

TIP-BASED NANOLITHOGRAPHY AND APPLICATION TO MOLYBDENUM
DISULFIDE DEVICES

BY

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DISSERTATION

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ABSTRACT

Advances in nanotechnology rely on the capability to fabricate nanometer scale structures and devices. Tip-based nanolithography (TBN) is a low-cost and versatile unconventional nanolithography technique that can be used to prototype novel devices. This dissertation reports the study of tip-based polymer nanostructure fabrication and the application of TBN to fabricate MoS₂ devices. The main contributions of this work are (i) understanding the effects of polymer properties and polymer melt flow on the size and shape of polymer nanostructures deposited from a heated tip, (ii) fabricating monolayer MoS₂ nanoribbon transistors as narrow as 30 nm using TBN, (iii) improving the mobility of hBN encapsulated monolayer MoS₂ transistors by cleaning and smoothing the interfaces with contact mode atomic force microscopy, (iv) demonstrating single-molecule sensing with monolayer MoS₂ nanoribbon-nanopore devices.

For TBN of polymer nanostructures, this work found nanometer scale capillary-driven flow governs polymer nanostructure deposition from a heated tip. Heated atomic force microscope (AFM) tips deposited 50 – 350 nm wide poly(methyl methacrylate) nanoribbons over a wide range of polymer molecular weight and deposition conditions. Both ribbon width and height increase with tip temperature and decrease with tip speed and polymer molecular weight. The width of the deposited polymer nanoribbons depends on capillary number (Ca) and is independent of tip temperature, tip speed and polymer molecular weight. Uniform and continuous deposition occurs only when $Ca \ll 1$, indicating that capillary-driven flow governs polymer transport.

For application of TBN to MoS₂ devices, this study described the fabrication of the first working transistor from monolayer MoS₂ with a channel width smaller than 100 nm to our

knowledge. Seven devices were fabricated with channel width ranging from 30 nm to 370 nm. The electrical properties (mobility, on/off ratio and subthreshold swing) of MoS₂ field-effect transistors (FETs) degrade after nanoribbon formation, while atomic layer deposition passivation improves mobility and on/off ratio but degrades subthreshold swing. One 30-nm-wide monolayer FET achieved a mobility of 8.53 cm²/Vs and an on/off ratio of 2×10⁵, on par with multilayer MoS₂ nanoribbon FETs reported to date.

This study also found cleaning and smoothing the interfaces with contact mode AFM could improve the mobility of hBN encapsulated monolayer MoS₂ FETs. The AFM cleaning process flattened hBN encapsulated monolayer MoS₂ and reduced the photoluminescence peak width of monolayer MoS₂, both of which indicate a reduction in interface traps. The mobility of four hBN encapsulated monolayer MoS₂ FETs increased by an average of 73% from 21.95±2.27 cm²/Vs to 38.03±6.12 cm²/Vs after AFM cleaning.

Finally, this work demonstrated DNA sensing with solid state nanopores integrated with monolayer MoS₂ nanoribbon transistors. Nanopores of 4-10 nm were drilled in ~ 100 nm wide hBN encapsulated monolayer MoS₂ nanoribbons. Translocation of 3kbp dsDNA through a monolayer MoS₂ nanoribbon-nanopore device was detected in ionic channel. Example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current were obtained.

Improved understanding of TBN of polymer nanostructures enhances the reproducibility and scalability of tip-based polymer nanofabrication. Monolayer MoS₂ nanoribbon field-effect transistors can be used as the building block for next generation low-power electronics. MoS₂ FET-nanopore devices could potentially enable fast and cheap DNA sequencing.

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CHAPTER 1: INTRODUCTION

1.1 Introduction

Nanotechnology is the engineering of materials, devices, and systems that have key features of size between 1 and 100 nanometers. Nanotechnology has revolutionized many fields such as digital electronics and biomedical diagnostics by scaling macroscopic devices into the nanometer scale and taking advantage of unique physics and properties at the nanometer scale. Advances in nanotechnology rely on the capability to fabricate nanometer scale structures and devices. The development of unconventional nanolithography techniques opens possibilities to fabricate novel nanodevices with superior performance. Understanding the physical mechanisms of nanolithography allows modeling and control of the nanolithography processes. Improved understanding of nanolithography can in turn be used to prototype novel nanodevices, explore new knowledge in nanotechnology, and ultimately develop new technologies that could potentially impact industries and society. For example, two-dimensional materials-based nanodevices show promise as next-generation alternatives to silicon technology, and nanopore sensors may be able to meet the need for cheaper and faster genome sequencing for personalized medicine.

1.2 Tip-Based Nanolithography

Nanolithography is the process of fabricating structures and devices with dimensions between 1 and 100 nanometers. Nanolithography can be classified into (i) mask-based lithography, such as deep ultraviolet lithography [1], extreme ultraviolet lithography [2], x-ray lithography [3] and nanoimprint lithography [4], and (ii) maskless lithography, such as electron beam lithography

[5], ion beam lithography [6], and tip-based nanolithography [7]. Mask-based lithography techniques are used for high-volume high-throughput production, whereas maskless lithography techniques are used for low-cost low-volume production, mask fabrication, and prototyping of novel devices.

Among maskless lithography techniques, tip-based nanolithography offers a high level of flexibility to process unconventional materials such as small organic molecules [8–10], DNA [11,12], protein [13,14] and novel two-dimensional materials [15–17], and nanometer scale imaging and positioning capabilities [7]. Tip-based nanolithography (TBN) uses a scanning probe to add, remove or modify materials at the tip-substrate interface. The scanning probe can be atomic force microscope (AFM) tip or a scanning tunneling microscope (STM) tip. The TBN patterning process can involve mechanical [18], thermal [19], chemical [20], electrical [7] or other interactions between the probe and the substrate.

One form of TBN is nanomachining, which uses an AFM tip to mechanically scratch a surface [18]. Nanomachining has been applied to remove materials from metals [21], semiconductors [22], polymers [23,24] and self-assembled monolayers [25]. However, the use of nanomachining is limited by lack of reliability due to unpredictable tip wear and tip contamination from debris during lithography [24].

Thermal scanning probe lithography (tSPL) is another form of TBN, which uses thermal decomposition and evaporation to pattern a thermally responsive resist [26]. tSPL could pattern resists at a half pitch down to 10 nm and then transfer the pattern into silicon [19]. Other examples of tSPL include fabrication of contact electrodes to monolayer MoS₂ with vanishing Schottky barriers [27] and fabrication of three-dimensional molecular resists at a resolution of ~15 nm [28]. While the thermal process in tSPL does not induce chemical reactions, thermochemical

nanolithography (TCNL) modifies materials from one chemical state to another via thermally activated chemical reactions localized at a heated tip [20]. Notable examples of TCNL include thermal reduction of graphene oxide into reduced graphene oxide with dimensions down to 12 nm and up to four orders of magnitude improvement in conductivity [29], and direct patterning of organic field-effect transistors by conversion of a precursor material into 70-100 nm wide pentacene nanoribbon array [30].

If the TBN patterning process utilizes an electric field between a conductive scanning probe and a substrate, the TBN method is classified as bias-induced scanning probe lithography (b-SPL). Oxidation scanning probe lithography (o-SPL) is one typical kind of b-SPL [7], in which a nanometer scale water bridge forms between the tip and the substrate, and an oxidation reaction between the tip and the sample surface takes place within the water meniscus. The size of the meniscus determines the resolution of the features obtained by o-SPL. Examples of o-SPL fabricated nanodevices include single-photon detectors [31], single-electron transistors [32], metal-oxide transistors [33], silicon nanowire field-effect transistors [34], graphene devices [35] and MoS₂ and WSe₂ field-effect transistors [15,36]. Other b-SPL examples include patterning of 2 nm organic structures with 6 nm periodicities by electric field induced cross-linking of the octane molecules in air [37], as well as one atom tall four atoms wide silicon wires fabricated by STM [38].

Finally, dip-pen nanolithography (DPN) is an additive form of TBN that uses an AFM tip to directly write inks onto a substrate, analogous to a quill pen writing with ink on paper [39]. Figure 1.1 shows the DPN process. A water meniscus forms between the AFM tip and the solid substrate. Ink molecules on the tip transport to the substrate through the water meniscus by diffusion. The size of the meniscus, which is controlled by relative humidity, affects the ink

transport rate, the effective tip-substrate contact area, and DPN resolution [40]. DPN can handle a wide range of materials from small organic molecules [8–10] to polymers [41,42], DNA [11,12] and proteins [13,14]. Due to its versatility, low-cost and ease of use, DPN has been used to prototype a variety of devices for nanoelectronics [43], chemical sensing [44–46] and biomedical diagnostics [47–50]. Thermal DPN (tDPN), uses an AFM cantilever with an integrated resistive heater at the tip to write inks that are solid at room temperature. During writing, the tip is heated to an elevated temperature, causing the ink to melt and flow onto the surface [51]. Compared with DPN, tDPN offers two main advantages: (i) the ink flow can be turned on and off by raising and lowering tip temperature, whereas DPN applies ink to the surface as long as the tip is engaged on the surface; (ii) the rate of the ink transport can be tuned by controlling the tip temperature.

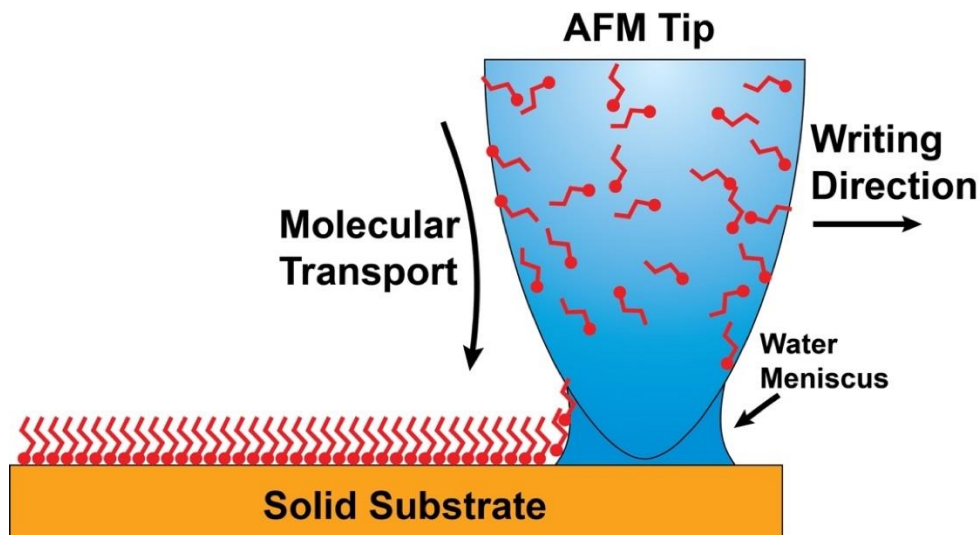


Figure 1.1 Schematic representation of the DPN process. A water meniscus forms between the AFM tip which is coated with “ink” molecules and the solid substrate. Ink molecules on the tip transport to the substrate through the water meniscus by diffusion.

1.3 MoS₂ Transistors

Field-effect transistor (FET) is the basic building block of modern digital circuits [52]. A typical FET consists of a semiconductor channel with electrodes at either end of the channel

referred to as the drain and the source. The channel is covered by a thin dielectric material, the gate dielectric, and capped with a control electrode, the gate. The gate controls the conductivity of the channel by changing the carrier concentration in the channel via electrostatic interactions. A transistor mostly operates as a switch: it is in the off state when the channel conductivity is low, and in the on state when the channel conductivity is high. An ideal transistor should be able to switch between the on and off states with minimal change in the gate electrode.

Silicon technology has evolved over the past five decades by scaling silicon transistors according to Moore's law, which states the number of transistors in a dense integrated circuit doubles about every two years [52]. However, Moore's law is coming to an end as the scaling of silicon transistors approaches its physical limit at 2–3 nm scale [53]. Two-dimensional materials are promising alternatives to silicon as transistor channel materials, as their atomic thickness allows a very high degree of electrostatic control, which is needed to achieve a sharp switching in transistors [54]. One class of two-dimensional (2D) materials is transition metal dichalcogenides (TMDCs), with MoS₂ being the most studied material of TMDCs [55]. MoS₂ has several advantages in device applications, because of its sizable bandgap (1.9 eV for monolayers and 1.29 eV for the bulk [56]), satisfactory electron mobility [57], good thermal stability up to 1,100 °C [58] and superior immunity to short-channel effects [59].

Figure 1.2 shows an example of a top-gated MoS₂ transistor. Figure 1.2(a) shows the schematic of the device structure. The device consists of a monolayer MoS₂ channel, gold electrodes as the source and the drain, HfO₂ as the top gate dielectric and gold on chromium as the top gate. Figure 1.2(b) shows the transfer curves of the device. The device had a high on/off ratio exceeding 10⁸, a low off-state current of 5 fA/μm, and a good subthreshold swing of 74 mV/dec.

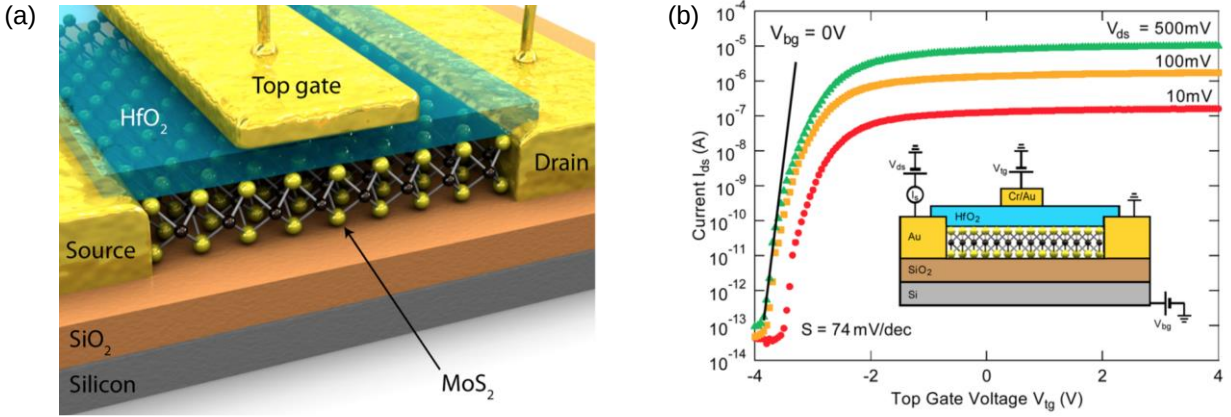


Figure 1.2 Encapsulated single-layer MoS₂ transistor. (a) Schematic of the transistor. The MoS₂ layer is connected by Au leads and encapsulated in 30 nm thick high- κ dielectric HfO₂ as top-gate dielectric. (b) Transfer curves of the device. For $V_{ds} = 500$ mV, the on/off ratio is $>10^8$ and the subthreshold swing $SS = 74$ mV/dec. Inset: Cross-sectional view of MoS₂ FET. [60]

The performance of MoS₂ transistors has been limited by large contact resistance between contact electrodes and MoS₂ [61]. (i) One major source of contact resistance is resist residues at the MoS₂-metal interface resulting from metal deposition with optical lithography [62] or electron beam lithography [27]. Ultra-high-vacuum metal evaporation [63] and thermal scanning probe lithography based fabrication [27] could create a cleaner interface between metals and MoS₂ and thus reduce contact resistance. (ii) Direct deposition of metal can significantly damage MoS₂ via kinetic energy transfer or chemical reaction between the metal atoms and MoS₂, which induces high contact resistance [64]. Monolayer hBN has been used as a tunnel layer to protect MoS₂ from damage and reduce contact resistance [65,66]. Recent use of both transferred electrodes [67] and soft indium contact metal [68] effectively prevented MoS₂ damage during metal deposition and resulted in van der Waals contact between 3D metals and 2D semiconductors. By transferring metal films (silver or platinum) with a work function that matches the conduction band or valence band edges of MoS₂, room-temperature extrinsic electron mobility of 260 cm²/Vs and extrinsic hole mobility of 175 cm²/Vs were achieved for multilayer MoS₂ [67]. With indium/gold electrodes,

a low contact resistance of $3\,000 \pm 300 \, \Omega \, \mu\text{m}$ and a high mobility of $167 \pm 20 \, \text{cm}^2/\text{Vs}$ were achieved for monolayer MoS₂ [68].

Lastly, the intrinsic electron mobilities of monolayer and few-layer MoS₂, excluding the effect of contact resistance, have been substantially below their theoretical phonon-scattering limit [69]. Intrinsic defects such as sulphur vacancies in MoS₂ [70,71] and extrinsic sources of disorders such as surface adsorbates [72] and charged impurities in the substrates [73] have limited the electrical performance of MoS₂. Defects in MoS₂ can be reduced by optimizing chemical vapor deposition growth process of MoS₂ [74] and by chemical repairing such as repairing sulfur vacancies by thiol chemistry [75]. High- κ dielectric and hBN passivation can be used to reduce surface adsorbates and improve the carrier mobility of MoS₂ transistors [60,76,77]. High- κ substrate instead of SiO₂ can reduce the Coulomb impurity scattering by dielectric screening [78], while hBN substrate has fewer charged impurities than oxide substrates [73]. Top and bottom hBN encapsulation has been the most effective way to reduce interface trap and Coulomb impurities [73]. Nevertheless, the density of charged impurities in hBN encapsulated MoS₂ ($\sim 3 \times 10^{11} \, \text{cm}^{-2}$ [69]) is still about one of magnitude higher than that of hBN encapsulated graphene ($\sim 5 \times 10^{10} \, \text{cm}^{-2}$ [79]), indicating that Coulomb impurities in MoS₂ partly come from the channel material itself, such as surface adsorbates and defects [73].

1.4 Nanopore Sensing

Nanopore sensing uses voltage to drive charged macromolecules through a nanopore in a membrane one molecule at a time and monitor how ionic current through the nanopore changes as single molecules pass through it [80]. The ionic current reveals useful information about the structure and dynamic motion of the molecule [81]. For instance, negatively charged DNA

molecules can thread through a nanopore in a membrane under a transmembrane electric field, leading to an observable blockade in the ionic current, as shown in Fig. 1.3.

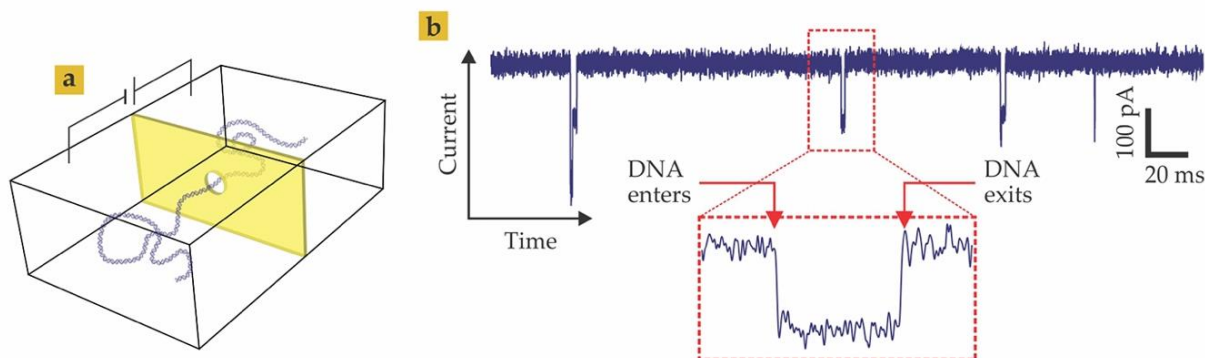


Figure 1.3 Threading DNA through a nanopore. (a) A negatively charged DNA molecule immersed in electrolyte solution can be coaxed through a nanopore by an electric field. (b) Experimental current trace of DNA molecules stochastically captured into a pore. The transiting molecule momentarily blocks the flow of ionic current through the pore by an amount that depends on the volume of the molecule within the pore constriction. [80]

Nanopores can be classified into three categories: biological, solid state, and hybrid. Biological nanopores consist of transmembrane proteins inserted in lipid bilayers. Representative examples of biological nanopores include the protein α -Hemolysin [82], produced by the bacterium *Staphylococcus aureus*, and the protein MspA [83], produced by *Mycobacteria*. α -Hemolysin has a ~ 10 nm long channel with a 1.4 nm wide constriction, and MspA has a 0.6 nm long 1.2 nm wide constriction [84]. Solid-state nanopores are nanometer-scale apertures formed in synthetic membranes. Nanopores can be formed by focused ion or electron beam sculpting [85,86], voltage-induced dielectric breakdown [87], chemical wet etching [88], and electrochemical reaction [89]. Nanopore sizes can be controlled atom by atom starting from sub-nm sizes [89,90] and nanopore geometries can be arbitrarily shaped [91]. Solid state nanopore channels can be functionalized to exhibit selectivity [92]. The membrane may consist of a wide range of materials, from the most commonly used silicon nitride [93] to aluminum oxide [94],

hafnium oxide [95] and atomically thick two-dimensional materials such as graphene [96], boron nitride [97], and molybdenum disulfide [98]. Glass nanocapillaries [99] with tens of nanometers wide tip openings are a variant of solid state nanopores, which are formed by laser glass pulling. Hybrid nanopores can be biological nanopores inserted in solid state nanopores like α -hemolysin proteins in silicon nitride pores [100], or DNA origami structures inserted in solid-state nanopores or lipid bilayers [101–103].

The basic biopolymer translocation process [80] is illustrated in Fig. 1.4. First, a biomolecule drifts into the capture zone by diffusion and then gets pulled toward the pore by electrophoretic force. The radius of the capture zone is defined by the competition between diffusion and electrophoresis and is typically around 1 μm . Second, the biomolecule arrives at the pore entrance as a randomly coiled blob. Third, one end of the strand aligns with the pore entrance and enters the pore, at an entropic cost on the order of $10 k_B T$, where k_B is Boltzmann's constant and T is temperature. Fourth, the strand begins to uncoil as the end moves through the pore, at an entropic cost of 2-3 $k_B T$. Finally, the strand transits the pore through a combination of electrophoretic drift and diffusion.

The capability of nanopores to sense single macromolecules enables a wide range of applications. Application examples include (i) biomedical diagnostic by detecting DNA base modifications such as methylation [104] and hydroxymethylation [105], (ii) protein sensing [106], (iii) RNA sequencing [107], (iv) chemical sensing with functionalized nanopores [108], and (v) biomimetic applications [109,110].

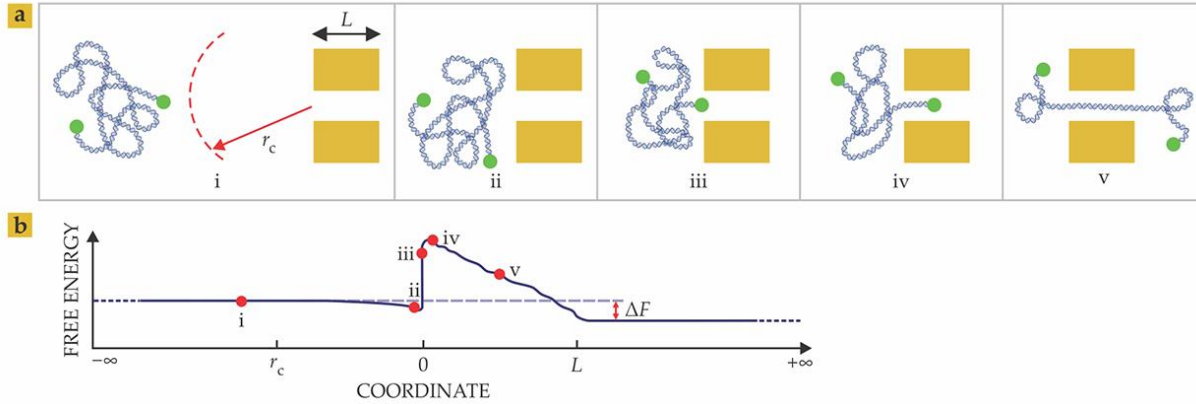


Figure 1.4 (a) The threading of a biopolymer strand through a nanopore of length L : (i) The charged polymer drifts into the capture zone; (ii) the biopolymer arrives at the pore with its ends unregistered with the pore entrance; (iii) one end of the strand aligns with the pore entrance and enters the pore; (iv) the strand begins to uncoil as the end moves through the pore; (v) the strand crosses the pore. (b) Free-energy landscape corresponding to the five stages in (a). ΔF is the net free energy gain by the translocating molecule. [80]

The most widely studied application of nanopores has been direct DNA sequencing [81]. The concept of nanopore sequencing is explained as follows: When a single DNA strand passes through a nanopore, the magnitude of the induced ionic current blockade is approximately proportional to the size of the base occupying the pore. Since the size differences among the four bases (adenine, guanine, cytosine, and thymine) are significant enough to yield current variations of ~ 10 pA in biological pores [111], specific ionic current levels can be associated with specific bases and thus be used to read out DNA sequences. Nanopore DNA sequencing was demonstrated in 2012 using biological nanopores (α -hemolysin [112] and MspA [113]) and then commercialized in 2015 by Oxford Nanopore Technologies. The state-of-the-art nanopore sequencing demonstrated a single-passage read accuracy of 95% [114]. Recent whole-genome sequencing of a human genome using MinION nanopore sequencers achieved an assembly accuracy of 99.8% at $30\times$ coverage, after incorporating complementary short-read sequencing data [115]. Compared with conventional DNA sequencing methods where long strands are fragmented into small pieces

(~ 100 bp) and then independently amplified and analyzed [116], nanopore sequencing can directly read long DNA strands (~ 1 megabase [115]) in a low-cost, high-throughput fashion without labeling or amplification. In addition, the extreme portability of nanopore sequencers enables real-time genomic surveillance of epidemics like Zika [117].

Despite the commercial development of biological nanopore sequencers, current nanopore sequencing technologies still lack the clinical accuracy for single-nucleotide variant calling [118]. Two error modes dominate the single-pass sequencing errors [119]: (i) distinct sequences with indistinguishable ionic signals, as multiple nucleobases in a strand of DNA contribute to each of the measured current levels, and (ii) irregular ratchet steps by the motor enzyme [120] used to slow DNA transport, as enzyme motion is stochastic. Apart from insufficient read accuracy, the use of biological nanopores is also limited by the fragility of lipid bilayers (6-10 hrs' lifetime [121]) and the susceptibility to extreme solution conditions (pH, temperature and salt concentration) [84].

Solid-state nanopores [85] are an inexpensive and versatile alternative to biological nanopores in nanopore sensing, owing to their mechanical, chemical and thermal robustness and durability [94], tunable pore dimensions [86], potential for integration into integrated circuits [122] and compatibility with alternative detection modalities that could improve sensitivity and resolution of nanopore based sequencing [123–126]. However, DNA sequencing with solid state nanopores has not yet been demonstrated, due to limitations in spatial resolution [127] and in temporal resolution [128].

The spatial resolution of a solid-state nanopore depends on the thickness of the membrane, because the measured signal is a convolution of the signals of all bases residing in the pore channel [127]. The thicker the membrane, the more bases would contribute to the detected ionic signal. For example, 10–30 nm thick conventional silicon nitride membrane is about 30–90 times the spacing

between nucleotides ~ 0.34 nm in a DNA molecule, so 30–90 nucleotides would be read simultaneously. Therefore, 2D monolayers of sub-nm thickness are explored to maximize the spatial resolution of nanopore sensing [96,129,130]. Nanopores fabricated in MoS₂ monolayers [98] demonstrated statistical discrimination of all four types of single nucleotides. In practice, the electric field near a pore extends outside the pore for a distance comparable to the diameter of the pore, so even pores in atomically thin membranes will be sensitive to the DNA bases that lie outside the pore on each side [127]. Raw ionic signal must be deconvoluted to recover the actual sequence [131].

The temporal resolution of a solid-state nanopore depends on DNA translocation speed, data sampling rate and the associated current noise level. Larger sampling rate have higher current noise [132]. Typical commercial current amplifiers used in nanopore experiments to measure pA–nA scale current have a bandwidth of 0.1 MHz [133]. Meanwhile, the translocation speed of dsDNA ranges from 0.2 to 50 base pairs per microsecond [80]. Under typical conditions, 2 to 500 bases will thread through a solid-state nanopore in the shortest resolvable time unit. Accordingly, the signal is averaged over 2 to 500 bases, so the sequence information of individual bases is hard to extract. Also, for translocations as fast as the cutoff frequency of the digital low-pass filter, the system will inevitably distort the raw ionic current data [134]. There are two ways to improve the temporal resolution of a solid-state nanopore: (i) increasing measurement bandwidth while reducing the electrical noise [135,136], and (ii) slowing DNA translocation [137]. An integrated complementary metal-oxide-semiconductor (CMOS) amplifier has been demonstrated with low noise recording at a bandwidth of 10 MHz [136]. Strategies for slowing DNA transport include maintaining viscosity or chemical potential gradient across the membrane [98,138,139], increasing DNA-counterion interactions [140] and enhancing DNA-pore interactions [128,141].

Alternative to nanopore ionic current, new readout mechanisms with integrated sensors may achieve the sensitivity and resolution required for nanopore based sequencing [81]. Integrated sensors with solid state nanopores include devices based on tunneling current [126,142] and field-effect transistors [143–145]. Figure 1.5 shows the schematics for these two novel nanopore architectures [81]. A tunneling detector integrated with a solid state nanopore might be able to sequence DNA, because the electrical signatures of A, G, C and T determined by their molecular orbitals are unique [146]. Single-molecule detection of TMP, GMP and CMP by electron tunneling current has been demonstrated with gold nanoelectrodes [142]. For DNA sequencing using a field-effect transistor integrated with a solid state nanopore, the FET signal due to local electric potential change upon DNA translocation can be regarded as a linear amplification of the ionic signal [143]. Thus, the FET signal preserves the base detection capability of the ionic signal with the potential to achieve higher resolution and integration density. Additional studies [147,148] indicate that the FET signal due to base-specific modulation of local density of states of FET nanopore edges could also be used to read DNA sequences.

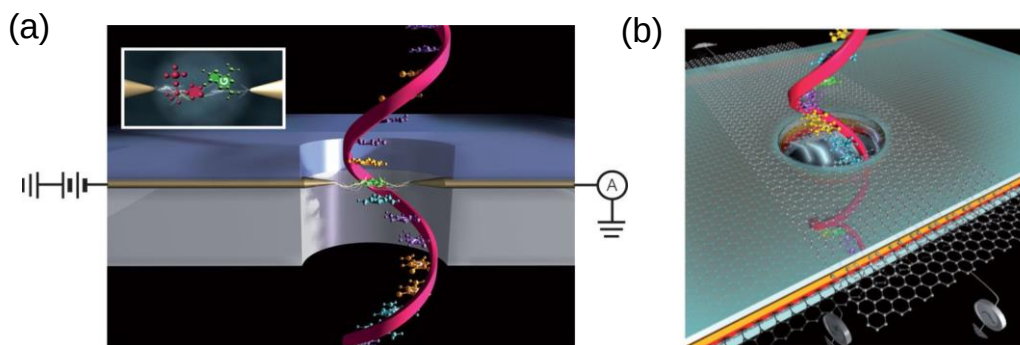


Figure 1.5 Alternative readout mechanisms for sequencing. (a) Schematic of ssDNA passing through a solid-state nanopore with an embedded tunneling detector [142]. Changes in the tunneling current as ssDNA passes through the nanopore could be used to read the sequence of bases in the DNA. Inset: top view showing a nucleotide in the nanogap between the electrodes of the tunneling detector. (b) Schematic of ssDNA passing through a solid-state nanopore a graphene nanoribbon with an embedded graphene gate. The graphene gate could be used to modulate the transverse conductance of the graphene nanoribbon. Changes in graphene current as ssDNA passes through the nanopore could be used to read the sequence of bases in the DNA [147]. [81]

1.5 Dissertation Overview

This dissertation reports the study of tip-based polymer nanostructure fabrication and the application of TBN to fabricate novel MoS₂ devices. The main contributions of this dissertation are (i) understanding the effects of polymer properties and polymer melt flow on feature sizes of polymer nanostructures deposited from a heated tip, (ii) prototyping monolayer MoS₂ nanoribbon transistors using TBN, (iii) improving the mobility of hBN encapsulated monolayer MoS₂ transistors by cleaning and smoothing the interfaces with contact mode atomic force microscopy, and (iv) nanopore sensing of DNA molecules by integrating monolayer MoS₂ nanoribbon transistors with solid state nanopores.

