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研究課題名（和文） Exploring the impact of confinement and defects on surface charge of 2D materials with controlled van der Waals nanochannels fabrication.

研究課題名（英文） Exploring the impact of confinement and defects on surface charge of 2D materials with controlled van der Waals nanochannels fabrication.

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研究成果の概要（和文）：この研究プロジェクトの目的は、2D材料ベースのナノチャネルを作成し、ファンデルワールス集合によって作成されたグラフェンまたはhBNナノチャネル内の2D材料に対する閉じ込めおよび表面欠陥の影響を調査することである。
グラファイト/hBNの剥離、様々な基板（SiN、SiO2 on Si、ガラス）へのフレーク転写など、アニール前の製造工程（最終工程）を完了させることができました。また、電子ビームリソグラフィーを使ってナノスケールのマスクを作製し、ナノチャネルのエッチングを行いました。さらに、ナノチャンネルを組み立てる膜を購入しました。

研究成果の学術的意義や社会的意義
ナノスケールの流体の流れは、独自の量子効果や表面効果により、より大きなスケールの流れとは大きく異なっています。これを理解することで、海水淡水化や青色エネルギー利用などのプロセスにおいて、より優れた性能を持つ膜の作成につながる可能性があります。その重要性にもかかわらず、ナノスケールの流れ、特に表面電荷と欠陥に関連する知識は、まだ限られています。表面電荷はナノスケールの流体挙動に大きく影響し、欠陥はこの電荷とその後の流れを変えることができます。ナノスケールの流れに依存する技術を発展させるためには、表面電荷と欠陥の相互作用についてより包括的に理解することが重要です。

研究成果の概要（英文）：The objective of this research project is to make 2D material based nanochannels to investigate the impact of confinement and surface defects on 2D materials within graphene or hBN nanochannels created through van der Waals assembly.
We successfully completed the fabrication steps before annealing (last steps): including graphite/hBN exfoliation, transfer of flakes to various desired substrates (SiN, SiO2 on Si, or glass). We also fabricated nanoscale masks using electron beam lithography, and performed etching of nanochannels. We bought the membranes on top of which the nanochannels are assembled.

研究分野： Nanofluidics and wetting

キーワード： nanofluidics　2D materials　graphene　flow　fluid mechanics

１．研究開始当初の背景

Nanofluidics, the study of fluid and ion transport at the nanoscale, has distinct features compared to fluid transport at larger scales. This difference stems from phenomena exclusive to the nanometer range, such as fluid slippage and electrostatic screening of charged surfaces by ions. These characteristics can be harnessed for crucial societal applications. For instance, the influence of surface charges is utilized in the creation of membranes for water desalination, blue-energy harvesting, and ultrafiltration. Despite the progress of nanofluidic technologies, we are still unable to achieve the remarkable selectivity and permeability of biological channels like aquaporins. The nanoscale restriction of these channels, such as roughly 0.5nm in aquaporins, could be the source of their superior properties, but the physics behind this is not yet fully understood. Recent nanofluidics experiments have shown an unforeseen link between the electronic properties of the confining material and macroscopic attributes. This coupling was first identified in nanotubes. Boron nitride nanotubes (BNNT) and carbon nanotubes (CNT), though possessing similar crystallographic properties, exhibit stark differences due to their electronic nature. This atomic-scale difference has a significant impact on macroscopic transport. Andre Geim's team in Manchester recently devised a new technique using a 2D form of these materials (graphene and hexagonal boron nitride - hBN). This novel approach allowed for the first-ever confinement of fluids in a purely 2D setup with atomic-level control over wall properties and confinement size. However, an unexpected finding emerged from these experiments. The surface charge in the van der Waals channels was significantly lower than that measured in nanotubes made of the same material. The cause of this discrepancy in surface charge is still unclear and needs to be comprehended for better nanofluidics design. Possible explanations include the difference in confinement or the possibility that the nanotubes, due to their fabrication method, have more defects than exfoliated graphene/hBN, resulting in a higher surface charge.

２．研究の目的

The main objective of this research project is to examine how defects and confinement influence the surface charge of 2D materials, namely graphene and boron nitride. The primary focus is to experimentally investigate and understand the individual impacts of these factors on the surface charge. The specific goal of the study is to decouple the effects of confinement and defects density on the surface charge.

