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研究課題名(和文) 信号増幅機能を備えた自己発電型グラフェンNEMS - ナノ粒子集積高精度環境センサ

研究課題名(英文) Highly-accurate and self-powered environmental sensor based on integrated graphene NEMS-nano particles with signal amplification

研究代表者

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研究成果の概要(和文)：トップゲート型グラフェン共振器を用いた水素とアルゴン混合ガスの質量センシングを報告した。長さ1 $\mu\text{m}$ 、幅500nmのGNEM共振器を作製し、チャンバの真空条件でQ値45でその共振周波数を95.5MHzとして測定した。～886zeptogramsの吸着分子質量の変化を $5.6\times 10^{-3}\text{Pa}$ から $6.2\times 10^{-3}\text{Pa}$ までの圧力レベル変化で測定した。また、ドーピングはグラフェン分子vdW錯体相互作用を必ずしも支配しないことを示した。さらに、活性炭官能化グラフェン電界効果トランジスタガスセンサにおいて、実空気中で100ppbの室温アンモニア感度を実証することに成功した。

研究成果の学術的意義や社会的意義

研究代表者らのグラフェン質量センサーは、軽量分子質量分析への応用の可能性を示している。さらに、グラフェンガスセンサーにおける最も弱い分子間メモリーは、ガス分子の同定のための方法を開発する際に特に有用である。また、研究代表者らの活性炭官能化グラフェンセンサーは、グラフェンの大気ドーピング制限を克服し、選択的大気アンモニアガス検出および同定を可能にする。したがって、これらのグラフェンセンサーは、環境および臨床用アンモニアガスセンサーに使用することができる。

研究成果の概要(英文)：We reported the mass sensing of Hydrogen and Argon mixture gas using a top-gated graphene resonator. 1  $\mu\text{m}$  length and 500 nm width GNEM resonator was fabricated and its resonant frequency was measured as 95.5 MHz with a Q factor of 45 in the vacuum condition of the chamber. The change in adsorbed molecule mass of ~886 zeptograms was measured with the pressure level change from  $5.6\times 10^{-3}\text{ Pa}$  to  $6.2\times 10^{-3}\text{ Pa}$ . Also, we showed that doping does not always dominate the graphene-molecule vdW complex interaction. Moreover, room temperature ammonia sensitivity of 100 parts-per-billion (ppb) in real air was successfully demonstrated in the activated carbon functionalized graphene field-effect transistor gas sensor.

研究分野：グラフェンガスセンサー

キーワード：Graphene Gas sensor Ammonia Acetone Mass sensing

1. 研究開始当初の背景

Ammonia and volatile organic components (VOCs) are present at different concentration levels in indoor air. Even relatively low concentration of these pollutants present in indoor air can constitute health hazard due to long time of impact. The required limit of detection of these ammonia and volatile organic gases concentration is in parts-per-billion (ppb) level. Moreover, exhaled breath contains ppb levels of ammonia and VOCs, which can serve as indicators of many physiological parameters indicating the status of disease. We have to establish the extreme sensitivity of these gas molecules in the real-time air environment.

2. 研究の目的

In the first part of this research work, we systematically study the graphene resonator mass sensing of Hydrogen and Argon gas mixture molecules under different pressure levels and the corresponding resonant frequency shifts and Q factor. This work is based on Graphene Nano-Electro-Mechanical (GNEM) fabrication technology. In the second part of this research work, we develop highly selective and extreme sensitive ppb level sensor to detect ammonia and volatile organic gas molecules by utilizing the activated carbon functionalized graphene.

