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論　　文　　題　　目	Thermal Transport in Suspended Graphene Phononic Crystal (GPnC)
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論文の内容の要旨

a. Research content

Background

With the advances in the field of electronics, it has become relevant to reflect on the ever-growing problem of management of waste heat and probe further into nanoscale heat transport as the devices are being vigorously scaled down to tens of nanometers. The physical entity that can help create thermal blockade is now defined as phononic crystals (PnCs) in the community- the terminology rooted into the word 'phonon' which represents the quanta of atomic vibration in materials. RFabrication of PnCs has become a subject of interest for the potential it offers for heat propagation control. Fabrication of intricate nanopatterns on materials like silicon and steel has long since been realized with the optimization of various focused ion beam (FIB) techniques. However, it has been reported that, with superior physical and mechanical properties i.e. Young's modulus (~1 TPa) and Debye temperature (~1900 K) graphene offers better flexibility and control of phonon contributions. In this work, we have reflected on the asymmetry in thermal transport in graphene phononic crystals as an initial study to understand thermal rectification characteristics in nanoscale devices.

Summary of results

First, the dispersion curves and transmission probability of graphene based phononic crystals by configuring different periodicity, porosity and pore shape were studied by Finite Element Method simulations. From the dispersion relations, obvious band flattening or distinct frequency regions were observed where phonon transmission was completely blocked. The analysis showed strong evidence of porosity and pore shape dependency on phononic band gap (PnBG) generation. For circular shaped nanopores, a very small PnBG opens at ~0.4 THz only at a high porosity over 0.73 which is extremely difficult to achieve using the current experimental facilities. To address this limitation, cross shaped nanopore pattern was introduced where PnBG opened at a porosity ~0.28. The PnBG was most obvious at

~0.9 THz for single nanometer neck length and completely disappeared when it increased to 10 nm indicating that the constrictions due to the narrow neck structure induced phonon modes confinement contributing to the suppression or flattening of the dispersion relation. At similar porosity and unit cell size, snowflake shaped pores exhibited phononic bandgap (PnBG) in gradually higher THz (~1.5 THZ) regime as the symmetric placement of the neck length along all the supercell edges reinforced the phonon confinement. Also, the snowflake shaped nanopattern gives the advantage of having larger neck lengths of ~10 nm (fig. 1).

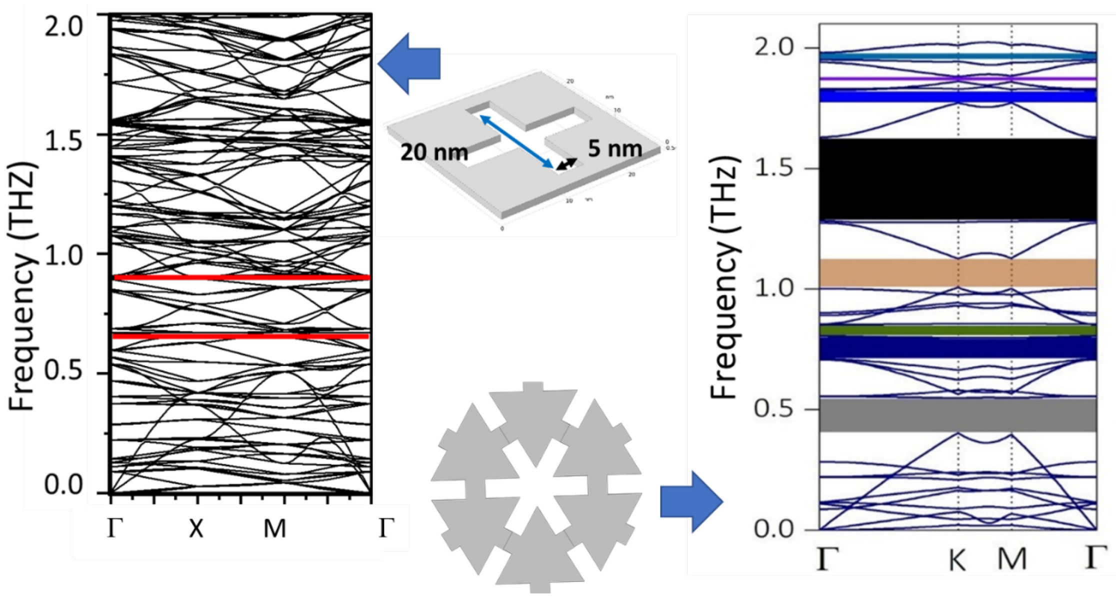

Figure 1: *Calculated dispersion relation for cross-shaped and snowflake-shaped nanopores with 28% porosity maintained for both cases.*

