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研究課題名（和文） Chirality engineering of single-walled carbon nanotubes by in situ TEM probing

研究課題名（英文） Chirality engineering of single-walled carbon nanotubes by in situ TEM probing

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研究成果の概要（和文）：単層カーボンナノチューブ（SWCNT）は、次世代のエネルギー効率の高いトランジスタとして期待されているが、カイラリティ（らせん構造）により、ナノチューブの1/3が金属になる。本プロジェクトでは、カイラリティを変換し、金属性ナノチューブを半導体に変化させる方法を開発した。その場TEMプロービングにより高温で機械的ストレスを与えることで、個々のナノチューブの局所的なカイラリティを変換することに成功しました。また、フィードバック制御により、金属から半導体への転移を実現した。カイラリティ変換されたナノチューブをチャネルとして用いて、チャネル長が2.8ナノメートルのナノトランジスタが作製されました。

研究成果の学術的意義や社会的意義
カーボンナノチューブのカイラリティ（らせん構造）を制御することは、エレクトロニクスへの応用において極めて重要である。本プロジェクトでは、個々のカーボンナノチューブの局所的なカイラリティを変換する手法を開発した。このカイラリティ変換により、金属性カーボンナノチューブは、ナノトランジスタを作製するための半導体へと変化した。この成果は、5ナノメートル以下のナノチューブトランジスタを開発することに貢献する。

研究成果の概要（英文）：Single-walled carbon nanotubes (SWCNTs) have superior electrical, mechanical, and thermal properties and are promising for the next generation energy-efficient transistors. However, depending on the chirality, 1/3 of the nanotubes are metallic. In this project, a method is developed to transform the chirality and change the metallic nanotubes into semiconductors. By using in situ transmission electron microscopy (TEM) probing technique and applying mechanical tension and high temperature, the local chirality of individual nanotubes was successfully transformed. Metal-to-semiconductor transition was realized by using closed-loop (feedback) control. Nanotransistors with the channel length as short as 2.8 nanometers were fabricated using the chirality-transformed nanotubes as channels and quantum transport was demonstrated at room temperature.

研究分野：ナノテクノロジー

キーワード：carbon nanotube　transistor　chirality　electron microscopy　quantum transport

１．研究開始当初の背景

SWCNTs are one-dimensional seamless tubular structures composed of single sheets of graphene and have exceptional electrical, mechanical, and thermal properties. Because of the superior scaling performance of the SWCNT based field-effect transistors (FETs), they have been considered by the International Technology Roadmap for Semiconductors (ITRS) as the most promising candidate channel material for the next generation energy-efficient transistors with the gate length scaling down to sub-10 nm region (Science 355, 271 (2017)). Recently, MIT has reported a SWCNT-based microprocessor comprising more than 14,000 CMOS FETs, using industry-standard processes, demonstrating the potential for large scale applications (Nature 572, 595-602 (2019)). However, there is a fundamental challenge to control the chirality, which determines the SWCNTs to be metallic or semiconducting. To realize the very-large-scale integration, it is estimated that the purity of the semiconducting nanotubes must reach 99.999999%, calling for the chirality control at individual SWCNT level. In the current project, it is proposed to modify the chirality of individual SWCNTs to control the metallicity by mechanical engineering and to investigate the transition mechanism by in situ TEM probing. To realize controlled modification of the SWCNTs' chirality, it is essential to understand the "key scientific question" of the fundamental chirality transition mechanism of the SWCNTs, including the stability of different chiralities, the critical conditions for initializing the transitions, and the transition path under the stimuli of bias, stress, and heat.

２．研究の目的

There are three purposes for this project: 1), Chirality transition mechanism: The first goal is to reveal the chirality transition mechanism and dynamics of SWCNTs under mechanical tension at a high temperature. 2), Metal-to-semiconductor transition: The second goal is to realize and control the metal-to-semiconductor transition of the SWCNTs by monitoring the chirality evolution through in situ electron diffraction and electrical transport measurement. 3), High performance sub-10 nm transistors: The third goal is to fabricate high performance transistors by using the chirality controlled semiconducting SWCNTs as the conducting channels.