３．研究の方法

Through this research project, we want to isolate the effect of molecular confinement. To this end, we build van der Waals channels with large confinement around 60-100 nm and measure the surface charge of such devices. At this scale, classical nanofluidics theory applies, therefore we will be able to identify the surface charge nature of such devices and directly compare it with the nanotubes surface charge. We will then elucidate how surface charge is affected when transitioning to

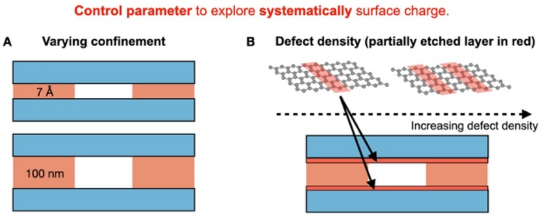

Fig. 1 *van der Waals channels control parameters for systematic surface charge study.*

molecular confinement by building channels with decreasing height (Fig. 1A).

Probing the effect of defects on surface charge is more difficult, as the defect density is hard to control and to quantify during fabrication. Through this research project, we want to artificially add -in a controlled way- defects to the channel's walls and to measure the impact of this defect density on the surface charge using ionic current measurement using high sensitivity current measurement using a patch clamp amplifier (Axopatch 200B). To do so, using van der Waals assembly, we will deposit a partially etched graphene (or boron nitride) monolayer on both inner surfaces of the nanometric vdW channels (Fig. 1B). Contrary to previous studies, we will have a control parameter (through the etched area perimeter) in order to study the defect density influence on surface charge.

４．研究成果

We will now describe the results of this research project. We prepared the high-sensitivity ion current measurement setup using a patch clamp amplifier, Axopatch 200B. We acquired custom made SiN membranes on top of which the channels are fabricated. Finally, while we did not perform ionic current measurements yet, we developed the fabrication process of the nanochannels with different confinement and prepared the etching process necessary for the defect control.

We describe below our results for the establishment of the fabrication process:

Global process of Van der Waals assembly of the nanochannels

The nanochannels are fabricated by van der Waals assembly. In short, it is made by stacking three layers of 2D materials (Fig.2). A relatively large 2D material flake such as graphene and hexagonal boron nitride (hBN) is obtained by exfoliation and then transferred to silicon nitride (SiN) /Si substrate as the bottom of channel. Then another thin flake is fabricated in the same way and patterned into stripes by electron beam lithography (EBL) and reactive ion etching (RIE). These stripes are transferred to the top of the bottom layer as a gap layer. Finally, a relatively thick flakes of graphite or hBN are transferred to cover the top and form a row of parallel channels. The height of the channels can be controlled by selecting the thickness of the gap layer and we can add a partially etched layer to add defects. We now

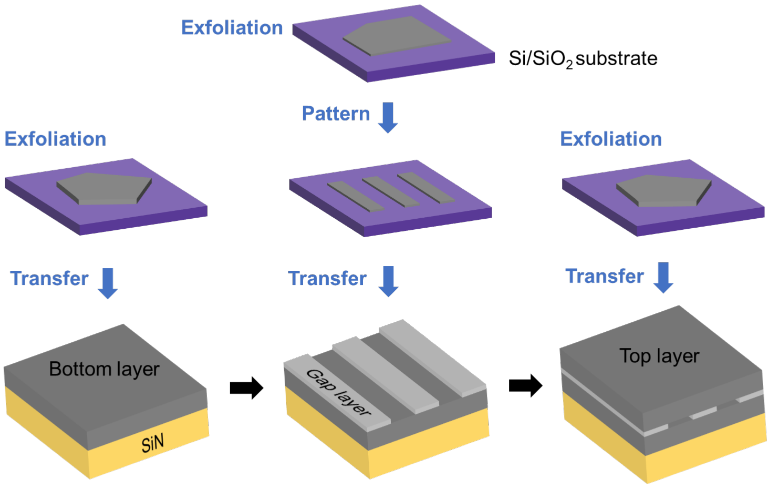

Fig. 2 Process of nanochannel fabrication.

Exfoliation

Graphite and hBN flakes of different thickness can be obtained by exfoliating from graphite and hBN crystals and followed by several exfoliations using tapes. Then the flakes can be put on a Si substrate with a thin layer of SiO_2 (100nm) by putting the tape over the chip, and slowly removing the tape. This way we can obtain very large flakes suitable for various characterizations and nanochannel fabrication. Figure. 3 shows some exfoliated large graphite and hBN flakes on SiO_2/Si substrate.