Next, a reproducible hybrid method was developed and demonstrated to successfully fabricate large area (in μm2 dimensions) suspended graphene nanomesh (GNM). The GNR are patterned into required dimensions using EBL and later suspended by buffered hydrofluoric acid (BHF) release with gold electrodes acting as a heater. The GNM is fabricated by milling periodic nanopores with as small as ~6 nm diameter on the suspended GNR by direct focused helium ion beam milling (HIBM). Taking advantage of the fidelity of HIBM, symmetric and asymmetric graphene nanomesh (GNM) samples were fabricated. As asymmetric GNM with nanopores patterned on half of the total area of the GNR is shown fig. 2(a). The concept of resistive thermometry was used to develop a 4-probe measurement method for thermal characterization of the prepared GNM devices which had 20 nm, 25 nm and 30 nm pitch and ~6nm diameter nanopores. With the base temperature maintained at 150K in a cryogenic vacuum probe station, joule heating was used to generate temperature at the metal electrode. With the measurement setup, resistance at the electrode was measured accurately and the corresponding temperature was calculated. By observing the change in temperature at the heater when there is GNM present, it was confirmed that some of the heat is dissipated through the GNM. The measurement was adopted to observe the trend of thermal dissipation through asymmetric and symmetric GNM by maintaining similar experimental conditions and most interestingly, characteristics of thermal rectification by introducing asymmetry in the GNM was observed when the heater position was changed. It was observed that the heat transport through the non-meshed area of the patterend GNR to the meshed area is larger compared to when the heater position is swapped and heat transport direction is from the meshed area to the non-meshed area (fig . 2(b))

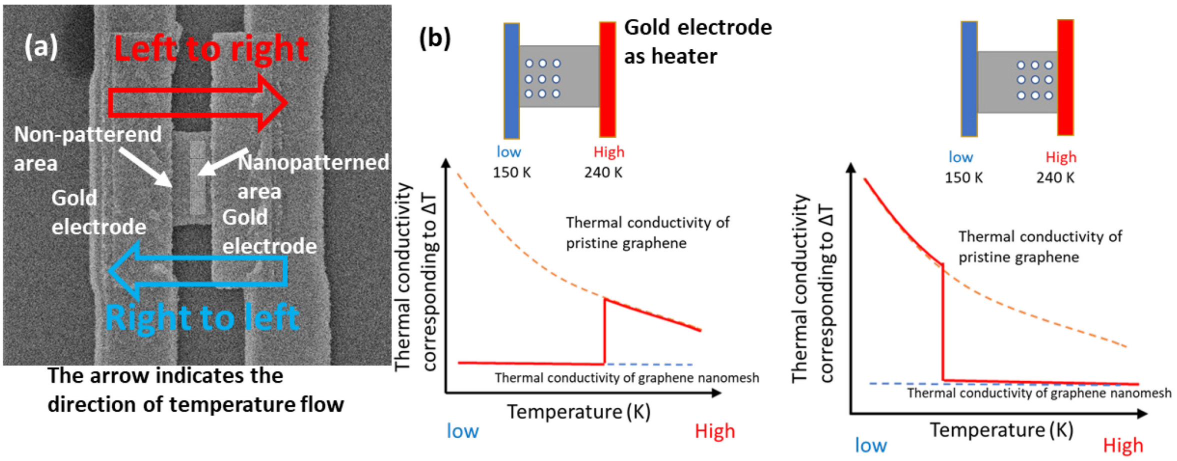

Figure 2: *(a) Suspended asymmetric GNM device with nanopores patterned on half of the entire GNR area. (b) Qualitative analysis of asymmetry of thermal transport for the fabricated device.*

b. Research objective

Controlling the thermal conductivity of a material independently of its electrical conductivity has always been an intriguing aspect for practical applications of thermoelectric materials. Research on thermal rectification is very important to establish the idea of controlling current induced heat transfer. Numerical simulations performed using continuum models of graphene PnCs in the COMSOL multiphysics platform provided the initial ideas and information to fabricate the GPnC device. A hybrid method by incorporating electron beam lithography (EBL) and helium ion beam milling (HIBM) was developed to fabricate graphene nanomesh (GNM) devices to study their thermal transport characteristics. A 4-terminal thermoelectric measurement method was established to detect the thermal transport through the fabricated GNM. This work provides the initial knowledge and ideas that could provide important information to the community to fabricate graphene based devices for thermal rectification applications.

c. Research accomplishment

Academic journals

1. Haque Mayeesha Masrura, Afsal Kareekunnan, Fayong Liu, Sankar Ganesh Ramaraj, Günter Ellrott, Ahmmed MM Hammam, Manoharan Muruganathan and Hiroshi Mizuta, Design of Graphene Phononic Crystals for Heat Phonon Engineering, Micromachines 2020, 11(7), 655 / DOI: 10.3 0655
2. Fayong Liu, Zhongwang Wang, Soya Nakanao, Shinichi Ogawa, Yukinori Morita, Marek Schmidt, Mayeesha Haque, Manoharan Muruganathan and Hiroshi Mizuta, Conductance Tunable Suspended Graphene Nanomesh by Helium Ion Milling, Micromachines 2020, 11(4), 387; DOI:10.3390/ mi11040387
3. M. E. Schmidt, T. Iwasaki, M. Muruganathan, M. Haque, NH Van, S. Ogawa and H. Mizuta, Structurally Controlled Large-Area 10 nm Pitch Graphene Nanomesh by Focused Helium Ion Beam Milling, ACS Applied Materials & Interfaces (2018), Vol.10, No. 12, pp. 10362-10368, DOI:10.1021/acsami.8b00427

