

**NANOSCALE TRIBOLOGY OF CHEMICAL VAPOR
DEPOSITED TUNGSTEN DISULFIDE (WS₂)
MONOLAYERS USING ATOMIC FORCE
MICROSCOPY**

HIMANSHU RAI



**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
MAY 2024**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2024

**Nanoscale Tribology of Chemical Vapor Deposited
Tungsten Disulfide (WS₂) Monolayers Using Atomic
Force Microscopy**

by

Himanshu Rai

Department of Materials Science and Engineering

Submitted

*in fulfilment of the requirements of the degree of
Doctor of Philosophy
to the*



Indian Institute of Technology Delhi

May 2024

Certificate

This is to certify that the thesis entitled “**Nanoscale Tribology of Chemical Vapor Deposited Tungsten Disulfide (WS₂) Monolayers Using Atomic Force Microscopy**” is being submitted by **Mr. Himanshu Rai** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**. This is a record of bona fide research work carried out by him under my supervision and guidance. The matter presented in this thesis has not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

Prof. Nitya Nand Gosvami

Associate Professor

Department of Materials Science and Engineering

Indian Institute of Technology Delhi

Acknowledgments

First and foremost, I would like to express my profound and sincere gratitude to my supervisor, Prof. Nitya Nand Gosvami, for his encouragement and excellent guidance throughout my tenure as a research scholar. This thesis would not have been possible without his timely and untiring guidance. His vast pool of ideas and tremendous enthusiasm for research and teaching has been a constant source of inspiration for me. The knowledge and experience gained from the research work, teaching assistantship, and various projects assigned to me will go a long way in guiding me through my future endeavors.

I would also like to thank my SRC members Prof. Bhabani K Satapathy, Prof. Sujeet Kumar Sinha, and Prof. Jayant Jain for their constant motivation. Their invaluable suggestions and comments have helped me tackle and overcome several challenges during my research work.

I want to thank the Department of Materials Science and Engineering for allowing me to use various instruments. A big thanks to my friends and seniors Dr. Prashant Mittal and Dr. Deepak Kumar for training me on various experimental techniques and providing me with guidance and support. A special thanks to my beloved colleagues - Dr. Aditya Gokhale, Dr. Himanshu Vashishtha, Dr. Vicky Nandal, Dr. Nooruddin Ansari, Dr. Shrikanth S, Dr. Aravi Muzaffar, Dr. Ranjeet Kumar, Dr. Amit Prasad, Dr. Kasimuthumaniyan S, Dr. Chetan Singh, Dr. Abhishek, Sourav, Junaid, Jitendra, Debottam, Shweta, Ashwani, Indrajeet, Sajid, and all my lab mates for making the workspace a lively place to work and learn.

I would also like to thank my incredible cycling companions - Dr. Vivek Chaudhary, Dr. Anand Jee, Dr. Kamal Agrawal, Kalyan Dash, and Abhishek Shukla. Together, we have

shared numerous unforgettable cycling adventures, joyously exploring the beautiful city of Delhi in weekends.

Finally, I would like to express my heartfelt gratitude to my family (my father, Shri Pankaj Kumar Rai; mother, Smt. Manju Rai; brother, Shri Ankit Rai; uncle, Shri Neeraj Kumar Rai) for their unwavering support, love, and encouragement throughout my journey in pursuing this Ph.D. degree. Their constant presence and belief in me have been the pillars that sustained my aspirations. I am deeply indebted to them for their immeasurable contributions to my academic and personal growth. From the beginning, you instilled a passion for learning and nurtured my curiosity. To my extended family (aunt, Smt. Anita Rai; cousin, Mohit Kumar Rai; niece, Anika Rai, and my whole Rai family), your continuous support and pride in my academic endeavors have fueled my determination. I am grateful for the love and care you have given, and I cherish the moments we have shared together.

To my wife (Akanksha Pandey) and my son (Ayushman Rai), your understanding and encouragement have been a source of inspiration. Your belief in my capabilities, even during the most trying times, pushed me to overcome obstacles and excel in my pursuits. The laughter and shared experiences we have had during this journey have kept me grounded and reminded me of the importance of family bonds. Thank you for being my cheerleader and for reminding me to celebrate every milestone, no matter how small.