Following this introductory chapter, Chapter 2 investigates the deposition of polymer nanostructures from a heated tip and elucidates the role of capillary-driven flow on deposited feature sizes during tDPN. Chapter 3 reports the fabrication of monolayer MoS₂ nanoribbon FETs as narrow as 30 nm, realized using tDPN. Chapter 4 reports on reducing interface voids and contaminants of hBN encapsulated monolayer MoS₂ by contact mode AFM to improve the electrical performance of monolayer MoS₂. Chapter 5 describes the design and fabrication of hBN encapsulated monolayer MoS₂ nanoribbon FET-nanopore devices for DNA sensing. Finally, Chapter 6 summarizes the main results of this dissertation and discusses future research directions based on the work described in this dissertation.

1.6 References

- [1] Hoffnagle J A, Hinsberg W D, Sanchez M and Houle F A 1999 Liquid Immersion Deep-Ultraviolet Interferometric Lithography *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **17** 3306
- [2] Gwyn C W, Stulen R, Sweeney D and Attwood D 1998 Extreme Ultraviolet Lithography *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **16** 3142
- [3] Smith H I and Schattenburg M L 1993 X-Ray Lithography from 500 to 30 Nm: X-Ray Nanolithography *IBM J. Res. Dev.* **37** 319–29
- [4] Chou S Y, Krauss P R and Renstrom P J 1996 Nanoimprint Lithography *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **14** 4129
- [5] Vieu C, Carcenac F, P épin A, Chen Y, Mejias M, Lebib A, Manin-Ferlazzo L, Couraud L and Launois H 2000 Electron Beam Lithography: Resolution Limits and Applications *Appl. Surf. Sci.* **164** 111–7
- [6] Watt F, Bettiol A A, Van Kan J A, Teo E J and Breese M B H 2005 Ion Beam Lithography and Nanofabrication: A Review *Int. J. Nanosci.* **04** 269–86
- [7] Garcia R, Knoll A W and Riedo E 2014 Advanced Scanning Probe Lithography *Nat. Nanotechnol.* **9** 577–87
- [8] Hong S, Zhu J and Mirkin C A 1999 Multiple Ink Nanolithography: Toward a Multiple-Pen Nano-Plotter *Science* **286** 523–5
- [9] Zhang Y, Salaita K, Lim J H and Mirkin C A 2002 Electrochemical Whittling of Organic Nanostructures *Nano Lett.* **2** 1389–92
- [10] Auletta T, Dordi B, Mulder A, Sartori A, Onclin S, Bruinink C M, P éter M, Nijhuis C A, Beijleveld H, Sch önherr H, Vancso G J, Casnati A, Ungaro R, Ravoo B J, Huskens J and Reinhoudt D N 2004 Writing Patterns of Molecules on Molecular Printboards *Angew. Chemie Int. Ed.* **43** 369–73
- [11] Demers L M, Ginger D S, Park S-J, Li Z, Chung S-W and Mirkin C A 2002 Direct Patterning of Modified Oligonucleotides on Metals and Insulators by Dip-Pen Nanolithography. *Science* **296** 1836–8
- [12] Chung S-W, Ginger D S, Morales M W, Zhang Z, Chandrasekhar V, Ratner M A and Mirkin C A 2005 Top-down Meets Bottom-up: Dip-Pen Nanolithography and DNA-Directed Assembly of Nanoscale Electrical Circuits *Small* **1** 64–9
- [13] Lim J-H, Ginger D S, Lee K-B, Heo J, Nam J-M and Mirkin C A 2003 Direct-Write Dip-Pen Nanolithography of Proteins on Modified Silicon Oxide Surfaces *Angew. Chemie Int. Ed.* **42** 2309–12
- [14] Lee K B, Lim J H and Mirkin C A 2003 Protein Nanostructures Formed via Direct-Write Dip-Pen Nanolithography *J. Am. Chem. Soc.* **125** 5588–9

- [15] Dago A I, Ryu Y K and Garcia R 2016 Sub-20nm Patterning of Thin Layer WSe₂ by Scanning Probe Lithography *Appl. Phys. Lett.* **109** 163103
- [16] Liu X, Chen K-S, Wells S A, Balla I, Zhu J, Wood J D and Hersam M C 2017 Scanning Probe Nanopatterning and Layer-by-Layer Thinning of Black Phosphorus *Adv. Mater.* **29** 1604121
- [17] Chen S, Kim S, Chen W, Yuan J, Bashir R, Lou J, van der Zande A M and King W P 2019 Monolayer MoS₂ Nanoribbon Transistors Fabricated by Scanning Probe Lithography *Nano Lett.* **19** 2092–8
- [18] Tseng A A 2011 Removing Material Using Atomic Force Microscopy with Single- and Multiple-Tip Sources *Small* **7** 3409–27
- [19] Ryu Cho Y K, Rawlings C D, Wolf H, Spieser M, Bisig S, Reidt S, Sousa M, Khanal S R, Jacobs T D B and Knoll A W 2017 Sub-10 Nanometer Feature Size in Silicon Using Thermal Scanning Probe Lithography *ACS Nano* **11** 11890–7
- [20] Szoszkiewicz R, Okada T, Jones S C, Li T De, King W P, Marder S R and Riedo E 2007 High-Speed, Sub-15nm Feature Size Thermochemical Nanolithography *Nano Lett.* **7** 1064–9
- [21] Irmer B, Blick R H, Simmel F, Gödel W, Lorenz H and Kotthaus J P 1998 Josephson Junctions Defined by a Nanoplough *Appl. Phys. Lett.* **73** 2051–3
- [22] Kawasegi N, Takano N, Oka D, Morita N, Yamada S, Kanda K, Takano S, Obata T and Ashida K 2006 Nanomachining of Silicon Surface Using Atomic Force Microscope With Diamond Tip *J. Manuf. Sci. Eng.* **128** 723
- [23] Shim W, Brown K A, Zhou X, Rasin B, Liao X, Schmucker A L and Mirkin C A 2013 Plow and Ridge Nanofabrication *Small* **9** 3058–62
- [24] Liu L, Shi J, Li M, Yu P, Yang T and Li G 2018 Fabrication of Sub-Micrometer-Sized MoS₂ Thin-Film Transistor by Phase Mode AFM Lithography *Small* **14** 1803273
- [25] Xu S, Miller S, Laibinis P E and Liu G 2002 Fabrication of Nanometer Scale Patterns within Self-Assembled Monolayers by Nanografting *Langmuir* **15** 7244–51
- [26] Cheong L L, Paul P, Holzner F, Despont M, Coady D J, Hedrick J L, Allen R, Knoll A W and Duerig U 2013 Thermal Probe Maskless Lithography for 27.5nm Half-Pitch Si Technology *Nano Lett.* **13** 4485–91
- [27] Zheng X, Calò A, Albisetti E, Liu X, Alharbi A S M, Arefe G, Liu X, Spieser M, Yoo W J, Taniguchi T, Watanabe K, Aruta C, Ciarrocchi A, Kis A, Lee B S, Lipson M, Hone J, Shahrjerdi D and Riedo E 2019 Patterning Metal Contacts on Monolayer MoS₂ with Vanishing Schottky Barriers Using Thermal Nanolithography *Nat. Electron.* **2** 17–25
- [28] Pires D, Hedrick J L, De Silva A, Frommer J, Gotsmann B, Wolf H, Despont M, Duerig U and Knoll A W 2010 Nanoscale Three-Dimensional Patterning of Molecular Resists by Scanning Probes *Science* **328** 732–5

- [29] Wei Z, Wang D, Kim S-Y Y S, Kim S-Y Y S, Hu Y, Yakes M K, Laracuenta A R, Dai Z, Marder S R, Berger C, King W P, De Heer W A, Sheehan P E and Riedo E 2010 Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics *Science* **328** 1373–6
- [30] Shaw J E, Stavrinou P N and Anthopoulos T D 2013 On-Demand Patterning of Nanostructured Pentacene Transistors by Scanning Thermal Lithography *Adv. Mater.* **25** 552–8
- [31] Delacour C, Pannetier B, Villegier J-C and Bouchiat V 2012 Quantum and Thermal Phase Slips in Superconducting Niobium Nitride (NbN) Ultrathin Crystalline Nanowire: Application to Single Photon Detection *Nano Lett.* **12** 3501–6
- [32] Matsumoto K, Gotoh Y, Maeda T, Dagata J A and Harris J S 2000 Room-Temperature Single-Electron Memory Made by Pulse-Mode Atomic Force Microscopy Nano Oxidation Process on Atomically Flat α -Alumina Substrate *Appl. Phys. Lett.* **76** 239–41
- [33] Snow E S and Campbell P M 1995 AFM Fabrication of Sub-10-Nanometer Metal-Oxide Devices with in Situ Control of Electrical Properties *Science* **270** 1639–41
- [34] Mart ínez R V., Mart ínez J and Garcia R 2010 Silicon Nanowire Circuits Fabricated by AFM Oxidation Nanolithography *Nanotechnology* **21** 245301
- [35] Masubuchi S, Arai M and Machida T 2011 Atomic Force Microscopy Based Tunable Local Anodic Oxidation of Graphene *Nano Lett.* **11** 4542–6
- [36] Espinosa F M, Ryu Y K, Marinov K, Dumcenco D, Kis A and Garcia R 2015 Direct Fabrication of Thin Layer MoS₂ Field-Effect Nanoscale Transistors by Oxidation Scanning Probe Lithography *Appl. Phys. Lett.* **106** 103503
- [37] Mart ínez R V., Losilla N S, Mart ínez J, Huttel Y and Garcia R 2007 Patterning Polymeric Structures with 2nm Resolution at 3nm Half Pitch in Ambient Conditions *Nano Lett.* **7** 1846–50
- [38] Weber B, Mahapatra S, Ryu H, Lee S, Fuhrer A, Reusch T C G, Thompson D L, Lee W C T, Klimeck G, Hollenberg L C L and Simmons M Y 2012 Ohm’s Law Survives to the Atomic Scale *Science* **335** 64–7
- [39] Piner R D, Zhu J, Xu F, Hong S and Mirkin C A 1999 “Dip-Pen” Nanolithography *Science* **283** 661–3
- [40] Brown K A, Eichelsdoerfer D J, Liao X, He S and Mirkin C A 2014 Material Transport in Dip-Pen Nanolithography *Front. Phys.* **9** 385–97
- [41] Chai J, Huo F, Zheng Z, Giam L R, Shim W and Mirkin C A 2010 Scanning Probe Block Copolymer Lithography. *Proc. Natl. Acad. Sci. U. S. A.* **107** 20202–6
- [42] McKendry R, Huck W T S, Weeks B, Fiorini M, Abell C and Rayment T 2002 Creating Nanoscale Patterns of Dendrimers on Silicon Surfaces with Dip-Pen Nanolithography *Nano Lett.* **2** 713–6

- [43] Shin Y-S, Son J Y, Jo M-H, Shin Y-H and Jang H M 2011 High-Mobility Graphene Nanoribbons Prepared Using Polystyrene Dip-Pen Nanolithography *J. Am. Chem. Soc.* **133** 5623–5
- [44] Su M, Li S and Dravid V P 2003 Miniaturized Chemical Multiplexed Sensor Array *J. Am. Chem. Soc.* **125** 9930–1
- [45] Tang Q and Shi S-Q 2008 Preparation of Gas Sensors via Dip-Pen Nanolithography *Sensors Actuators B Chem.* **131** 379–83
- [46] Martínez-Otero A, González-Monje P, MasPOCH D, Hernando J and Ruiz-Molina D 2011 Multiplexed Arrays of Chemosensors by Parallel Dip-Pen Nanolithography *Chem. Commun.* **47** 6864
- [47] Lee K B, Kim E Y, Mirkin C A and Wolinsky S M 2004 The Use of Nanoarrays for Highly Sensitive and Selective Detection of Human Immunodeficiency Virus Type 1 in Plasma *Nano Lett.* **4** 1869–72
- [48] Sekula S, Fuchs J, Weg-Remers S, Nagel P, Schuppler S, Fragala J, Theilacker N, Franzreb M, Wingren C, Ellmark P, Borrebaeck C A K, Mirkin C A, Fuchs H and Lenhert S 2008 Multiplexed Lipid Dip-Pen Nanolithography on Subcellular Scales for the Templating of Functional Proteins and Cell Culture *Small* **4** 1785–93
- [49] Mitsakakis K, Sekula-Neuner S, Lenhert S, Fuchs H and Gizeli E 2012 Convergence of Dip-Pen Nanolithography and Acoustic Biosensors towards a Rapid-Analysis Multi-Sample Microsystem *Analyst* **137** 3076
- [50] Hirtz M, Brglez J, Fuchs H and Niemeyer C M 2015 Selective Binding of DNA Origami on Biomimetic Lipid Patches *Small* **11** 5752–8
- [51] Sheehan P E, Whitman L J, King W P and Nelson B A 2004 Nanoscale Deposition of Solid Inks via Thermal Dip Pen Nanolithography *Appl. Phys. Lett.* **85** 1589–91
- [52] Streetman B G and Banerjee S 2015 Solid State Electronic Devices (Pearson)
- [53] Waldrop M M 2016 The Chips Are down for Moore’s Law *Nature* **530** 144–7
- [54] Lembke D, Bertolazzi S and Kis A 2015 Single-Layer MoS₂ Electronics *Acc. Chem. Res.* **48** 100–10
- [55] Manzeli S, Ovchinnikov D, Pasquier D, Yazyev O V. and Kis A 2017 2D Transition Metal Dichalcogenides *Nat. Rev. Mater.* **2** 17033
- [56] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically Thin MoS₂: A New Direct-Gap Semiconductor *Phys. Rev. Lett.*
- [57] Kaasbjerg K, Thygesen K S and Jacobsen K W 2012 Phonon-Limited Mobility in n-Type Single-Layer MoS₂ from First Principles *Phys. Rev. B - Condens. Matter Mater. Phys.* **85** 115317
- [58] Spalvins T 1987 A Review of Recent Advances in Solid Film Lubrication *J. Vac. Sci.*

- [59] Desai S B, Madhvapathy S R, Sachid A B, Llinas J P, Wang Q, Ahn G H, Pitner G, Kim M J, Bokor J, Hu C, Wong H-S P and Javey A 2016 MoS₂ Transistors with 1-Nanometer Gate Lengths *Science* **354** 99–102
- [60] Radisavljevic B, Radenovic A, Brivio J, Giacometti i V, Kis A, Giacometti V and Kis A 2011 Single-Layer MoS₂ Transistors *Nat. Nanotechnol.* **6** 147–50
- [61] Allain A, Kang J, Banerjee K and Kis A 2015 Electrical Contacts to Two-Dimensional Semiconductors *Nat. Mater.* **14** 1195–205
- [62] Shao P-Z, Zhao H-M, Cao H-W, Wang X-F, Pang Y, Li Y-X, Deng N-Q, Zhang J, Zhang G-Y, Yang Y, Zhang S and Ren T-L 2016 Enhancement of Carrier Mobility in MoS₂ Field Effect Transistors by a SiO₂ Protective Layer *Appl. Phys. Lett.* **108** 203105
- [63] English C D, Shine G, Dorgan V E, Saraswat K C and Pop E 2016 Improved Contacts to MoS₂ Transistors by Ultra-High Vacuum Metal Deposition *Nano Lett.* **16** 3824–30
- [64] Kim C, Moon I, Lee D, Choi M S, Ahmed F, Nam S, Cho Y, Shin H-J, Park S and Yoo W J 2017 Fermi Level Pinning at Electrical Metal Contacts of Monolayer Molybdenum Dichalcogenides *ACS Nano* **11** 1588–96
- [65] Wang J, Yao Q, Huang C-W, Zou X, Liao L, Chen S, Fan Z, Zhang K, Wu W, Xiao X, Jiang C and Wu W-W 2016 High Mobility MoS₂ Transistor with Low Schottky Barrier Contact by Using Atomic Thick h-BN as a Tunneling Layer *Adv. Mater.* **28** 8302–8
- [66] Cui X, Shih E-M, Jauregui L A, Chae S H, Kim Y D, Li B, Seo D, Pistunova K, Yin J, Park J-H, Choi H-J, Lee Y H, Watanabe K, Taniguchi T, Kim P, Dean C R and Hone J C 2017 Low-Temperature Ohmic Contact to Monolayer MoS₂ by van Der Waals Bonded Co/ h -BN Electrodes *Nano Lett.* **17** 4781–6
- [67] Liu Y, Guo J, Zhu E, Liao L, Lee S-J, Ding M, Shakir I, Gambin V, Huang Y and Duan X 2018 Approaching the Schottky–Mott Limit in van Der Waals Metal–Semiconductor Junctions *Nature* **557** 696–700
- [68] Wang Y, Kim J C, Wu R J, Martinez J, Song X, Yang J, Zhao F, Mkhoyan A, Jeong H Y and Chhowalla M 2019 Van Der Waals Contacts between Three-Dimensional Metals and Two-Dimensional Semiconductors *Nature* **568** 70–4
- [69] Cui X, Lee G-H, Kim Y D, Arefe G, Huang P Y, Lee C-H, Chenet D A, Zhang X, Wang L, Ye F, Pizzocchero F, Jessen B S, Watanabe K, Taniguchi T, Muller D A, Low T, Kim P and Hone J 2015 Multi-Terminal Transport Measurements of MoS₂ Using a van Der Waals Heterostructure Device Platform *Nat. Nanotechnol.* **10** 534–40
- [70] Roy S, Choi W, Jeon S, Kim D-H, Kim H, Yun S J, Lee Y, Lee J, Kim Y-M and Kim J 2018 Atomic Observation of Filling Vacancies in Monolayer Transition Metal Sulfides by Chemically Sourced Sulfur Atoms *Nano Lett.* **18** 4523–30
- [71] Qiu H, Xu T, Wang Z, Ren W, Nan H, Ni Z, Chen Q, Yuan S, Miao F, Song F, Long G,

- Shi Y, Sun L, Wang J and Wang X 2013 Hopping Transport through Defect-Induced Localized States in Molybdenum Disulphide *Nat. Commun.* **4** 2642
- [72] Ahn J-H, Parkin W M, Naylor C H, Johnson A T C and Drndić M 2017 Ambient Effects on Electrical Characteristics of CVD-Grown Monolayer MoS₂ Field-Effect Transistors *Sci. Rep.* **7** 4075
- [73] Yu Z, Ong Z-Y, Li S, Xu J-B, Zhang G, Zhang Y-W, Shi Y and Wang X 2017 Analyzing the Carrier Mobility in Transition-Metal Dichalcogenide MoS₂ Field-Effect Transistors *Adv. Funct. Mater.* **27** 1604093
- [74] Chen W, Zhao J, Zhang J, Gu L, Yang Z, Li X, Yu H, Zhu X, Yang R, Shi D, Lin X, Guo J, Bai X and Zhang G 2015 Oxygen-Assisted Chemical Vapor Deposition Growth of Large Single-Crystal and High-Quality Monolayer MoS₂ *J. Am. Chem. Soc.* **137** 15632–5
- [75] Yu Z, Pan Y, Shen Y, Wang Z, Ong Z-Y, Xu T, Xin R, Pan L, Wang B, Sun L, Wang J, Zhang G, Zhang Y W, Shi Y and Wang X 2014 Towards Intrinsic Charge Transport in Monolayer Molybdenum Disulfide by Defect and Interface Engineering *Nat. Commun.* **5** 5290
- [76] Kim S Y, Park S and Choi W 2016 Enhanced Carrier Mobility of Multilayer MoS₂ Thin-Film Transistors by Al₂O₃ Encapsulation *Appl. Phys. Lett.* **109** 152101
- [77] Zou X, Huang C-W, Wang L, Yin L-J, Li W, Wang J, Wu B, Liu Y, Yao Q, Jiang C, Wu W-W, He L, Chen S, Ho J C and Liao L 2016 Dielectric Engineering of a Boron Nitride/Hafnium Oxide Heterostructure for High-Performance 2D Field Effect Transistors *Adv. Mater.* **28** 2062–9
- [78] Yu Z, Ong Z Y, Pan Y, Cui Y, Xin R, Shi Y, Wang B, Wu Y, Chen T, Zhang Y W, Zhang G and Wang X 2016 Realization of Room-Temperature Phonon-Limited Carrier Transport in Monolayer MoS₂ by Dielectric and Carrier Screening *Adv. Mater.* **28** 547–52
- [79] Yamoah M A, Yang W, Pop E and Goldhaber-Gordon D 2017 High-Velocity Saturation in Graphene Encapsulated by Hexagonal Boron Nitride *ACS Nano* **11** 9914–9
- [80] Muthukumar M, Plesa C and Dekker C 2015 Single-Molecule Sensing with Nanopores *Phys. Today* **68** 40–6
- [81] Venkatesan B M and Bashir R 2011 Nanopore Sensors for Nucleic Acid Analysis *Nat. Nanotechnol.* **6** 615–24
- [82] Kasianowicz J J, Brandin E, Branton D and Deamer D W 1996 Characterization of Individual Polynucleotide Molecules Using a Membrane Channel *Proc. Natl. Acad. Sci. U. S. A.* **93** 13770–3
- [83] Derrington I M, Butler T Z, Collins M D, Manrao E, Pavlenok M, Niederweis M and Gundlach J H 2010 Nanopore DNA Sequencing with MspA *Proc. Natl. Acad. Sci. U. S. A.* **107** 16060–5
- [84] Haque F, Li J, Wu H-C, Liang X-J and Guo P 2013 Solid-State and Biological Nanopore

for Real-Time Sensing of Single Chemical and Sequencing of DNA *Nano Today* **8** 56–74

- [85] Li J, Stein D, McMullan C, Branton D, Aziz M J and Golovchenko J A 2001 Ion-Beam Sculpting at Nanometre Length Scales *Nature* **412** 166–9
- [86] Storm A J, Chen J H, Ling X S, Zandbergen H W and Dekker C 2003 Fabrication of Solid-State Nanopores with Single-Nanometre Precision *Nat. Mater.* **2** 537–40
- [87] Kwok H, Briggs K and Tabard-Cossa V 2014 Nanopore Fabrication by Controlled Dielectric Breakdown ed A Hall *PLoS One* **9** e92880
- [88] Park S R, Peng H and Ling X S 2007 Fabrication of Nanopores in Silicon Chips Using Feedback Chemical Etching *Small* **3** 116–9
- [89] Feng J, Liu K, Graf M, Lihter M, Bulushev R D, Dumcenco D, Alexander D T L, Krasnozhan D, Vuletic T, Kis A and Radenovic A 2015 Electrochemical Reaction in Single Layer MoS₂ : Nanopores Opened Atom by Atom *Nano Lett.* **15** 3431–8
- [90] Feng J, Liu K, Graf M, Dumcenco D, Kis A, Di Ventra M and Radenovic A 2016 Observation of Ionic Coulomb Blockade in Nanopores *Nat. Mater.* **15** 850–5
- [91] Liu K, Lihter M, Sarathy A, Caneva S, Qiu H, Deiana D, Tileli V, Alexander D T L, Hofmann S, Dumcenco D, Kis A, Leburton J-P and Radenovic A 2017 Geometrical Effect in 2D Nanopores *Nano Lett.* **17** 4223–30
- [92] Iqbal S M, Akin D and Bashir R 2007 Solid-State Nanopore Channels with DNA Selectivity *Nat. Nanotechnol.* **2** 243–8
- [93] Li J, Gershow M, Stein D, Brandin E and Golovchenko J A 2003 DNA Molecules and Configurations in a Solid-State Nanopore Microscope *Nat. Mater.* **2** 611–5
- [94] Venkatesan B M, Dorvel B, Yemenicioglu S, Watkins N, Petrov I and Bashir R 2009 DNA Sensors: Highly Sensitive, Mechanically Stable Nanopore Sensors for DNA Analysis *Adv. Mater.* **21** 2771–6
- [95] Larkin J, Henley R, Bell D C, Cohen-Karni T, Rosenstein J K and Wanunu M 2013 Slow DNA Transport through Nanopores in Hafnium Oxide Membranes *ACS Nano* **7** 10121–8
- [96] Garaj S, Hubbard W, Reina A, Kong J, Branton D and Golovchenko J A 2010 Graphene as a Subnanometre Trans-Electrode Membrane *Nature* **467** 190–3
- [97] Liu S, Lu B, Zhao Q, Li J, Gao T, Chen Y, Zhang Y, Liu Z, Fan Z, Yang F, You L and Yu D 2013 Boron Nitride Nanopores: Highly Sensitive DNA Single-Molecule Detectors *Adv. Mater.* **25** 4549–54
- [98] Feng J, Liu K, Bulushev R D, Khlybov S, Dumcenco D, Kis A and Radenovic A 2015 Identification of Single Nucleotides in MoS₂ Nanopores *Nat. Nanotechnol.* **10** 1070–6
- [99] Steinbock L J, Otto O, Chimere C, Gornall J and Keyser U F 2010 Detecting DNA Folding with Nanocapillaries *Nano Lett.* **10** 2493–7

- [100] Hall A R, Scott A, Rotem D, Mehta K K, Bayley H and Dekker C 2010 Hybrid Pore Formation by Directed Insertion of α -Haemolysin into Solid-State Nanopores *Nat. Nanotechnol.* **5** 874–7
- [101] Wei R, Martin T G, Rant U and Dietz H 2012 DNA Origami Gatekeepers for Solid-State Nanopores *Angew. Chemie Int. Ed.* **51** 4864–7
- [102] Bell N A W, Engst C R, Ablay M, Divitini G, Ducati C, Liedl T and Keyser U F 2012 DNA Origami Nanopores *Nano Lett.* **12** 512–7
- [103] Langecker M, Arnaut V, Martin T G, List J, Renner S, Mayer M, Dietz H and Simmel F C 2012 Synthetic Lipid Membrane Channels Formed by Designed DNA Nanostructures. *Science* **338** 932–6
- [104] Shim J, Humphreys G I, Venkatesan B M, Munz J M, Zou X, Sathe C, Schulten K, Kosari F, Nardulli A M, Vasmatazis G and Bashir R 2013 Detection and Quantification of Methylation in DNA Using Solid-State Nanopores *Sci. Rep.* **3** 1389
- [105] Wanunu M, Cohen-Karni D, Johnson R R, Fields L, Benner J, Peterman N, Zheng Y, Klein M L and Drndic M 2011 Discrimination of Methylcytosine from Hydroxymethylcytosine in DNA Molecules *J. Am. Chem. Soc.* **133** 486–92
- [106] Bell N A W and Keyser U F 2016 Digitally Encoded DNA Nanostructures for Multiplexed, Single-Molecule Protein Sensing with Nanopores *Nat. Nanotechnol.* **11** 645–51
- [107] Garalde D R, Snell E A, Jachimowicz D, Sipos B, Lloyd J H, Bruce M, Pantic N, Admassu T, James P, Warland A, Jordan M, Ciccone J, Serra S, Keenan J, Martin S, McNeill L, Wallace E J, Jayasinghe L, Wright C, Blasco J, Young S, Brocklebank D, Juul S, Clarke J, Heron A J and Turner D J 2018 Highly Parallel Direct RNA Sequencing on an Array of Nanopores *Nat. Methods* **15** 201–6
- [108] Haque F, Lunn J, Fang H, Smithrud D and Guo P 2012 Real-Time Sensing and Discrimination of Single Chemicals Using the Channel of Phi29 DNA Packaging Nanomotor *ACS Nano* **6** 3251–61
- [109] Kowalczyk S W, Kapinos L, Blosser T R, Magalhães T, van Nies P, Lim R Y H and Dekker C 2011 Single-Molecule Transport across an Individual Biomimetic Nuclear Pore Complex *Nat. Nanotechnol.* **6** 433–8
- [110] Yusko E C, Johnson J M, Majd S, Prangkio P, Rollings R C, Li J, Yang J and Mayer M 2011 Controlling Protein Translocation through Nanopores with Bio-Inspired Fluid Walls *Nat. Nanotechnol.* **6** 253–60
- [111] Church G, Deamer D W, Branton D, Baldarelli R and Kasianowicz J 1998 Characterization of Individual Polymer Molecules Based on Monomer-Interface Interactions
- [112] Cherf G M, Lieberman K R, Rashid H, Lam C E, Karplus K and Akeson M 2012 Automated Forward and Reverse Ratcheting of DNA in a Nanopore at 5-Å Precision *Nat.*

- [113] Manrao E A, Derrington I M, Laszlo A H, Langford K W, Hopper M K, Gillgren N, Pavlenok M, Niederweis M and Gundlach J H 2012 Reading DNA at Single-Nucleotide Resolution with a Mutant MspA Nanopore and Phi29 DNA Polymerase *Nat. Biotechnol.* **30** 349–53
- [114] Volden R, Palmer T, Byrne A, Cole C, Schmitz R J, Green R E and Vollmers C 2018 Improving Nanopore Read Accuracy with the R2C2 Method Enables the Sequencing of Highly Multiplexed Full-Length Single-Cell CDNA. *Proc. Natl. Acad. Sci. U. S. A.* **115** 9726–31
- [115] Jain M, Koren S, Miga K H, Quick J, Rand A C, Sasani T A, Tyson J R, Beggs A D, Dilthey A T, Fiddes I T, Malla S, Marriott H, Nieto T, O’Grady J, Olsen H E, Pedersen B S, Rhie A, Richardson H, Quinlan A R, Snutch T P, Tee L, Paten B, Phillippy A M, Simpson J T, Loman N J and Loose M 2018 Nanopore Sequencing and Assembly of a Human Genome with Ultra-Long Reads *Nat. Biotechnol.* **36** 338–45
- [116] Shendure J, Balasubramanian S, Church G M, Gilbert W, Rogers J, Schloss J A and Waterston R H 2017 DNA Sequencing at 40: Past, Present and Future *Nature* **550** 345–53
- [117] Quick J, Loman N J, Duraffour S, Simpson J T, Severi E, Cowley L, Bore J A, Koundouno R, Dudas G, Mikhail A, Ou édraogo N, Afrough B, Bah A, Baum J H J, Becker-Ziaja B, Boettcher J P, Cabeza-Cabrero M, Camino-S áchez Á, Carter L L, Doerrbecker J, Enkirch T, Dorival I G-, Hetzelt N, Hinzmann J, Holm T, Kafetzopoulou L E, Koropogui M, Kosgey A, Kuisma E, Logue C H, Mazzarelli A, Meisel S, Mertens M, Michel J, Ngabo D, Nitzsche K, Pallasch E, Patrono L V, Portmann J, Repits J G, Rickett N Y, Sachse A, Singethan K, Vitoriano I, Yemanaberhan R L, Zekeng E G, Racine T, Bello A, Sall A A, Faye O, Faye O, Magassouba N, Williams C V., Amburgey V, Winona L, Davis E, Gerlach J, Washington F, Monteil V, Jourdain M, Bererd M, Camara A, Somlare H, Camara A, Gerard M, Bado G, Baillet B, Delaune D, Nebie K Y, Diarra A, Savane Y, Pallawo R B, Gutierrez G J, Milhano N, Roger I, Williams C J, Yattara F, Lewandowski K, Taylor J, Rachwal P, J. Turner D, Pollakis G, Hiscox J A, Matthews D A, Shea M K O, Johnston A M, Wilson D, Hutley E, Smit E, Di Caro A, W äfel R, Stoecker K, Fleischmann E, Gabriel M, Weller S A, Koivogui L, Diallo B, Ke ãa S, et al 2016 Real-Time, Portable Genome Sequencing for Ebola Surveillance *Nature* **530** 228–32
- [118] Peters B A, Kermani B G, Sparks A B, Alferov O, Hong P, Alexeev A, Jiang Y, Dahl F, Tang Y T, Haas J, Robasky K, Zaranek A W, Lee J-H, Ball M P, Peterson J E, Perazich H, Yeung G, Liu J, Chen L, Kennemer M I, Pothuraju K, Konvicka K, Tsoupko-Sitnikov M, Pant K P, Ebert J C, Nilsen G B, Baccash J, Halpern A L, Church G M and Drmanac R 2012 Accurate Whole-Genome Sequencing and Haplotyping from 10 to 20 Human Cells *Nature* **487** 190–5
- [119] Deamer D, Akeson M and Branton D 2016 Three Decades of Nanopore Sequencing *Nat. Biotechnol.* **34** 518–24
- [120] Lieberman K R, Cherf G M, Doody M J, Olasagasti F, Kolodji Y and Akeson M 2010 Processive Replication of Single DNA Molecules in a Nanopore Catalyzed by Phi29 DNA

