conduction simulations. The measurements were carried out in a liquid-nitrogen cooled cryostat under high vacuum.

(3) Theoretical simulations. To reveal the physical mechanisms of phonon transport in the graphene nanostructures, we collaborated with Purdue University for the phonon Boltzmann tranport simulations. The input parameters in the BTE simulation code include the sample sizes, internal heat generation rate, specific heat, phonon group velocity and bulk mean free path (mfp). The specific heat was calculated from the phonon density of states. The phonon group velocity was calculated from the phonon dispersion relation of graphene.

4．研究成果

(1) The as-grown test device and graphene samples. We successfully fabricated as-grown graphene samples along with the test devices. Several suspended GNR samples with ~40 nm width and ~250 nm length were repeatedly fabricated with the 8-terminal device, and some ~25 nm-wide GNR samples were fabricated with the 10-terminal device. Not all the samples were successfully measured for the thermal and thermoelectric properties, because the fragile suspended samples as well as the Ni nanofilms can be easily burnout during the measurements (Fig. 3(a)). Besides, there was too much Ni residue on the ~25 nm-wide GNR samples because of the sensitive synthesis conditions as we changed the device structure, and thus it was quite difficult to extract reliable property data for the ~25 nm-wide samples. Finally, we collected repeatable data for the ~40 nm-wide samples, from which we achieved record-high thermoelectric performance of graphene.

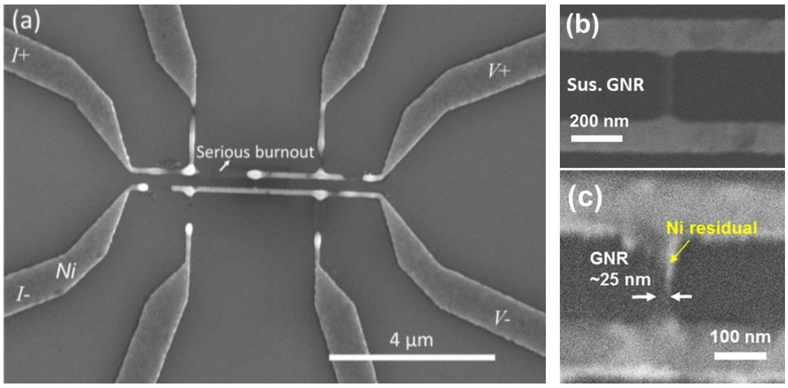

Fig. 3 SEM images of the as-grown test device and graphene samples. (a) An 8-terminal device that is burnout during the measurement. (b) A suspended GNR with ~40 nm width and ~250 nm length. (c) A suspended GNR with ~25 nm width.