HIMANSHU RAI

Abstract

Two-dimensional (2D) materials are single or few-layered structures with a thickness of only a few atoms possessing extraordinary electronic and mechanical properties. 2D materials have a crystal lattice structure with weak interlayer interactions, resulting in low frictional forces between the layers. Even a single layer of 2D material can reduce friction efficiently due to the inert and atomically smooth nature of the top layer. There are numerous ways through which 2D materials can be prepared, but the chemical vapor deposition (CVD) method is highly used due to its capability to produce large-size flakes and mass production. 2D materials such as transition metal dichalcogenides (TMDs) have attained specific attention due to their remarkable thermal and mechanical properties and layer-dependent band gap. Molybdenum disulfide (MoS_2) is the representative TMD as it has been used as a solid lubricant for decades due to its extraordinary lubrication properties at high temperatures and in a vacuum; however, there are other TMDs that can provide better tribological properties than MoS_2 such as tungsten disulfide (WS_2). WS_2 provides a better coefficient of friction (COF), high thermal and chemical stability, good load-carrying capacity, and is also naturally abundant similar to MoS_2 . In the present study, the tribological behavior of the CVD-grown WS_2 monolayer was investigated at the nanoscale using atomic force microscopy (AFM).

Structural defects in CVD-grown WS_2 monolayers are ubiquitous and cannot be avoided. Defects can be classified as point defects (zero-dimensional), line defects (one-dimensional), and surface defects (two-dimensional). Point defects such as sulfur (S) vacancies are common in CVD-grown WS_2 monolayers, as the S vacancy has the lowest formation energy. The tribological behavior of the CVD-grown WS_2 monolayers in the presence of point defects was investigated using AFM under ambient conditions. AFM experiments were performed within the interior and near the edge of the WS_2 monolayers.

Higher load-carrying capacity was observed within the interior as compared to near the edge of the WS₂ monolayer. The variation in the concentration of S vacancies in the WS₂ monolayer was found to be the main reason for the varying wear behavior within the interior and near the edge. The non-uniform distribution of S vacancies was estimated using Raman and photoluminescence (PL) spectroscopy.

WS₂ monolayers can be used as a solid lubricant in tribological applications for the long run; however, the possibility of the formation of wrinkles over time cannot be neglected. Wrinkles are generally formed due to the strain relaxation, which is accumulated during CVD growth due to the difference in the thermal expansion coefficient between the WS₂ monolayer and the SiO₂ substrate. The nanoscale tribological behavior of the aged WS₂ monolayer in the presence of wrinkles and the effect of change in surface chemistry was investigated using AFM. Lower load-carrying capacity (~ ten-fold reduction) was observed in the presence of wrinkles than the freshly grown WS₂ monolayers due to the stress concentration near the wrinkles. Interestingly, higher COF was also observed in the aged sample in a wrinkle-free area. XPS of the aged sample shows the formation of tungsten oxides over the surface with time, which is known to increase friction.

Based on the atomic arrangement, the WS₂ monolayer can exist in phases such as 1H, 1T, and 1T' phases. These phases have distinct mechanical and optoelectronic properties. The frictional behavior of 1H and 1T' phases was investigated using AFM in ambient conditions. AFM measurements reveal a significant friction contrast between the two phases, with the 1H phase displaying higher friction (~ 52%) than the 1T' phase due to the distinct lattice structures and higher binding and interlayer surface energy barrier of the 1H phase. Surprisingly, under repeated scanning at constant stress, the friction of the 1H phase gradually decreases, eventually matching the lower friction values of the 1T' phase. It was observed that the phase transformation is irreversible and is strongly dependent on contact

stresses and is accelerated as the contact stress is increased by increasing the applied normal load.

In summary, the present study investigates the nanoscale tribological behavior of CVD-grown WS₂ monolayers using AFM under ambient conditions for tribological applications.