Polymerase *J. Am. Chem. Soc.* **132** 17961–72

- [121] Venkatesan B M, Polans J, Comer J, Sridhar S, Wendell D, Aksimentiev A and Bashir R 2011 Lipid Bilayer Coated Al₂O₃ Nanopore Sensors: Towards a Hybrid Biological Solid-State Nanopore *Biomed. Microdevices* **13** 671–82
- [122] Uddin A, Yemenicioglu S, Chen C H, Corigliano E, Milaninia K and Theogarajan L 2013 Integration of Solid-State Nanopores in a 0.5 µm CMOS Foundry Process *Nanotechnology* **24** 155501
- [123] Gracheva M E, Xiong A, Aksimentiev A, Schulten K, Timp G and Leburton J-P 2006 Simulation of the Electric Response of DNA Translocation through a Semiconductor Nanopore–Capacitor *Nanotechnology* **17** 622–33
- [124] Girdhar A, Sathe C, Schulten K and Leburton J-P 2013 Graphene Quantum Point Contact Transistor for DNA Sensing *Proc. Natl. Acad. Sci. U. S. A.* **110** 16748–53
- [125] Lagerqvist J, Zwolak M and Di Ventra M 2006 Fast DNA Sequencing via Transverse Electronic Transport *Nano Lett.* **6** 779–82
- [126] Ivanov A P, Instuli E, McGilvery C M, Baldwin G, McComb D W, Albrecht T and Edel J B 2011 DNA Tunneling Detector Embedded in a Nanopore *Nano Lett.* **11** 279–85
- [127] Lindsay S 2016 The Promises and Challenges of Solid-State Sequencing *Nat. Nanotechnol.* **11** 109–11
- [128] Banerjee S, Wilson J, Shim J, Shankla M, Corbin E A, Aksimentiev A and Bashir R 2015 Slowing DNA Transport Using Graphene-DNA Interactions *Adv. Funct. Mater.* **25** 936–46
- [129] Schneider G F, Kowalczyk S W, Calado V E, Pandraud G, Zandbergen H W, Vandersypen L M K and Dekker C 2010 DNA Translocation through Graphene Nanopores *Nano Lett.* **10** 3163–7
- [130] Merchant C A, Healy K, Wanunu M, Ray V, Peterman N, Bartel J, Fischbein M D, Venta K, Luo Z, Johnson A T C and Drndić M 2010 DNA Translocation through Graphene Nanopores *Nano Lett.* **10** 2915–21
- [131] Jain M, Fiddes I T, Miga K H, Olsen H E, Paten B and Akeson M 2015 Improved Data Analysis for the MinION Nanopore Sequencer *Nat. Methods* **12** 351–6
- [132] Edel J B and Albrecht T 2013 Engineered Nanopores for Bioanalytical Applications: A Volume in Micro and Nano Technologies (William Andrew)
- [133] Graf M, Lihter M, Thakur M, Georgiou V, Topolancik J, Ilic B R, Liu K, Feng J, Astier Y and Radenovic A 2019 Fabrication and Practical Applications of Molybdenum Disulfide Nanopores *Nat. Protoc.* **14** 1130–68
- [134] Larkin J, Henley R Y, Muthukumar M, Rosenstein J K and Wanunu M 2014 High-Bandwidth Protein Analysis Using Solid-State Nanopores *Biophys. J.* **106** 696–704

- [135] Balan A, Machielse B, Niedzwiecki D, Lin J, Ong P, Engelke R, Shepard K L and Drndić M 2014 Improving Signal-to-Noise Performance for DNA Translocation in Solid-State Nanopores at MHz Bandwidths *Nano Lett.* **14** 7215–20
- [136] Shekar S, Niedzwiecki D J, Chien C-C, Ong P, Fleischer D A, Lin J, Rosenstein J K, Drndić M and Shepard K L 2016 Measurement of DNA Translocation Dynamics in a Solid-State Nanopore at 100ns Temporal Resolution *Nano Lett.* **16** 4483–9
- [137] Fologea D, Uplinger J, Thomas B, McNabb D S and Li J 2005 Slowing DNA Translocation in a Solid-State Nanopore *Nano Lett.* **5** 1734–7
- [138] Luan B and Zhou R 2018 Spontaneous Transport of Single-Stranded DNA through Graphene–MoS₂ Heterostructure Nanopores *ACS Nano* **12** 3886–91
- [139] He Y, Tsutsui M, Scheicher R H, Fan C, Taniguchi M and Kawai T 2013 Mechanism of How Salt-Gradient-Induced Charges Affect the Translocation of DNA Molecules through a Nanopore *Biophys. J.* **105** 776–82
- [140] Goto Y, Yanagi I, Matsui K, Yokoi T and Takeda K 2018 Identification of Four Single-Stranded DNA Homopolymers with a Solid-State Nanopore in Alkaline CsCl Solution *Nanoscale* **10** 20844–50
- [141] Krishnakumar P, Gyarfas B, Song W, Sen S, Zhang P, Krstić P and Lindsay S 2013 Slowing DNA Translocation through a Nanopore Using a Functionalized Electrode *ACS Nano* **7** 10319–26
- [142] Tsutsui M, Taniguchi M, Yokota K and Kawai T 2010 Identifying Single Nucleotides by Tunnelling Current *Nat. Nanotechnol.* **5** 286–90
- [143] Xie P, Xiong Q, Fang Y, Qing Q and Lieber C M 2012 Local Electrical Potential Detection of DNA by Nanowire-Nanopore Sensors *Nat. Nanotechnol.* **7** 119–25
- [144] Traversi F, Raillon C, Benameur S M, Liu K, Khlybov S, Tosun M, Krasnozhan D, Kis A and Radenovic A 2013 Detecting the Translocation of DNA through a Nanopore Using Graphene Nanoribbons *Nat. Nanotechnol.* **8** 939–45
- [145] Heerema S J, Vicarelli L, Pud S, Schouten R N, Zandbergen H W and Dekker C 2018 Probing DNA Translocations with Inplane Current Signals in a Graphene Nanoribbon with a Nanopore *ACS Nano* **12** 2623–33
- [146] Zwolak M and Di Ventra M 2005 Electronic Signature of DNA Nucleotides via Transverse Transport *Nano Lett.* **5** 421–4
- [147] Nelson T, Zhang B and Prezhdo O V. 2010 Detection of Nucleic Acids with Graphene Nanopores: Ab Initio Characterization of a Novel Sequencing Device *Nano Lett.* **10** 3237–42
- [148] Farimani A B, Min K and Aluru N R 2014 DNA Base Detection Using a Single-Layer MoS₂ *ACS Nano* **8** 7914–22

CHAPTER 2: NANOMETER-SCALE CAPILLARY-DRIVEN FLOW GOVERNS POLYMER NANOSTRUCTURE DEPOSITION FROM A HEATED TIP

2.1 Introduction

Polymer nanostructures are important for nanoelectronics [1], organic electronics [2], wearable electronics [3], and biosensing [4]. One method for fabricating polymer nanostructures is dip-pen nanolithography (DPN), which is a nanofabrication technique that can produce sub-100 nm patterns of polymers [5,6], DNA [7,8], proteins [9,10] and small organic molecules [11–13]. In DPN, an atomic force microscope (AFM) tip directly writes inks onto a substrate [14]. Due to its versatility, low-cost and ease of use, DPN has been used to prototype a variety of devices for nanoelectronics [15], chemical sensing [16–18] and biomedical diagnostics [19–22]. Thermal DPN (tDPN), uses an AFM cantilever with an integrated resistive heater at the tip to write inks that are solid at room temperature. During writing, the tip is heated to an elevated temperature, causing the ink to melt and flow onto the surface [23]. tDPN is well suited for fabricating polymer nanostructures, because the tip temperature offers precise control over feature size and deposition rate [24,25]. tDPN can fabricate polymer nanostructures that have electrical or chemical functions [26,27] or that can be used as a masking layer for further nanofabrication [28,29].

Despite a number of publications that describe the applications of polymer nanostructures [30], only a few publications investigate the underlying physics of polymer ink transport during nanofabrication. The lack of understanding of ink transport mechanisms limits the reproducibility

and scalability of polymer nanofabrication. Experimental studies found that ink viscosity [31,32], surface energy [31,33], Laplace pressure within the polymer [31], and thermo-Marangoni effects [31] all play important roles in polymer ink transport. One study analyzed the mechanical forces that cause flow from the tip to the substrate, and found that both Laplace pressure forces and thermo-Marangoni forces are likely to drive polymer flow [31]. Despite these efforts to understand the mechanisms that underlie the transport of polymer inks, there remains a lack of understanding how the size and shape of the deposited polymer nanostructures depends upon polymer properties and the temperature, size, and speed of the tip.

This chapter investigates the effect of polymer properties and polymer melt flow on feature sizes of polymer nanostructures deposited from a heated tip, by studying the size of the polymer nanostructures over a wide range of polymer molecular weight and deposition conditions. Heated AFM tips deposited 50 – 350 nm wide poly(methyl methacrylate) nanoribbons by varying tip temperature between 204 and 335 °C, tip speed between 20 and 500 nm/s and polymer molecular weight between 16 500 and 542 900. We found both ribbon width and normalized ribbon height by radius of gyration can be generalized as a function of capillary number, independent of tip temperature, tip speed and polymer molecular weight. Scaling analysis of various factors affecting polymer feature sizes confirmed that capillary number governs feature size during thermal deposition of polymer nanostructures.

2.2 Experimental Method

Figure 2.1(a) shows the deposition of a Poly(methyl methacrylate) (PMMA) nanoribbon from a heated tip. Figures 2.1(b) and 2.1(c) show examples of PMMA nanoribbons that were deposited at increasing tip temperatures from left to right over the range 221-283 °C at a constant

tip speed of 100 nm/s. The polymer nanoribbons shown in these images are of typical sizes and shapes presented in this study. The deposited polymer height is denoted as h and width as w , which are used for subsequent analysis.

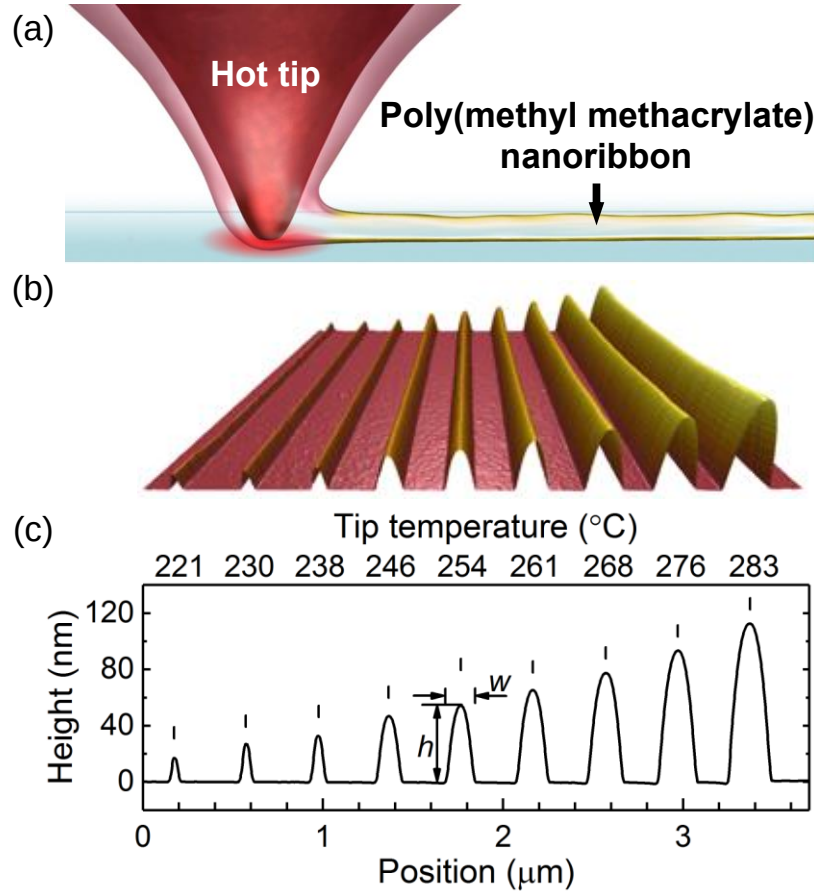


Figure 2.1 (a) Schematic of a PMMA nanoribbon deposited from a hot AFM tip. (b) AFM topology of nine PMMA ($M_w = 98,100$) nanoribbons deposited at increasing tip temperatures from left to right at constant tip speed of 100 nm/s. (c) Cross-section profile of the polymer nanoribbons shown in (b). The ribbon height h and the ribbon width w shown here are used for subsequent analysis.

The heated atomic force microscope cantilever tips were fabricated from single crystal silicon and coated with ultra-nanocrystalline diamond (UNCD) [34]. The diamond coating promotes resistance to tip wear and fouling and has good adhesion with the polymer ink. The silicon cantilever legs were doped with phosphorus at a concentration of 2.51×10^{16} atoms/cm² and

the region near the cantilever tip was doped with phosphorus at a lower concentration of 2.51×10^{13} atoms/cm². Thus, the region near the cantilever tip had a high electrical resistance and the cantilever legs had low electrical resistance; the dopant distribution promotes local heating near the cantilever tip when current flows through the device. We measured the tip temperature using a Renishaw InVia Raman microscope, and calibrated the cantilever temperature based on the temperature dependence of the cantilever electrical resistance [35], which varied over the range 2-7 k Ω . The electrical resistance temperature calibration allowed us to accurately control the cantilever temperature over the range 50-500 °C using a closed-loop feedback circuit [36]. Two diamond-coated tips were used in the experiment, with a radius of curvature of 56 nm (Tip I) and 125 nm (Tip II) respectively.

Table 2.1 summarizes the polymers used in the experiments, which were commercially available PMMA samples from Polysciences Inc. The samples are labeled as PMMA16, PMMA98 and PMMA542 by their molecular weight M_w . Molecular weight and polydispersity (M_w/M_n) were characterized using gel permeation chromatography. Tacticity was measured with proton nuclear magnetic resonance spectroscopy, and the amounts of syndiotactic (st), heterotactic (ht), and isotactic (it) triads were determined by integrating over the peaks at 0.85, 1.02, and 1.21 ppm, respectively [37].

Table 2.1 Characterization of the Poly(methyl methacrylate) samples

sample	M_w (g/mol)	M_n (g/mol)	M_w/M_n	tacticity
				st, ht, it (%)
PMMA16	16 500	10 900	1.508	51:32:17
PMMA98	98 100	59 900	1.638	52:36:12
PMMA542	542 900	297 900	1.822	54:35:11

To coat the tip with polymer ink [25], we used a micro-positioning stage to bring the tip in contact with a thin PMMA fiber under stereo microscope, and then resistively heated the tip to a temperature of 200-250 °C, which is above the PMMA melting point of 160 °C [38]. The PMMA melted and flowed to wet the end of the UNCD-coated cantilever and tip. We then withdrew the tip from the fiber and turned off the heat. Each loading step resulted in approximately 100 pg of polymer loaded onto the cantilever, as determined by the change in the AFM cantilever resonant frequency before and after inking [31]. In some cases, the tip was ready to deposit uniform, narrow ribbons of PMMA immediately after inking. Occasionally the loading step caused an excess of polymer on the tip, resulting in the deposition of very wide and thick ribbons. In these cases, the deposition was excessive for the first several features, and then the deposition quickly stabilized.

We deposited polymer nanoribbons of PMMA16, PMMA98 and PMMA542 on a room-temperature 300 nm SiO₂/Si substrate, while varying tip temperatures from 204 °C to 335 °C and tip speeds from 20 nm/s to 500 nm/s. The maximum temperature was limited to prevent PMMA decomposition. PMMA decomposes at temperatures above 280 °C, with a half decomposition temperature of 337 °C and a thermal decomposition rate of 5.2%/min at 350 °C [38]. To minimize the impact polymer of decomposition, the total writing time above 280 °C was limited to 5 minutes before re-inking. The deposited polymer ribbons were uniform throughout the writing process, indicating that decomposition was negligible. Before writing, the substrate was cleaned with a piranha solution bath at 120 °C for 10 minutes, thoroughly rinsed with deionized water and blow-dried with nitrogen gas. After writing, we used a commercial AFM cantilever tip with a nominal tip radius of 7 nm and a resonant frequency of 70 kHz to measure the deposited features in tapping mode. The fast scan direction was perpendicular to the polymer nanoribbons, minimizing the measurement error of ribbon width.

2.3 Experimental Results and Discussion

Figure 2.2 shows the mass flow rate of PMMA from the moving hot tip to the substrate. Mass flow rate is calculated as the product of the nanoribbon cross-section area, tip speed, and PMMA density ($\rho = 1.13 \text{ g/cm}^3$ [39]). Figure 2.2(a) shows the mass flow rate as a function of tip temperature for PMMA16, PMMA98 and PMMA542. Mass flow rate, over the range 5 ag/s to 3 fg/s, increases exponentially with tip temperature. To understand the exponential dependence of mass flow rate on tip temperature, we plotted the mass flow rate as a function of polymer melt viscosity in Fig. 2.2(b). Zero-shear viscosity η_0 of the PMMA samples was calculated using Williams-Landel-Ferry shift parameters found with PMMA100A in Ref. [37]. Figure 2.2(b) shows the mass flow rate decreases sub-linearly with viscosity, over four orders of magnitude in viscosity. The mass flow rate is nearly linear with viscosity for each of the three PMMA samples in Fig. 2.2(b), suggesting that polymer melt viscosity governs mass transport from the moving hot tip to the substrate.

Figure 2.2(c) shows the mass flow rate as a function of tip temperature for PMMA98 at three different tip speeds. Surprisingly, mass flow rate decreases with tip speed at each tip temperature, and this dependence weakens at higher tip temperature. We rule out thermal Marangoni force, Laplace pressure force, and shear force as possible explanations for this trend. The first two do not depend on tip speed, while the third should increase rather than decrease the flow rate [31]. We suggest that there is a fourth driving force: long-range van der Waals force. At low tip speed, the ink can spread onto the surface before the heated tip moves away, while at high speed the polymer cannot flow before the tip moves away. At higher tip temperature, other driving forces such as thermal Marangoni force and Laplace pressure force dominate, so the dependence of mass flow rate on V_{tip} weakens. If we exclude data points with ribbon height $h < 20 \text{ nm}$, which

are indicated in the gray zone in Fig. 2.2(c), then the mass flow rate does not depend upon on tip speed. Therefore, long-range force also drives mass flow and cannot be ignored for the deposition of < 20 nm tall features.

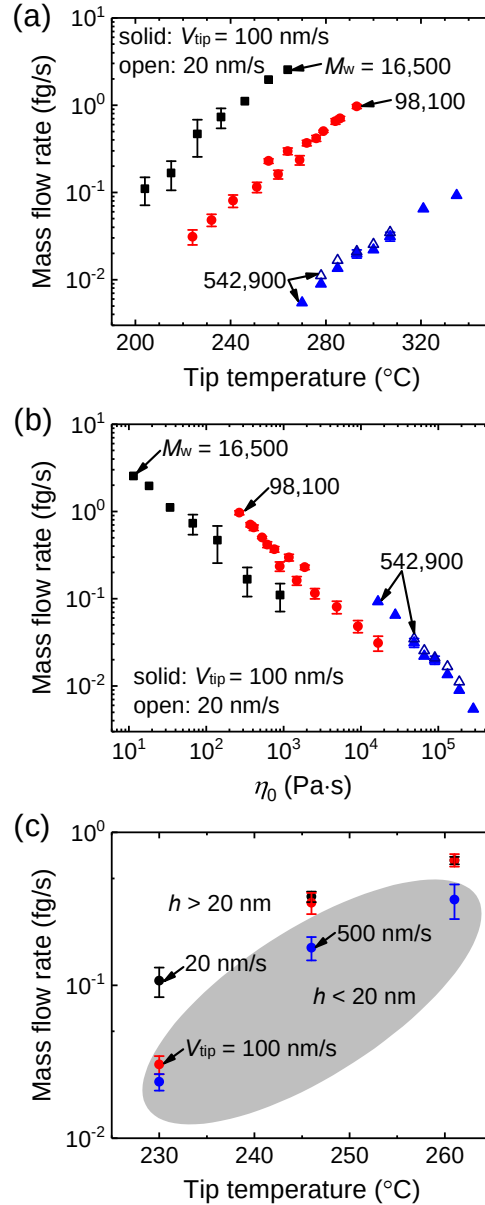


Figure 2.2 Mass flow rate of PMMA ($M_w = 16,500, 98,100, 542,900$) from a heated tip to SiO₂ substrate as a function of (a) tip temperature and (b) polymer viscosity η_0 . (c) Mass flow rate of PMMA ($M_w = 98,100$) as a function of tip temperature for three different tip speeds. Data points in the gray zone correspond to ribbon height < 20 nm, and data points outside the gray zone correspond to ribbon height > 20 nm.

Figure 2.3 summarizes all the measured PMMA nanoribbon sizes as a function of tip temperature, tip speed and polymer molecular weight. The raw data of Figs. 2.3(a) and 2.3(b) correspond to Tip I and those of Figs. 2.3(c) and 2.3(d) correspond to Tip II. Figures 2.3(a) and 2.3(b) show the nanoribbon width and height of PMMA98 as a function of tip speed over the range 20-500 nm/s and tip temperature over the range 230-261 °C. Both width and height decrease with tip speed and increase with tip temperature. Figures 2.3(c) and 2.3(d) show the nanoribbon width and height of PMMA16, PMMA98 and PMMA542 as a function of tip temperature over the range 204-335 °C at a tip speed of 100 nm/s. Additional data of PMMA542 nanoribbons written at 20 nm/s are also included. Both width and height increase with tip temperature and decrease with polymer molecular weight. Taken altogether, nanoribbon width and height increase with tip temperature and decrease with tip speed and polymer molecular weight. We can make three general comments about these observations. (1) Increasing tip temperature enhances polymer melt mobility, so more polymer melts flow from the tip to the substrate per ink deposition time, which increases nanoribbon width and height. (2) Increasing tip speed reduces the time during which ink can flow at a particular location, which decreases the nanoribbon width and height. (3) Polymers of higher molecular weight are less mobile, which results in smaller ribbon width and height. We are thus able to control the size of the deposited polymer nanoribbon by changing tip temperature, tip speed and polymer molecular weight.

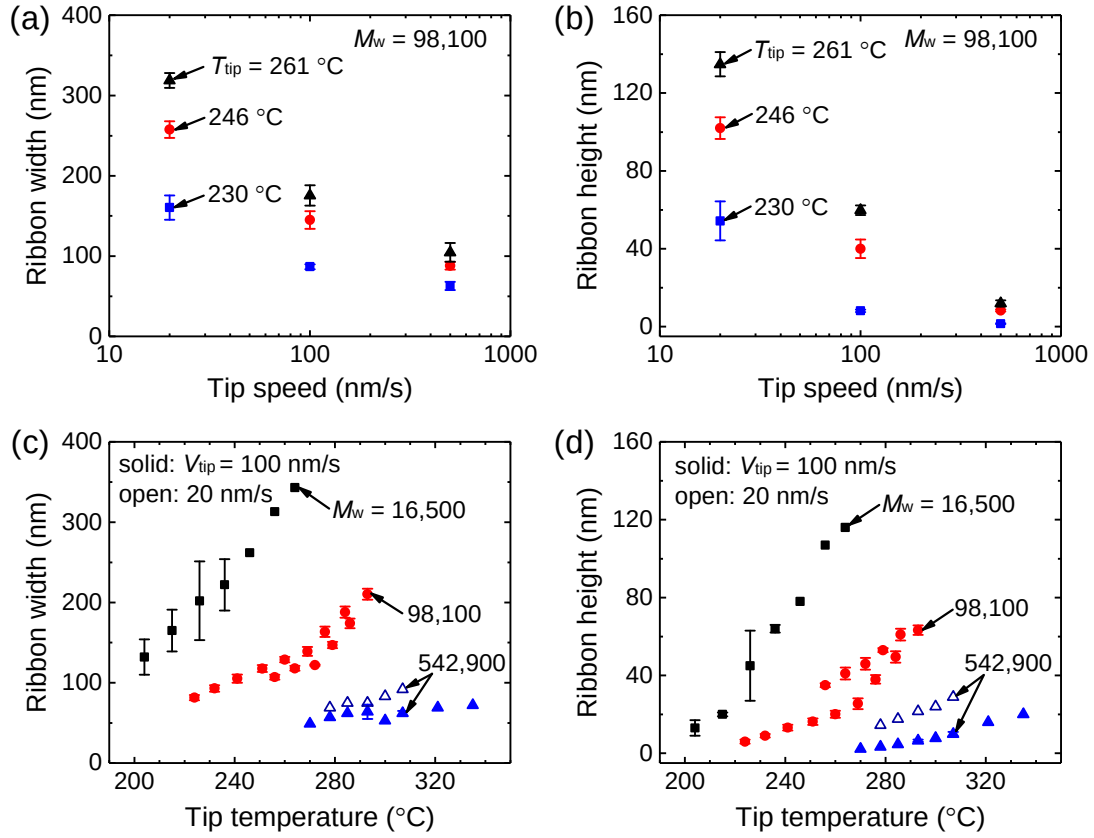


Figure 2.3 Ribbon width (a) and height (b) of PMMA98 as a function of tip speed at three different tip temperatures. Ribbon width (c) and height (d) as a function of tip temperature for three different molecular weights. The solid symbols indicate a tip speed of 100 nm/s and the open symbol indicates a tip speed of 20 nm/s.

To investigate the relation between polymer melt dynamics and resulting polymer nanoribbon sizes, we studied nanoribbon width and height as a function of capillary number Ca , which describes the relative importance of viscous stress to surface tension stress in polymer melts. $Ca = \eta_0 V_p / \gamma$, where η_0 is the zero-shear polymer viscosity, V_p is the characteristic polymer velocity, and γ is the polymer melt surface tension. We assumed that V_p is proportional to tip speed V_{tip} and approximated capillary number as $Ca \sim \eta_0 V_{tip} / \gamma$. The parameters η_0 and γ were evaluated at tip temperature.

Figure 2.4 shows nanoribbon width as a function of Ca . Figure 2.4(a) shows ribbon width of PMMA98 as a function of Ca at different tip speeds. Ribbon widths of different tip speeds are collinear and decrease monotonically with Ca to the power of -0.34. Figure 2.4(b) shows ribbon width of PMMA16, PMMA98 and PMMA542 as a function of Ca . Ribbon widths of different molecular weights are also collinear and decrease with Ca to the power of -0.19. The results of Fig. 2.4 reveal that ribbon width decreases monotonically with Ca , independent of tip temperature, tip speed and polymer molecular weight. The raw data of Figs. 2.4(a) and 2.4(b) are from two different tips (Tip I and Tip II), and it is likely that the difference in tip shape caused the difference in the exponents.

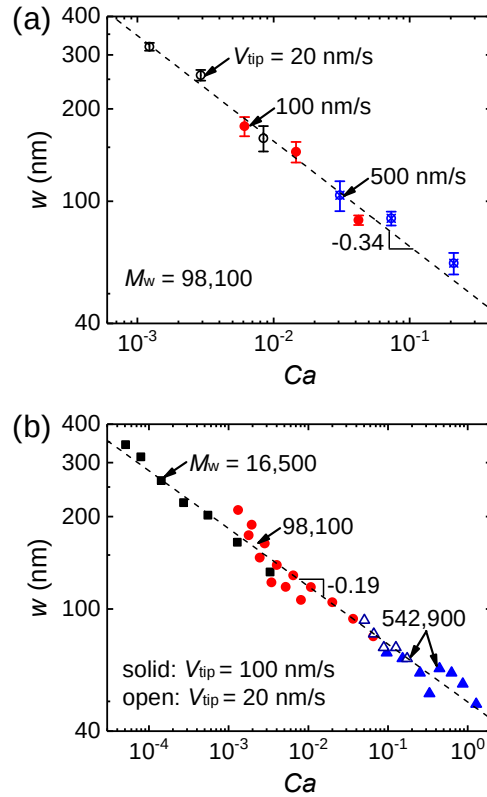


Figure 2.4 (a) Ribbon width w of PMMA98 as a function of capillary number Ca at three different tip speeds. (b) Ribbon width w as a function of capillary number Ca for three different molecular weights. Dashed lines give the best fits to data.

Figure 2.5 shows the dependence of nanoribbon height on viscosity, polymer size and Ca . Figures 2.5(a) and 2.5(b) show ribbon height as a function of viscosity. The ribbon height-viscosity relation varies with tip speed and polymer molecular weight, even though height decreases with viscosity for any one molecular weight and tip speed. To explore whether the size of the polymer molecule affects the deposition, we normalized ribbon height by radius of gyration as h/R_g , and plotted h/R_g as a function of Ca in Figs. 2.5(c) and 2.5(d). Figures 2.5(c) and 2.5(d) show that $h/R_g \sim Ca^x$, $x = -0.5$ when $h \gtrsim R_g$ & $x < -0.5$ when $h \lesssim R_g$, which does not depend upon tip temperature, tip speed and polymer molecular weight. $x = -0.5$ when $h \gtrsim R_g$ is consistent with a previous tDPN study using poly(3-dodecylthiophene) ink [40], but we do not know whether $h/R_g \sim Ca^{-1/2}$ is valid for all polymer inks when $h \gtrsim R_g$, which remains a topic for further exploration. $x < -0.5$ when $h \lesssim R_g$ can be explained by polymer-substrate interaction: The carbonyl groups of PMMA are attracted by the hydroxyl groups of the silicon dioxide, so near-substrate PMMA is less mobile than its bulk [41,42] and η_0 of the bulk underestimates effective viscosity for $h \lesssim R_g$, resulting in $x < -0.5$. Finally, we note that the dependence of h on R_g could be ascribed to thin-film confinement [43], which does not affect in-plane polymer mobility [44,45], so there is no explicit dependence of w on R_g .