3. 研究の方法

(1) Zeptogram Level Mass Sensing of Light Weight Gas Molecules Using Graphene Nanomechanical (GNEM) Resonator [1]:

Silicon substrate with SiO<sub>2</sub> thickness of 285 nm and Chemical vapor deposition (CVD) graphene from Graphene Platform Corp. are used for the graphene resonator fabrication. CVD graphene was transferred on to the silicon substrate and its Raman spectra at different positions clearly showed the G peak at ~1580 cm<sup>-1</sup> and the 2D peak at ~2700 cm<sup>-1</sup>. Moreover, significantly weak D-peak (~1350 cm<sup>-1</sup>) and shape of the 2D-peak indicated the monolayer nature of the CVD graphene. Fig. 1 shows the important steps of device fabrication processes. Graphene nanoribbons (GNR) was patterned using electron beam lithography (EBL) and reactive ion etching (RIE) processes with 4 Pa pressure and 10 W Oxygen plasma. GNR with 1 μm length and 500 nm width was fabricated.

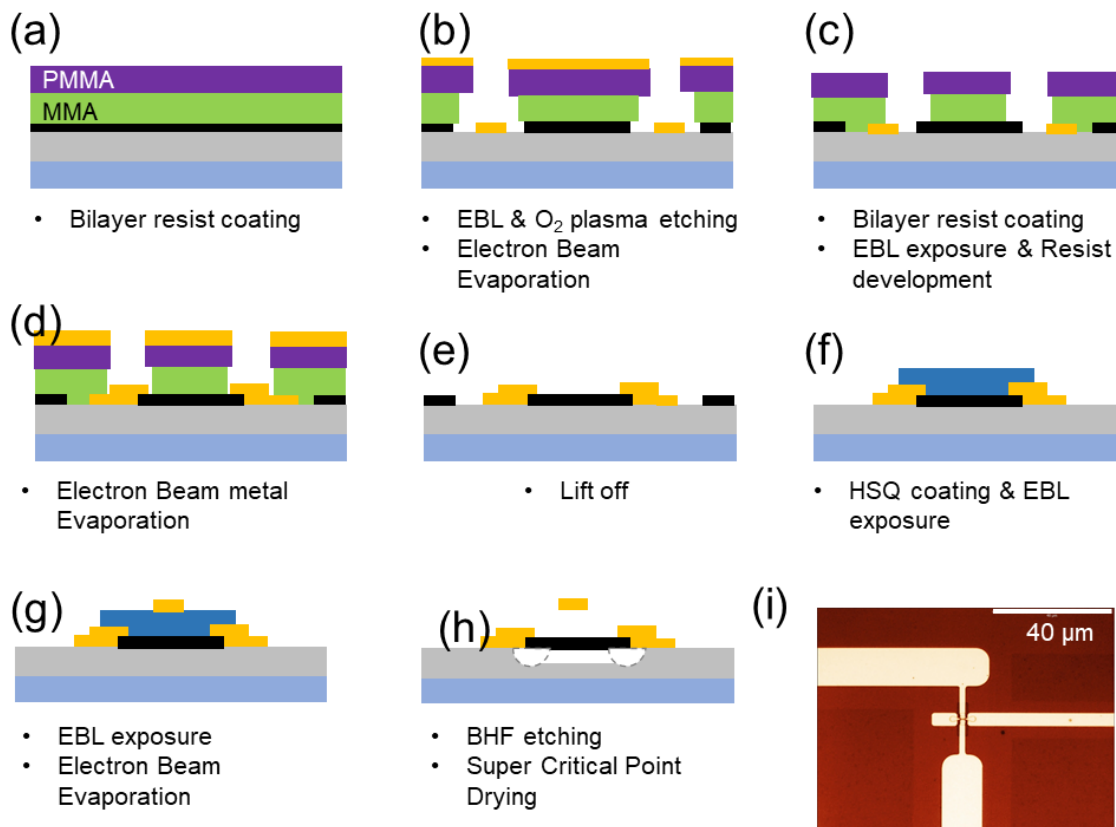


Fig. 1 (a)-(h) Schematic diagrams of top gated graphene resonator fabrication processes with CVD graphene on Si substrate with 285 nm SiO<sub>2</sub> (i) Optical microscope image of the fabricated top-gated graphene resonator.