３．研究の方法

The project is aimed to elucidate the fundamental mechanism of the chirality transitions of SWCNTs under mechanical and thermal stimuli, to realize controlled metal-to-semiconductor transformation, by using the in situ TEM probing method. Experiments will be carried out by using a unique dual-probe STM-TEM holder. A nanoscale transistor will be fabricated by using the CNT as a conducting channel, the two probes as source and gate electrodes, and the fixed electrode as the drain. To modify the structure, mechanical tension and pulsed Joule heating will be applied through the piezo-controlled STM probes. Chirality changes will be characterized by high resolution TEM and electron diffraction. Electrical transport properties will be measured with the transistor configuration, to determine the metallicity. The output chirality and transport properties are related to the input control to form a close loop for optimizing the engineering process, by using a LabVIEW program. Therefore, desired specific chirality and metal-to-semiconductor transformation could be realized after several cycles.

４．研究成果

4-1 Metal-to-semiconductor chirality transition and fabrication of 2.8 nm SWCNT transistors

The main goal of the project is to realize the chirality transition and the controlled metal-to-semiconductor transformation to fabricate sub-10 nm carbon nanotube transistors. Using in situ transmission electron microscopy, we applied heating and mechanical strain to alter the local chirality and thereby control the electronic properties of individual single-wall carbon nanotubes (Fig. 1). A controlled metal-to-semiconductor transition was realized to create nanotube transistors with a semiconducting nanotube channel covalently bonded between a metallic nanotube source and drain. Additionally, quantum transport at room temperature was demonstrated for the fabricated nanotube transistors with a channel length as short as 2.8 nanometers.(*1*)

Another main goal is to understand the mechanism of the nanotube chirality transition, in this work, a transition trend toward a larger chiral angle region was observed and explained in terms of orientation-dependent dislocation formation energy. The work was published in Science (D.-M. Tang *et al.*, *Science* **374**, 1616-1620 (2021).), and was highlighted by the press release in NIMS, AIST and University of Tokyo, and was reported by the news media such as Nikkei.

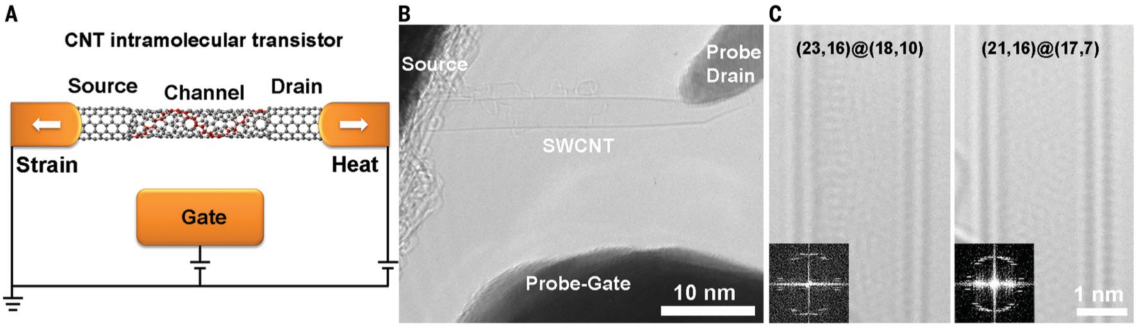

Fig. 1. Fabrication and characterization of CNT intramolecular transistors. (A) Schematic of a CNT intramolecular transistor with local chirality altered by mechanical strain and Joule heating. (B) TEM image of a SWCNT transistor with a fixed source electrode, a probe as drain electrode, and another probe as gate electrode. (C) Lattice-resolved TEM images and corresponding FFT patterns of a DWCNT before and after the chirality transition.