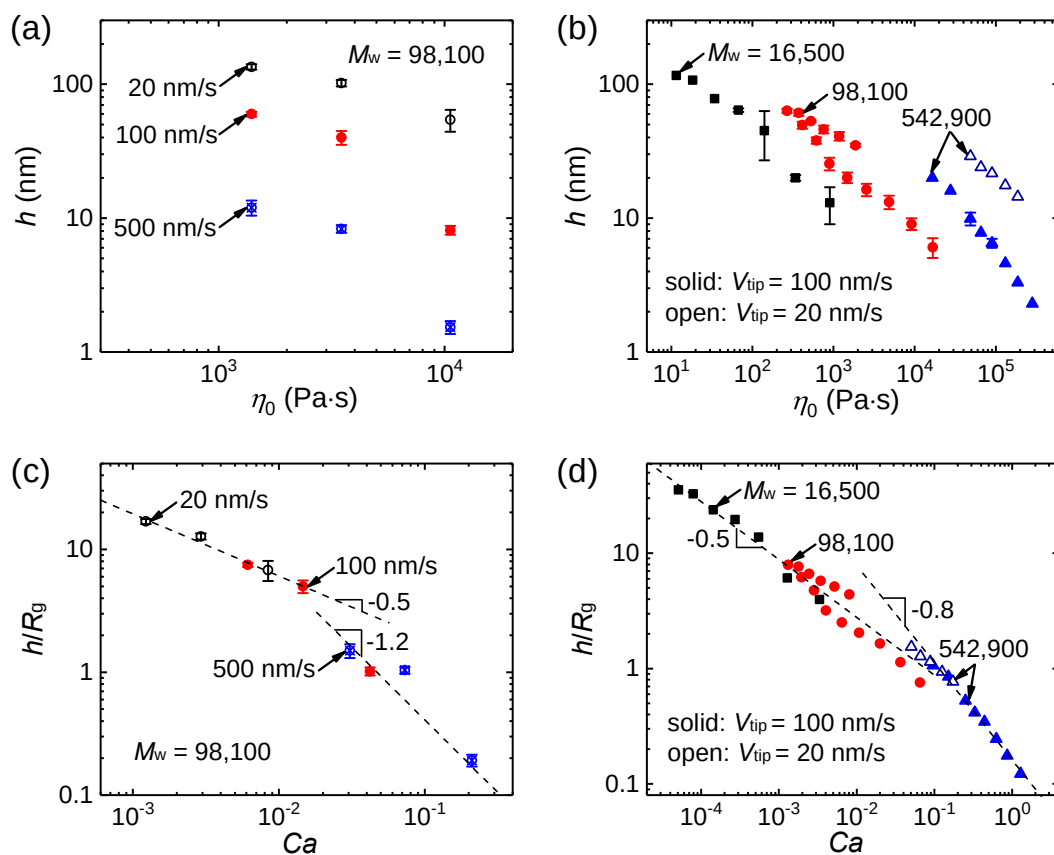


Figure 2.5 (a) Ribbon height h of PMMA98 as a function of viscosity η_0 at three different tip speeds. (b) Ribbon height h as a function of viscosity η_0 for three different molecular weights. (c) Ribbon height h in (a) normalized by radius of gyration R_g as a function of capillary number Ca . (d) Ribbon height h in (b) normalized by radius of gyration R_g as a function of capillary number Ca . Dashed lines give the best fits to data.

Figure 2.6 shows the correlation of ribbon height h with ribbon width w . Figure 2.6(a) shows that h and w are linearly correlated as $h = 0.54w - 37$ regardless of tip speed. Figure 2.6(b) also shows a linear correlation between nanoribbon width and height as $h = 0.32w - 14$, despite difference in polymer molecular weight. Additionally, independent linear fits (not shown here) for different tip speeds in Fig. 2.6(a) and for different molecular weights in Fig. 2.6(b) all satisfy the relation that $h = A*w + B$, where $A > 0$, $B < 0$. $A > 0$ shows that height growth and ink spreading are

positively correlated, as in dot patterning of fluid inks by DPN [31–33], while $B < 0$ implies a greater-than-zero initial meniscus size.

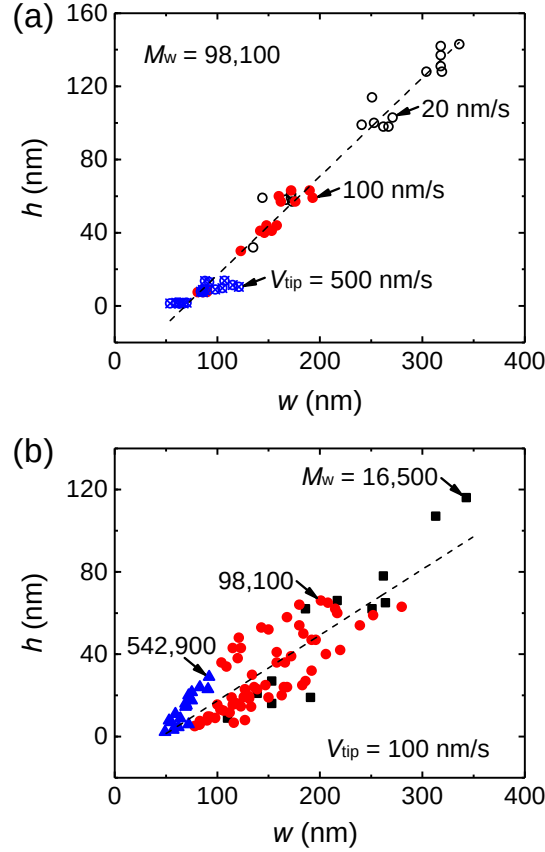


Figure 2.6 Correlation of ribbon height h with ribbon width w for (a) PMMA98 at different tip speeds and (b) PMMA16, PMMA98 and PMMA542 at a tip speed of 100 nm/s. Dashed lines give the best fits to data.

2.4 Modeling the Polymer Flow

The goal of the modeling is to explain why capillary number Ca governs polymer ribbon deposition in tDPN. First, we use dimensional analysis to show that Ca controls ribbon size. For any tDPN system, ribbon width w depends on ink viscosity η , surface tension γ , tip speed V_{tip} and initial meniscus size a . The dimensions of η , γ , V_{tip} and a can be expressed by mass M , time T and length L as $\eta \sim M/LT$, $\gamma \sim M/T^2$, $V_{\text{tip}} \sim L/T$, $a \sim w_{\text{min}} \sim L$, where a is approximated as the minimum

ribbon width $w_{\min}$. Apply the Buckingham π theorem [46] to identify the key nondimensional groups, we find that $w/w_{\min} = f(Ca = \eta V_{\text{tip}}/\gamma)$. Likewise, $h/R_g = f(Ca)$, whereas h depends on η , γ , V_{tip} and R_g .

The preceding analysis presumes a steady, uniform ink temperature during ribbon writing. We can assess the validity of this assumption by studying the time scales of heat and mass transport. Ink velocity due to thermocapillarity can be approximately calculated as $V_{\text{TC}} = d\gamma/dT \times (\Delta T/\eta)$ [47]. Assuming that $d\gamma/dT = 0.08 \text{ mN}/(\text{m K})$ for PMMA [38], the temperature difference between tip and substrate is $\Delta T = 200 \text{ }^\circ\text{C}$, η ranges over $1 \times 10^1 - 3 \times 10^5 \text{ Pa}\cdot\text{s}$, and the ink velocity is $5 \times 10^{-5} - 1.6 \text{ m/s}$. For polymer flowing at these velocities, the time required to form a 100 nm wide ribbon is 30 ns – 1 ms. In the experiments, tip speed ranges over 20 – 500 nm/s. Thus, within a period of 1 ms, the the tip deposits a nanoribbon with width 0.02 – 0.5 nm. Within this same period of time, the thermal penetration depth $\delta \sim \sqrt{\alpha t}$ is 8 μm , where $\alpha = 6.3 \times 10^{-8} \text{ m}^2/\text{s}$ is the thermal diffusivity of PMMA [38]. Because the ribbon length deposited is much smaller than the distance of thermal penetration from the heated tip, we can infer that the ribbon remains at the temperature of the tip during this period. We conclude that within the timescale of ink spreading onto the surface, the ink remains at the tip temperature.

We now use a simple model [31] to discuss how the forces acting on the polymer scale with Ca . The tip is modeled as a cylinder with radius r and height h_{tip} , and the polymer on the tip is a thin film with thickness t . Assuming a no-slip condition on the tip and the substrate, the shear stress scales as $\tau \sim \eta V_{\text{tip}}/t$, and the shear force scales as $F_\tau = 2\pi r t \tau \sim 2\pi r \eta V_{\text{tip}}$. The force due to thermocapillary effect scales as $F_{\Delta T} \sim 2\pi r (d\gamma/dT) \Delta T \sim 2\pi r \gamma$. The force due to the local curvature κ of the ink-air interface scales as $F_{\Delta P} \sim 2\pi r \kappa^{-1} \gamma \kappa = 2\pi r \gamma$. Finally, the viscous force resisting polymer flow scales as $F_{\text{visc}} \sim 2\pi r h_{\text{tip}} \eta V_p/t \sim 2\pi r h_{\text{tip}} \eta V_{\text{tip}}/t$. Applying force balance $F_\tau + F_{\Delta T} + F_{\Delta P}$

$= F_{\text{visc}}$, we have $F_{\tau}/F_{\text{visc}} \sim Ca/(Ca + 2)$ and $F_{\text{TC}}/F_{\text{visc}} \sim F_{\Delta\text{P}}/F_{\text{visc}} \sim 1/(Ca + 2)$. We define capillary force $F_{\gamma} \equiv F_{\Delta\text{T}} + F_{\Delta\text{P}}$, so we have $F_{\gamma}/F_{\text{visc}} \sim 2/(Ca + 2)$. Further discussion of this model, along with experimental validation, is available in reference [31].

Based on this model, Fig. 2.7(a) shows how polymer melt deposition varies with capillary number Ca . When $Ca \ll 1$, capillary force F_{γ} is much larger than shear force F_{τ} , which results in the deposition of nanoribbons of uniform width and height. Nanoribbon sizes can be regulated by tip speed and tip temperature. When $Ca \sim 1$, capillary force F_{γ} is as large as shear force F_{τ} , causing the deposition of irregular polymer features. Figures 2.7(b)-(e) show examples of irregular polymer nanostructures deposited when $Ca \sim 1$. When $Ca \gg 1$, capillary force F_{γ} is much smaller than shear force F_{τ} , and there is no deposition at all. In sum, good deposition occurs only when $Ca \ll 1$, i.e., when capillary force is much larger than shear force. Polymer melt deposition is driven by capillary force, but not by tip shear force.

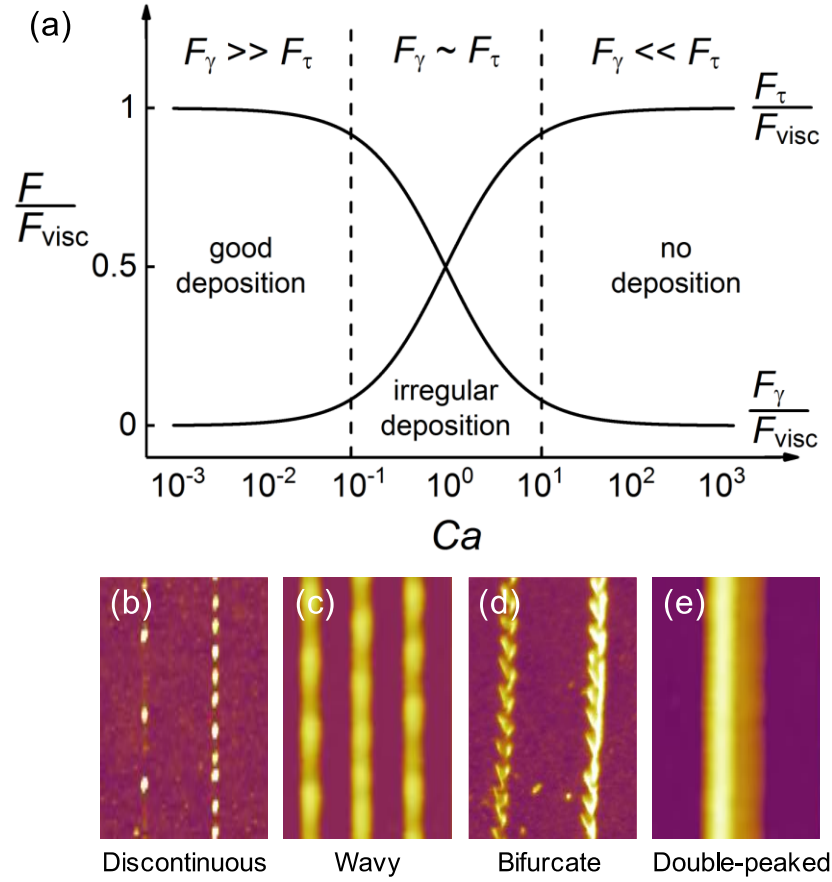


Figure 2.7 (a) Concept plot for polymer melt deposition at varying Ca . Four typical types of irregular polymer deposition: (b) discontinuous, (c) wavy, (d) bifurcate and (e) double-peaked.

Finally, we use this model to analyze the final shape of the deposited polymer. Figure 2.8(a) shows a typical AFM cross section profile of the deposited polymer nanoribbons, which consists of a spherical cap in the center and a protruding foot surrounding the cap. The foot height is b and the foot length is f_1 . The existence of a protruding foot indicates polymer melt slip at the surface [48]. No precursor film can be detected, as is the usual case under partial wetting [49,50]. In the lubrication approximation, if we ignore the thermo-Marangoni force and long-range force, and apply a local balance between viscous force and capillary force due to local curvature, we find $b/f_1 \cong Ca^{1/3}$ [48]. Figure 2.8(b) reveals that b/f_1 scales as $Ca^{0.36 \pm 0.03}$ for PMMA98 at the tip speed of 100 nm/s, very close to $Ca^{1/3}$ as predicted by the model. The validity of this simplified model

implies that Laplace pressure is the dominant driving force over thermal-Marangoni force and long-range force in the protruding foot region.

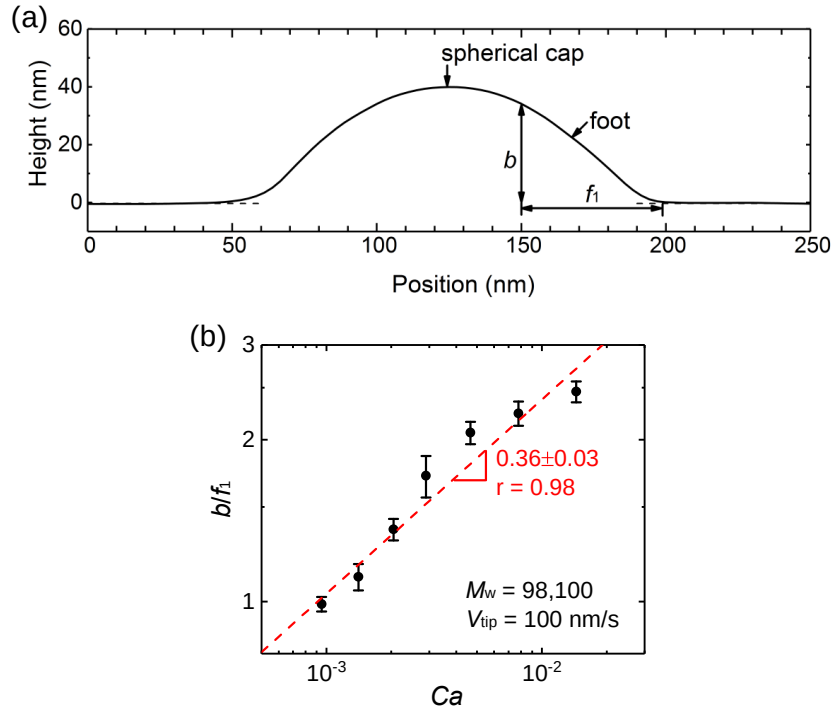


Figure 2.8 (a) A typical AFM cross section profile of the deposited polymer nanoribbons, which consists of a spherical cap in the center and a protruding foot surrounding the cap. The foot height is b and the foot length is f_1 . (b) The ratio of foot height b to foot length f_1 as a function of capillary number Ca in log-log plot. PMMA ($M_w = 98,100$) was deposited at a tip speed of 100 nm/s. The power law fits relatively well with $r = 0.98$ and a power of 0.36 ± 0.03 .

2.5 Conclusions

We investigated the role of capillary-driven polymer melt flow on thermal deposition of polymer nanostructures. We studied the deposition of PMMA nanoribbons from a moving heated AFM tip onto SiO₂ by varying tip temperature between 204 and 335 °C, tip speed between 20 and 500 nm/s and polymer molecular weight between 16 500 and 542 900. Polymer melt mass flow rate varied nearly linearly with polymer viscosity for each of the three PMMA samples, indicating that polymer melt viscosity governs mass transport from the moving hot tip to the substrate. Mass

flow rate decreased with tip speed when writing < 20 nm tall ribbons, which we ascribe to the effect of long-range forces. Both ribbon width and height increase with tip temperature and decrease with tip speed and polymer molecular weight.

Capillary number Ca governs the size of the polymer nanostructures over a wide range of polymer molecular weight and deposition conditions. The nanoribbon width can be described by a monotonic function of Ca , independent of tip temperature, tip speed and polymer molecular weight. For high molecular weight polymers, ribbon height normalized by radius of gyration is also a monotonic function of Ca . An analytical model of polymer flow also shows that Ca governs the size of the polymer nanoribbon. Uniform and continuous deposition occurs only when $Ca \ll 1$, i.e., when capillary force outweighs tip shear force, indicating that polymer melt deposition is caused by capillary force but not by tip shear force. Strong correlation of ribbon height with ribbon width suggests that height growth and polymer spreading are coupled processes. Finally, we found protruding foot in the final shape of ribbon cross section, suggesting that Laplace pressure causes slip within the polymer melt.

This work provides a framework to study feature sizes of thermally deposited polymer nanostructures and predict the size and shape of deposited polymers as a function of capillary number. Our results imply that narrower polymer ribbons can be achieved at larger capillary number, while irregularly shaped ribbons will be deposited when capillary number approaches one. Future work could further investigate instabilities in polymer flow that occur when $Ca \sim 1$, i.e., when viscous force balances surface tension and inadequate capillary driving force may lead to intermittent or unstable writing, also when tip shear force is as large as capillary force and may affect the shape of deposited polymer via local tip structure.

2.6 References

- [1] Bai J, Zhong X, Jiang S, Huang Y and Duan X 2010 Graphene Nanomesh *Nat. Nanotechnol.* **5** 190–4
- [2] Hu Z, Tian M, Nysten B and Jonas A M 2009 Regular Arrays of Highly Ordered Ferroelectric Polymer Nanostructures for Non-Volatile Low-Voltage Memories *Nat. Mater.* **8** 62–7
- [3] Xu J, Wang S, Wang G J N, Zhu C, Luo S, Jin L, Gu X, Chen S, Feig V R, To J W F, Rondeau-Gagné S, Park J, Schroeder B C, Lu C, Oh J Y, Wang Y, Kim Y H, Yan H, Sinclair R, Zhou D, Xue G, Murmann B, Linder C, Cai W, Tok J B-H, Chung J W and Bao Z 2017 Highly Stretchable Polymer Semiconductor Films through the Nanoconfinement Effect *Science* **355** 59–64
- [4] Xia L, Wei Z and Wan M 2010 Conducting Polymer Nanostructures and Their Application in Biosensors *J. Colloid Interface Sci.* **341** 1–11
- [5] Chai J, Huo F, Zheng Z, Giam L R, Shim W and Mirkin C A 2010 Scanning Probe Block Copolymer Lithography. *Proc. Natl. Acad. Sci. U. S. A.* **107** 20202–6
- [6] McKendry R, Huck W T S, Weeks B, Fiorini M, Abell C and Rayment T 2002 Creating Nanoscale Patterns of Dendrimers on Silicon Surfaces with Dip-Pen Nanolithography *Nano Lett.* **2** 713–6
- [7] Demers L M, Ginger D S, Park S-J, Li Z, Chung S-W and Mirkin C A 2002 Direct Patterning of Modified Oligonucleotides on Metals and Insulators by Dip-Pen Nanolithography. *Science* **296** 1836–8
- [8] Chung S-W, Ginger D S, Morales M W, Zhang Z, Chandrasekhar V, Ratner M A and Mirkin C A 2005 Top-down Meets Bottom-up: Dip-Pen Nanolithography and DNA-

Directed Assembly of Nanoscale Electrical Circuits *Small* **1** 64–9

- [9] Lim J-H, Ginger D S, Lee K-B, Heo J, Nam J-M and Mirkin C A 2003 Direct-Write Dip-Pen Nanolithography of Proteins on Modified Silicon Oxide Surfaces *Angew. Chemie Int. Ed.* **42** 2309–12
- [10] Lee K B, Lim J H and Mirkin C A 2003 Protein Nanostructures Formed via Direct-Write Dip-Pen Nanolithography *J. Am. Chem. Soc.* **125** 5588–9
- [11] Hong S, Zhu J and Mirkin C A 1999 Multiple Ink Nanolithography: Toward a Multiple-Pen Nano-Plotter *Science* **286** 523–5
- [12] Zhang Y, Salaita K, Lim J H and Mirkin C A 2002 Electrochemical Whittling of Organic Nanostructures *Nano Lett.* **2** 1389–92
- [13] Auletta T, Dordi B, Mulder A, Sartori A, Onclin S, Bruinink C M, Péter M, Nijhuis C A, Beijleveld H, Schönherr H, Vancso G J, Casnati A, Ungaro R, Ravoo B J, Huskens J and Reinhoudt D N 2004 Writing Patterns of Molecules on Molecular Printboards *Angew. Chemie Int. Ed.* **43** 369–73
- [14] Piner R D, Zhu J, Xu F, Hong S and Mirkin C A 1999 “Dip-Pen” Nanolithography *Science* **283** 661–3
- [15] Shin Y-S, Son J Y, Jo M-H, Shin Y-H and Jang H M 2011 High-Mobility Graphene Nanoribbons Prepared Using Polystyrene Dip-Pen Nanolithography *J. Am. Chem. Soc.* **133** 5623–5
- [16] Su M, Li S and Dravid V P 2003 Miniaturized Chemical Multiplexed Sensor Array *J. Am. Chem. Soc.* **125** 9930–1
- [17] Tang Q and Shi S-Q 2008 Preparation of Gas Sensors via Dip-Pen Nanolithography *Sensors Actuators B Chem.* **131** 379–83

- [18] Martínez-Otero A, González-Monje P, MasPOCH D, Hernando J and Ruiz-Molina D 2011 Multiplexed Arrays of Chemosensors by Parallel Dip-Pen Nanolithography *Chem. Commun.* **47** 6864
- [19] Lee K B, Kim E Y, Mirkin C A and Wolinsky S M 2004 The Use of Nanoarrays for Highly Sensitive and Selective Detection of Human Immunodeficiency Virus Type 1 in Plasma *Nano Lett.* **4** 1869–72
- [20] Sekula S, Fuchs J, Weg-Remers S, Nagel P, Schuppler S, Fragala J, Theilacker N, Franzreb M, Wingren C, Ellmark P, Borrebaeck C A K, Mirkin C A, Fuchs H and Lenhert S 2008 Multiplexed Lipid Dip-Pen Nanolithography on Subcellular Scales for the Templating of Functional Proteins and Cell Culture *Small* **4** 1785–93
- [21] Mitsakakis K, Sekula-Neuner S, Lenhert S, Fuchs H and Gizeli E 2012 Convergence of Dip-Pen Nanolithography and Acoustic Biosensors towards a Rapid-Analysis Multi-Sample Microsystem *Analyst* **137** 3076
- [22] Hirtz M, Brglez J, Fuchs H and Niemeyer C M 2015 Selective Binding of DNA Origami on Biomimetic Lipid Patches *Small* **11** 5752–8
- [23] Sheehan P E, Whitman L J, King W P and Nelson B A 2004 Nanoscale Deposition of Solid Inks via Thermal Dip Pen Nanolithography *Appl. Phys. Lett.* **85** 1589–91
- [24] Somnath S and King W P 2013 Heated Atomic Force Cantilever Closed Loop Temperature Control and Application to High Speed Nanotopography Imaging *Sensors Actuators, A Phys.* **192** 27–33
- [25] Hu H, Banerjee S, Estrada D, Bashir R and King W P 2015 Tip-Based Nanofabrication of Arbitrary Shapes of Graphene Nanoribbons for Device Applications *RSC Adv.* **5** 37006–12

- [26] Yang M, Sheehan P E, King W P and Whitman L J 2006 Direct Writing of a Conducting Polymer with Molecular-Level Control of Physical Dimensions and Orientation *J. Am. Chem. Soc.* **128** 6774–5
- [27] Szoszkiewicz R, Okada T, Jones S C, Li T De, King W P, Marder S R and Riedo E 2007 High-Speed, Sub-15nm Feature Size Thermochemical Nanolithography *Nano Lett.* **7** 1064–9
- [28] Lee W-K, Robinson J T, Gunlycke D, Stine R R, Tamanaha C R, King W P and Sheehan P E 2011 Chemically Isolated Graphene Nanoribbons Reversibly Formed in Fluorographene Using Polymer Nanowire Masks *Nano Lett.* **11** 5461–4
- [29] Chen S, Kim S, Chen W, Yuan J, Bashir R, Lou J, van der Zande A M and King W P 2019 Monolayer MoS₂ Nanoribbon Transistors Fabricated by Scanning Probe Lithography *Nano Lett.* **19** 2092–8
- [30] Brown K A, Eichelsdoerfer D J, Liao X, He S and Mirkin C A 2014 Material Transport in Dip-Pen Nanolithography *Front. Phys.* **9** 385–97
- [31] Felts J R, Somnath S, Ewoldt R H and King W P 2012 Nanometer-Scale Flow of Molten Polyethylene from a Heated Atomic Force Microscope Tip *Nanotechnology* **23** 215301
- [32] Liu G, Zhou Y, Banga R S, Boya R, Brown K A, Chipre A J, Nguyen S T and Mirkin C A 2013 The Role of Viscosity on Polymer Ink Transport in Dip-Pen Nanolithography *Chem. Sci.* **4** 2093
- [33] Eichelsdoerfer D J, Brown K A and Mirkin C A 2014 Capillary Bridge Rupture in Dip-Pen Nanolithography *Soft Matter* **10** 5603–8
- [34] Fletcher P C, Felts J R, Dai Z, Jacobs T D, Zeng H, Lee W, Sheehan P E, Carlisle J A, Carpick R W and King W P 2010 Wear-Resistant Diamond Nanoprobe Tips with

- Integrated Silicon Heater for Tip-Based Nanomanufacturing *ACS Nano* **4** 3338–44
- [35] Lee J, Beechem T, Wright T L, Nelson B A, Graham S and King W P 2006 Electrical, Thermal, and Mechanical Characterization of Silicon Microcantilever Heaters *J. Microelectromechanical Syst.* **15** 1644–55
- [36] Somnath S, Corbin E A and King W P 2011 Improved Nanotopography Sensing via Temperature Control of a Heated Atomic Force Microscope Cantilever *IEEE Sens. J.* **11** 2664–70
- [37] Fuchs K, Friedrich C and Weese J 1996 Viscoelastic Properties of Narrow-Distribution Poly (Methyl Methacrylates) *Macromolecules* **9297** 5893–901
- [38] Van Krevelen D W and Te Nijenhuis K 2009 Properties of Polymers : Their Correlation with Chemical Structure ; Their Numerical Estimation and Prediction from Additive Group Contributions (Elsevier)
- [39] Fetters L J, Lohse D J, Richter D, Witten T A and Zirkel A 1994 Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties *Macromolecules* **27** 4639–47
- [40] Lee W-K K, Yang M, Laracuenta A R, King W P, Whitman L J and Sheehan P E 2012 Direct-Write Polymer Nanolithography in Ultra-High Vacuum vol 3 (Beilstein-Institut)
- [41] Li R N, Chen F, Lam C H and Tsui O K C 2013 Viscosity of PMMA on Silica: Epitome of Systems with Strong Polymer-Substrate Interactions *Macromolecules* **46** 7889–93
- [42] Keddie J L, Jones R A L and Cory R A 1994 Interface and Surface Effects on the Glass-Transition Temperature in Thin Polymer Films *Faraday Discuss.* **98** 219
- [43] Rowland H D, King W P, Pethica J B and Cross G L W 2008 Molecular Confinement Accelerates Deformation of Entangled Polymers during Squeeze Flow *Science* **322** 720–4

- [44] Soles C L and Ding Y 2008 Materials Science: Nanoscale Polymer Processing *Science* **322** 689–90
- [45] Jones R, Kumar S, Ho D, Briber R and Russell T 1999 Chain Conformation in Ultrathin Polymer Films *Nature* **400** 146–9
- [46] Lienhard J H 2011 A Heat Transfer Textbook (Courier Corporation)
- [47] Hadland P H, Balasubramaniam R, Wozniak G and Subramanian R S 1999 Thermocapillary Migration of Bubbles and Drops at Moderate to Large Marangoni Number and Moderate Reynolds Number in Reduced Gravity *Exp. Fluids* **26** 240–8
- [48] De Gennes P G 1985 Wetting: Statics and Dynamics *Rev. Mod. Phys.* **57** 827–63
- [49] Snoeijer J H and Andreotti B 2013 Moving Contact Lines: Scales, Regimes, and Dynamical Transitions *Annu. Rev. Fluid Mech.* **45** 269–92
- [50] Soleymaniha M and Felts J R 2018 Measurement of Nanoscale Molten Polymer Droplet Spreading Using Atomic Force Microscopy *Rev. Sci. Instrum.* **89** 033703

CHAPTER 3: MONOLAYER MOLYBDENUM DISULFIDE NANORIBBON TRANSISTORS FABRICATED BY SCANNING PROBE LITHOGRAPHY

3.1 Introduction

MoS₂, a widely studied transition metal dichalcogenide semiconductor, is potentially well suited for electronic applications, due to its large bandgap (1.9 eV for monolayers), acceptable mobility, and two-dimensional atomic layer structure that allows for a high degree of electrostatic control over its electrical conductivity [1,2]. Field-effect transistors from monolayer MoS₂ can achieve current on/off ratio larger than 10⁸, room-temperature carrier mobility of ~150 cm²/Vs, and near-thermionic subthreshold swing, making monolayer MoS₂ a promising candidate for low-power electronics [1,3–6]. Because of these intriguing electronic characteristics, there has been significant research into electronic devices made from MoS₂, however the field is still immature and considerable challenges remain, especially for the realization of nanometer-scale devices.

Nanometer-scale MoS₂ transistors are desired for high device density and low power operation [3,7,8], however there are only a few published articles that describe the fabrication of these devices, owing to the difficulty of device fabrication. For example, multi-layer MoS₂ with thickness 5-15 nm (7-25 layers) were formed into nanoribbons as narrow as 40-65 nm using electron beam lithography (EBL) [9–11]. Transistors based on these multi-layer ribbons had current on/off ratios of 10⁵-10⁷ and room-temperature mobility of 1.25-31 cm²/Vs. In one study, a monolayer MoS₂ transistor with channel width 200 nm was fabricated using oxidation scanning

probe lithography [12]. The monolayer transistor had a current on/off ratio of 200 and room-temperature mobility of $0.12 \text{ cm}^2/\text{Vs}$. Smaller structures have been demonstrated in monolayer MoS_2 , for example 20 nm structures fabricated using EBL [13], and 10 nm structures fabricated using helium ion beam milling [14]. These structures were however not integrated into working transistors. To our knowledge, there has been no published article that describes a working transistor device from monolayer MoS_2 with a channel width smaller than 100 nm.

A key technical challenge for the fabrication of monolayer MoS_2 transistors is the compatibility of the materials and the materials processing. For example, even low electron doses used in EBL can induce defects such as sulfur vacancies in monolayer MoS_2 [15,16], which has a more sensitive surface than multilayer MoS_2 due to higher surface to volume ratio [17]. Ion beam lithography can also damage sensitive electronic materials [18,19]. As an alternative to these processes, we propose SPL, which avoids the exposure of device materials to radiation [20]. SPL has been shown to overcome materials and process compatibility issues, and fabricate nanoelectronic devices such as silicon nanowire transistors [21,22], graphene devices [23–27], and WSe_2 transistors [28].