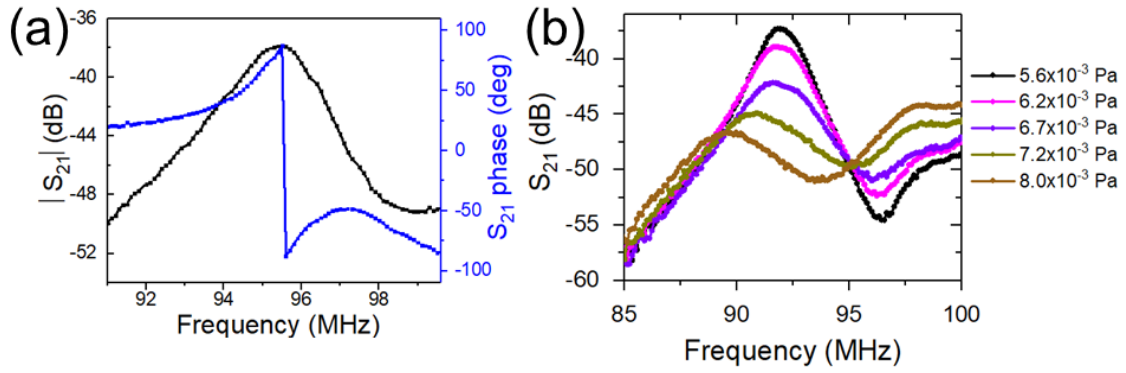


Fig. 2 (a) Measured transmission S-parameter characteristics of the doubly clamped graphene resonator measured in vacuum condition ( $1.1 \times 10^{-4}$  Pa). The black and blue lines represents the magnitude and phase characteristics of the transmission S parameter, respectively. (b) Measured S-parameter characteristics of doubly clamped graphene resonator in Ar + H<sub>2</sub> (9:1) mixture gas at the different pressures.

Metal contact to GNR was realized with Cr/Au (5/100 nm) EBL, electron beam evaporation, and lift-off processes. After this GNR device fabrication process, we realized a sacrificial layer (80 nm) on GNR by using hydrogen-silsesquioxane (HSQ). This resist is converted to SiO<sub>2</sub> layer after the EBL electron beam exposure. A top gate electrode with Cr/Au = 5/140 nm, and 200 nm length was fabricated on this sacrificial layer (Fig. 1g). CVD graphene defects were reduced using hydrogen annealing process. As a final step, sacrificial layer HSQ turned SiO<sub>2</sub> and SiO<sub>2</sub> under GNR are selectively removed by buffered HF etching. Supercritical point drying process was used in order to suspend GNR resonator without any stiction to the substrate (Fig. 1h). Fig. 1(i) shows the optical image of the fabricated device.

Fig. 2 (a) shows the measurement results of transmission S-parameter  $S_{21}$  in vacuum condition. As a result of this measurement, a resonance peak ( $f_0$ ) is observed to be 95.5 MHz. The quality factor (Q) is estimated to be 45 from the 3 dB bandwidth characteristics. 180° phase change at the resonant peak indicates change in the resonator reactance at the resonant frequency. In order to measure the inertial mass of Ar+H<sub>2</sub> mixture gas, different pressure levels of this mixture gas was introduced in the vacuum chamber and then transmission characteristics of the resonator was measured. Fig. 2 (b) shows the measurement results of the resonator at different pressure levels. The resonant frequency systematically decreased with the increase in the pressure, which is ascribed to increase in the adsorption of the mixture gas molecules onto the resonator. The change in adsorbed molecules mass of ~886 zeptogram was measured with the pressure level change from  $5.6 \times 10^{-3}$  Pa to  $6.2 \times 10^{-3}$  Pa. First-principles simulation with van der Waals (vdW) correction showed smaller effective charge transfer between graphene and H<sub>2</sub> molecule. However, Argon and graphene interaction is purely based on vdW interaction. These results clearly indicate the possibility of using graphene nanomechanical resonator for light weight molecules mass spectrometry applications.