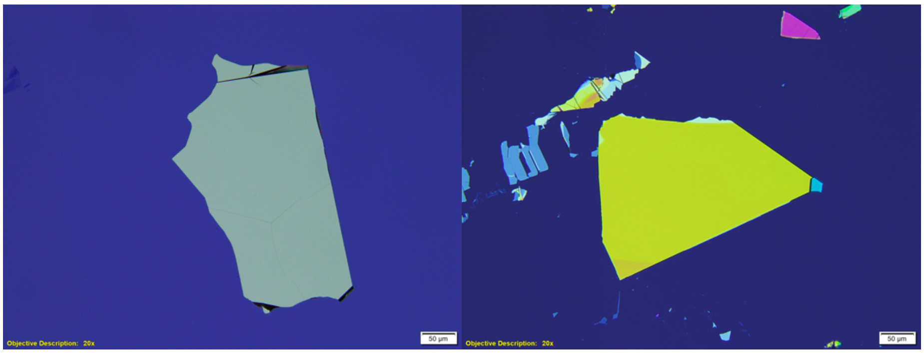

Fig. 3 Example of exfoliated graphite and hBN flakes on SiO_2/Si substrate.

Transfer

The 2D material flakes on the Si/SiO_2 substrate can be transferred to other substrate by several methods. Here we used the wet transfer method. First, the Si/SiO_2 substrate with 2D materials on top is spin-coated with a 100 nm polymethyl methacrylate (PMMA) layer. Then a piece of tape with a hole is used to support the PMMA film and cover the area where the flake to transfer is. The substrate (Si/SiO2) is subsequently etched in KOH solution so that the flake covered by PMMA and tape detachs from the substrate and float on the solution. After rinsing the flake in pure water, it can be transferred to any substrate using our transfer station. The transfer station consists of three parts: a microscope, a movable platform for fixing and heating the substrate, and a movable cantilever that can stick the tape with 2D materials (Fig. 4 left). The tape containing 2D material flake can be moved with cantilever to the aim location under the microscope and contact with the new substrate. In this way, the 2D material and PMMA can adhere to the new substrate because of van der Waals force. Finally, we can remove the PMMA by hot acetone and the 2D material flake is transferred successfully. Fig. 4 (right) shows a graphite and a hBN flake transferred to quartz surface.

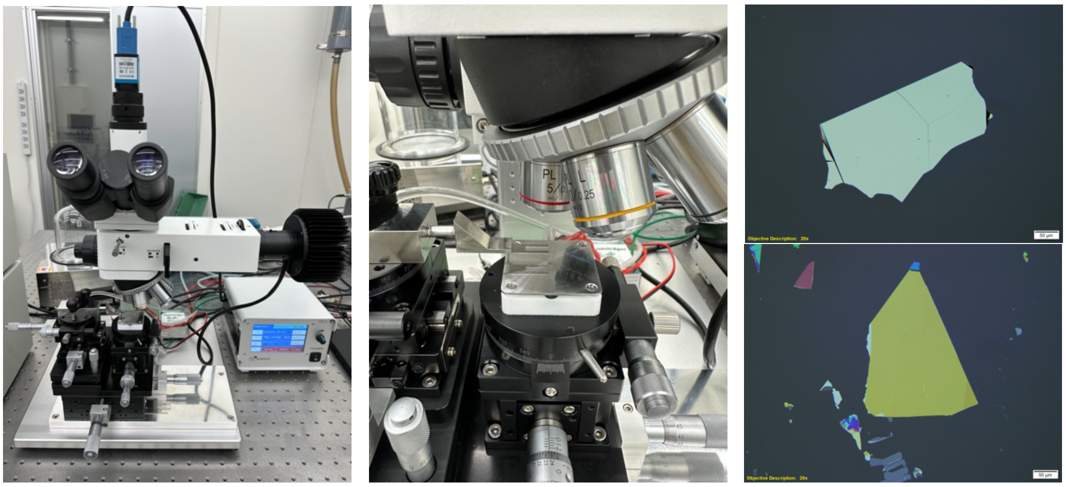

Fig. 4 Transfer stage and transferred graphite and hBN flakes on quartz surface.