This chapter reports the fabrication of monolayer MoS_2 nanoribbon FETs as narrow as 30 nm, realized using SPL. An atomic force microscope (AFM) tip deposited a nanometer scale constricted polymer on a prefabricated microribbon FET as etch mask and XeF_2 etched unmasked MoS_2 , forming a nanoribbon FET. One 30-nm-wide monolayer FET achieved a mobility of $8.53 \text{ cm}^2/\text{Vs}$ and an on/off ratio of 2×10^5 , on par with multilayer MoS_2 nanoribbon FETs reported to date. We found the electrical properties of MoS_2 FET degrade after nanoribbon formation, while atomic layer deposition (ALD) of high- κ dielectric on nanoribbon devices improves mobility and

on/off ratio. Finally, we observed increase in threshold voltage after nanoribbon formation and decrease in threshold voltage after ALD passivation.

3.2 Design and Fabrication

Figure 3.1 shows the device design and fabrication process flow. Figures 3.1(a) and 3.1(b) show the top and side views of the monolayer MoS₂ nanoribbon FET and its components and electrical connections. The device consists of a narrow monolayer MoS₂ channel, electrical contacts for the source and drain consisting of 30 nm gold on 5 nm nickel, a 285 nm SiO₂ gate dielectric, and a degenerately p-doped silicon back gate. A layer of 10 nm Al₂O₃ provides passivation. Figure 3.1(c) illustrates the device fabrication process flow. The fabrication started with growth of monolayer MoS₂ by chemical vapor deposition [29] on a SiO₂/Si substrate (i). Atomic force microscopy and Raman spectroscopy confirmed that the MoS₂ is a monolayer, as shown in Fig. 3.2. Figure 3.2(a) shows that the thickness of the MoS₂ flake is 0.67 nm, consistent with previous CVD grown and exfoliated monolayers [4,30]; Figure 3.2(b) shows that the Raman peak difference is 18.1 cm⁻¹, which also corresponds to monolayer MoS₂ [31]. Contact electrodes were defined using optical lithography, forming a single-layer MoS₂ microribbon device. We fabricated seven devices with various feature sizes. The channel width varied over the range 6.9 - 37.5 μm and channel length varied over the range 3.9 - 6.9 μm.

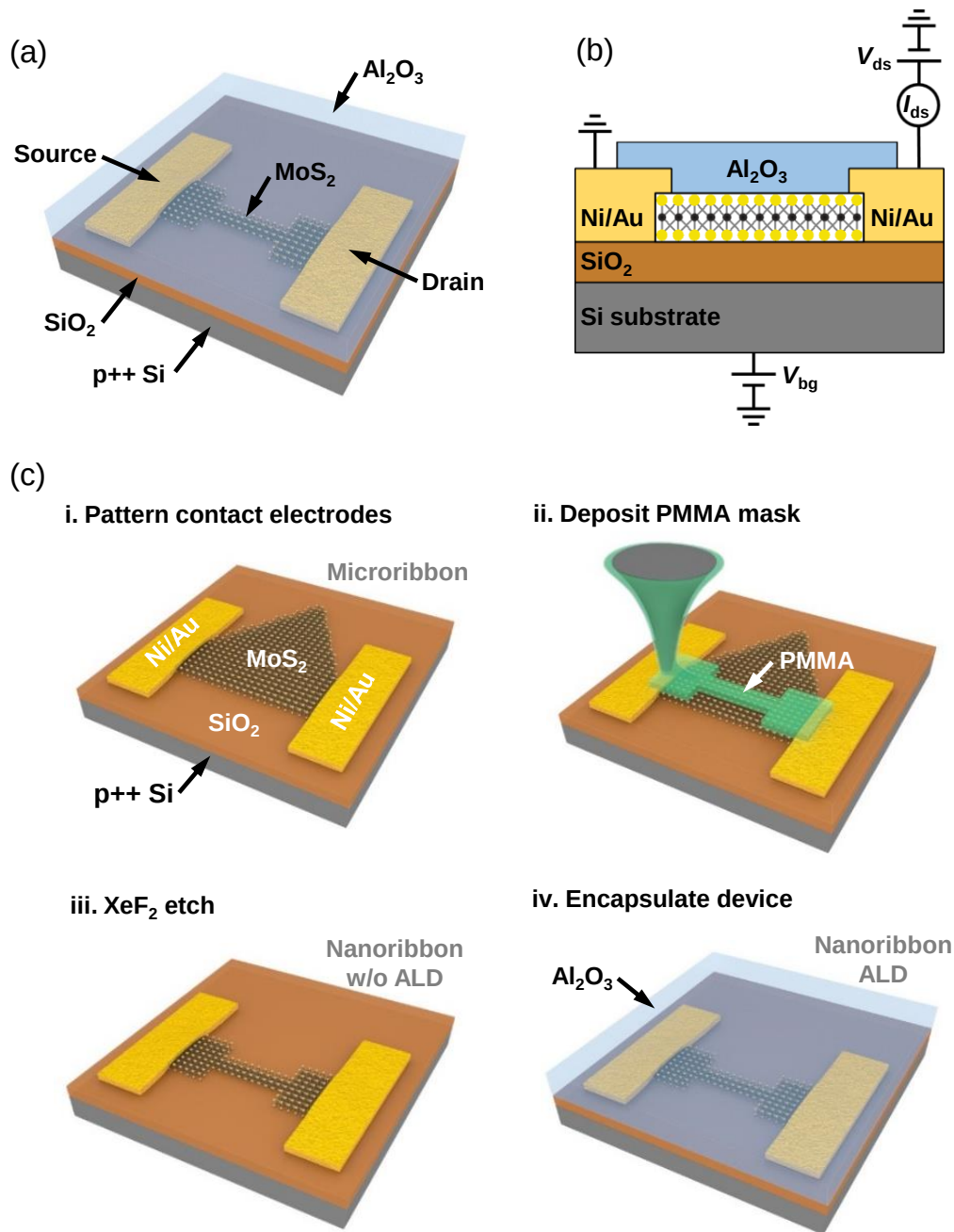


Figure 3.1 (a) Schematic of the monolayer MoS₂ nanoribbon FET. (b) Cross-sectional view of the FET, along with the electrical connections used to characterize the device. (c) Process flow for device fabrication.

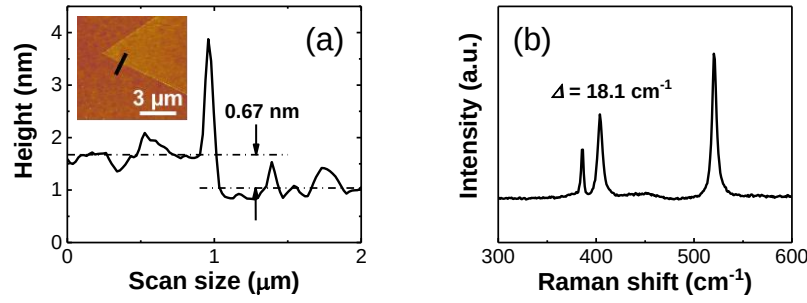


Figure 3.2 (a) Line scan of monolayer MoS_2 measured along the black line in the AFM image shown in the inset. (b) Raman spectrum of monolayer MoS_2 .

We used thermal dip-pen nanolithography (tDPN) [23,32] to form constrictions in the microribbons (ii). In tDPN, a heated AFM tip writes a solid ink onto a substrate and the temperature gradient between the tip and the substrate controls the ink flow. In this process, a diamond-coated AFM cantilever tip [33] deposited a narrow ribbon of Poly(methyl methacrylate) (PMMA) ($M_w = 542,900$) across the electrodes. The deposited polymer serves as an etch mask in subsequent steps. We were able to tailor the width of the deposited lines by controlling polymer mask deposition from the heated AFM tip [34], with lower tip temperature and higher tip speed producing narrower ribbons. The tip temperature ranged from 210 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ and the tip speed ranged from 100 nm/s to 1000 nm/s. To protect the MoS_2 -metal contact during etching, the tip also deposited larger regions of PMMA near both contacts. Figure 3.3 shows the typical AFM topology of the PMMA mask deposited by a heated AFM tip onto a MoS_2 microribbon transistor. The mask consists of two PMMA nanoribbons across the source and the drain, connected to 1 μm wide 2-3 μm long PMMA microribbons on each side. Next, we used XeF_2 gas [35] to etch the unmasked MoS_2 , forming a MoS_2 nanoribbon device (iii). We choose XeF_2 vapor over plasma etching because XeF_2 has higher selectivity of MoS_2 to PMMA. Figure 3.4 shows the Raman spectra of three tip-defined MoS_2 microribbon channels, and the spectra for an as-grown CVD MoS_2 flake. None of the three

samples exhibit peak shift in E'_{2g} or A_{1g} , confirming that the tDPN process does not damage the MoS_2 [16]. Finally, on some transistors, we used atomic layer deposition to encapsulate the nanoribbon device with 10 nm Al_2O_3 (iv). The ALD passivation layer was introduced with the goal of improving carrier mobility [36] and slowing degradation [37] by protecting the devices from air and water vapor. Table 3.1 summarizes the dimensions and electronic characteristics of seven monolayer MoS_2 nanoribbon transistors fabricated using this process, with width ranging from 30 nm to 370 nm. Devices A-C were passivated with 10 nm ALD Al_2O_3 , while Devices D-G were unpassivated.

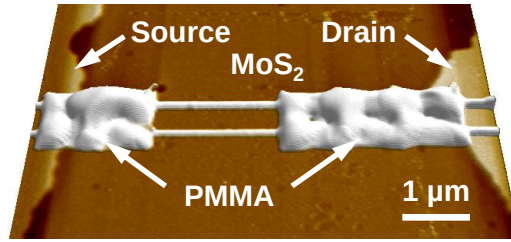


Figure 3.3 AFM topography of the PMMA mask on a MoS_2 microribbon transistor deposited by thermal dip-pen nanolithography (tDPN).

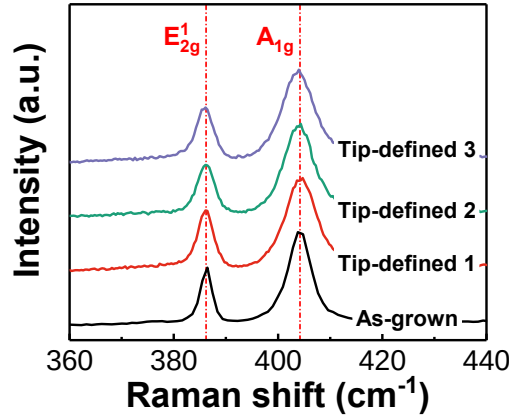


Figure 3.4 Typical Raman spectrum of an as-grown CVD monolayer MoS_2 flake and Raman spectra of three MoS_2 microribbon channels defined by tDPN.

Table 3.1 Summary of monolayer MoS₂ nanoribbon FETs^a

Device	W (nm)	L (μm)	μ (cm ² /Vs)	I _{on} /I _{off}	SS (V/dec)
A	30	0.16	8.53	2×10 ⁵	8.2
B	36	1.93	1.05	1×10 ³	12.8
C	60	2.95	4.33	4×10 ⁴	10.1
D	154	1.42	0.36	2×10 ³	6.0
E	230	3.75	1.71	2×10 ⁴	6.4
F	270	1.26	4.18	1×10 ⁶	5.6
G	370	2.10	1.19	1×10 ⁵	5.1

^aDevices A-C were passivated with 10 nm ALD Al₂O₃ while Devices D-G were unpassivated

Figure 3.5 shows an example MoS₂ monolayer nanoribbon device, Device B from Table 3.1. Figure 3.5(a) shows the false-colored scanning electron microscopy (SEM) image of the device, and Figure 3.5(b) shows the magnified SEM image. The images exhibit a 36 nm wide, 1.93 μm long nanoribbon in series with two microribbon segments, showing that our SPL technique is capable of fabricating continuous MoS₂ nanoribbons of *L/W* aspect ratio 54.

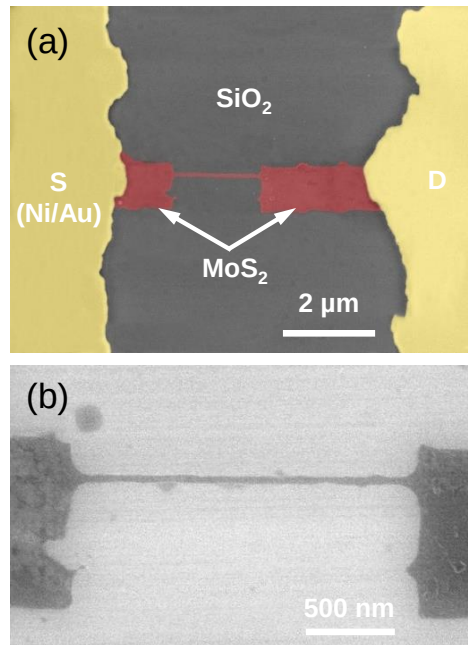


Figure 3.5 (a) False-colored SEM image of a 36-nm-wide monolayer MoS₂ nanoribbon device (Device B). (b) Magnified SEM image of the MoS₂ nanoribbon device shown in (a).

3.3 Results and Discussion

Figure 3.6 shows the transfer and output characteristics of a monolayer MoS₂ FET (Device C in Table 3.1) that was measured at each stage of fabrication – as a microribbon, after patterning down to a nanoribbon with tDPN, and after coating with an ALD passivation layer. The microribbon and nanoribbon have very different aspect ratios ($L/W = 0.48$ for the microribbon and 49 for the nanoribbon), and the nanoribbon is in series with two microribbon segments. To normalize the measurements, the effective conductivity per square is calculated as $\sigma_{\square} = I_{ds}/V_{ds} \sum (L/W)$, where $\sum (L/W)$ is the sum of L/W over all the channel segments in series. Figure 3.6(a) shows the transfer curves of the microribbon (black), and the nanoribbon before (red) and after ALD passivation (blue). Three important metrics of a field-effect transistor were extracted from the transfer curves: extrinsic field-effect mobility $\mu = d\sigma_{\square}/C_g dV_{bg}$, current on/off ratio I_{on}/I_{off} , and subthreshold swing SS . The mobility is calculated using the gate dielectric capacitance per unit area of 285-nm-thick SiO₂ ($C_g = 12.1$ nF/cm²).

The microribbon transistor in Figure 3.6 is 11.6 μm wide and 5.6 μm long, with a mobility of 25.54 cm²/Vs, a current on/off ratio of 1×10^6 , and a subthreshold swing of 2.3 V/dec. These values are typical of monolayer microribbon transistors on SiO₂/Si substrates [38–41]. After nanoribbon formation, the device had a nanoribbon that is 60 nm wide and 2.95 μm long, and the electronic properties changed to a mobility of 0.97 cm²/Vs, a current on/off ratio of 5×10^3 and a subthreshold swing of 6.4 V/dec. Several factors could affect the observed reduction in mobility and on/off ratio after nanoribbon formation, such as increased edge disorder from etching, a more prominent role of edge roughness and defects in nanoribbons, or increased surface scattering due to the presence of PMMA residue. The increased subthreshold swing likely resulted from increased interface trap density.

After ALD passivation, the nanoribbon device had a mobility of $4.33 \text{ cm}^2/\text{Vs}$, a current on/off ratio of 4×10^4 and a subthreshold swing of 10.1 V/dec . The increase in mobility and current on/off can be attributed to charged impurity screening by the high-k dielectric passivation. Increase in subthreshold swing likely resulted from higher interface trap density. The ALD process could have introduced additional interface traps due to the presence of H_2O in the reaction [42]. The transfer curves of the nanoribbon device are noisy compared with that of the microribbon device. The increased noise after nanoribbon formation is a result of contributions from 1) larger carrier number fluctuations in the channel due to increased density of interface traps which capture and release carriers [6] and 2) mobility fluctuation in the narrow channel [43]. Finally, the hysteresis in nanoribbon device is significantly larger than that in microribbon device, which can be explained by increased density of defects and traps in nanoribbons [44].

Figures 3.6(b)-(d) show the output characteristics of the microribbon device, and the nanoribbon device before and after ALD passivation. Figure 3.6(b) shows a linear dependence of drain current on drain-source voltage for the nickel-contacted MoS_2 microribbon transistor, indicating ohmic contacts at room temperature [45]. Figure 3.6(c) shows a nonlinear dependence of drain current on drain-source voltage for the nanoribbon device before ALD passivation. Since the contacts on the original device did not change, this indicates that a Schottky barrier was created between the MoS_2 microribbon channel and the nanoribbon channel. Figure 3.6(d) shows a linear dependence of drain current on drain-source voltage for the nanoribbon device after ALD passivation, indicating a reduction of the Schottky barrier height. Our hypothesis for this behavior is that the Fermi level of nanoribbons is lower than that of microribbons, as the nanoribbons were more heavily p-doped by higher ratio of edge defects and adsorbates [9,46–49], which creates a

Schottky barrier between each pair of microribbon channel and nanoribbon channel. After ALD passivation, edge adsorbates were reduced, so the Schottky barrier height decreased.

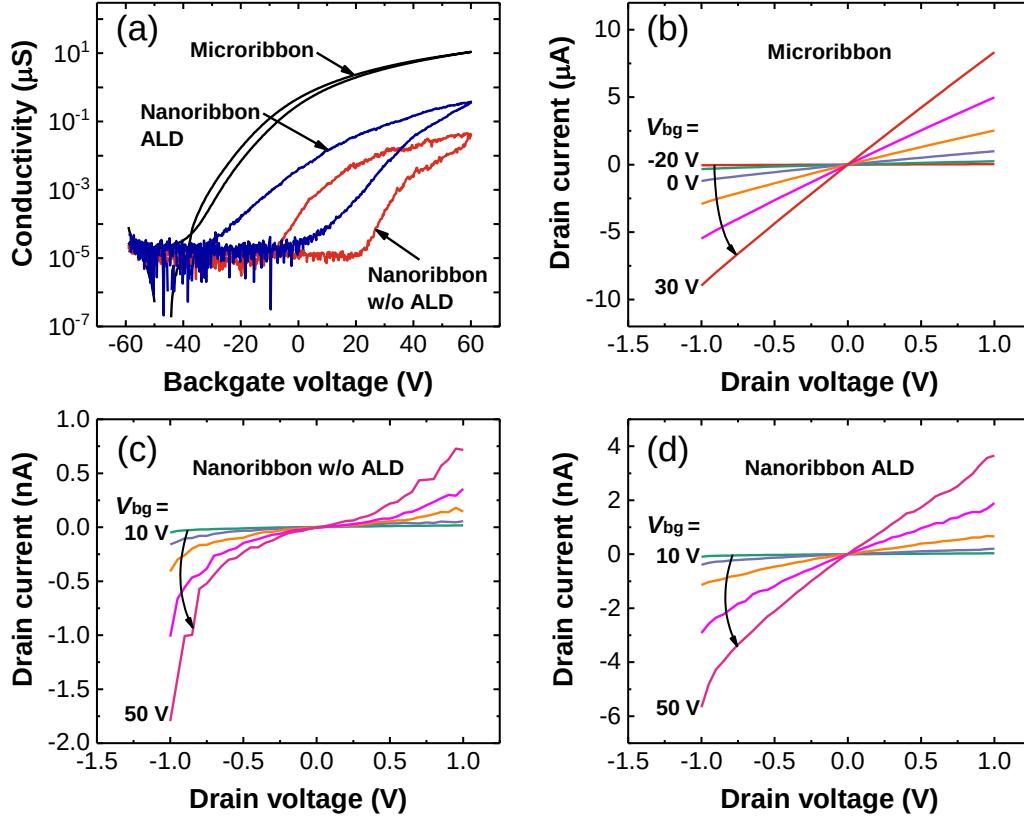


Figure 3.6 Electrical performance of a monolayer MoS₂ FET (Device C). (a) Transfer curves of the microribbon device and the nanoribbon device before and after ALD passivation. $V_{ds} = 0.5\text{ V}$. (b) Output curves of the microribbon device. (c) Output curves of the nanoribbon device before ALD passivation. (d) Output curves of the nanoribbon device after ALD passivation. V_{bg} was swept with 10 V step in (b) – (d).

Next, we compare the electronic behavior of different nanoribbon transistors, summarized in Table 3.1. The range in extrinsic field-effect mobility was $0.36 - 8.53\text{ cm}^2/\text{Vs}$, the range in current on/off ratio ranged was $10^3 - 10^6$, and the range in subthreshold swing was $5.1 - 12.8\text{ V/dec}$. In comparison, 5-15 nm thick multilayer MoS₂ nanoribbon devices reported in the literature had a mobility of $1.25 - 31\text{ cm}^2/\text{Vs}$, a current on/off ratio of $10^5 - 10^7$ and a subthreshold swing of $1 - 10\text{ V/dec}$ [9–11]. Considering that Coulomb scattering is weaker for thicker channels due to increased

interaction distance between interfacial Coulomb impurities and charge carriers in the channel [50], our monolayer nanoribbon devices have reasonable electrical properties compared with published values for multilayer nanoribbon devices. Finally, both Device A and Device C exhibited a current on/off ratio larger than 10^4 , which is much higher than that of graphene nanoribbon FETs of similar width [51] and comparable with that of 1-nm-wide graphene nanoribbon FETs [52].

To probe the impact of nanoribbon width on device performance, Figure 3.7 compares the transfer characteristics of two unpassivated nanoribbon devices that were fabricated on the same MoS₂ flake: a 30-nm-wide device (Device A) and a 60-nm-wide device (Device C). Device A had a field-effect mobility of 0.12 cm²/Vs, a current on/off ratio of 1×10^4 and a subthreshold swing of 6.5 V/dec, while Device C had a field-effect mobility of 2.76 cm²/Vs, a current on/off ratio of 3×10^4 and a subthreshold swing of 4.0 V/dec. Device A had a smaller mobility and a lower on/off ratio than Device C, which may be explained by a more prominent role of edge roughness in narrower nanoribbons. In addition, Device A had a larger subthreshold swing than Device C, which indicates that narrower nanoribbon devices have a higher density of interface traps.

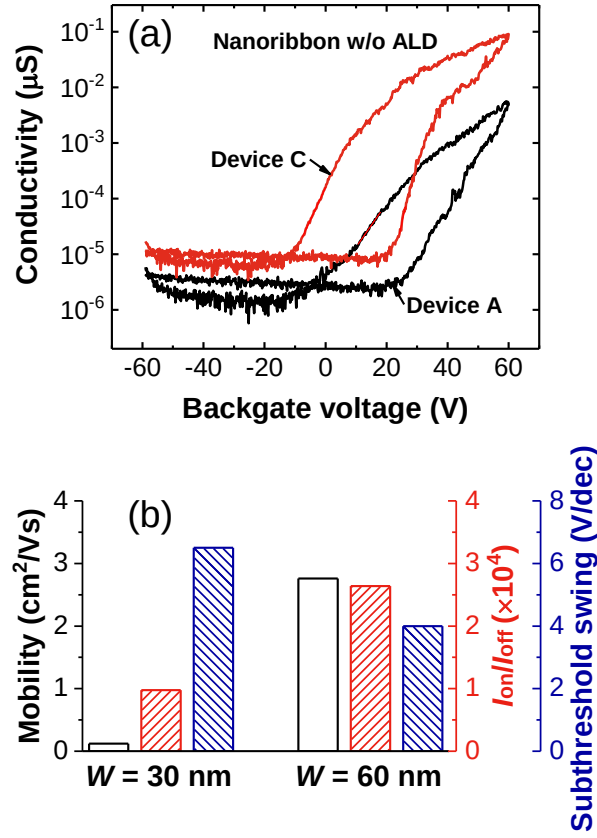


Figure 3.7 (a) Transfer curves of nanoribbon Device A ($W = 30$ nm) and Device C ($W = 60$ nm) before ALD passivation. $V_{ds} = 1$ V. (b) Comparison of the mobility, on to off ratio, and subthreshold swing of the two widths.

Finally, we studied the effect of nanoribbon patterning and ALD passivation on threshold voltage. Threshold voltage V_T was extracted by linear extrapolation [53] for the reverse sweep at $V_{ds} = 0.1$ V, as shown in Fig. 3.8. Although the threshold voltage of the microribbon devices varied widely, all of the threshold voltages increased after nanoribbon patterning, consistent with the observed positive threshold voltage shift in multi-layer (9-18 layers) MoS₂ nanoribbon transistors [9]. On average, threshold voltage increased by 21 V after nanoribbon formation, likely due to carrier depletion by surface adsorbates (e.g. water) [9,11,54]. After ALD passivation, the threshold

voltage of all three nanoribbon transistors (Devices A, B and C) decreased, which can be ascribed to reduced adsorbates [40].

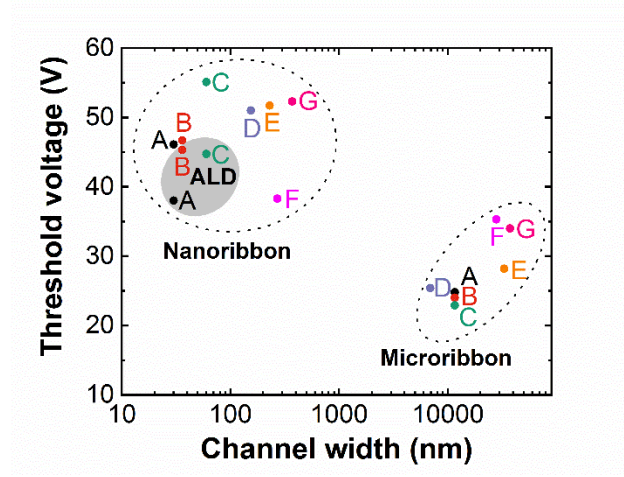


Figure 3.8 Threshold voltage as a function of channel width of all the devices listed in Table 3.1. Nanoribbon devices after ALD passivation are shown in the gray zone.

3.4 Conclusions and Future Work

In summary, we demonstrated the fabrication of single-layer MoS₂ nanoribbon transistors with channel width as narrow as 30 nm, by depositing a polymer etch mask with a heated AFM tip on prefabricated microribbon transistors to create ultra-narrow channel transistors. Of all the fabricated nanoribbon devices, with width ranging from 30 nm to 370 nm, the mobility ranged from 0.36 cm²/Vs to 8.53 cm²/Vs, the on/off ratio ranged from 1×10³ to 1×10⁶, and the subthreshold swing ranged from 5.1 V/dec to 12.8 V/dec. We examined the electrical properties of the device at each stage of fabrication and found that the electrical properties (mobility, on/off ratio and subthreshold swing) degrade after nanoribbon formation, while ALD passivation improves mobility and on/off ratio but degrades subthreshold swing. Change in the output characteristics indicates that a Schottky barrier was created after nanoribbon formation, and the Schottky barrier height was reduced after ALD passivation. By comparing a 30-nm-wide device

with a 60-nm-wide device that were fabricated on the same MoS₂ flake, we found that the narrower device had a smaller mobility, a lower on/off ratio and a larger subthreshold swing. We also observed that the threshold voltage increased after nanoribbon formation and decreased after ALD passivation.

Several steps could be taken to further improve the electrical performance of the MoS₂ nanoribbon transistors. First, the MoS₂ could be encapsulated before fabrication, perhaps with layers of hBN, which would reduce MoS₂ exposure to contaminants during processing [55,56]. The hBN could also be used as the gate dielectric material. Compared to SiO₂, hBN has fewer Coulomb impurities and traps and is atomically flat [50]. Second, the contacts could be selected to have a lower work function that would result in reduced contact resistance and improved extrinsic field-effect mobility [57–59]. Recent articles have reported good contacts to MoS₂ using ultra-high-vacuum metal deposition [60] or SPL based fabrication [61], both of which would be highly compatible with the present work. Third, the devices could be smaller. The ultimate resolution of tDPN depends on ink type, surface chemistry and tip shape [23,34,62]. For instance, deposition of 10 nm wide nanoparticle rows has been demonstrated with tDPN [62], which could potentially serve as etch mask for nanoribbon fabrication. The channels could be shorter as well in order to reduce channel resistance. Finally, since scanning probe lithography can be parallelized to scale up [63–65], we envision that the entire fabrication process consisting of CVD growth, optical lithography and SPL can be applied to manufacture ultra-scaled MoS₂ devices at the wafer scale.