सार

द्वि-आयामी (२डी) पदार्थ असाधारण इलेक्ट्रॉनिक और यांत्रिक गुणों वाली केवल कुछ परमाणुओं की मोटाई वाली एकल या कुछ-परत संरचनाएं होती हैं। २डी पदार्थों में कमजोर अंतःपरत अन्योन्यक्रिया के साथ एक क्रिस्टल जाली संरचना होती है, जिसके परिणामस्वरूप परतों के बीच कम घर्षण बल होता है। यहां तक कि २डी पदार्थ की एक परत भी शीर्ष परत की निष्क्रिय और परमाणु रूप से चिकनी प्रकृति के कारण घर्षण को कुशलता से कम कर सकती है। ऐसे कई तरीके हैं जिनके माध्यम से २डी पदार्थ तैयार की जा सकती है, लेकिन बड़े आकार के गुच्छे और बड़े पैमाने पर उत्पादन करने की क्षमता के कारण रासायनिक वाष्प जमाव (सी.वी.डी.) विधि का अत्यधिक उपयोग किया जाता है। ट्रांज़िशन धातु डाइक्लोजेनाइड्स (टी.एम.डी.) जैसी २डी पदार्थों ने अपने उल्लेखनीय तापीय और यांत्रिक गुणों और परत-निर्भर बैंड गैप के कारण विशेष ध्यान आकर्षित किया है। मोलिब्डेनम डाइसल्फाइड (MoS_2) प्रतिनिधि टी.एम.डी. है क्योंकि उच्च तापमान और निर्वात में इसके असाधारण स्नेहन गुणों के कारण इसका उपयोग दशकों से एक ठोस स्नेहक के रूप में किया जाता रहा है; हालाँकि, ऐसे अन्य टी.एम.डी. भी हैं जो MoS_2 से बेहतर जनजातीय गुण प्रदान कर सकते हैं जैसे टंगस्टन डाइसल्फाइड (WS_2)। WS_2 घर्षण का बेहतर गुणांक (COF), उच्च तापीय और रासायनिक स्थिरता, अच्छी भार वहन क्षमता प्रदान करता है, और MoS_2 के समान स्वाभाविक रूप से प्रचुर मात्रा में भी है। वर्तमान अध्ययन में, परमाणु

बल सूक्ष्मदर्शी (ए.एफ.एम.) का उपयोग करके नैनोस्केल पर सी.वी.डी.-विकसित WS_2 एकल परत के जनजातीय व्यवहार की जांच की गई थी।

सी.वी.डी.-विकसित WS_2 एकल परत में संरचनात्मक दोष सर्वव्यापी हैं और इन्हें टाला नहीं जा सकता है। दोषों को बिंदु दोष (शून्य-आयामी), रेखा दोष (एक-आयामी), और सतह दोष (द्वि-आयामी) के रूप में वर्गीकृत किया जा सकता है। सी.वी.डी.-विकसित WS_2 एकल परत में सल्फर (S) रिक्तियों जैसे बिंदु दोष आम हैं, क्योंकि S रिक्ति में सबसे कम गठन ऊर्जा होती है। परिवेशी परिस्थितियों में ए.एफ.एम. का उपयोग करके बिंदु दोषों की उपस्थिति में सी.वी.डी.-विकसित WS_2 एकल परत के जनजातीय व्यवहार की जांच की गई। ए.एफ.एम. प्रयोग WS_2 एकल परत के आंतरिक और किनारे के पास किए गए। WS_2 एकल परत के किनारे की तुलना में आंतरिक भाग में अधिक भार वहन करने की क्षमता देखी गई। WS_2 एकल परत में S रिक्तियों की सांद्रता में भिन्नता को आंतरिक और किनारे के पास अलग-अलग रगड़ के व्यवहार का मुख्य कारण पाया गया। S रिक्तियों के गैर-समान वितरण का अनुमान रमन और फोटोल्यूमिनसेंस (पी.एल.) स्पेक्ट्रोस्कोपी का उपयोग करके लगाया गया था।

WS_2 एकल परत का उपयोग लंबे समय तक जनजातीय अनुप्रयोगों में एक ठोस स्नेहक के रूप में किया जा सकता है; हालाँकि, समय के साथ झुर्रियाँ बनने की संभावना को नज़रअंदाज नहीं किया जा सकता है। झुर्रियाँ आम तौर पर तनाव छूट के कारण बनती हैं,