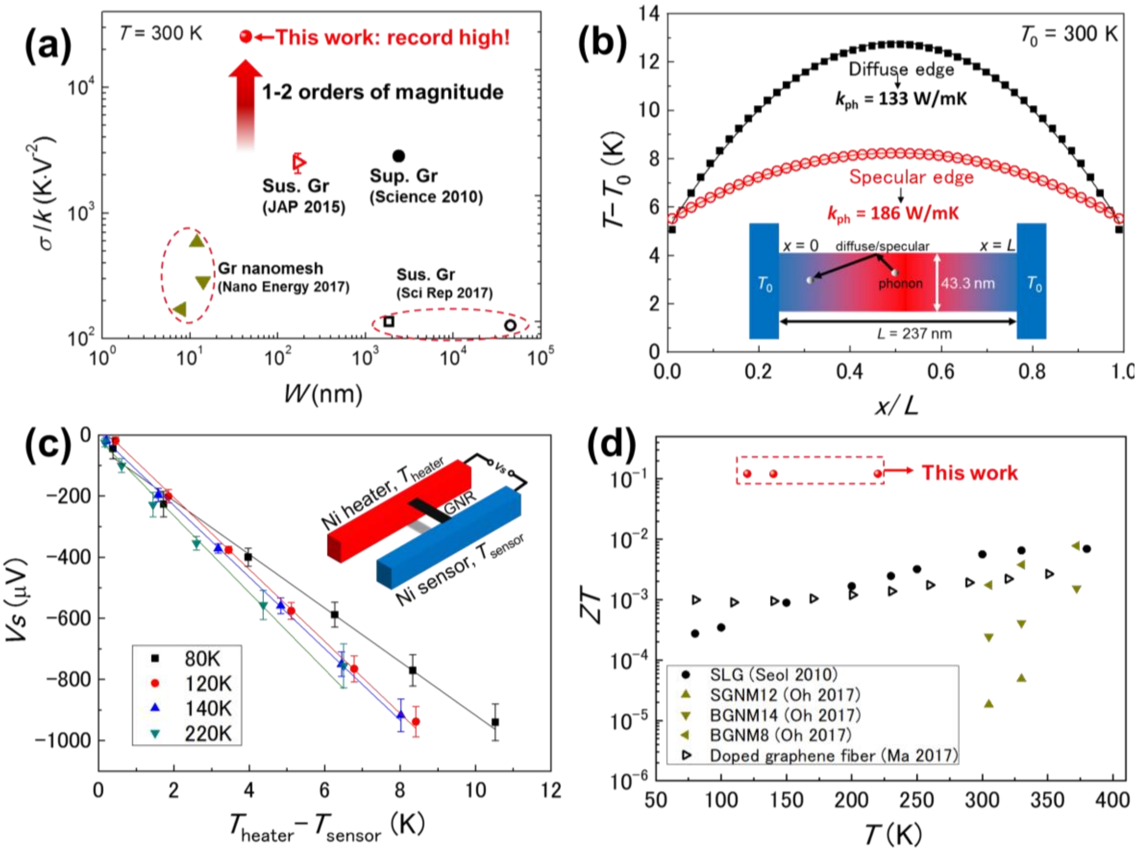

Fig. 4 Thermal and thermoelectric measurement results for the ~40 nm-wide and ~250 nm-long suspended GNRs. (a) Record-high ratio of electrical to thermal conductivities. (b) Phonon Boltzmann transport simulation results that reveal the mechanisms of the largely reduced thermal conductivity. (c) Seebeck voltages versus the temperature difference, from which the enhanced Seebeck coefficients were measured. (d) Record-high dimensionless thermoelectric figure of merit for graphene based materials.

(2) Record-high thermoelectric performance of graphene. The electrical and thermal conductivities of the ~40 nm-wide and ~250 nm-long sample were measured at 20 K steps between 120 K and 360 K. The electrical conductivity (σ) is on the order of 10^6 S/m, among the highest values reported for graphene in the literature. The thermal conductivity (k) is (224±16) W/mK at 300 K, only about 1/10 of that of large pristine graphene. Thus, the thermal conductivity is significantly reduced while the electrical conductivity is maintained at a high level. The ratio of electrical to thermal conductivity (σ/k) reached record-high values of 2.27×10^4 K/V^2 to 7.29×10^4 K/V^2 at 120-360 K (Fig. 4(a)). Phonon Boltzmann transport simulations (Fig. 4(b)) reveal that the enhancement of σ/k is mainly attributed to disparate electron and phonon mean free paths as well as the defect-free samples.

The Seebeck coefficient (S) was obtained by linear fitting of the V_s versus (T_{heater}-T_{sensor}) data in Fig. 4(c), which changes from (-87.7±5.2) μV/K to (-125.7±7.1) μV/K as the temperature increases from 80 K to 220 K, enhanced by a factor of 2-6 as compared to bulk graphene at the corresponding temperatures. The enhanced thermopower in nanostructured graphene is mainly attributed to the opening of band gap. Finally, the figure of merit ($ZT = S^2\sigma T/k$) of the as-grown 40 nm-wide GNRs reached 0.12 at 120-220 K. ZT of our samples should also be no less than 0.1 if we reasonably assume the room-temperature Seebeck coefficient to be no less than -120 μV/K. This ZT value is 2-4 orders of magnitude higher than all the reported ZT values of graphene-based materials (Fig. 4(d)).

５．主な発表論文等

〔雑誌論文〕　計9件（うち査読付論文　9件／うち国際共著　6件／うちオープンアクセス　0件）

１．著者名 Li, Qin-Yi; Takahashi, Koji; Zhang, Xing;	４．巻 134
２．論文標題 Frequency-domain Raman method to measure thermal diffusivity of one-dimensional microfibers and nanowires	５．発行年 2019年
３．雑誌名 International Journal of Heat and Mass Transfer	６．最初と最後の頁 539-546
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.ijheatmasstransfer.2019.01.057	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Li, Qin-Yi; Katakami, Koki; Ikuta, Tatsuya; Kohno, Masamichi; Zhang, Xing; Takahashi, Koji;	４．巻 141
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２．論文標題 Variable-spot-size laser-flash Raman method to measure in-plane and interfacial thermal properties of 2D van der Waals heterostructures	５．発行年 2018年
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２．論文標題 Enhanced Thermoelectric Performance of As-Grown Suspended Graphene Nanoribbons	５．発行年 2019年
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掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsnano.9b03521	査読の有無 有
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3．雑誌名 The Journal of Physical Chemistry Letters	6．最初と最後の頁 3744～3749
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpclett.9b00718	査読の有無 有
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〔学会発表〕　計15件（うち招待講演　4件／うち国際学会　10件）

1．発表者名 Li Qin-Yi
2．発表標題 Enhancing thermoelectric efficiency of graphene via nanostructuring
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2．発表標題 Record-high thermoelectric efficiency of graphene nanoribbons
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１．発表者名
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４．発表年
2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

研究成果に関するニュース「Thermoelectric performance of graphene gets a boost」(https://www.kyushu-u.ac.jp/en/researches/view/137)

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
研究協力者	加藤　俊顕 (Kato Toshiaki)	東北大学・准教授	

６．研究組織（つづき）

	氏名 （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
研究協力者	阮　修林 (Ruan Xiulin)	パデュー大学・Professor	