## (2) Adsorbed Molecules as Interchangeable Dopants and Scatterers with a Van der Waals Bonding Memory in Graphene Sensors [2]:

Molecular adsorption induced doping and scattering play a central role in the detection mechanism of graphene gas sensors. However, while the doping contributions in electric field enhanced gas sensing is well studied, an understanding of the effects of scattering is still lacking. In this work, the scattering contribution of the graphene-molecule van der Waals (vdW) complex is studied under various electric fields and the associated vdW bonding retention in the complex is investigated (Fig. 3). We show that contrary to the generally opined view, doping does not always dominate the graphene-molecule vdW complex interaction and consequently the conductivity response in graphene sensors, rather the vdW complex interaction only shows doping dominated interaction at zero electric field while scattering increases with electric field modulation. The experimentally observed electric field dependent scattering response agrees with electron difference density analysis from density functional theory (DFT)

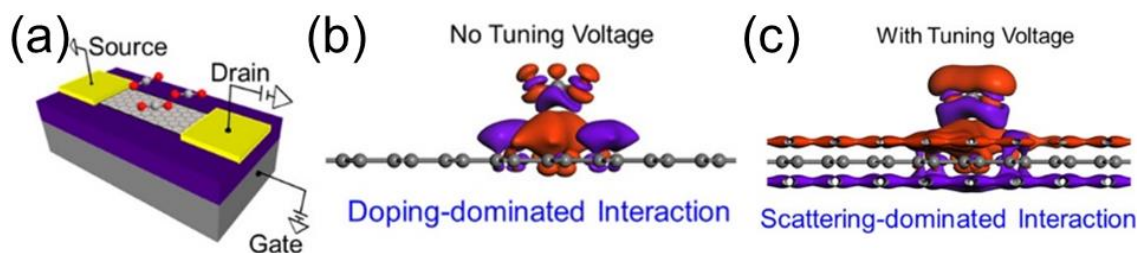


Fig. 3 (a) Schematic diagram of the GFET sensor Visualization of the electron difference density at an isovalue of  $8 \times 10^{-4}$  electron/Å<sup>3</sup> for a CO<sub>2</sub> molecule adsorbed on the graphene surface at different tuning voltages of (b) 0.15 V/Å (i.e., TV = 40 V), (c) 0.0 V/Å (i.e., TV = 0 V) Red regions = electron rich regions and purple regions = electron-deficient regions.

calculations which shows that scattering is directly dependent on the electric field induced molecular-reorientation as well as the redistribution and delocalization of charge in the graphene-gas molecule vdW complex. Furthermore, ‘vdW bonding memory’ i.e. retention of electric field-induced vdW bonding states after turning off the electric field is observed and shown to result from the high binding energies of the vdW complexes, which are an order of magnitude higher than the sensing measurement thermal energy. This ‘vdW bonding memory’ in the graphene-molecule complexes is important for the molecular identification of adsorbed gases based on their tunable charge transfer characteristics.

### (3) Activated Carbon Functionalized Graphene for Room Temperature parts-per-billion (ppb)-Level Ammonia and Acetone Gas Sensing:

Sensitivity, selectivity in real air and gas specific electronic responses are highly desired in graphene based gas sensors. An activated carbon functionalized graphene field effect transistor (ACF-GFET) gas sensor consisting of few ten-nm porous activated carbon on graphene with a room temperature ammonia sensitivity of 100 ppb in real air and a response time of ~3 seconds was successfully achieved (Fig. 4). Furthermore, a proof-of-concept for a gas specific electronic response, charge neutrality point disparity (CNPD), based on the charge neutrality point difference between tuning voltage (TV) induced graphene-gas molecule van der Waals (vdW) complexes of opposite TV polarities is demonstrated. The CNPD values obtained from pristine graphene and the ACF-GFET sensor increased with tuning voltage (TV) and tuning time and were characteristic for various gas environments: nitrogen, oxygen, dry air as well as ppb concentrations of ammonia and acetone in different environments. Density Functional Theory (DFT) simulations show that the CNPD values originate from the TV induced high energy graphene-gas vdW interactions which result in signature TV-dependent charge transfer and unique molecular dynamics effects. Based on these