जो WS_2 एकल परत और SiO_2 सब्सट्रेट के बीच तापीय विस्तार गुणांक में अंतर के कारण सी.वी.डी. विकास के दौरान जमा होती है। झुर्रियों की उपस्थिति में वृद्ध WS_2 एकल परत के नैनोस्केल जनजातीय व्यवहार और सतह रसायन विज्ञान में परिवर्तन के प्रभाव की जांच ए.एफ.एम. का उपयोग करके की गई थी। झुर्रियों के पास तनाव की सघनता के कारण ताजा विकसित WS_2 एकल परत की तुलना में झुर्रियों की उपस्थिति में कम भार वहन करने की क्षमता ($\sim$ दस गुना कमी) देखी गई। दिलचस्प बात यह है कि पुराने नमूने में झुर्रियों से मुक्त क्षेत्र में भी उच्च COF देखा गया। पुराने नमूने का एक्स.पी.एस. समय के साथ सतह पर टंगस्टन ऑक्साइड के गठन को दर्शाता है, जो घर्षण को बढ़ाने के लिए जाना जाता है।

परमाणु व्यवस्था के आधार पर, WS_2 एकल परत 1H, 1T, और 1T' अवस्थाओं में मौजूद हो सकता है। इन अवस्थाओं में विशिष्ट यांत्रिक और ऑप्टोइलेक्ट्रॉनिक गुण होते हैं। परिवेशी परिस्थितियों में ए.एफ.एम. का उपयोग करके 1H और 1T' अवस्थाओं के घर्षण व्यवहार की जांच की गई। ए.एफ.एम. माप दो अवस्थाओं के बीच एक महत्वपूर्ण घर्षण विरोधाभास को प्रकट करता है, जिसमें 1H अवस्था विशिष्ट जाली संरचनाओं और उच्च बंधन और अंतःपरत सतह ऊर्जा अवरोध के कारण 1T' अवस्था की तुलना में उच्च घर्षण ($\sim 52\%$) प्रदर्शित करता है। आश्चर्यजनक रूप से, निरंतर तनाव पर बार-बार स्कैन करने पर, 1H अवस्था का घर्षण धीरे-धीरे कम हो जाता है, अंततः 1T' अवस्था के निचले घर्षण

मूल्यों से मेल खाता है। यह देखा गया कि अवस्था परिवर्तन अपरिवर्तनीय है और संपर्क तनावों पर दृढ़ता से निर्भर है और लागू सामान्य भार में वृद्धि के कारण संपर्क तनाव बढ़ने पर यह तेज हो जाता है।

संक्षेप में, वर्तमान अध्ययन जनजातीय अनुप्रयोगों के लिए परिवेशी परिस्थितियों में ए.एफ.एम. का उपयोग करके सी.वी.डी.-विकसित WS_2 एकल परत के नैनोस्केल जनजातीय व्यवहार की जांच करता है।

Table of Contents

Certificate	i
Acknowledgments	iii
Abstract.....	v
Table of Contents	xiii
List of Figures.....	xvii
Chapter 1 Introduction	1
1.1 Chapter plan of Thesis	3
Chapter 2 Literature Review	5
2.1 Background of tribology	5
2.1.1 Friction.....	6
2.2 Tribology on the small scale	14
2.2.1 Friction at small scale	15
2.2.2 Wear at small-scale	18
2.2.3 Summary	19
2.3 2D materials.....	20
2.3.1 Graphene	21
2.3.2 TMDs	22
2.3.3 Synthesis of 2D materials	25
2.3.4 Defects in TMDs.....	33
2.3.5 Effect of defects on tribology of 2D materials.....	36