4-2 In situ TEM measurements of the temperature mapping of Joule-heated carbon nanotubes

An important question about the nanotube chirality transition is the temperature during the plastic deformation under Joule heating and mechanical strain. In this work, we mapped the temperature distribution of suspended carbon nanotubes down to the 5-nm level inside a transmission electron microscope, by using electron energy-loss plasmon spectroscopy. The nanotubes are Joule heated in-situ, by individually contacting them using a biasing holder. The nanotubes can withstand temperatures of over 2000 K without breaking (Fig. 2). The temperature reaches its maximum around the nanoprobe contact, due to the comparatively large electrical resistance and small thermally-conductive area. These results verify the expected robustness of these structures and confirm them as ideal candidates for applications as interconnects under extremely high current densities and temperatures. (O. Cretu*, D. M. Tang*, et al., Carbon 201, 1025-1029 (2023).)(*2*)

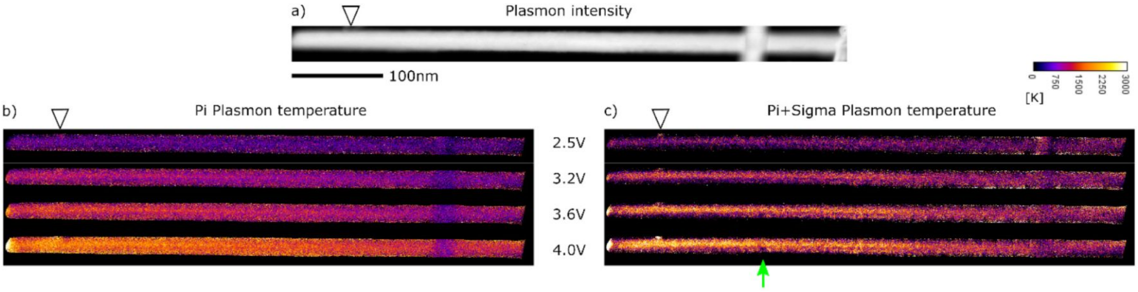

Fig. 2 a) Plasmon intensity map for one of the Joule-heated CNTs. b), c) Plasmon shift-derived temperature map as a function of the applied bias, calculated from the Pi and Pi + Sigma plasmons, respectively.

4-3 Growth mechanism of carbon nanotubes by in situ TEM

Ultimately, the performance of the CNT transistors is determined by the structure of the nanotubes. And it is critical to understand the growth mechanism for controlling the fine structures including the chirality. In this project, environmental TEM(*3-5*), high throughput growth(*6, 7*) and machine learning have been used to investigate the growth mechanism of CNTs. For example, we investigated the phase evolution of cobalt (Co) catalyst NPs during the incubation, nucleation, and growth stages of CNTs under near-atmospheric pressure using an in situ close-cell environmental transmission electron microscope (ETEM), as shown in Fig. 3. Strict statistical analysis of the electron diffractograms was performed to accurately identify the phases of the catalyst NPs. It was found that the NPs belong to an orthorhombic Co_3C phase that remained unchanged during CNT growth. (Y. Wang *et al.*, *ACS Nano* **14**, 16823-16831 (2020).)

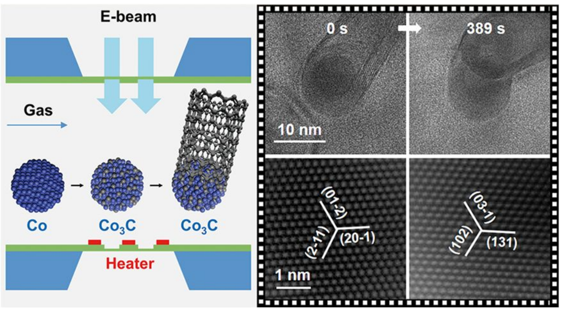

Fig. 3 Schematic and TEM images of carbon nanotubes growing from a Co catalyst nanoparticle.