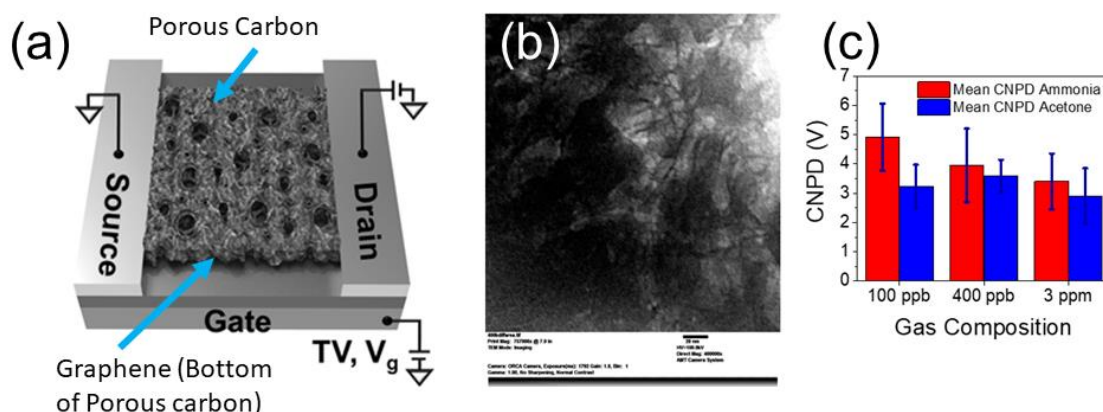


Fig. 4 (a) Device schematics of ACF-GFET sensor showing porous ACF on graphene (b) TEM image (bright field) showing porous activated carbon on graphene. Dark regions are activated carbon, while bright regions are pores leading to graphene. Scale bar is 20 nm. (c) Variation of CNPD value for ammonia and acetone using pristine graphene.

fabrication methods, Zinc Oxide nanoparticles can also be integrated with the suspended graphene to realize self-powered environmental sensor.

References:

[1] Muruganathan, Manoharan, Hiroya Miyashita, Jothiramalingam Kulothungan, Marek E. Schmidt, and Hiroshi Mizuta. "Zeptogram level mass sensing of light weight gas molecules using graphene nanomechanical (GNEM) resonator." In *2018 IEEE SENSORS*, pp. 1-4. IEEE, 2018.

[2] Agbonlahor, Osazuwa G., Muruganathan, Manoharan, Tomonori Imamura, and Hiroshi Mizuta. "Adsorbed Molecules as Interchangeable Dopants and Scatterers with a Van der Waals Bonding Memory in Graphene Sensors." *ACS sensors* 5, no. 7 (2020): 2003-2009.

#### 4. 研究成果

##### (1) Key Achievements:

We achieved fast detection of ammonia within in 2 minutes through the gate voltage modulation of the carrier density of graphene and polarization of the ammonia molecule. This fast detection time and shift in the charge neutrality point are achieved due to the charge transfer between graphene and ammonia facilitated by gate voltage modulation.

Contrary to the generally opined view, we clarified that the doping does not always dominate the graphene–molecule van der Waals (vdW) complex interaction and the vdW complex interaction only shows doping-dominated interaction at zero electric fields while scattering increases with electric field modulation. The “vdW bonding memory” phenomenon was also discovered, and we concluded that it results from the high binding energies of the vdW complexes, which are an order of magnitude higher than the sensing measurement thermal energy.