2.3.6 TMDs as lubricants	41
2.3.7 WS ₂ as a solid lubricant	51
2.3.8 Summary	55
Chapter 3 Motivation and Objectives	57
Chapter 4 Materials and Methodologies.....	61
4.1 Introduction.....	61
4.2 Sample preparation	61
4.2.1 CVD growth of WS ₂ monolayer	61
4.3 Material characterization techniques	62
4.3.1 Optical microscopy	62
4.3.2 Raman and PL spectroscopy	62
4.3.3 XPS	62
4.4 AFM.....	63
4.4.1 Working principle of AFM	63
4.4.2 Experimental setup of an AFM.....	65
4.4.3 Calibration of normal and lateral forces	66
4.4.4 Nanoscale friction and wear behavior using AFM under ambient conditions..	67
Chapter 5 Nanotribology of Chemical Vapor Deposited WS₂ Monolayers.....	69
5.1 Introduction.....	69
5.2 Results and discussion	69
5.2.1 Raman and PL spectroscopy of WS ₂ monolayers.....	69

5.2.2 Nanoscale friction and wear measurements.....	72
5.3 Summary	83
Chapter 6 Nanotribology of CVD-Grown Aged WS₂ Monolayer: The Role of Wrinkles and Surface Chemistry	85
6.1 Introduction.....	85
6.2 Results and discussion	85
6.2.1 Initial characterization	85
6.2.2 AFM imaging of wrinkles.....	87
6.2.3 Friction and wear behavior of the wrinkled WS ₂ monolayers.....	90
6.3 Friction and wear behavior of the wrinkle-free regions.....	94
6.4 Summary	98
Chapter 7 Nanotribology of CVD-grown Mixed-Phase WS₂ Monolayers	101
7.1 Introduction.....	101
7.2 Results and discussion	101
7.2.1 Fluorescence microscopy, Raman, and PL spectroscopy of mixed-phase WS ₂ monolayers.....	101
7.2.2 Nanotribological behavior of WS ₂ monolayers containing mixture of 1H and 1T' phases.....	103
7.3 Summary	108
Chapter 8 Conclusions and Future Work	111
8.1 Conclusions.....	111

8.2 Future work.....	112
References.....	115

List of Figures

Figure 2.1 A schematic of a system shows various factors influencing tribological properties [9].	6
Figure 2.2 The schematic illustrates the scenario of a block sliding on a surface, where W represents the normal load exerted by the block's weight, and F denotes the friction force acting between the block and the surface.	7
Figure 2.3 Stribeck curve illustrating the COF variation with speed, the viscosity of the lubricant, and the applied normal load [14].	13
Figure 2.4 Schematic illustrates the difference in the contact pressure and contact size between macro, micro, and nanoscale tribology [16].	15
Figure 2.5 Various parameters and mechanisms that affect wear at the nanoscale [18].	19
Figure 2.6 Various types of 2D layered materials [22].	21
Figure 2.7 Properties of graphene [23].	22
Figure 2.8 The atomic structure of TMDs can be categorized into two main phases: a) T phase and b) H phase. (c) The molecular structures of 2D TMDs can be represented using ball-and-stick models, which showcase the five different phase structures commonly observed in TMDs [2].	24
Figure 2.9 Various routes to fabricate 2D materials [26].	26
Figure 2.10 Schematic showing various factors that affect the thermodynamics and growth of 2D materials in a CVD process [36].	29
Figure 2.11 The schematic setup includes a quartz tube furnace with a horizontal configuration (upper), a SiO ₂ /Si substrate placed inside the tube (bottom), and a quartz boat	

loaded with WS ₂ precursor powder (middle) positioned in the center of the furnace [46].	31
Figure 2.12 Raman spectra of the WS ₂ sample: red line-monolayer, green line-bilayer, blue line-multilayer, and black line-bulk [46].	32
Figure 2.13 PL spectra of WS ₂ layers [46].	32
Figure 2.14 A classification of defects in 2D TMDs. (a) 0D defects such as vacancies and adatoms [56]. (b) 1D defects such as grain boundaries and edges [57]. (c) 2D defects such as folding, wrinkling, rippling, and scrolling [58].	35
Figure 2.15 (a) The figure illustrates the friction force profiles along two different directions: parallel (represented by the blue color) and perpendicular (represented by the red color) to the probe scan direction. The profiles depict both forward and backward scan directions, with sharp peaks indicating the higher friction associated with wrinkles. In the red profile, which is perpendicular to the probe scan direction, the wrinkle-free graphene exhibits minor peaks originating from ripples and puckers. Conversely, the blue profile shows no distinct ripples. Schematics in figures (b) and (c) provide visual representations of graphene puckering at the probe contact area. The illustrations highlight that greater deformation occurs perpendicular to the ripple lines due to the lower bending stiffness, contributing to the observed frictional differences [63].	37
Figure 2.16 (a) Illustration of the friction behavior of GWs at a load of 0 nN. The friction loops and corresponding cross-sectional profiles of the GW are shown when the scanning direction is vertical to the direction of the wrinkle. (b) Shows the peak lateral force variation as a function of wrinkle heights. (c) Shows the peak lateral force variations with applied loads. (d) AFM topographic images of W1 and W3 before and after measurements [64].	39