3.5 References

- [1] Lembke D, Bertolazzi S and Kis A 2015 Single-Layer MoS₂ Electronics *Acc. Chem. Res.* **48** 100–10
- [2] Radisavljevic B and Kis A 2013 Mobility Engineering and a Metal–Insulator Transition in Monolayer MoS₂ *Nat. Mater.* **12** 815–20
- [3] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides *Nat. Nanotechnol.* **7** 699–712
- [4] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Single-Layer MoS₂ Transistors *Nat. Nanotechnol.* **6** 147–50
- [5] Yu Z, Ong Z Y, Pan Y, Cui Y, Xin R, Shi Y, Wang B, Wu Y, Chen T, Zhang Y W, Zhang G and Wang X 2016 Realization of Room-Temperature Phonon-Limited Carrier Transport in Monolayer MoS₂ by Dielectric and Carrier Screening *Adv. Mater.* **28** 547–52
- [6] Vu Q A, Fan S, Lee S H, Joo M-K, Yu W J and Lee Y H 2018 Near-Zero Hysteresis and Near-Ideal Subthreshold Swing in h-BN Encapsulated Single-Layer MoS₂ Field-Effect Transistors *2D Mater.* **5** 031001
- [7] Schwierz F 2010 Graphene Transistors *Nat. Nanotechnol.* **5** 487–96
- [8] Fiori G, Bonaccorso F, Iannaccone G, Palacios T, Neumaier D, Seabaugh A, Banerjee S K and Colombo L 2014 Electronics Based on Two-Dimensional Materials *Nat. Nanotechnol.* **9** 768–79
- [9] Liu H, Gu J and Ye P D 2012 MoS₂ Nanoribbon Transistors: Transition from Depletion Mode to Enhancement Mode by Channel-Width Trimming *IEEE Electron Device Lett.* **33** 1273–5
- [10] Stampfer B, Zhang F, Illarionov Y Y, Knobloch T, Wu P, Walzl M, Grill A, Appenzeller J and Grasser T 2018 Characterization of Single Defects in Ultrascaled MoS₂ Field-Effect Transistors *ACS Nano* **12** 5368–75
- [11] Zhang F, Lee C-H, Robinson J A and Appenzeller J 2018 Exploration of Channel Width Scaling and Edge States in Transition Metal Dichalcogenides *Nano Res.* **11** 1768–74
- [12] Espinosa F M, Ryu Y K, Marinov K, Dumcenco D, Kis A and Garcia R 2015 Direct Fabrication of Thin Layer MoS₂ Field-Effect Nanoscale Transistors by Oxidation Scanning Probe Lithography *Appl. Phys. Lett.* **106** 103503
- [13] Wei G, Lenferink E J, Czaplewski D A and Stern N P 2017 Width-Dependent Photoluminescence and Anisotropic Raman Spectroscopy from Monolayer MoS₂ Nanoribbons
- [14] Fox D S, Zhou Y, Maguire P, O’Neill A, Ó’Coileáin C, Gatensby R, Glushenkov A M, Tao T, Duesberg G S, Shvets I V., Abid M, Abid M, Wu H-C, Chen Y, Coleman J N,

- Donegan J F and Zhang H 2015 Nanopatterning and Electrical Tuning of MoS₂ Layers with a Subnanometer Helium Ion Beam *Nano Lett.* **15** 5307–13
- [15] Matsunaga M, Higuchi A, He G, Yamada T, Krüger P, Ochiai Y, Gong Y, Vajtai R, Ajayan P M, Bird J P and Aoki N 2016 Nanoscale-Barrier Formation Induced by Low-Dose Electron-Beam Exposure in Ultrathin MoS₂ Transistors *ACS Nano* **10** 9730–7
- [16] Parkin W M, Balan A, Liang L, Das P M, Lamparski M, Naylor C H, Rodríguez-Manzo J A, Johnson A T C, Meunier V and Drndić M 2016 Raman Shifts in Electron-Irradiated Monolayer MoS₂ *ACS Nano* **10** 4134–42
- [17] Kim C, Moon I, Lee D, Choi M S, Ahmed F, Nam S, Cho Y, Shin H-J, Park S and Yoo W J 2017 Fermi Level Pinning at Electrical Metal Contacts of Monolayer Molybdenum Dichalcogenides *ACS Nano* **11** 1588–96
- [18] Kalhor N, Boden S A and Mizuta H 2014 Sub-10nm Patterning by Focused He-Ion Beam Milling for Fabrication of Downscaled Graphene Nano Devices *Microelectron. Eng.* **114** 70–7
- [19] Zhao S, Xue J, Wang Y and Yan S 2012 Effect of SiO₂ Substrate on the Irradiation-Assisted Manipulation of Supported Graphene: A Molecular Dynamics Study *Nanotechnology* **23** 285703
- [20] Garcia R, Knoll A W and Riedo E 2014 Advanced Scanning Probe Lithography *Nat. Nanotechnol.* **9** 577–87
- [21] Martínez R V., Martínez J and Garcia R 2010 Silicon Nanowire Circuits Fabricated by AFM Oxidation Nanolithography *Nanotechnology* **21** 245301
- [22] Ryu Y K, Chiesa M and Garcia R 2013 Electrical Characteristics of Silicon Nanowire Transistors Fabricated by Scanning Probe and Electron Beam Lithographies *Nanotechnology* **24** 315205
- [23] Lee W-K, Robinson J T, Gunlycke D, Stine R R, Tamanaha C R, King W P and Sheehan P E 2011 Chemically Isolated Graphene Nanoribbons Reversibly Formed in Fluorographene Using Polymer Nanowire Masks *Nano Lett.* **11** 5461–4
- [24] Lee W K, Haydell M, Robinson J T, Laracuente A R, Cimpoiasu E, King W P and Sheehan P E 2013 Nanoscale Reduction of Graphene Fluoride via Thermochemical Nanolithography *ACS Nano* **7** 6219–24
- [25] Hu H, Banerjee S, Estrada D, Bashir R and King W P 2015 Tip-Based Nanofabrication of Arbitrary Shapes of Graphene Nanoribbons for Device Applications *RSC Adv.* **5** 37006–12
- [26] Wei Z, Wang D, Kim S-Y Y S, Kim S-Y Y S, Hu Y, Yakes M K, Laracuente A R, Dai Z, Marder S R, Berger C, King W P, De Heer W A, Sheehan P E and Riedo E 2010 Nanoscale Tunable Reduction of Graphene Oxide for Graphene Electronics *Science* **328** 1373–6

- [27] Zhang K, Fu Q, Pan N, Yu X, Liu J, Luo Y, Wang X, Yang J and Hou J 2012 Direct Writing of Electronic Devices on Graphene Oxide by Catalytic Scanning Probe Lithography *Nat. Commun.* **3** 1194
- [28] Dago A I, Ryu Y K and Garcia R 2016 Sub-20nm Patterning of Thin Layer WSe₂ by Scanning Probe Lithography *Appl. Phys. Lett.* **109** 163103
- [29] Najmaei S, Liu Z, Zhou W, Zou X, Shi G, Lei S, Yakobson B I, Idrobo J-C, Ajayan P M and Lou J 2013 Vapour Phase Growth and Grain Boundary Structure of Molybdenum Disulphide Atomic Layers *Nat. Mater.* **12** 754–9
- [30] Zhan Y, Liu Z, Najmaei S, Ajayan P M and Lou J 2012 Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate *Small* **8** 966–71
- [31] Li H, Zhang Q, Yap C C R, Tay B K, Edwin T H T, Olivier A and Baillargeat D 2012 From Bulk to Monolayer MoS₂: Evolution of Raman Scattering *Adv. Funct. Mater.* **22** 1385–90
- [32] Sheehan P E, Whitman L J, King W P and Nelson B A 2004 Nanoscale Deposition of Solid Inks via Thermal Dip Pen Nanolithography *Appl. Phys. Lett.* **85** 1589–91
- [33] Fletcher P C, Felts J R, Dai Z, Jacobs T D, Zeng H, Lee W, Sheehan P E, Carlisle J A, Carpick R W and King W P 2010 Wear-Resistant Diamond Nanoprobe Tips with Integrated Silicon Heater for Tip-Based Nanomanufacturing *ACS Nano* **4** 3338–44
- [34] Felts J R, Somnath S, Ewoldt R H and King W P 2012 Nanometer-Scale Flow of Molten Polyethylene from a Heated Atomic Force Microscope Tip *Nanotechnology* **23** 215301
- [35] Huang Y, Wu J, Xu X, Ho Y, Ni G, Zou Q, Koon G K W, Zhao W, Castro Neto A H, Eda G, Shen C and Özyilmaz B 2013 An Innovative Way of Etching MoS₂: Characterization and Mechanistic Investigation *Nano Res.* **6** 200–7
- [36] Qiu H, Pan L, Yao Z, Li J, Shi Y and Wang X 2012 Electrical Characterization of Back-Gated Bi-Layer MoS₂ Field-Effect Transistors and the Effect of Ambient on Their Performances *Appl. Phys. Lett.* **100** 123104
- [37] Gao J, Li B, Tan J, Chow P, Lu T M and Koratkar N 2016 Aging of Transition Metal Dichalcogenide Monolayers *ACS Nano* **10** 2628–35
- [38] Late D J, Liu B, Matte H S S R, Dravid V P and Rao C N R 2012 Hysteresis in Single-Layer MoS₂ Field Effect Transistors *ACS Nano* **6** 5635–41
- [39] Amani M, Chin M L, Mazzoni A L, Burke R A, Najmaei S, Ajayan P M, Lou J and Dubey M 2014 Growth-Substrate Induced Performance Degradation in Chemically Synthesized Monolayer MoS₂ Field Effect Transistors *Appl. Phys. Lett.* **104** 203506
- [40] He G, Ghosh K, Singiseti U, Ramamoorthy H, Somphonsane R, Bohra G, Matsunaga M, Higuchi A, Aoki N, Najmaei S, Gong Y, Zhang X, Vajtai R, Ajayan P M and Bird J P 2015 Conduction Mechanisms in CVD-Grown Monolayer MoS₂ Transistors: From Variable-Range Hopping to Velocity Saturation *Nano Lett.* **15** 5052–8

- [41] Ahn J-H, Parkin W M, Naylor C H, Johnson A T C and Drndić M 2017 Ambient Effects on Electrical Characteristics of CVD-Grown Monolayer MoS₂ Field-Effect Transistors *Sci. Rep.* **7** 4075
- [42] Smithe K K H, Suryavanshi S V., Muñoz Rojo M, Tedjarati A D and Pop E 2017 Low Variability in Synthetic Monolayer MoS₂ Devices *ACS Nano* **11** 8456–63
- [43] Song J G, Kim S J, Woo W J, Kim Y, Oh I K, Ryu G H, Lee Z, Lim J H, Park J and Kim H 2016 Effect of Al₂O₃ Deposition on Performance of Top-Gated Monolayer MoS₂-Based Field Effect Transistor *ACS Appl. Mater. Interfaces* **8** 28130–5
- [44] Sangwan V K, Arnold H N, Jariwala D, Marks T J, Lauhon L J and Hersam M C 2013 Low-Frequency Electronic Noise in Single-Layer MoS₂ Transistors *Nano Lett.* **13** 4351–5
- [45] Kaushik N, Mackenzie D M A, Thakar K, Goyal N, Mukherjee B, Boggild P, Petersen D H and Lodha S 2017 Reversible Hysteresis Inversion in MoS₂ Field Effect Transistors *npj 2D Mater. Appl.* **1** 34
- [46] Das S, Chen H Y, Penumatcha A V and Appenzeller J 2013 High Performance Multilayer MoS₂ Transistors with Scandium Contacts *Nano Lett.* **13** 100–5
- [47] Lee S Y, Kim U J, Chung J, Nam H, Jeong H Y, Han G H, Kim H, Oh H M, Lee H, Kim H, Roh Y G, Kim J, Hwang S W, Park Y and Lee Y H 2016 Large Work Function Modulation of Monolayer MoS₂ by Ambient Gases *ACS Nano* **10** 6100–7
- [48] Tongay S, Zhou J, Ataca C, Liu J, Kang J S, Matthews T S, You L, Li J, Grossman J C and Wu J 2013 Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating *Nano Lett.* **13** 2831–6
- [49] Zhang K, Borys N J, Bersch B M, Bhimanapati G R, Xu K, Wang B, Wang K, Labella M, Williams T A, Haque M A, Barnard E S, Fullerton-Shirey S, Schuck P J and Robinson J A 2017 Deconvoluting the Photonic and Electronic Response of 2D Materials: The Case of MoS₂ *Sci. Rep.* **7** 16938
- [50] Yu Z, Ong Z-Y, Li S, Xu J-B, Zhang G, Zhang Y-W, Shi Y and Wang X 2017 Analyzing the Carrier Mobility in Transition-Metal Dichalcogenide MoS₂ Field-Effect Transistors *Adv. Funct. Mater.* **27** 1604093
- [51] Li X, Wang X, Zhang L, Lee S and Dai H 2008 Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors *Science* **319** 1229–32
- [52] Llinas J P, Fairbrother A, Borin Barin G, Shi W, Lee K, Wu S, Yong Choi B, Braganza R, Lear J, Kau N, Choi W, Chen C, Pedramrazi Z, Dumsclaff T, Narita A, Feng X, Müllen K, Fischer F, Zettl A, Ruffieux P, Yablonovitch E, Crommie M, Fasel R and Bokor J 2017 Short-Channel Field-Effect Transistors with 9-Atom and 13-Atom Wide Graphene Nanoribbons *Nat. Commun.* **8** 633
- [53] Schroder D K 2005 Semiconductor Material and Device Characterization: Third Edition (Hoboken, New Jersey: John Wiley & Sons)

- [54] Estrada D, Dutta S, Liao A and Pop E 2010 Reduction of Hysteresis for Carbon Nanotube Mobility Measurements Using Pulsed Characterization *Nanotechnology* **21** 085702
- [55] Cui X, Lee G-H, Kim Y D, Arefe G, Huang P Y, Lee C-H, Chenet D A, Zhang X, Wang L, Ye F, Pizzocchero F, Jessen B S, Watanabe K, Taniguchi T, Muller D A, Low T, Kim P and Hone J 2015 Multi-Terminal Transport Measurements of MoS₂ Using a van Der Waals Heterostructure Device Platform *Nat. Nanotechnol.* **10** 534–40
- [56] Allain A, Kang J, Banerjee K and Kis A 2015 Electrical Contacts to Two-Dimensional Semiconductors *Nat. Mater.* **14** 1195–205
- [57] Liu Y, Wu H, Cheng H C, Yang S, Zhu E, He Q, Ding M, Li D, Guo J, Weiss N O, Huang Y and Duan X 2015 Toward Barrier Free Contact to Molybdenum Disulfide Using Graphene Electrodes *Nano Lett.* **15** 3030–4
- [58] Chee S-S, Seo D, Kim H, Jang H, Lee S, Moon S P, Lee K H, Kim S W, Choi H and Ham M-H 2019 Lowering the Schottky Barrier Height by Graphene/Ag Electrodes for High-Mobility MoS₂ Field-Effect Transistors *Adv. Mater.* **31** 1804422
- [59] English C D, Shine G, Dorgan V E, Saraswat K C and Pop E 2016 Improved Contacts to MoS₂ Transistors by Ultra-High Vacuum Metal Deposition *Nano Lett.* **16** 3824–30
- [60] Zheng X, Calò A, Albisetti E, Liu X, Alharbi A S M, Arefe G, Liu X, Spieser M, Yoo W J, Taniguchi T, Watanabe K, Aruta C, Ciarrocchi A, Kis A, Lee B S, Lipson M, Hone J, Shahrjerdi D and Riedo E 2019 Patterning Metal Contacts on Monolayer MoS₂ with Vanishing Schottky Barriers Using Thermal Nanolithography *Nat. Electron.* **2** 17–25
- [61] Lee W K, Dai Z, King W P and Sheehan P E 2010 Maskless Nanoscale Writing of Nanoparticle–Polymer Composites and Nanoparticle Assemblies Using Thermal Nanoprobes *Nano Lett.* **10** 129–33
- [62] Salaita K, Wang Y, Fragala J, Vega R A, Liu C and Mirkin C A 2006 Massively Parallel Dip-Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays *Angew. Chemie Int. Ed.* **45** 7220–3
- [63] Somnath S, Kim H J, Hu H and King W P 2014 Parallel Nanoimaging and Nanolithography Using a Heated Microcantilever Array *Nanotechnology* **25** 014001
- [64] Carroll K M, Lu X, Kim S, Gao Y, Kim H J, Somnath S, Polloni L, Sordan R, King W P, Curtis J E and Riedo E 2014 Parallelization of Thermochemical Nanolithography *Nanoscale* **6** 1299–304

CHAPTER 4: CLEANING AND SMOOTHING THE INTERFACES OF HEXAGONAL BORON NITRIDE ENCAPSULATED MONOLAYER MOLYBDENUM DISULFIDE WITH CONTACT MODE ATOMIC FORCE MICROSCOPY

4.1 Introduction

Two-dimensional materials, such as MoS₂, are being explored as an alternative to silicon for next generation low-power electronic applications, because their atomic thickness allows a very high degree of electrostatic control over their electrical conductivity [1]. MoS₂ monolayers have several advantages as a transistor channel material, because of its sizable bandgap (1.9 eV [2]), satisfactory electron mobility [3], good thermal stability up to 1,100 °C [4] and superior immunity to short-channel effects [5]. However, due to its high surface-to-volume ratio, the electrical performance of MoS₂ is limited by extrinsic factors such as Coulomb impurities and charge traps in substrate materials [6] and surface adsorbates [7–9].

hBN encapsulation is an effective method in reducing extrinsic disorders and improving the mobility of MoS₂ field-effect transistors (FETs). First, hBN encapsulation could protect MoS₂ from contaminations from the device fabrication process [10] and reduce scattering from ambient adsorbates [11]. Second, compared to SiO₂ and high- κ dielectric substrates, hBN has fewer Coulomb impurities and traps and is atomically flat [11,12]. Third, monolayer hBN can serve as a tunneling layer to improve the contact between MoS₂ and metal and reduce contact resistance [13]. The state-of-the-art hBN encapsulated monolayer MoS₂ FETs had a record-high low-temperature

mobility of $1,020 \text{ cm}^2/\text{Vs}$ [10], a near-ideal subthreshold swing of 63 mV/dec and a current on/off ratio of 10^9 [11].

Despite improved electrical performance of MoS_2 transistors with hBN encapsulation, hBN encapsulated MoS_2 stacks prepared by mechanical transfer techniques typically have trapped contaminants and voids between hBN and MoS_2 [14]. These interface impurities act as charge traps or Coulomb impurities and obscure the intrinsic behavior of MoS_2 . Thermal annealing is often used to reduce interface contaminants, but the random nature of annealing could also cause trapped contaminants to accumulate in clusters rather than remove them from the interface of two-dimensional (2D) layers [11]. Alternatively, contact mode atomic force microscopy (AFM) can be used to remove interface contaminants between 2D layers in a controllable fashion [15]. AFM cleaning improved the mobility of graphene on hBN by a factor of 65% to 250% [16]. Likewise, the mobility of hBN encapsulated monolayer MoS_2 may also be improved by AFM cleaning.

This chapter reports improving the mobility of hBN encapsulated monolayer MoS_2 FETs by cleaning and smoothing their interfaces with contact mode AFM. We showed that the AFM cleaning process flattened hBN encapsulated monolayer MoS_2 and reduced the photoluminescence peak width of monolayer MoS_2 , both of which indicate a reduction in interface traps between hBN and MoS_2 . One MoS_2 FET fabricated on AFM cleaned hBN encapsulated monolayer MoS_2 achieved a high mobility of $73.01 \text{ cm}^2/\text{Vs}$. Finally, the mobility of all four hBN encapsulated monolayer MoS_2 FETs improved by an average of 73% after AFM cleaning, while the hysteresis of these four devices also increased from 1% to 20%.

4.2 Experimental Method

Figure 4.1 shows the concept of AFM cleaning of stacked 2D layers. As shown in Fig. 4.1(a), as-transferred 2D stacks have trapped contaminants and voids between the 2D layers. A clean transfer technique [18] results in intimate contacts between layers where the interface contaminants and voids are absent. By scanning the surface of the stacked 2D layers with an AFM tip in contact mode, contact force applied by the AFM tip squeezes trapped contaminants and voids out from the interface of stacked 2D layers and flattens the stacked 2D layers, while pushing surface contaminants along the scan direction.

All AFM cleaning and measurement experiments were performed with an Asylum MFP-3D AFM system. The cleaning tips typically had a nominal tip radius of 8 nm and a spring constant of 3 N/m. However, when the device had large surface contaminants which could not be displaced by the cleaning tip with 8 nm tip radius, a blunter tip with 25 nm tip radius and a spring constant of 0.45 N/m was used. The cleaning force was determined by first engaging the tip on the sample at a tiny force of 10 nN, and then increasing the force at a step size of 10 nN while cleaning the device, until the AFM image of the device did not look cleaner. The appropriate AFM cleaning force was in the range of 60 – 90 nN for hBN encapsulated monolayer MoS₂. The scan size for AFM cleaning varied from 3 μ m to 7 μ m, depending on the desired size of the cleaning region. The scan rate was typically 1-2 Hz, which corresponds to a scan speed as high as 28 μ m/s. The scan rate was limited by the control system of the MFP-3D, which could be greatly increased using a video-rate AFM system [17]. The density of scan lines was typically 5 nm/line, which was smaller than the tip radius and ensured that contaminants were pushed out of the cleaned region rather than accumulating between scan lines. To avoid redeposition of contaminants from the cleaning tip, we used a different tip for imaging the device after cleaning. The imaging tip had a

nominal tip radius of 8 nm, a typical spring constant of 40 N/m, and a typical resonance frequency of 325 kHz. Devices were imaged in tapping mode to minimize the interaction between the imaging tip and the device surface. The imaging process did not affect the device surface, as repeated imaging of the same area produced identical AFM images.

Figures 4.1(b)-(e) demonstrates the change in the AFM images of an hBN encapsulated monolayer MoS₂ stack on a SiO₂/Si substrate after AFM cleaning at a contact force of 65 nN. Figures 4.1(b) and 4.1(d) show the device as-transferred. The rough line scan in Fig. 4.1(d) indicates trapped contaminants and voids between hBN and MoS₂. Figures 4.1(c) and 4.1(e) show the device after AFM cleaning. Compared against the line scan in Fig. 4.1(b), the smoother line scan in Fig. 4.1(e) indicates reduced interface contaminants and voids.

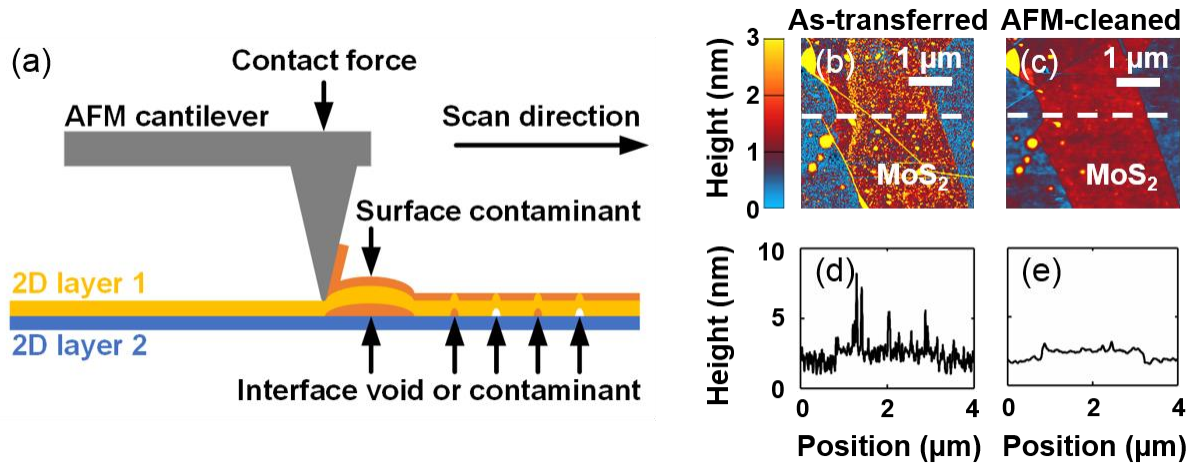


Figure 4.1 (a) Schematic of the AFM cleaning technique. AFM images of hBN encapsulated monolayer MoS₂ (b) as-transferred and (c) after AFM cleaning. (d)(e) Line scans along the dashed white lines in (b) and (c), respectively.

4.3 Results and Discussion

First, we demonstrate that our AFM cleaning process does not damage monolayer MoS₂. Figure 4.2 shows the Raman spectrum of the AFM-cleaned region and the as-transferred region of the same hBN encapsulated monolayer MoS₂ flake. The applied contact force between the AFM

tip and the sample during AFM cleaning was 90 nN. The AFM-cleaned region exhibits no obvious peak shift in E_{2g}^1 or A_{1g} from the as-transferred region, confirming that the AFM cleaning process at a contact force of up to 90 nN does not damage monolayer MoS_2 [19].

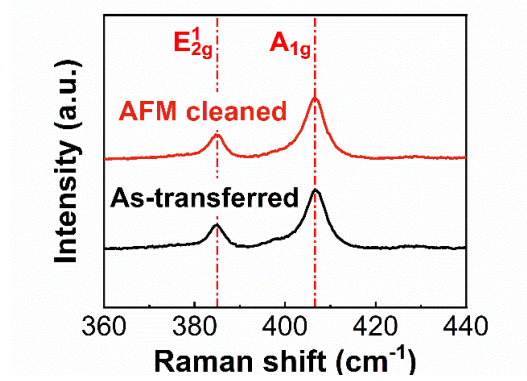


Figure 4.2 Raman spectrum of the AFM cleaned region and the as-transferred region of an hBN encapsulated monolayer MoS_2 flake.

Then we show the effect of AFM cleaning on the photoluminescence (PL) response of hBN encapsulated monolayer MoS_2 in Fig. 4.3. The AFM cleaning force was 65 nN. The as-transferred region had an average PL peak width of 84 ± 3 meV, while the AFM-cleaned region had a smaller average PL peak width of 70 ± 3 meV. Therefore, the AFM cleaning process improved PL peak width, indicating that AFM cleaning reduces interface trap density [11].

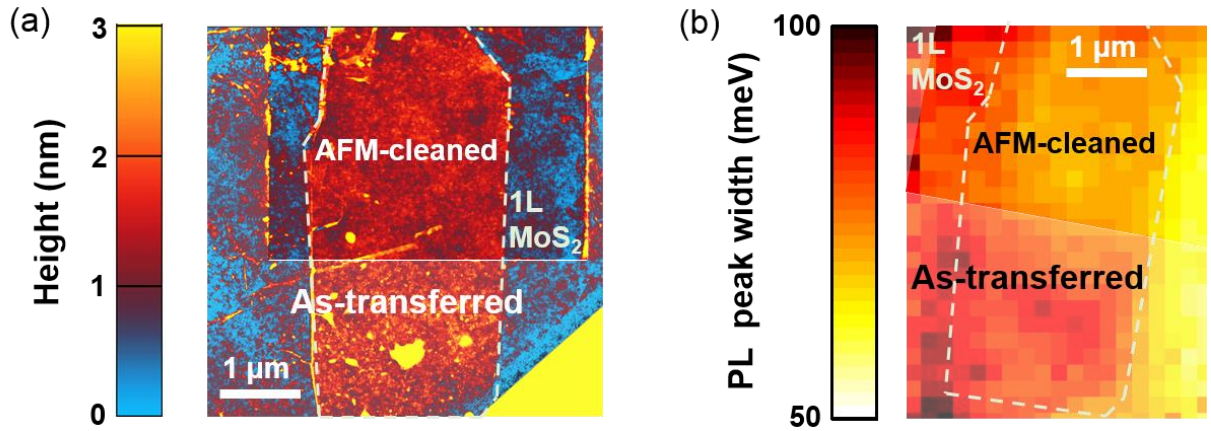


Figure 4.3 (a) Comparison of (a) AFM topography and (b) photoluminescence response of AFM-cleaned vs as-transferred hBN encapsulated monolayer MoS_2 .

An example of a MoS₂ FET fabricated on AFM-cleaned hBN encapsulated monolayer MoS₂ is shown in Fig. 4.4. Figure 4.4(a) shows the schematic of the device structure. The device consists of hBN encapsulated monolayer MoS₂ as the channel, and gold on nickel as the source and the drain, 8 nm thick bottom hBN and 300 nm thick silicon dioxide as the gate dielectric and a conductive silicon as the back gate. The top monolayer hBN also serves as a tunnel layer to inject electrons from metal contacts into monolayer MoS₂. The device had a width of 2.4 μm and a length of 1.0 μm , as shown in Fig. 4.4(b). Figure 4.4(c) shows the transfer curve of the FET characterized in air. The device achieved an extrinsic electron mobility of 73.01 cm²/Vs, which is among the highest for monolayer MoS₂ [10,20–22].

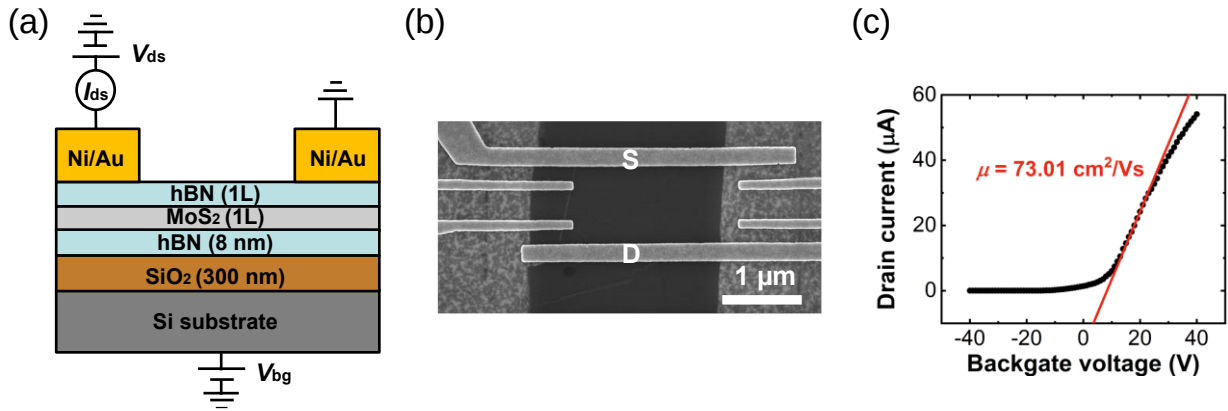


Figure 4.4 (a) Cross-sectional view of a device fabricated on an AFM-cleaned flake, along with the electrical connections used to characterize the devices. (b) SEM image of the FET. (c) Transfer curve of the FET. $V_{ds} = 1 \text{ V}$.

Lastly, we studied the effect of AFM cleaning on the electrical performance of hBN encapsulated monolayer MoS₂ FETs, as shown in Fig. 4.5. We fabricated a total of four devices on the same as-transferred hBN encapsulated monolayer MoS₂ stack and characterized the devices in air before and after AFM cleaning. The AFM cleaning force was 85 nN, with a tip radius of 25 nm and a scan speed of 17 $\mu\text{m/s}$. The device structure is identical to the one shown in Fig. 4.4(a). Figure 4.5(a) shows the AFM topology of the devices (Devices A-D) before AFM cleaning. Figure

4.5(b) shows the AFM topology after AFM cleaning. The average surface roughness decreased from 1.22 nm to 0.20 nm after cleaning. Figure 4.5(c) shows the transfer curves of the four FETs characterized in air before and after AFM cleaning, and Fig. 4.5(d) shows the change in mobility. The mobility of four devices increased by an average of 73% after AFM cleaning, from 21.95 ± 2.27 cm^2/Vs to 38.03 ± 6.12 cm^2/Vs . The hysteresis of the devices also increased from 1% to 20% after cleaning. Whether AFM cleaning caused the increase in hysteresis remains to be explored.

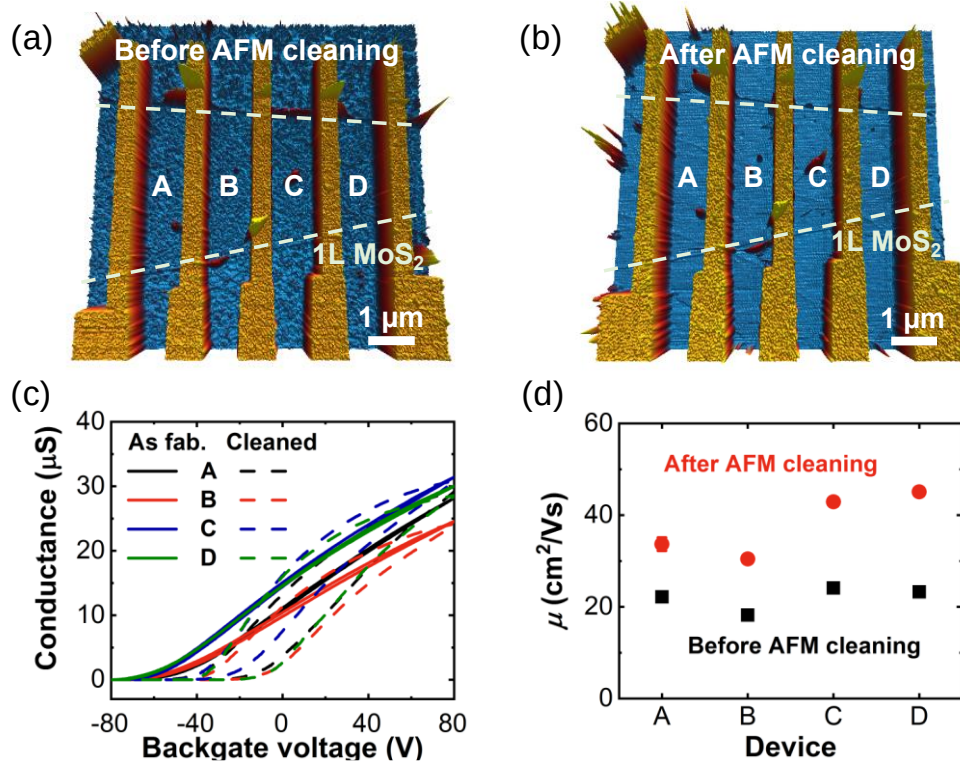


Figure 4.5 (a) AFM topography of hBN encapsulated monolayer MoS₂ FETs (a) before and (b) after AFM cleaning. (c) Transfer curve of the FETs. $V_{\text{ds}} = 0.1$ V. (d) Change in mobilities before and after AFM cleaning.