As the final main achievement, we developed a new method to distinguish various gas via the tuning voltage induced charge transfer characteristics. The charge neutrality point difference was observed in various environments: dry air, 100% N<sub>2</sub> and 100% O<sub>2</sub>, Ammonia/N<sub>2</sub>, Ammonia (84 ppm, 5ppb, 1ppb)/Real Air, Acetone (3ppm)/Real Air, and Ethanol (50 ppb)/Real Air. For the high sensitivity gas detection, activated carbon functionalization of the graphene was developed. Also, methods to coat various nanoparticles such as ZnO was developed and characterized.

##### (2) Comparison with competing groups in Japan and worldwide:

For ppb level sensing of various gases, a group such as A. Geim (University of Manchester) has reported observations by changing the Hall resistance using a Hall element, but in this case, a strong magnetic field device was indispensable. In Japan, sensing of ppb-level gases in real air environment is under the progress. Our sensing and detection methods overcome atmospheric doping of graphene while enabling selective atmospheric gas detection and identification, thus enabling graphene’s atmospheric applications in environmental and clinical ammonia gas sensors.

##### 3) Future prospect:

Our graphene gas sensing method is easy to apply in terms of both size and cost of the sensor element. Also, this principle can be applied to detection of other chemical molecules (especially volatile organic molecules such as formaldehyde that cause sick building syndrome). It is highly possible that our sensor and detection method will be a promising candidate technology for high-speed, and ultra-sensitive environment sensing.

5. 主な発表論文等

〔雑誌論文〕 計6件（うち査読付論文 6件/うち国際共著 6件/うちオープンアクセス 1件）

1. 著者名 Schmidt Marek E., Muruganathan Manoharan, Kanzaki Teruhisa, Iwasaki Takuya, Hammam Ahmed M. M., Suzuki Shunei, Ogawa Shinichi, Mizuta Hiroshi	4. 巻 15
2. 論文標題 Dielectric Screening Reduction Induced Large Transport Gap in Suspended Sub 10 nm Graphene Nanoribbon Functional Devices	5. 発行年 2019年
3. 雑誌名 Small	6. 最初と最後の頁 1903025 ~ 1903025
掲載論文のDOI (デジタルオブジェクト識別子) 10.1002/smll.201903025	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
1. 著者名 Kulothungan Jothiramalingam, Muruganathan Manoharan, Mizuta Hiroshi	4. 巻 153
2. 論文標題 Modulation of twisted bilayer CVD graphene interlayer resistivity by an order of magnitude based on in-situ annealing	5. 発行年 2019年
3. 雑誌名 Carbon	6. 最初と最後の頁 355 ~ 363
掲載論文のDOI (デジタルオブジェクト識別子) 10.1016/j.carbon.2019.07.036	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 Kareekunnan Afsal, Muruganathan Manoharan, Mizuta Hiroshi	4. 巻 11
2. 論文標題 Electrically controlled valley states in bilayer graphene	5. 発行年 2019年
3. 雑誌名 Nanoscale	6. 最初と最後の頁 14707 ~ 14711
掲載論文のDOI (デジタルオブジェクト識別子) 10.1039/C9NR03621K	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 Iwasaki Takuya, Wang Zhongwang, Muruganathan Manoharan, Mizuta Hiroshi	4. 巻 12
2. 論文標題 Formation of quantum dot in graphene single nanoconstriction	5. 発行年 2019年
3. 雑誌名 Applied Physics Express	6. 最初と最後の頁 025004 ~ 025004
掲載論文のDOI (デジタルオブジェクト識別子) 10.7567/1882-0786/aaf993	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 Agbonlahor Osazuwa G., Muruganathan Manoharan, Imamura Tomonori, Mizuta Hiroshi	4. 巻 5
2. 論文標題 Adsorbed Molecules as Interchangeable Dopants and Scatterers with a Van der Waals Bonding Memory in Graphene Sensors	5. 発行年 2020年
3. 雑誌名 ACS Sensors	6. 最初と最後の頁 2003 ~ 2009
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acssensors.0c00403	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 Kareekunnnan Afsal, Muruganathan Manoharan, Mizuta Hiroshi	4. 巻 101
2. 論文標題 Manipulating Berry curvature in hBN/bilayer graphene commensurate heterostructures	5. 発行年 2020年
3. 雑誌名 Physical Review B	6. 最初と最後の頁 195406
掲載論文のDOI (デジタルオブジェクト識別子) 10.1103/PhysRevB.101.195406	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8件 (うち招待講演 1件 / うち国際学会 4件)