Figure 2.17 The figures present high-resolution images showcasing the surface topography and friction characteristics of MoS ₂ following helium ion irradiation. (a) and (b) show the surface topography and friction images, respectively, after irradiation. Corresponding surface line profiles are shown in (c). (d) and (e) show the surface topography and friction images, respectively, after irradiation with a higher dose, and the corresponding surface line profiles are shown in (f) [65].	41
Figure 2.18 Possible 2D nanosheet mechanisms to reduce friction and wear [70].	43
Figure 2.19 (a) Optical, (b) topographic, and (c) friction (forward force) images of various 2D materials, (d) friction decreases with the increasing number of 2D layers [77].	45
Figure 2.20 (a) The hexagonal symmetric structure of single-layer MoX ₂ (where X can be S, Se, or Te) is illustrated using a ball-and-stick model, which includes both top and side views. (b) Lattice parameters for each TMD supercell. (c) The friction loops acquired through AFM are displayed to represent the friction behavior of the sample. The AFM probe slides perpendicular to the long axis of the cantilever during the measurement process. (d) Representative friction traces were obtained using MD simulations [78].	46
Figure 2.21 COF of 2L MoS ₂ , 4L MoS ₂ , 12L MoS ₂ , and 1L graphene were determined at low pressure after undergoing up to 10 sliding cycles. In comparison, SiO ₂ /Si was subjected to only one sliding cycle to determine its friction coefficient [81].	48
Figure 2.22 COF with the varying normal load shows variation in friction as the diamond tip scratches the MoS ₂ layer [80].	49
Figure 2.23 (a) The experimental setup for the friction test is shown in the schematic diagram. (b) The friction coefficient of the continuous monolayer MoS ₂ was measured under a normal load of 0.1 mN, and its variation with the cycle number was recorded. The optical microscopy image of the sliding track after the test is presented as an inset. (c) The	

friction coefficient of the continuous monolayer MoS ₂ was measured as a function of the normal load and cycle number, with the load being increased every 20 cycles at the same location. The optical microscopy image of the sliding track after the test is included as an inset. (d) The spatial variation of the friction coefficient along the sliding track was measured as a function of the cycle number. [84].	50
Figure 2.24 (a) COF values variations and (b) steel ball wear rate of different coated samples. The substrates with dimple array, line array, and four-leaf clover array textures were referred to as DSC, LSC, and CSC, respectively. Additionally, polished cemented carbide substrates coated with WS ₂ were labeled as PSC [6].	53
Figure 2.25 The surface properties of the WS ₂ , MoSe ₂ , and WSe ₂ monolayer flakes were characterized, including topography (a0-a2), friction maps (b0-b2), and load-dependent friction (c0-c2). The normal force measured the combined force of adhesion and applied load, with a dotted dashed line marking the point of zero applied load [89].	55
Figure 4.1 Illustration of the schematic of the CVD process to grow WS ₂ monolayers on a SiO ₂ /Si substrate [90].	62
Figure 4.2 The force-distance curve shows different operating modes of AFM [91].	65
Figure 4.3 (a) A schematic shows an AFM experimental setup. (b) Drive AFM components utilized to perform AFM experiments.	66
Figure 5.1 (a) Optical image showing a WS ₂ monolayer flake (b) Raman and (c) PL spectra collected from the four different points marked on the WS ₂ monolayer in (a). (d) Representative optical micrograph showing WS ₂ monolayer flake and corresponding (e) PL intensity and (f) PL position map.	71