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５．主な発表論文等

〔雑誌論文〕　計8件（うち査読付論文　8件／うち国際共著　8件／うちオープンアクセス　3件）

１．著者名 Ma Ruixue、Qiu Lu、Zhang Lili、Tang Dai-Ming、Wang Yang、Zhang Bingsen、Ding Feng、Liu Chang、Cheng Hui-Ming	４．巻 16
２．論文標題 Nucleation of Single-Wall Carbon Nanotubes from Faceted Pt Catalyst Particles Revealed by in Situ Transmission Electron Microscopy	５．発行年 2022年
３．雑誌名 ACS Nano	６．最初と最後の頁 16574～16583
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsnano.2c06012	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 Wang Yang、Qiu Lu、Zhang Lili、Tang Dai-Ming、Ma Ruixue、Ren Cui-Lan、Ding Feng、Liu Chang、Cheng Hui-Ming	４．巻 8
２．論文標題 Growth mechanism of carbon nanotubes from Co-W-C alloy catalyst revealed by atmospheric environmental transmission electron microscopy	５．発行年 2022年
３．雑誌名 Science Advances	６．最初と最後の頁 eabo5686
掲載論文のDOI（デジタルオブジェクト識別子） 10.1126/sciadv.abo5686	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

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２．論文標題 Nanometer-level temperature mapping of Joule-heated carbon nanotubes by plasmon spectroscopy	５．発行年 2023年
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２．論文標題 Semiconductor nanochannels in metallic carbon nanotubes by thermomechanical chirality alteration	５．発行年 2021年
３．雑誌名 Science	６．最初と最後の頁 1616～1620
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2．論文標題 Precise Identification of the Active Phase of Cobalt Catalyst for Carbon Nanotube Growth by In Situ Transmission Electron Microscopy	5．発行年 2020年
3．雑誌名 ACS Nano	6．最初と最後の頁 16823～16831
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsnano.0c05542	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

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2．論文標題 1000 Wh L-1 lithium-ion batteries enabled by crosslink-shrunk tough carbon encapsulated silicon microparticle anodes	5．発行年 2021年
3．雑誌名 National Science Review	6．最初と最後の頁 1~11
掲載論文のDOI（デジタルオブジェクト識別子） 10.1093/nsr/nwab012	査読の有無 有
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2．論文標題 High-throughput screening and machine learning for the efficient growth of high-quality single-wall carbon nanotubes	5．発行年 2021年
3．雑誌名 Nano Research	6．最初と最後の頁 NA
掲載論文のDOI（デジタルオブジェクト識別子） 10.1007/s12274-021-3387-y	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

〔学会発表〕　計3件（うち招待講演　1件／うち国際学会　3件）

１．発表者名
Yongjia Zheng, Akihito Kumamoto, Rong Xiang, Kaoru Hisama, Keigo Otsuka, Yuta Sato, Taiki Inoue, Shohei Chiashi, Daiming Tang, Qiang Zhang, Anton Anisimov, Esko Kauppinen, Kazu Suenaga, Yuichiro Ikuhara, Shigeo Maruyama

２．発表標題
Growth mechanism and handedness relation of one-dimensional van der Waals heterostructures

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International Conference on the Science and Application of Nanotubes and Low-Dimensional Materials (NT21)（国際学会）

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2021年

１．発表者名
Dai-Ming Tang

２．発表標題
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３．学会等名
IV INTERNATIONAL SYMPOSIUM "MODERN MATERIALS SCIENCE" (MMS-2020)（招待講演）（国際学会）

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Dai-Ming Tang

２．発表標題
Mechanical properties of 2D materials by in situ TEMfrom atomic sheets to batteries

３．学会等名
MANA International Symposium 2021（国際学会）

４．発表年
2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

室温で量子輸送可能な2.8 nmのカーボンナノチューブトランジスタ
https://www.nims.go.jp/news/press/2021/12/202112240.html
RT Quantum Transport in a 2.8 nm CNT Transistor
https://www.nims.go.jp/eng/news/press/2021/12/202112240.html
室温で量子輸送可能な2.8nmのカーボンナノチューブトランジスタの作製
https://www.nikkei.com/article/DGXLRSP624537_23122021000000/
ナノチューブからトランジスタ　物質・材料研究機構など
https://www.nikkei.com/article/DGXZQOUC207NI0Q2A120C2000000/?n_cid=SNSTWT&n_tw=1643833828

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

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関