Electron beam lithography (EBL) and reactive ion etching (RIE)

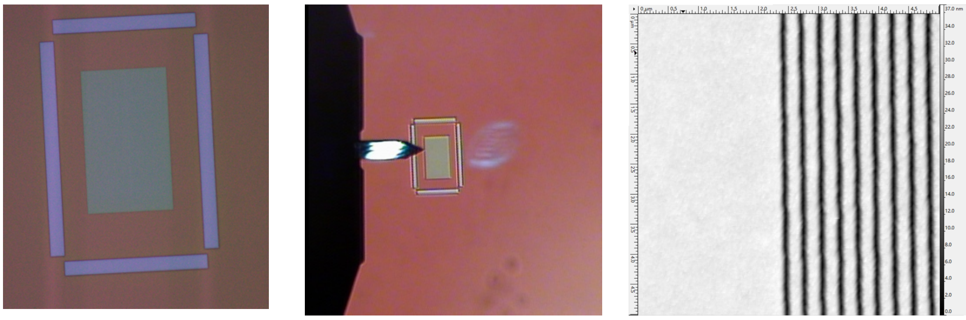

Fig. 5 AFM measurement of EBL sample

For patterning the gap layer into stripes, we also first spinning coat a layer of photoresist like PMMA on the top of Si/SiO$_2$ substrate with 2D material flakes and then write parallel lines with a width of about 100 nm by EBL. Fig. 5 shows the Atomic Force Microscope (AFM) measurement of resist surface after EBL. Subsequently, the 2D material can be partially etched by RIE while resist can act as a mask. We tested the etching speed of RIE for graphite and hBN by measuring the depth of etched micron scale lines after etching for different times (Fig. 6). It is found that the etching rate for graphite is about 5 nm/min and 9 nm/min for hBN.

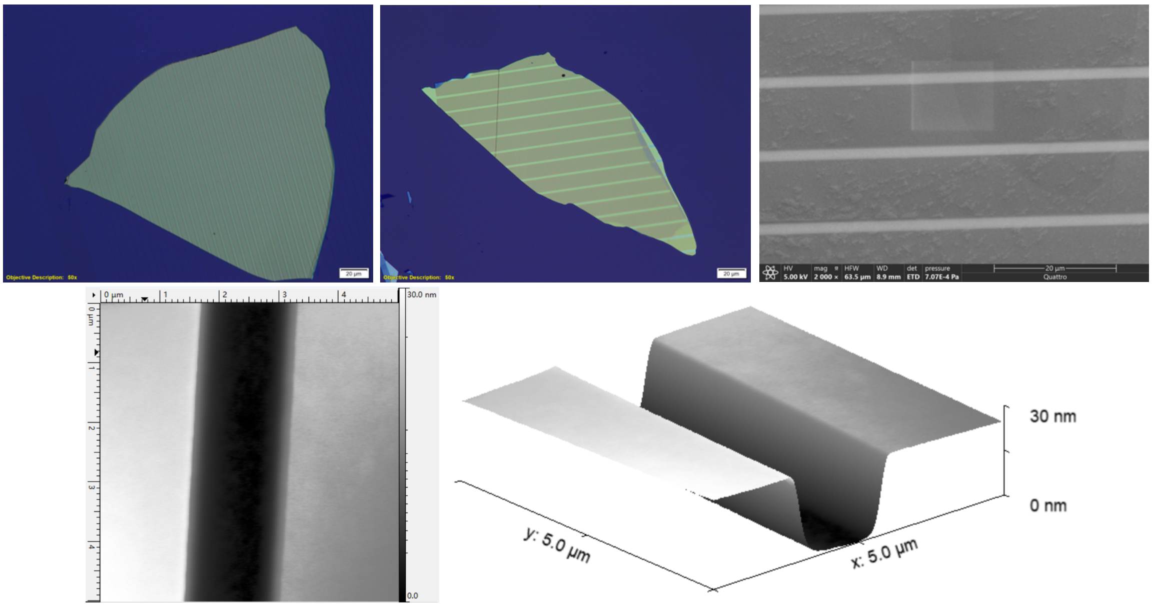

Fig. 6 Etching test. (top left, top middle) Image of etched graphite flakes; (top right) SEM image of etched graphite in (top middle); (bottom) AFM measurement of etched channel on graphite in (a).

We are now going to perform ionic current measurements to measure the surface charge and understand how it is influenced by the surface defects and the confinement.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計0件

〔図書〕　計0件

〔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

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