Figure 5.2 (a) AFM topographic image ($13\ \mu\text{m} \times 13\ \mu\text{m}$) of the CVD-grown WS_2 monolayer, and (b) the line profile showing the thickness around 1 nm [97]. The abrupt change in the height near the edge is possible due to the edge overshoot artifact [98]. 72

Figure 5.3 (a) Friction force vs. applied normal load measured on the CVD-grown WS_2 monolayer on SiO_2/Si substrate within the interior of the WS_2 monolayer, showing an abrupt increase in the friction force due to sudden wear. (b) Zoomed-out friction channel image showing the experiment region and (c) the line profile showing no abrupt change in the friction force in the experiment region. (d) Zoomed-out friction channel image showing experiment region, a clear friction contrast between the experiment region and outer area is visible, and (e) the line profile showing an abrupt increase in friction in the experiment region. Zoomed-out images shown in Figure 5.3 were obtained at a lower normal load ($\sim 0.1\ \mu\text{N}$). 74

Figure 5.4 (a) Zoomed-out topographic image of the experiment region with no wear and (b) the line profile showing no variation in the experiment region. (c) Zoomed-out topographic image of the experiment region when sudden wear occurred and (b) the line profile showing the wear of the monolayer in the experiment region. These experiments were performed within the interior of the WS_2 monolayer. 75

Figure 5.5 Friction force vs. normal load for the interior region, along with the topographical images showing the wear of the WS_2 monolayer with the increasing normal load. 76

Figure 5.6 (a) Friction force vs. applied normal load measured on the CVD-grown WS_2 monolayer, near the edge of the monolayer, on SiO_2/Si substrate showing a sudden and gradual increase in the friction force. (b) Zoomed-out friction channel image showing experiment region and (c) the line profile showing higher friction force in the worn-out area

of experiment region. (d) Zoomed-out friction channel image showing experiment region, and (e) the line profile showing variation in the friction force. Zoomed-out images shown in Fig. 4b & c were obtained at a lower normal load ($\sim 0.1 \mu\text{N}$).....	78
Figure 5.7 (a) Zoomed-out topographic image of the experiment region when there is sudden wear of the monolayer, and (b) the line profile showing wear in the experiment region. (c) Zoomed-out topographic image of the experiment region when wear occurred gradually with increasing normal load and (b) the line profile showing wear in the experiment region. These experiments were performed near the edge of the WS_2 monolayer.	79
Figure 5.8 Friction force vs. normal load for the edge region (sudden wear) along with the topographical images showing the wear of the WS_2 with the increasing normal load.....	80
Figure 5.9 Friction force vs. normal load for the edge region (gradual wear), along with the topographical images showing the wear of the WS_2 monolayer with the increasing load.	80
Figure 5.10 Blind estimated tip shape (a) before and (b) after experiments. Tip check (c) before and (d) after exp.....	81
Figure 5.11 Schematic showing the wear of monolayer WS_2 after performing the sliding experiments (a) within the interior and (b) near the edge. The black color dashed square shows the AFM experiment region.....	83
Figure 6.1 (a) Raman and (b) PL spectra of the aged WS_2 confirming the presence of monolayer [108].....	86
Figure 6.2 XPS plot of freshly grown WS_2 monolayer. (a) Survey scan, (b) C-scan, (c) O-scan, (d) W-scan, and (e) S-scan are presented.	87

Figure 6.3 (a) Low magnification AFM topographic image and (b) friction force map of the aged WS₂ monolayer shows wrinkles. (c) Higher magnification AFM topographic image of a wrinkle shows height profile in the inset, (d) corresponding friction force map of the wrinkle shows higher friction on the wrinkle. A friction loop across the wrinkle is shown in the inset.....89

Figure 6.4 High-magnification 3D topographic AFM image of a wrinkle shows height contrast between the wrinkle and the WS₂ monolayer.89