4.4 Conclusions and Future Work

In conclusion, we demonstrated that cleaning and smoothing the interfaces of hBN encapsulated monolayer MoS₂ with contact mode AFM could improve the mobility of MoS₂ transistors. AFM cleaning reduced the surface roughness and the PL peak width of hBN

encapsulated monolayer MoS₂, both of which indicate a reduction in interface traps. One MoS₂ FET fabricated on AFM cleaned hBN encapsulated monolayer MoS₂ achieved a mobility of 73.01 cm²/Vs, which is among the highest for monolayer MoS₂. Finally, the mobility of four hBN encapsulated monolayer MoS₂ FETs improved by an average of 73% from 21.95±2.27 cm²/Vs to 38.03±6.12 cm²/Vs after AFM cleaning. However, the hysteresis of these four devices also increased from 1% to 20%. Whether the increase in hysteresis resulted from AFM cleaning or changes in ambient conditions remains to be explored.

To minimize the effect of ambient adsorbates on device testing, we should fabricate and characterize devices on AFM-cleaned and as-transferred regions side-by-side. After transferring hBN encapsulated monolayer MoS₂ onto a SiO₂/Si substrate, clean half of the 2D stack with an AFM tip and leave the other half as-transferred. Then fabricate devices on both AFM-cleaned and as-transferred regions. Since the environmental conditions would be the same for all the FETs on the same substrate, we can conclude the effect of AFM cleaning by comparing the electrical performance of hBN encapsulated monolayer MoS₂ FETs fabricated on AFM-cleaned regions and on as-transferred regions.

4.5 References

- [1] Lembke D, Bertolazzi S and Kis A 2015 Single-Layer MoS₂ Electronics *Acc. Chem. Res.* **48** 100–10
- [2] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically Thin MoS₂: A New Direct-Gap Semiconductor *Phys. Rev. Lett.*
- [3] Kaasbjerg K, Thygesen K S and Jacobsen K W 2012 Phonon-Limited Mobility in n-Type Single-Layer MoS₂ from First Principles *Phys. Rev. B - Condens. Matter Mater. Phys.* **85** 115317
- [4] Spalvins T 1987 A Review of Recent Advances in Solid Film Lubrication *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **5** 212–9
- [5] Desai S B, Madhvapathy S R, Sachid A B, Llinas J P, Wang Q, Ahn G H, Pitner G, Kim M J, Bokor J, Hu C, Wong H-S P and Javey A 2016 MoS₂ Transistors with 1-Nanometer Gate Lengths *Science* **354** 99–102
- [6] Yu Z, Ong Z Y, Pan Y, Cui Y, Xin R, Shi Y, Wang B, Wu Y, Chen T, Zhang Y W, Zhang G and Wang X 2016 Realization of Room-Temperature Phonon-Limited Carrier Transport in Monolayer MoS₂ by Dielectric and Carrier Screening *Adv. Mater.* **28** 547–52
- [7] Late D J, Liu B, Matte H S S R, Dravid V P and Rao C N R 2012 Hysteresis in Single-Layer MoS₂ Field Effect Transistors *ACS Nano* **6** 5635–41
- [8] Qiu H, Pan L, Yao Z, Li J, Shi Y and Wang X 2012 Electrical Characterization of Back-Gated Bi-Layer MoS₂ Field-Effect Transistors and the Effect of Ambient on Their Performances *Appl. Phys. Lett.* **100** 123104
- [9] Ahn J-H, Parkin W M, Naylor C H, Johnson A T C and Drndić M 2017 Ambient Effects on Electrical Characteristics of CVD-Grown Monolayer MoS₂ Field-Effect Transistors *Sci. Rep.* **7** 4075
- [10] Cui X, Lee G-H, Kim Y D, Arefe G, Huang P Y, Lee C-H, Chenet D A, Zhang X, Wang L, Ye F, Pizzocchero F, Jessen B S, Watanabe K, Taniguchi T, Muller D A, Low T, Kim P and Hone J 2015 Multi-Terminal Transport Measurements of MoS₂ Using a van Der Waals Heterostructure Device Platform *Nat. Nanotechnol.* **10** 534–40
- [11] Vu Q A, Fan S, Lee S H, Joo M-K, Yu W J and Lee Y H 2018 Near-Zero Hysteresis and Near-Ideal Subthreshold Swing in h-BN Encapsulated Single-Layer MoS₂ Field-Effect Transistors *2D Mater.* **5** 031001
- [12] Lee C, Rathi S, Khan M A, Lim D, Kim Y, Yun S J, Youn D-H, Watanabe K, Taniguchi T and Kim G-H 2018 Comparison of Trapped Charges and Hysteresis Behavior in HBN Encapsulated Single MoS₂ Flake Based Field Effect Transistors on SiO₂ and HBN Substrates *Nanotechnology* **29** 335202
- [13] Wang J, Yao Q, Huang C-W, Zou X, Liao L, Chen S, Fan Z, Zhang K, Wu W, Xiao X,

- Jiang C and Wu W-W 2016 High Mobility MoS₂ Transistor with Low Schottky Barrier Contact by Using Atomic Thick h-BN as a Tunneling Layer *Adv. Mater.* **28** 8302–8
- [14] Purdie D G, Pugno N M, Taniguchi T, Watanabe K, Ferrari A C and Lombardo A 2018 Cleaning Interfaces in Layered Materials Heterostructures *Nat. Commun.* **9** 5387
- [15] Rosenberger M R, Chuang H J, McCreary K M, Hanbicki A T, Sivaram S V. and Jonker B T 2018 Nano-"Squeegee" for the Creation of Clean 2D Material Interfaces *ACS Appl. Mater. Interfaces* **10** 10379–87
- [16] Goossens A M, Calado V E, Barreiro A, Watanabe K, Taniguchi T and Vandersypen L M K 2012 Mechanical Cleaning of Graphene *Appl. Phys. Lett.* **100** 073110
- [17] Pizzocchero F, Gammelgaard L, Jessen B S, Caridad J M, Wang L, Hone J, Bøggild P and Booth T J 2016 The Hot Pick-up Technique for Batch Assembly of van Der Waals Heterostructures *Nat. Commun.* **7** 11894
- [18] Song B, Xi N, Yang R, Lai K W C and Qu C 2011 Video Rate Atomic Force Microscopy (AFM) Imaging Using Compressive Sensing *2011 11th IEEE International Conference on Nanotechnology (IEEE)* pp 1056–9
- [19] Parkin W M, Balan A, Liang L, Das P M, Lamparski M, Naylor C H, Rodríguez-Manzo J A, Johnson A T C, Meunier V and Drndić M 2016 Raman Shifts in Electron-Irradiated Monolayer MoS₂ *ACS Nano* **10** 4134–42
- [20] Cui X, Shih E-M, Jauregui L A, Chae S H, Kim Y D, Li B, Seo D, Pistunova K, Yin J, Park J-H, Choi H-J, Lee Y H, Watanabe K, Taniguchi T, Kim P, Dean C R and Hone J C 2017 Low-Temperature Ohmic Contact to Monolayer MoS₂ by van Der Waals Bonded Co/ h -BN Electrodes *Nano Lett.* **17** 4781–6
- [21] Liu Y, Wu H, Cheng H C, Yang S, Zhu E, He Q, Ding M, Li D, Guo J, Weiss N O, Huang Y and Duan X 2015 Toward Barrier Free Contact to Molybdenum Disulfide Using Graphene Electrodes *Nano Lett.* **15** 3030–4
- [22] Wang Y, Kim J C, Wu R J, Martinez J, Song X, Yang J, Zhao F, Mkhoyan A, Jeong H Y and Chhowalla M 2019 Van Der Waals Contacts between Three-Dimensional Metals and Two-Dimensional Semiconductors *Nature* **568** 70–4

CHAPTER 5: MONOLAYER MOLYBDENUM DISULFIDE NANORIBBON-NANOPORE DEVICES FOR SINGLE- MOLECULE SENSING

5.1 Introduction

Nanopore sensing uses voltage to drive charged macromolecules through a nanopore in a membrane and monitor how ionic current through the nanopore changes as single molecules pass through it [1]. Nanopore sensors enable label-free analysis of charged biopolymers with sub-nanometer precision, and thus are suitable for DNA sequencing applications [2]. Solid-state nanopore sensors are one of the nanopore technologies that could potentially meet the need for cheaper and faster genome sequencing, owing to their mechanical, chemical and thermal robustness and durability, compatibility with complementary metal-oxide-semiconductor (CMOS) technology and potential for integration into wafer-scale circuits [3].

Limitations in temporal resolution preclude DNA sequencing with solid state nanopores. The temporal resolution of a solid-state nanopore depends on DNA translocation speed, measurement bandwidth and the associated current noise level. 1-10 MHz sampling rate is needed to resolve individual nucleotides, as DNA molecules translocate through a solid state nanopore at the speed of 1 base/ μ s or faster [2]. However, the ionic noise at such bandwidth is too high to resolve genome sequence information [4,5]. One solution to achieve the temporal resolution required for DNA sequencing is to slow DNA translocation down from ~ 1 base/ μ s to ~ 1 base/ms [6–8]. Strategies for slowing DNA transport include maintaining viscosity or chemical potential

gradient across the membrane [7,9,10], increasing DNA-counterion interactions [8] and enhancing DNA-pore interactions [11,12]. Another solution is to reduce the electrical noise at high bandwidth [4,5]. An integrated complementary metal-oxide-semiconductor (CMOS) amplifier has been demonstrated with low noise recording at a bandwidth of 10 MHz [5]. Alternatively, new readout mechanisms with integrated sensors, like field-effect transistors (FETs), may achieve the signal-to-noise ratio needed for high bandwidth solid state nanopore sequencing [2].

Only a few publications report nanopore sensing with FET-nanopore devices, due to the complexity of device fabrication. The first FET-nanopore device [13] was fabricated with synthesized silicon nanowires as the nanoscale FET, where the silicon nanowires were 30-50 nm in diameter and less than 200 nm long. Simultaneous detection of DNA translocation in both ionic current and FET conductance signals was demonstrated, and the sensor signal was found to be a linear amplification of the ionic current signal for the local potential sensing mechanism. To improve the spatial sensing resolution, solid-state nanopores integrated with ~ 100 nm wide graphene nanoribbon transistors were fabricated [14]. Graphene is only 0.335 nm thick, equivalent to the spacing between two bases in a DNA chain. To increase the sensitivity of graphene nanoribbons to local potential changes near the nanopore, $30\text{ nm} \times 30\text{ nm}$ short and narrow graphene nanoribbon transistors were fabricated [15]. While FET signals of reported FET-nanopore devices could detect DNA translocation through nanopores, their signal-to-noise ratio (~ 5) was not large enough for DNA sequencing applications. FET-nanopore devices with large signal-to-noise ratio are needed to enable solid-state nanopore based DNA sequencing.

We propose that monolayer MoS_2 nanoribbon FET-nanopore devices are potentially well suited for nanopore based single molecule sensing and DNA sequencing: (1) As a semiconducting electronic material, MoS_2 has better sensitivity to local electric potential changes and thus larger

FET signal-to-noise ratio than graphene. (2) As with graphene, MoS₂ monolayers have similar thickness to the spacing between two bases in a DNA chain (~ 0.34 nm), providing excellent spatial resolution. (3) Nanoribbons improve the sensitivity to localized effects near the nanopore.

This chapter presents the design and fabrication of hBN encapsulated monolayer MoS₂ nanoribbon FET-nanopore devices, which consist of nanopores of 4-10 nm in ~ 100 nm wide hBN/MoS₂/hBN nanoribbons. We demonstrate the detection of dsDNA translocation thru a monolayer MoS₂ nanoribbon-nanopore device in ionic channel. Finally, we show example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current.

5.2 Design and Fabrication

Figure 5.1 shows the structure of the monolayer MoS₂ nanoribbon FET-nanopore device and the concept for its operation. Figures 5.1(a) and 5.1(b) show the side view and a three-dimensional representation of the FET-nanopore device, which consists of an hBN encapsulated monolayer MoS₂ nanoribbon channel, electrical contacts for the source and drain consisting of 30 nm gold on 5 nm nickel, and a solid state nanopore inside the nanoribbon. The top and bottom hBN encapsulation reduces MoS₂ exposure to contaminants during processing [16], and reduces interface traps and Coulomb impurities [17]. The top hBN is a monolayer, which is also used as a tunnel layer to inject carriers from Ni/Au metal contacts into monolayer MoS₂ [18]. The bottom hBN is about 5 nm thick. The 10-20 nm thick bottom layer of SiN_x provides mechanical support, the 10 nm bottom layer of Al₂O₃ serves as an etch stop during nanoribbon formation [19], and the 24 nm top layer of Al₂O₃ provides top side passivation to prevent leakage [20].

Figure 5.1(c) shows the concept of simultaneous detection of DNA translocation with the FET-nanopore device. A transmembrane voltage V_{ionic} drives negatively charged DNA molecules

from the *cis* chamber to the *trans* chamber via the nanopore channel. As a DNA molecule moves thru the nanopore, the ionic current I_{ionic} drops due to volumetric blockage of the ionic channel. Upon DNA translocation, the local potential distribution around the nanopore also changes, which changes the electrostatic gate modulating the MoS₂ current I_{ds} and thus the MoS₂ current. As a result, both ionic current and MoS₂ current can detect DNA translocation thru a nanopore in a MoS₂ nanoribbon simultaneously.

There are two regions of electronic operations where the MoS₂ FET can operate to detect DNA translocation: region I where the MoS₂ current increases exponentially with ionic voltage, and region II where the MoS₂ current increases quadratically or linearly with ionic voltage [21]. When the FET operates in region I, the MoS₂ signal due to DNA translocation is small in magnitude but large in change of order of magnitude from the baseline current. When the FET operates in region II, the MoS₂ signal is large in magnitude but small in change of order of magnitude. In low-frequency (< 10 kHz) measurement where flicker noise dominates, the signal-to-noise ratio (SNR) scales with the order of magnitude change in current upon DNA translocation [22], so the MoS₂ current has a higher SNR in region I than in region II.

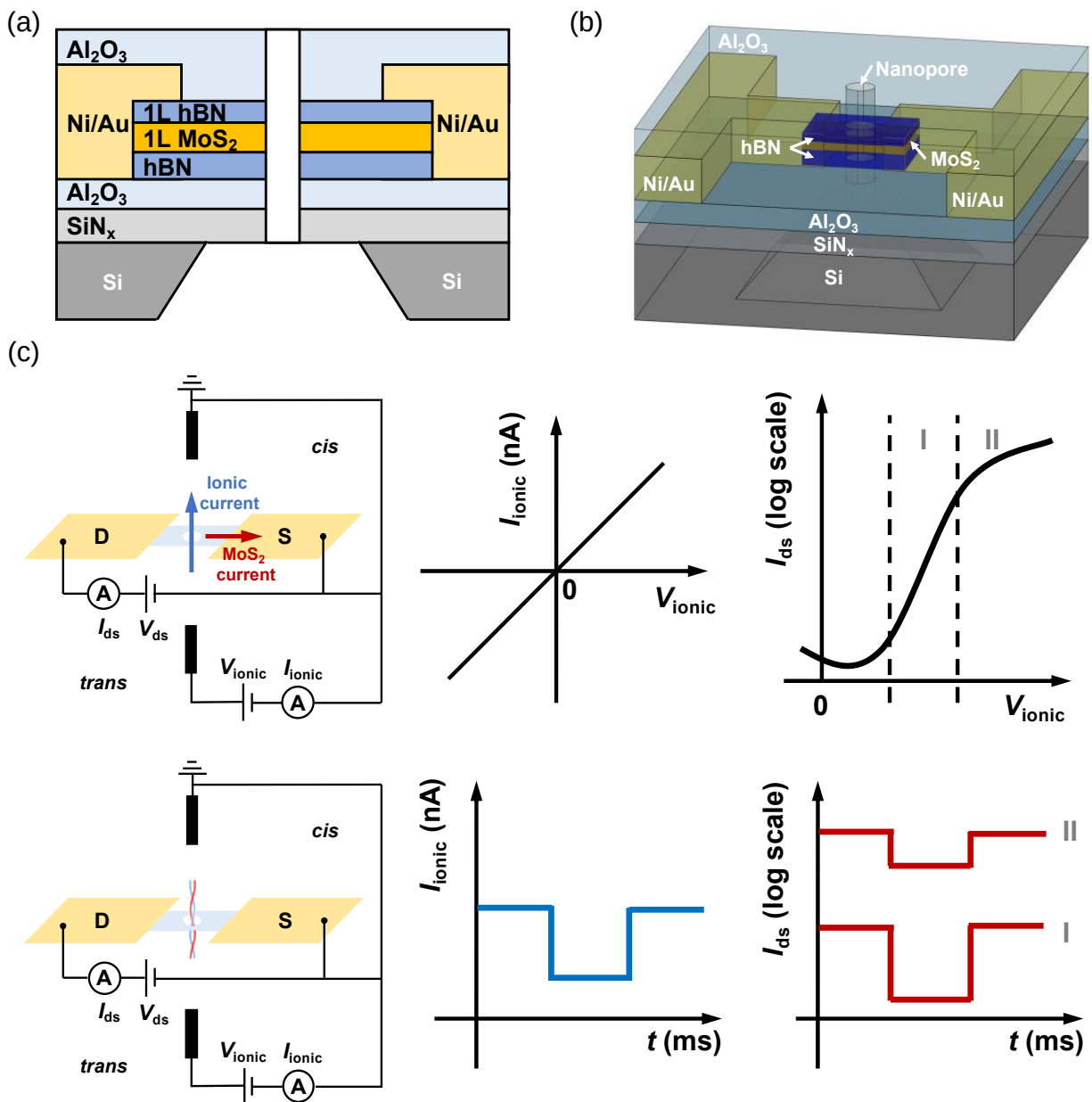
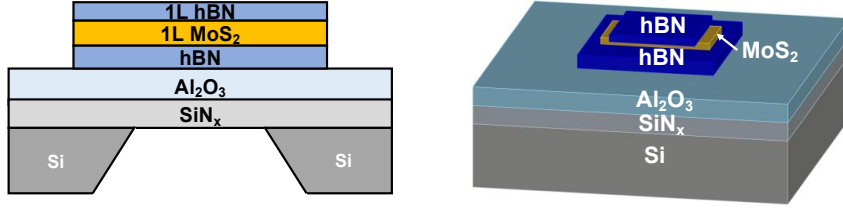


Figure 5.1 (a) Schematic of an hBN encapsulated monolayer MoS_2 nanoribbon-nanopore device. (b) 3D representation of the device. (c) Concept of measurement. As a DNA molecule translocates thru a nanopore, the ionic current drops as DNA partly blocks the ionic channel. Upon DNA translocation, the local potential around the nanopore also changes, which results in change in MoS_2 current via electrostatic gating. As a result, ionic current and MoS_2 current can simultaneously detect DNA translocation thru a nanopore in a MoS_2 nanoribbon.

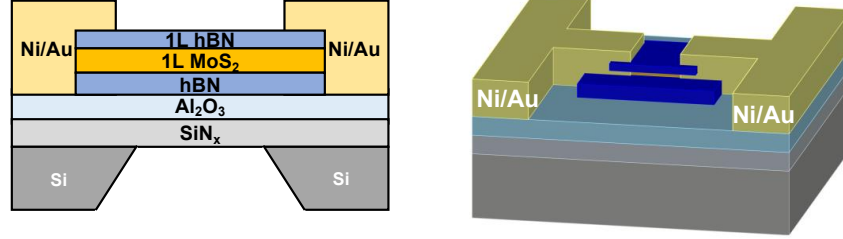
Figure 5.2 shows the device fabrication process. Fabrication started with transferring hBN encapsulated monolayer MoS_2 onto a silicon nitride membrane (i). MoS_2 and hBN of desired

thickness were prepared by mechanical exfoliation with Scotch tape, and then transferred together as a stack onto a silicon nitride membrane. The transfer process is described in detail in ref [23]. Before transfer, commercial silicon nitride membranes (Norcada Inc.) were passivated with 10 nm Al_2O_3 using atomic layer deposition (ALD) and then patterned with contact pads and alignment markers using optical lithography. After transfer, the 2D stack was cleaned with an AFM tip in contact mode [24] to reduce the interface traps and voids. The applied contact force was around 100 nN. Then contact electrodes consisting of 30 nm gold on 5 nm nickel were defined on hBN encapsulated monolayer MoS_2 to form the source and the drain using e-beam lithography (ii). Next, thermal dip-pen nanolithography shaped the hBN/ MoS_2 /hBN stack into a nanoribbon (iii). The steps are identical to the fabrication of monolayer MoS_2 nanoribbons as detailed in ref [19]. Finally, the device was passivated with 24 nm Al_2O_3 and then a 3-10 nm nanopore was drilled in the nanoribbon using focused electron beams (iv). 2 nm Al seed layer [25] was evaporated before ALD deposition of 22 nm Al_2O_3 at 250 °C to promote the deposition of ALD Al_2O_3 on hBN and MoS_2 .

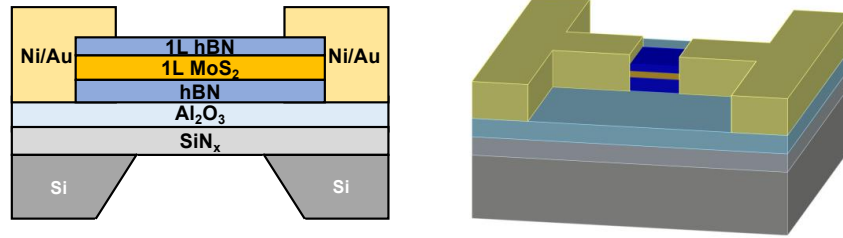
i. Transfer hBN/MoS₂/hBN onto membrane



ii. Pattern contact electrodes



iii. Shape 2D stack into nanoribbon



iv. Drill nanopore in nanoribbon

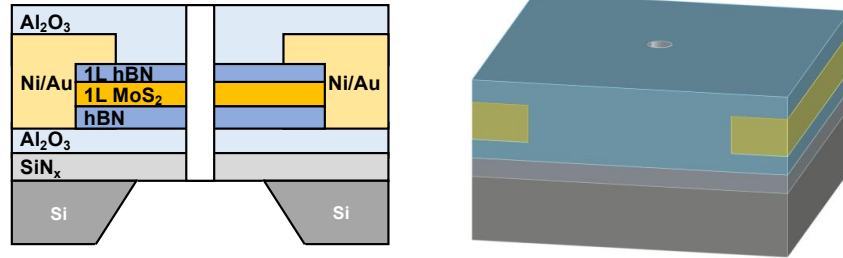


Figure 5.2 Device fabrication procedure. (i) hBN encapsulated monolayer MoS₂ were transferred onto Al₂O₃/SiN_x membranes. (ii) Contact electrodes were patterned onto hBN encapsulated monolayer MoS₂ using ebeam lithography. (iii) hBN/MoS₂/hBN stacks were shaped into nanoribbons using thermal dip-pen nanolithography. (iv) Nanoribbons were passivated with ALD Al₂O₃ and then nanopores were drilled in the nanoribbons using focused electron beams.

Figure 5.3 shows an example of the device fabrication. Figure 5.3(a) shows the optical image of transferred hBN/MoS₂/hBN stack on membrane. Figure 5.3(b) shows the SEM image of contact electrodes patterned on hBN/MoS₂/hBN stack. Figure 5.3(c) shows an 89 nm wide hBN

encapsulated monolayer MoS₂ nanoribbon formed using thermal dip-pen nanolithography. Figure 5.3(d) shows the TEM images of a 5.9 nm * 8.6 nm nanopore in the nanoribbon.

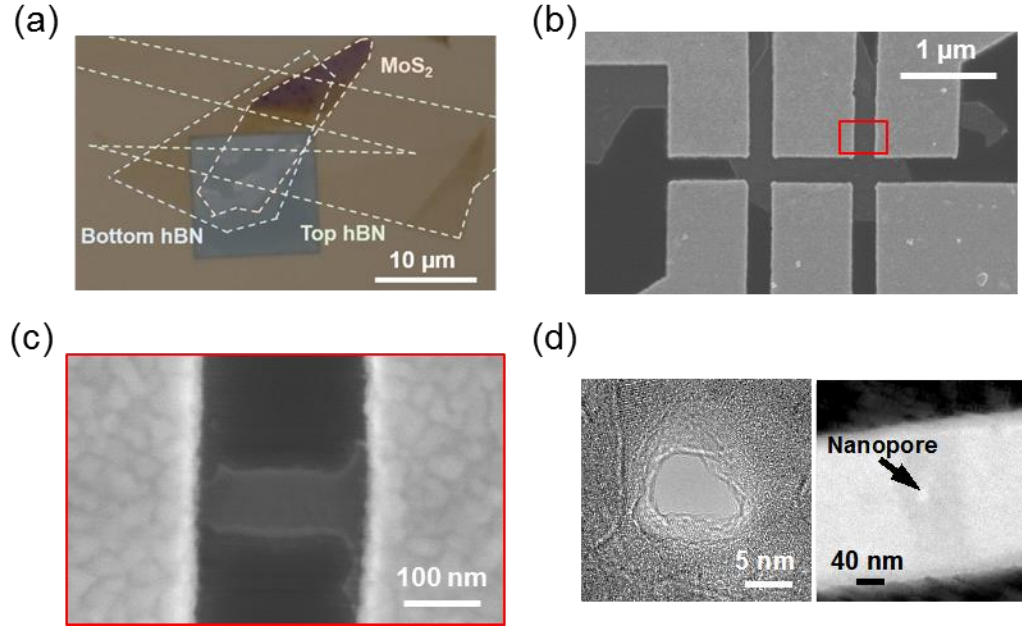


Figure 5.3 Example of device fabrication. (a) Optical image of hBN/MoS₂/hBN stack transferred onto membrane. (b) SEM image of contact electrodes patterned on hBN/MoS₂/hBN stack with ebeam lithography. (c) SEM image of an hBN/MoS₂/hBN nanoribbon patterned with thermal dip-pen nanolithography. (d) TEM images of a nanopore drilled in a nanoribbon using focused electron beams.

After fabrication, the FET-nanopore devices were first characterized in air with a probe station, and then characterized in KCl solution under liquid gating. Figure 5.4 shows the characterization of a FET-nanopore device. Figure 5.4(a) shows the cross-sectional view of the device. A 30 nm thick PMMA residue was left on the hBN/MoS₂/hBN nanoribbon after XeF₂ etch, probably because moisture in the sample reacted with XeF₂ and produced F radicals, which fluorinated PMMA into Teflon-like polymer [26]. Figures 5.4(b) and 5.4(c) show the STEM images of 4.1 nm * 5.7 nm nanopore in a 100 nm wide nanoribbon. Figure 5.4(d) shows the I-V characteristic of the MoS₂ nanoribbon in air after nanopore drilling, which yields a conductance of ~ 0.5 nS. Figure 5.4(e) shows the I-V characteristic of the liquid-gated MoS₂ nanoribbon with

a nanopore in 1 M KCl, 10 mM Tris and 1 M EDTA. Unexpectedly, the MoS₂ current decreases with ionic voltage, which does not conform to the n-type behavior of the MoS₂ device with Ni/Au contacts. One possible explanation is that the MoS₂ nanoribbon operated in off state and the MoS₂ current was dominated by leakage, which could possibly increase with ionic voltage. Figure 5.4(f) shows the I-V characteristic of the nanopore in the nanoribbon in 1 M KCl, with a nanopore conductance of 10.2 nS. Assuming a truncated double-cone pore structure [27,28], the pore conductance G can be calculated as $G = \frac{\pi d^2}{4} \sigma \left(\frac{\delta \tan \alpha + 1}{h + h_{\text{eff}} \delta \tan \alpha} \right)$ [27], where d is the nanopore diameter, $\sigma = 102.1$ mS/cm is the ionic conductivity of 1 M KCl, $h = 80$ nm is the total membrane thickness, $h_{\text{eff}} \approx h/3$ is the length of the cylindrical region of the nanopore, $\square = (h - h_{\text{eff}})/d$, and $\alpha \approx 30^\circ$ is the cone half-angle. The calculated pore diameter based on observed conductance value is 6.8 nm. It is possible that the nanopore was enlarged due to electrochemical etching.

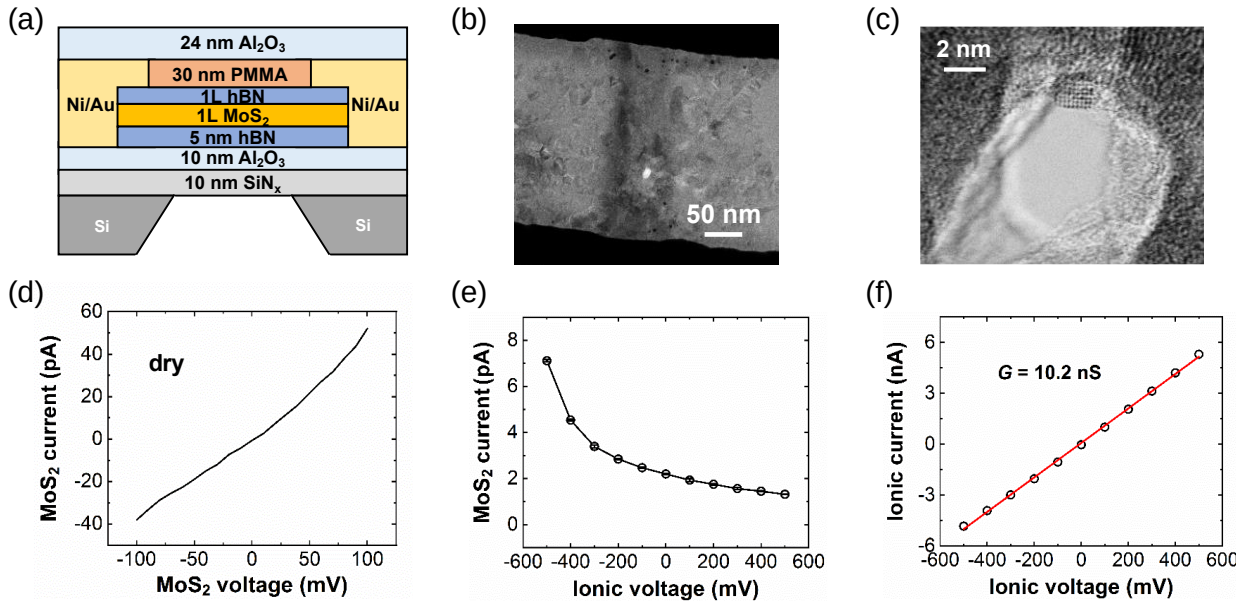


Figure 5.4 Device characterization. (a) Cross-sectional view of a nanoribbon-nanopore device (nanopore not shown). (b) STEM image of the nanoribbon with a nanopore in it. (c) STEM image of the nanopore. (d) I-V characteristic of the MoS₂ nanoribbon in air after nanopore drilling. (e) I-V characteristic of the liquid-gated MoS₂ nanoribbon with a nanopore in 1 M KCl. $V_{\text{ds}} = 50$ mV. (f) I-V characteristic of the nanopore in 1 M KCl. Dots are experimental points and the red line is a linear fit to data.

5.3 Results and Discussion

First, we demonstrate the detection of DNA translocation thru a nanopore in a monolayer MoS₂ nanoribbon in ionic channel, as shown in Fig. 5.5. We added 3kbp dsDNA into the *cis* chamber and applied an ionic voltage of 500 mV in 1M KCl. We used the nanoribbon-nanopore device described in Fig. 5.4, which had a calculated pore size of 6.8 nm in diameter. Figure 5.5(a) shows a sample ionic current trace low-pass filtered at 10 kHz at a sampling rate of 100 kHz. Figure 5.5(b) shows representative translocation sample events of the 3kbp dsDNA thru the nanopore. Current blockade versus event dwell for $n = 134$ events are plotted in Fig. 5.5(c). Figure 5.5(d) shows the event dwell time histogram. A mono-exponential decay function with a time constant of 56 ± 10 μ s was fitted into the dwell-time distribution. Longer events are more likely to be DNA translocations which involve significant DNA-pore interactions, while shorter events ($t < 100$ μ s) could be DNA collisions [29]. Figure 5.5(e) shows the current blockade histogram. A Gaussian function with a mean blockade of 384 ± 5 pA was fitted to into the current blockade distribution. The noise level was around 150 pA, so the SNR in ionic channel was around 2.6. The signal-to-noise ratio can be improved by reducing the membrane thickness and pore size.