International conferences

1. Phononic bandgap formation in single nanometer graphene nanomesh
M. Haque, M. E. Schmidt, M. Muruganathan, I. Katayama, J. Takeda, S. Ogawa, H. Mizuta
The 1st JAIST World Conference (JWC2018), Nomi, 27-28 February 2018 (Poster presentation)
2. Phononic Bandgap Engineering in Single Nanometer Graphene Nanomesh
Mayeesha M. Haque, Marek E. Schmidt, M. Muruganathan, I. Katayama, J. Takeda, S. Ogawa, H. Mizuta
Joint Conference of the 16th International Conference on Phonon Scattering in Condensed Matter (Phonons 2018) and the 4th International Conference on Phononics and Thermal Energy Science (PTES 2018), Nanjing, China, 31 May - 3 June 2018 (Oral presentation)

National conferences (in chronological order)

1. Effects of structural dimensions on phonon bandgaps in nanopatterned graphene phononic crystals
Mayeesha M. Haque, Marek E. Schmidt, Takuya Iwasaki, Manoharan Muruganathan, Hiroshi Mizuta
第 78 回応用物理学会秋季学術講演会
2. Graphene Nanophononics: Sample fabrication and FEM Simulation I
Mayeesha M. Haque, Seiya Kubo, Marek E. Schmidt, Manoharan Muruganathan, Shinichi Ogawa, Hiroshi Mizuta
第 2 回フォノンエンジニアリング研究会
2018 年 7 月 13 日-14 日、KKR ホテル熱海
3. Fabrication process and thermal conductivity measurement setup of graphene phononic crystal

M. Haque, S. Kubo, M. E. Schmidt, M. Muruganathan, S. Ogawa, H. Mizuta
第 79 回応用物理学会秋季学術講演会
2018 年 9 月 18 日-21 日、名古屋国際会議場

Keywords: Graphene phononic crystal, Graphene nanomesh, Helium ion beam milling, Phononic bandgap, Resistive thermometry, Thermal rectification.

論文審査の結果の要旨

原子層材料グラフェンのヤング率は＞1 TPa とシリコンに比べて一桁大きく、またデバイ温度は約 2800 K と非常に高い。そのためグラフェンナノ電子機械(GNEM)振動子の共振周波数（すなわち TA フォノンの基底モードエネルギー）は、シリコンのナノ振動子より数倍高くなる。この優れた機械的性質は、熱フォノンの制御のために必要となる超微細構造の寸法への要求を緩和するという大きな利点をもたらす。本研究は、GNEM 技術で宙吊りにしたグラフェンに、ビーム径 ＜1 nm の集束ヘリウムイオンビームミリング（HIBM）を用いた超微細加工技術を駆使して、直径、間隔 ～ 10 nm の2次元ナノ孔アレイ(グラフェンフォノニック結晶：GPnC)を作製し、サブ THz～数 THz 帯域のフォノニックバンドギャップ(PnBG)を形成して、熱伝導を制御するとともに熱整流作用の発現を目的とした。

本研究では、まず、3次元有限要素シミュレーションにより、円形ナノ孔直径を3～8nm、孔ピッチを 10～25 nm の範囲で変化させた GPnC のエネルギー分散特性を解析した。円形ナノ孔 GPnC では、有限の PnBG を形成するために、隣接するナノ孔間ネック幅を～1 nm まで微細化することが必要であることわかった。次に、クロス型およびスノーフレーク型ナノ孔構造を提案し、同様の解析行った結果、六角形状に配置したスノーフレーク型ナノ孔 GPnC では、孔ピッチ 25 nm でも広範囲の構造パラメータに渡り広い PnBG が形成され、真性グラフェンに対して～1／5 程度まで熱伝導度を低減できることを見出した。

また、HIBM 技術によって、宙吊り単層グラフェン膜上に、直径～6 nm，ネック幅～9 nm 円形ナノ孔 GPnC を、全面（FM：フルメッシュ）、半面（HM：ハーフメッシュ）で形成し、その両端に4端子電極（マイクロヒータ・センサ兼用）を備えたデバイス作製した。まず、これらの GPnC の電気伝導特性を環境温度 85K～400K の範囲で測定し、FM-、HM-GPnC ともに電気特性は対称であること確認した。次に、HM-GPnC チャネル有・無の2素子に対して、両端のヒータ・センサの位置を入れ替えてヒータ電極の温度低下を測定する手法で、HM-GPnC を介した熱リークを測定した結果、HM-GPnC 側にヒータを置いた方が高い熱伝導特性を示すことを初めて見出した。一方、全面ナノ孔を形成した FM-GPnC 構造では、このような非対称熱伝導は観測されなかった。HM-GPnC に対して見積もられた熱整流性は最大で～66 %であった。

以上、本論文は、宙吊りにした非対称 GPnC 構造が熱整流性を示す原理実験に初めて成功した研究であり、ナノスケールサーマルエンジニアリングという新技術の今後の発展において学術上・応用上両方の観点から極めて価値の高いものである。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。