Figure 6.5 (a) The effect of normal load on the friction measured on wrinkled WS₂ monolayer. Above 300 nN normal load, friction force increased abruptly, likely due to the complete wear of the WS₂ monolayer, and the tip encounters the underlying substrate (SiO₂/Si). (b) Zoomed-out friction force map of the experimental region (shown in white color dashed square). (c) The line profile across the friction force map (white color solid line drawn in the middle) shows an abrupt increase in the friction force in the experimental region. From the upper left, clockwise around the boundary: The images show the wear of the aged WS₂ monolayer with the increasing normal load (the corresponding normal load is mentioned in the inset); wear can be observed initiating near wrinkles.92

Figure 6.6 Topographic image of the perpendicular and parallel wrinkle at low and high normal loads in (a), (b), (d), and (e). (c) and (f) show topographic line profile across wrinkles (red and blue color lines in topographic images) at two different normal loads revealing wear of perpendicular wrinkle and flattening of the wrinkle oriented parallel to sliding direction.93

Figure 6.7 (a) Friction vs. normal load shows a jump in the friction at a lower normal load of ~ 150 nN for perpendicular wrinkle, whereas no such sudden jump is observed for parallel wrinkle. Zoomed-out friction force map of the experimental area (white color

dashed square) showing (b) perpendicular wrinkle with the worn region where friction contrast is much brighter and (c) parallel wrinkle with uniform friction contrast due to lack of wear.94

Figure 6.8 Variation in the lateral force and wrinkle height when sliding an AFM tip across a wrinkle at various applied normal loads from 45 nN to 200 nN.....94

Figure 6.9 (a) The effect of normal load on the friction of the wrinkled WS₂ monolayer. However, above 1000 nN normal load, friction force increased abruptly due to the wear of monolayer WS₂, and the tip encounters the underlying substrate (SiO₂/Si). (b) Zoomed-out friction force map of the experimental region in white color dashed square. (c) The line profile across the friction force map (white color solid line drawn in Fig. (b)) shows an abrupt increase in the friction force in the experimental region.97

Figure 6.10 (a) A comparison of friction loop and (b) adhesion (pull-off force) between fresh and aged (wrinkle-free region) WS₂ monolayer. The aged sample shows higher friction and lower adhesion force than the fresh WS₂ sample.97

Figure 6.11 XPS plot of aged WS₂ monolayer. (a) A survey scan indicates the presence of W, S, C, and O in the aged sample. The intensity of C is higher in the aged sample due to the adsorption of hydrocarbons on the monolayer surface over time. (b) C-scan, (c) O-scan, (d) W, and (e) S-scan.98

Figure 6.12 (a) Zoomed-out friction force map of the experimental region (in white color dashed square). (b) The line profile across the friction force map (white color solid line drawn in the middle) shows reduced friction in the middle, highlighted by the black color dashed circle.....98

Figure 7.1 (a) Fluorescent micrograph of the WS₂ monolayer flakes revealing contrast (bright and dark regions) within the flake. (b) and (c) Raman spectra of the bright and dark

regions of five random locations (B1 to B5 and D1 to D5). (d) PL spectra of the bright and dark regions (B1, B2 and D1, D2). Raman and PL spectra confirm the presence of 1H and 1T' phases in the WS₂ monolayer. 103

Figure 7.2 (a) AFM friction force map of the WS₂ monolayer flake revealing 1H and 1T' phases within the flake before the experiment (the experimental region is shown by black color dashed square). (b) Friction force variation of both phases with the increasing no. of cycles at constant stress. All seven cycles are shown at the boundary of the friction plot starting from the left top corner clockwise. (c) The friction force map of the WS₂ monolayer shows the experimental region after the experiment. 107

Figure 7.3 (a) AFM topographic image of the experimental region revealing no significant height difference between the two phases (1H and 1T' phase), which can lead to friction contrast. (b) The corresponding friction map shows lower friction in the 1T' phase as compared to the 1H phase. 107

Figure 7.4 (a) No. of cycles vs. normal load shows a decreasing trend as lower no. of scans are required for transformation (1H phase to 1T' phase) with the increasing normal loads. (b) Friction transformation rate dependence on contact pressure. Transformation rate is exponential with the increasing contact pressures. 108