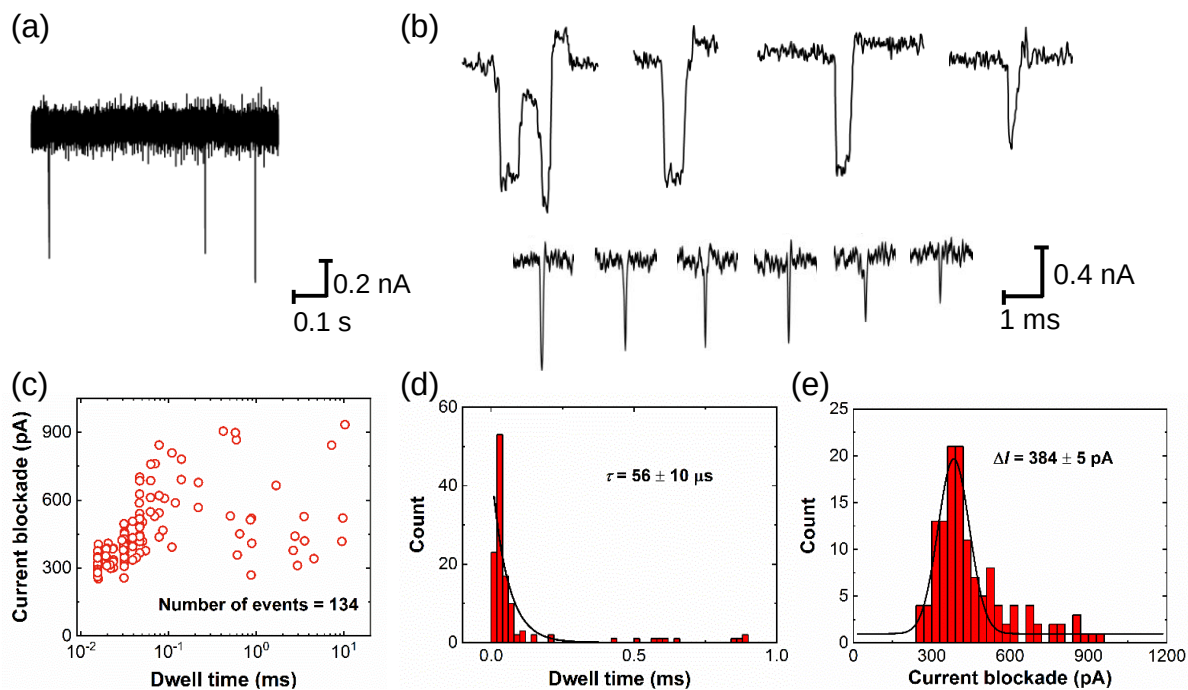


Figure 5.5 Detection of 3kbp dsDNA translocation in ionic channel at $V_{\text{ionic}} = 500$ mV. (a) Ionic current trace of DNA transport. (b) Representative DNA transport events. (c) Current blockade versus dwell time for 134 events. (d) Corresponding event dwell time histogram with a time constant of 56 ± 10 μs . The black line is an exponential fit to data. (e) Corresponding current blockade histogram with a mean blockade of 384 ± 5 pA. The black line is a Gaussian fit to data.

Finally, we present the initial results of simultaneous detection of DNA translocation in ionic current and MoS₂ current, as shown in Fig. 5.6. Figure 5.6(a) shows the STEM image of a 3.8 nm * 9.3 nm nanopore, with an area-equivalent diameter of 6.2 nm. Figure 5.6(b) shows the STEM image of the nanopore inside a 100 nm wide nanoribbon. Figure 5.6(c) shows the I-V characteristic of the MoS₂ nanoribbon after nanopore drilling in air with backside silicon grounded. The device had unexpectedly large gate leakage and nonzero drain current at zero drain-source bias. The cause of large gate leakage remains unclear. The device would exhibit unusual ionic current with contributions from gate leakage during DNA sensing but could still be tested. Figure 5.6(d) shows the device schematic along with the electrical connections used for liquid measurement. Figure 5.6(e) shows the I-V characteristic of the nanopore in 1 M KCl, 10 mM Tris

and 1 mM EDTA. Dots are experimental points, and the dashed red line is a theoretical I-V curve with a nanopore conductance of 13.8 nS, calculated by assuming a truncated double-cone pore structure [27,28]. The theoretical curve matches fairly well with the experimental data points at $V_{\text{ionic}} \leq 200$ mV. Figure 5.6(f) shows the I-V characteristic of the liquid-gated MoS₂ nanoribbon with a nanopore in 1 M KCl. The MoS₂ current remained small ~ 0.9 pA and almost constant as the ionic voltage was swept from -300 mV to 300 mV, indicating that the MoS₂ nanoribbon FET was operating in the off state. Figure 5.6(g) shows example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current, which mark the first possible simultaneous detection of DNA translocation in ionic and MoS₂ channels. A total of 7 correlated events were detected in 20 min. The *cis* chamber was grounded. We added 3kbp dsDNA into the *trans* chamber and applied an ionic voltage of -300 mV to -400 mV to drive DNA thru the nanopore. Unexpectedly, current enhancement of ~ 2 nA was observed in ionic channel upon possible DNA translocations. Current enhancement caused by DNA translocation was previously reported for low KCl concentrations < 400 mM [30] but may be associated with gate leakage for this device. MoS₂ signals in events#1-3 scaled as the time derivative of the ionic current, indicating that these MoS₂ signals were dominated by capacitive coupling [31]. MoS₂ signals in events #4-7 scaled linearly with the ionic current and may have resulted from effects other than capacitive coupling: the effect of local potential change is unlikely, as the MoS₂ current remained flat over 600 mV ionic voltage in Fig. 5.6(f); other effects such as the base-specific alternation of the local density of states of the MoS₂ edges [32] have not been experimentally validated, but may explain the 5 pA scale MoS₂ current. Ionic voltage and drain-source voltage also changed upon DNA translocation thru the pore, probably due to capacitive coupling. To confirm correlated events are indeed caused

by DNA translocation, we still need to apply different ionic voltages and observe changes in dwell time of ionic and MoS₂ signals for future devices.

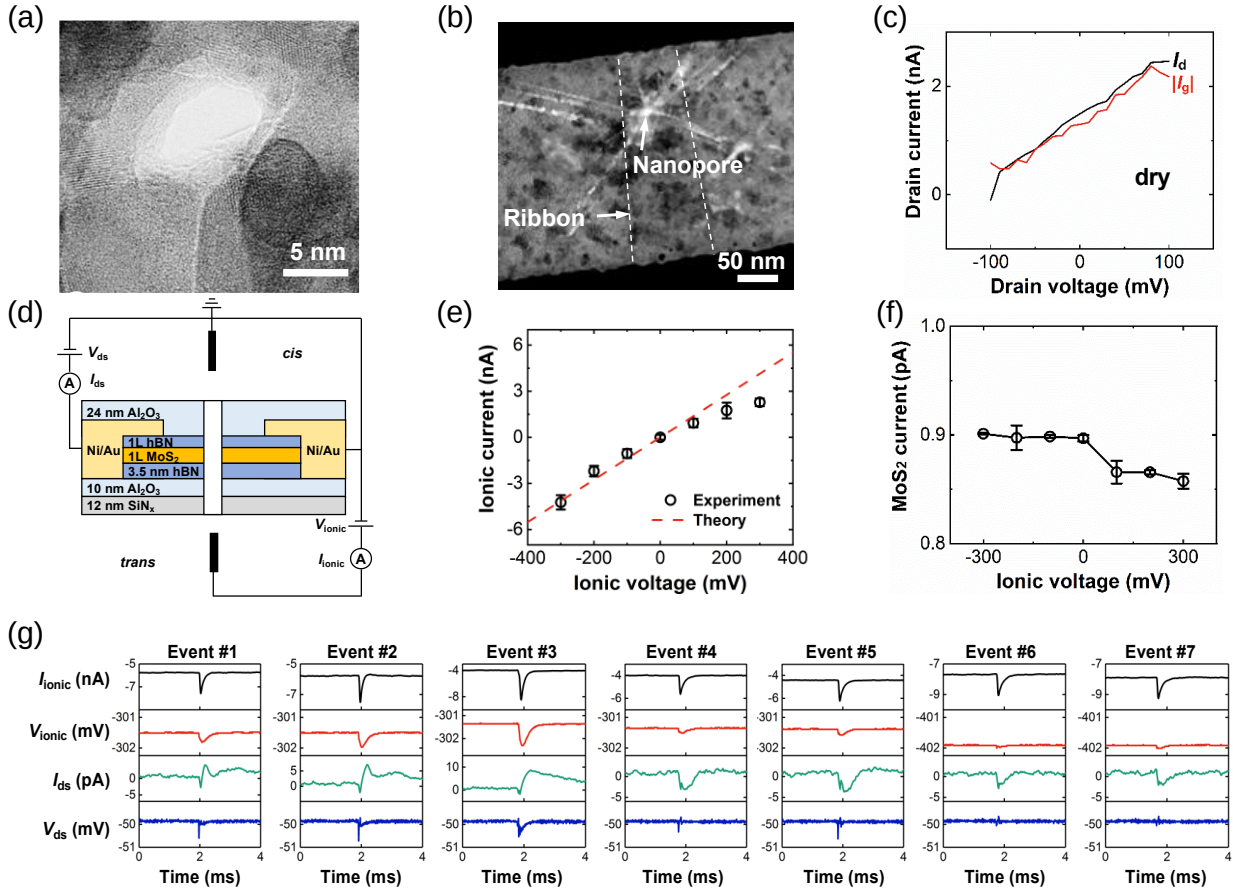


Figure 5.6 Simultaneous detection of DNA translocation in ionic current and MoS₂ current. (a) STEM image of the nanopore. (b) STEM image of the nanopore in a nanoribbon. (c) I-V characteristic of the MoS₂ nanoribbon in air with backside silicon grounded. (d) Device schematic along with the electrical components used for liquid measurement. (e) I-V characteristic of the nanopore in 1 M KCl. (f) I-V characteristic of the liquid-gated MoS₂ nanoribbon with a nanopore in 1 M KCl. $V_{ds} = 10$ mV. (g) Seven example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current. $V_{ds} = -50$ mV and $V_{ionic} = -300$ mV or -400 mV.

5.4 Conclusions and Future Work

In this chapter, we designed and fabricated hBN encapsulated monolayer MoS₂ nanoribbon FET-nanopore devices. Nanopores of 4-10 nm were drilled in ~ 100 nm wide hBN/MoS₂/hBN nanoribbons. FET-nanopore devices were characterized in air and in KCl under liquid gating. We

demonstrated the detection of 3kbp dsDNA translocation thru a monolayer MoS₂ nanoribbon-nanopore device in ionic channel. A total of 134 events were recorded with a time constant of 56 ± 10 μ s and a mean current blockade of 384 ± 5 pA at an ionic voltage of 500 mV. Finally, we showed seven example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current. The ionic signal was about 2 nA and the MoS₂ signal about 5 pA. Whether these correlated events were caused by DNA translocation remains to be confirmed.

To attain the goal of simultaneous detection of DNA translocation in ionic and MoS₂ channels, future work should tackle the following two main challenges: The first challenge is that the MoS₂ nanoribbon FETs were mostly in the off state after nanopore drilling and could not be turned on during nanopore sensing under available ionic voltage. Thus, we were unable to detect DNA translocation in MoS₂ signal due to the effect of local potential change. To turn on MoS₂ nanoribbon, we can use thinner ALD Al₂O₃ as the gate dielectric or use higher-k dielectric such as HfO₂ [33]. We can also try to left shift the threshold voltage of MoS₂ nanoribbon, e.g., via electron doping of the oxide layer [34]. The second challenge is that 24 nm top ALD Al₂O₃ were fully etched within a few hours under even small ionic voltage bias, preventing thorough investigation of the FET-nanopore device performance. To reduce the electrochemical etching of Al₂O₃, we can use 10 mM KCl instead of 1 M KCl on the device side [14].

5.5 References

- [1] Muthukumar M, Plesa C and Dekker C 2015 Single-Molecule Sensing with Nanopores *Phys. Today* **68** 40–6
- [2] Venkatesan B M and Bashir R 2011 Nanopore Sensors for Nucleic Acid Analysis *Nat. Nanotechnol.* **6** 615–24
- [3] Dekker C 2007 Solid-State Nanopores *Nat. Nanotechnol.* **2** 209–15
- [4] Balan A, Machielse B, Niedzwiecki D, Lin J, Ong P, Engelke R, Shepard K L and Drndić M 2014 Improving Signal-to-Noise Performance for DNA Translocation in Solid-State Nanopores at MHz Bandwidths *Nano Lett.* **14** 7215–20
- [5] Shekar S, Niedzwiecki D J, Chien C-C, Ong P, Fleischer D A, Lin J, Rosenstein J K, Drndić M and Shepard K L 2016 Measurement of DNA Translocation Dynamics in a Solid-State Nanopore at 100ns Temporal Resolution *Nano Lett.* **16** 4483–9
- [6] Kowalczyk S W, Wells D B, Aksimentiev A and Dekker C 2012 Slowing down DNA Translocation through a Nanopore in Lithium Chloride *Nano Lett.* **12** 1038–44
- [7] Feng J, Liu K, Bulushev R D, Khlybov S, Dumcenco D, Kis A and Radenovic A 2015 Identification of Single Nucleotides in MoS₂ Nanopores *Nat. Nanotechnol.* **10** 1070–6
- [8] Goto Y, Yanagi I, Matsui K, Yokoi T and Takeda K 2018 Identification of Four Single-Stranded DNA Homopolymers with a Solid-State Nanopore in Alkaline CsCl Solution *Nanoscale* **10** 20844–50
- [9] Luan B and Zhou R 2018 Spontaneous Transport of Single-Stranded DNA through Graphene–MoS₂ Heterostructure Nanopores *ACS Nano* **12** 3886–91
- [10] He Y, Tsutsui M, Scheicher R H, Fan C, Taniguchi M and Kawai T 2013 Mechanism of How Salt-Gradient-Induced Charges Affect the Translocation of DNA Molecules through a Nanopore *Biophys. J.* **105** 776–82
- [11] Banerjee S, Wilson J, Shim J, Shankla M, Corbin E A, Aksimentiev A and Bashir R 2015 Slowing DNA Transport Using Graphene-DNA Interactions *Adv. Funct. Mater.* **25** 936–46
- [12] Krishnakumar P, Gyarfas B, Song W, Sen S, Zhang P, Krstić P and Lindsay S 2013 Slowing DNA Translocation through a Nanopore Using a Functionalized Electrode *ACS Nano* **7** 10319–26
- [13] Xie P, Xiong Q, Fang Y, Qing Q and Lieber C M 2012 Local Electrical Potential Detection of DNA by Nanowire-Nanopore Sensors *Nat. Nanotechnol.* **7** 119–25
- [14] Traversi F, Raillon C, Benameur S M, Liu K, Khlybov S, Tosun M, Krasnozhon D, Kis A and Radenovic A 2013 Detecting the Translocation of DNA through a Nanopore Using Graphene Nanoribbons *Nat. Nanotechnol.* **8** 939–45

- [15] Heerema S J, Vicarelli L, Pud S, Schouten R N, Zandbergen H W and Dekker C 2018 Probing DNA Translocations with Inplane Current Signals in a Graphene Nanoribbon with a Nanopore *ACS Nano* **12** 2623–33
- [16] Cui X, Lee G-H, Kim Y D, Arefe G, Huang P Y, Lee C-H, Chenet D A, Zhang X, Wang L, Ye F, Pizzocchero F, Jessen B S, Watanabe K, Taniguchi T, Muller D A, Low T, Kim P and Hone J 2015 Multi-Terminal Transport Measurements of MoS₂ Using a van Der Waals Heterostructure Device Platform *Nat. Nanotechnol.* **10** 534–40
- [17] Yu Z, Ong Z-Y, Li S, Xu J-B, Zhang G, Zhang Y-W, Shi Y and Wang X 2017 Analyzing the Carrier Mobility in Transition-Metal Dichalcogenide MoS₂ Field-Effect Transistors *Adv. Funct. Mater.* **27** 1604093
- [18] Wang J, Yao Q, Huang C-W, Zou X, Liao L, Chen S, Fan Z, Zhang K, Wu W, Xiao X, Jiang C and Wu W-W 2016 High Mobility MoS₂ Transistor with Low Schottky Barrier Contact by Using Atomic Thick h-BN as a Tunneling Layer *Adv. Mater.* **28** 8302–8
- [19] Chen S, Kim S, Chen W, Yuan J, Bashir R, Lou J, van der Zande A M and King W P 2019 Monolayer MoS₂ Nanoribbon Transistors Fabricated by Scanning Probe Lithography *Nano Lett.* **19** 2092–8
- [20] Banerjee S, Shim J, Rivera J, Jin X, Estrada D, Solovyeva V, You X, Pak J, Pop E, Aluru N and Bashir R 2013 Electrochemistry at the Edge of a Single Graphene Layer in a Nanopore *ACS Nano* **7** 834–43
- [21] Sarkar D, Liu W, Xie X, Anselmo A C, Mitragotri S and Banerjee K 2014 MoS₂ Field-Effect Transistor for Next-Generation Label-Free Biosensors *ACS Nano* **8** 3992–4003
- [22] Parkin W M and Drndić M 2018 Signal and Noise in FET-Nanopore Devices *ACS Sensors* **3** 313–9
- [23] Pizzocchero F, Gammelgaard L, Jessen B S, Caridad J M, Wang L, Hone J, Bøggild P and Booth T J 2016 The Hot Pick-up Technique for Batch Assembly of van Der Waals Heterostructures *Nat. Commun.* **7** 11894
- [24] Rosenberger M R, Chuang H J, McCreary K M, Hanbicki A T, Sivaram S V. and Jonker B T 2018 Nano-"Squeegee" for the Creation of Clean 2D Material Interfaces *ACS Appl. Mater. Interfaces* **10** 10379–87
- [25] Kim S, Nah J, Jo I, Shahrjerdi D, Colombo L, Yao Z, Tutuc E and Banerjee S K 2009 Realization of a High Mobility Dual-Gated Graphene Field-Effect Transistor with Al₂O₃ Dielectric *Appl. Phys. Lett.* **94** 062107
- [26] Madou M J 2018 Fundamentals of Microfabrication (CRC Press)
- [27] Kim M J, Wanunu M, Bell D C and Meller A 2006 Rapid Fabrication of Uniformly Sized Nanopores and Nanopore Arrays for Parallel DNA Analysis *Adv. Mater.* **18** 3149–53
- [28] Venkatesan B M, Dorvel B, Yemenicioglu S, Watkins N, Petrov I and Bashir R 2009 DNA Sensors: Highly Sensitive, Mechanically Stable Nanopore Sensors for DNA

Analysis *Adv. Mater.* **21** 2771–6

- [29] Wanunu M, Sutin J, McNally B, Chow A and Meller A 2008 DNA Translocation Governed by Interactions with Solid-State Nanopores *Biophys. J.* **95** 4716–25
- [30] Smeets R M M, Keyser U F, Krapf D, Wu M Y, Dekker N H and Dekker C 2006 Salt Dependence of Ion Transport and DNA Translocation through Solid-State Nanopores *Nano Lett.* **6** 89–95
- [31] Puster M, Balan A, Rodríguez-Manzo J A, Danda G, Ahn J H, Parkin W and Drndić M 2015 Cross-Talk between Ionic and Nanoribbon Current Signals in Graphene Nanoribbon-Nanopore Sensors for Single-Molecule Detection *Small* **11** 6309–16
- [32] Farimani A B, Min K and Aluru N R 2014 DNA Base Detection Using a Single-Layer MoS₂ *ACS Nano* **8** 7914–22
- [33] Shim J, Rivera J A and Bashir R 2013 Electron Beam Induced Local Crystallization of HfO₂ Nanopores for Biosensing Applications *Nanoscale* **5** 10887
- [34] Lu M-Y, Wu S-C, Wang H-C and Lu M-P 2018 Time-Evolution of the Electrical Characteristics of MoS₂ Field-Effect Transistors after Electron Beam Irradiation *Phys. Chem. Chem. Phys.* **20** 9038–44

CHAPTER 6: CONCLUSIONS AND FUTURE OUTLOOK

This dissertation reports the study of polymer nanostructure deposition from a heated tip and the application of tip-based nanolithography (TBN) to fabricate MoS₂ devices. For TBN of polymer nanostructures, we elucidated the effect of polymer properties and polymer melt flow on the size and shape of polymer nanostructures deposited from a heated tip, by studying the size of deposited PMMA nanostructures over a wide range of polymer molecular weight, tip temperature and tip speed. We found both ribbon width and height increase with tip temperature and decrease with tip speed and polymer molecular weight. For PMMA over a wide range of polymer molecular weight, the width of the deposited polymer nanoribbons depends on capillary number (Ca) and is independent of tip temperature, tip speed and polymer molecular weight. For high molecular weight polymers deposited with features close to the polymer radius of gyration, polymer molecular weight also influenced the size of the deposited polymer ribbon. We found that uniform and continuous deposition occurs only when $Ca \ll 1$, i.e, when capillary force outweighs tip shear force, indicating that polymer melt deposition is caused by capillary force but not by tip shear force. This work provides a framework to study feature sizes of thermally deposited polymer nanostructures and predict the size and shape of deposited polymers as a function of capillary number, which enables better control of the speed and resolution at which polymer nanostructures can be fabricated.

For application of TBN to MoS₂ devices, we demonstrated first-of-its-kind fabrication of monolayer MoS₂ nanoribbon transistors with sub-100 nm channel width. Fabricating monolayer MoS₂ nanoribbon transistors with electron or ion beam lithography is challenging, because high-

energy beams can damage sensitive electronic materials with high surface-to-volume ratios like MoS₂ monolayers. Tip-based nanolithography overcomes such materials and process compatibility issues by avoiding the exposure of device materials to radiation. An atomic force microscope (AFM) tip deposited a nanometer scale constricted polymer on a prefabricated microribbon field-effect transistor (FET) as etch mask and XeF₂ etched unmasked MoS₂, forming a nanoribbon FET. We fabricated seven devices with channel width ranging from 30 nm to 370 nm, and the fabrication process was carefully studied by electronic measurements made at each process step. One 30-nm-wide monolayer FET achieved a mobility of 8.53 cm²/Vs and an on/off ratio of 2×10⁵, on par with multilayer MoS₂ nanoribbon FETs reported to date. We found that the electrical properties (mobility, on/off ratio and subthreshold swing) degrade after nanoribbon formation, while ALD passivation improves mobility and on/off ratio but degrades subthreshold swing. Change in the output characteristics indicates that a Schottky barrier was created after nanoribbon formation, and the Schottky barrier height was reduced after ALD passivation. By comparing a 30-nm-wide device with a 60-nm-wide device that were fabricated on the same MoS₂ flake, we found that the narrower device had a smaller mobility, a lower on/off ratio and a larger subthreshold swing. We also observed that the threshold voltage increased after nanoribbon formation and decreased after ALD passivation. Lastly, our MoS₂ nanoribbon fabrication technique also applies to other 2D materials, representing a crucial advancement in 2D nanoelectronics fabrication technology.

The performance of MoS₂ transistors has been limited by extrinsic disorders such as charged impurities and interface traps. hBN encapsulation is an effective method in reducing interface traps and charged impurities. However, conventional mechanical stacking technique used in hBN encapsulation unavoidably introduces trapped contaminants and voids between hBN and MoS₂, which act as charged impurities or interface traps and limit the intrinsic behavior of MoS₂.

We showed that cleaning hBN encapsulated monolayer MoS₂ with contact mode AFM could reduce surface contaminants and surface roughness. Further examination with photoluminescence (PL) showed that AFM cleaning improved PL peak width, indicating that AFM cleaning reduced interface traps. We fabricated a monolayer MoS₂ FET on AFM cleaned hBN encapsulated monolayer MoS₂ and achieved a high mobility of 73.01 cm²/Vs. Finally, we found the mobility of four hBN encapsulated monolayer MoS₂ FETs improved by an average of 73% from 21.95 ± 2.27 cm²/Vs to 38.03 ± 6.12 cm²/Vs after AFM cleaning. However, we found the hysteresis of these four devices also increased from 1% to 20%, which may be explained by the effect of ambient adsorbates. Results are inconclusive because it remains unclear whether AFM cleaning caused the increase in hysteresis.

In addition, we integrated monolayer MoS₂ nanoribbon transistors with solid state nanopores to fabricate MoS₂ FET-nanopore devices for DNA sensing. Nanopores of 4-10 nm were drilled in ~ 100 nm wide hBN encapsulated MoS₂ nanoribbons. We demonstrated the detection of 3kbp dsDNA translocation thru a monolayer MoS₂ nanoribbon-nanopore device in ionic channel. Finally, we showed seven example events of simultaneous detection of DNA translocation in ionic current and MoS₂ current. The ionic signal was about 2 nA and the MoS₂ signal about 5 pA. Whether these correlated events were caused by DNA translocation remains to be confirmed.

6.1 Future Outlook

6.1.1 Tip-Based Nanolithography of Polymer Nanostructures

First, our results of TBN of polymer nanostructures imply that narrower polymer ribbons can be achieved at larger capillary number, while irregularly shaped ribbons will be deposited

when capillary number approaches one. Future work could further investigate instabilities in polymer flow that occur when $Ca \sim 1$, i.e., when viscous force balances surface tension and inadequate capillary driving force may lead to intermittent or unstable writing. Based on contact mechanics, the ultimate resolution of TBN determined by the diameter of the contact area between a typical diamond-coated AFM tip and a hard surface is smaller than 10 nm. Understanding the limiting process of polymer melt deposition may help us realize the ultimate resolution of TBN at around 10 nm.

Second, it is worthwhile testing the universality of the governing role of Ca on the size of tip-deposited polymer nanostructures with other commonly used polymers, such as polyethylene and polystyrene. Also, the effect of other polymer properties such as polydispersity, crystallinity, branching on the size of polymer nanostructures deposited from a heated tip can be investigated.

6.1.2 Monolayer MoS₂ Nanoribbon Field-Effect Transistors

Several steps could be taken to further improve the electrical performance of monolayer MoS₂ nanoribbon transistors. First, the MoS₂ could be encapsulated before fabrication, perhaps with layers of hBN, which would reduce MoS₂ exposure to contaminants during processing [1,2]. The hBN could also be used as the gate dielectric material. Compared to SiO₂, hBN has fewer Coulomb impurities and traps and is atomically flat [3]. Second, better contacts are needed to reduce contact resistance and improve extrinsic field-effect mobility. Recent articles have reported small contact resistance with van der Waals contacts between metals and MoS₂ using transferred electrodes [4] or soft indium contact metal [5], both of which would be highly compatible with the present work. Third, the devices could be smaller. The ultimate resolution of tDPN depends on ink type, surface chemistry and tip shape [6–8]. For instance, deposition of 10 nm wide nanoparticle

rows has been demonstrated with tDPN [8], which could potentially serve as etch mask for nanoribbon fabrication. The channels could be shorter as well in order to reduce channel resistance.

6.1.3 DNA Sequencing with Solid State Nanopores

To realize DNA sequencing with solid state nanopores, we need to improve both temporal and spatial resolutions of solid state nanopores. Local sensors integrated with solid state nanopores, such as MoS₂ FETs, are promising to improve the temporal resolution by offering a better signal-to-noise ratio (SNR) than ionic signals. High bandwidth measurements of FET-nanopore devices coupled with techniques to slow DNA transport could potentially achieve single nucleotide temporal resolution. If we can obtain signals due to base-specific interactions between MoS₂ edges and DNA bases [9], then we may achieve 2-3 bases spatial resolution with monolayer MoS₂ FETs; otherwise, we need to reduce the total membrane thickness to sub-5 nm to obtain a spatial resolution of 15 bases or better [10,11]. Finally, we can incorporate MspA biological nanopores into MoS₂ FET-nanopore sensors [12], complementing whatever is available in commercial biological nanopore sequencers with high SNR MoS₂ FET signals and robust and durable solid state membranes.

6.2 References

- [1] Cui X, Lee G-H, Kim Y D, Arefe G, Huang P Y, Lee C-H, Chenet D A, Zhang X, Wang L, Ye F, Pizzocchero F, Jessen B S, Watanabe K, Taniguchi T, Muller D A, Low T, Kim P and Hone J 2015 Multi-Terminal Transport Measurements of MoS₂ Using a van Der Waals Heterostructure Device Platform *Nat. Nanotechnol.* **10** 534–40
- [2] Vu Q A, Fan S, Lee S H, Joo M-K, Yu W J and Lee Y H 2018 Near-Zero Hysteresis and Near-Ideal Subthreshold Swing in h-BN Encapsulated Single-Layer MoS₂ Field-Effect Transistors *2D Mater.* **5** 031001
- [3] Yu Z, Ong Z-Y, Li S, Xu J-B, Zhang G, Zhang Y-W, Shi Y and Wang X 2017 Analyzing the Carrier Mobility in Transition-Metal Dichalcogenide MoS₂ Field-Effect Transistors *Adv. Funct. Mater.* **27** 1604093
- [4] Liu Y, Guo J, Zhu E, Liao L, Lee S-J, Ding M, Shakir I, Gambin V, Huang Y and Duan X 2018 Approaching the Schottky–Mott Limit in van Der Waals Metal–Semiconductor Junctions *Nature* **557** 696–700
- [5] Wang Y, Kim J C, Wu R J, Martinez J, Song X, Yang J, Zhao F, Mkhoyan A, Jeong H Y and Chhowalla M 2019 Van Der Waals Contacts between Three-Dimensional Metals and Two-Dimensional Semiconductors *Nature* **568** 70–4
- [6] Lee W-K, Robinson J T, Gunlycke D, Stine R R, Tamanaha C R, King W P and Sheehan P E 2011 Chemically Isolated Graphene Nanoribbons Reversibly Formed in Fluorographene Using Polymer Nanowire Masks *Nano Lett.* **11** 5461–4
- [7] Felts J R, Somnath S, Ewoldt R H and King W P 2012 Nanometer-Scale Flow of Molten Polyethylene from a Heated Atomic Force Microscope Tip *Nanotechnology* **23** 215301
- [8] Lee W K, Dai Z, King W P and Sheehan P E 2010 Maskless Nanoscale Writing of

Nanoparticle–Polymer Composites and Nanoparticle Assemblies Using Thermal

Nanoprobes *Nano Lett.* **10** 129–33

- [9] Farimani A B, Min K and Aluru N R 2014 DNA Base Detection Using a Single-Layer MoS₂ *ACS Nano* **8** 7914–22
- [10] Venta K, Shemer G, Puster M, Rodríguez-Manzo J A, Balan A, Rosenstein J K, Shepard K and Drndić M 2013 Differentiation of Short, Single-Stranded DNA Homopolymers in Solid-State Nanopores *ACS Nano* **7** 4629–36
- [11] Lee M-H, Kumar A, Park K-B, Cho S-Y, Kim H-M, Lim M-C, Kim Y-R and Kim K-B 2015 A Low-Noise Solid-State Nanopore Platform Based on a Highly Insulating Substrate *Sci. Rep.* **4** 7448
- [12] Hall A R, Scott A, Rotem D, Mehta K K, Bayley H and Dekker C 2010 Hybrid Pore Formation by Directed Insertion of α -Haemolysin into Solid-State Nanopores *Nat. Nanotechnol.* **5** 874–7