1. 発表者名 H. Mizuta, G. Agbonlahor, H. Miyashita, K. Taketomi, J. Lee, N. Huynh and M. Muruganathan
2. 発表標題 Graphene Nano-Electro-Mechanical (NEM) Devices and Extension to Sensor Applications
3. 学会等名 The Semiconductor Process Integration 11 Symposium in 236th ECS Meeting (招待講演) (国際学会)
4. 発表年 2019年

1. 発表者名 Kareekunnnan Afsal, Manoharan Muruganathan, Hiroshi Mizuta
2. 発表標題 Valley Hall Effect in Ungated Bilayer Graphene
3. 学会等名 Recent Progress in Graphene & 2D Materials Research (国際学会)
4. 発表年 2019年

1. 発表者名 R. Sankar Ganesh, Gabriel Agbonlahor, H. Maki, M. Manoharan, H. Mizuta
2. 発表標題 High sensitive detection of Acetone gas using Graphene nanoribbon sensor
3. 学会等名 第67回応用物理学会春季学術講演会
4. 発表年 2020年

1. 発表者名 Osazuwa Gabriel Agbonlahor, Manoharan Muruganathan, Hiroshi Mizuta
2. 発表標題 Atmosphere-Specific Response in Graphene Field-Effect Transistors
3. 学会等名 第67回応用物理学会春季学術講演会
4. 発表年 2020年

1. 発表者名 M. Muruganathan, H. Miyashita, J. Kulothungan, M. Schmidt, H. Mizuta
2. 発表標題 Zeptogram Level Mass Sensing of Light Weight Gas Molecules Using Graphene Nanomechanical (GNEM) Resonator
3. 学会等名 IEEE Sensors 2018 (国際学会)
4. 発表年 2018年～2019年

1. 発表者名 M. Muruganathan, H. V. Ngoc, J. Kulothungan, M. Schmidt, H. Mizuta
2. 発表標題 Low-Voltage Multifunctional Graphene Nanoelectromechanical Devices
3. 学会等名 International Conference on Global Research and Education, Inter-Academia (国際学会)
4. 発表年 2018年～2019年



1. 発表者名 Osazuwa Gabriel Agbonlahor, Jothiramalingam Kulothungan, Manoharan Muruganathan, and Hiroshi Mizuta
2. 発表標題 Detection of ammonia via charge transfer-induced shift of graphene charge neutrality point
3. 学会等名 第79回応用物理学会秋季学術講演会
4. 発表年 2018年～2019年

1. 発表者名 K. Taketomi, S. Taniuchi, H. Sakai, S. Saito, M. Mahoharan, H. Mizuta
2. 発表標題 Sensing of N2/Acetone mixed gas using graphene nanoribbon
3. 学会等名 第79回応用物理学会秋季学術講演会
4. 発表年 2018年～2019年

〔図書〕 計1件

1. 著者名 Muruganathan Manoharan, Mizuta Hiroshi	4. 発行年 2019年
2. 出版社 Springer	5. 総ページ数 19
3. 書名 Nanotechnology Characterization Tools for Environment, Health, and Safety	

〔産業財産権〕

〔その他〕

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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
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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
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