Abstract

Tribological Properties of Ultrathin Films for MEMS Applications

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2014

The friction and wear properties of ultrathin films of graphene, graphene oxide (GO) and reduced GO at nanoscale were investigated using friction force microscopy (FFM). Graphene and GO were found to reduce friction for sliding between a Si AFM tip and SiO$_2$ surfaces by $\sim$6 and $\sim$2 times respectively. As a solid lubricant, GO was found to wear under small normal load, while graphene was found to be highly wear resistant. The higher propensity for wear of GO as compared to graphene may limit its usefulness as coatings for micro/nano-electro-mechanical systems (M/NEMS) with high contact stress applications. Adhesion of GO has been found to increase with elevated relative humidity. Effect of chemical structure on the friction and wear properties of GO was then investigated to overcome the challenge for GO as a solid lubricant. It was found that reduced GO exhibited higher anti-wear properties than GO and proves to be effective in designing coatings for M/NEMS with tunable properties.
Acknowledgements

I would never have been able to finish this work without the assistance of many people, including my supervisor, lab mates, funding agencies, friends and my family.

Foremost, I would like to express my deepest gratitude to my advisor Prof. Tobin Filleter for his support, patience, motivation, enthusiasm, and immense knowledge that guided me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my graduate study.

Secondly, my sincere thanks goes to my lab mates who provided me with critical insights, encouragements as well as happiness while enjoying the beauty of research into this cutting edge field.

Thirdly, I would like to thank the funding agencies and academic collaborators that supported this work. I would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and Canada Foundation for Innovation (CFI) for the support of research and infrastructure funding. This work has also been supported by other academic researchers at the University of Toronto. Specially I would like to acknowledge Rana Sodhi & Peter Brodersen (University of Toronto) and James Jonkman (University Health Network). Besides the support from research, I would also like to thank many other colleagues and friends with whom I have enjoyed a great time at the University of Toronto.

Last but not least I’d like to express me special thanks to my family who has stood behind me and always encouraged me with love and support throughout my graduate study and research.
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Chapter 1

Forward

1.1 Motivation

The miniaturization of electrical circuits and systems in the integrated circuit (IC) industry has greatly improved the world’s economy and enhanced people’s lives. The miniaturization of devices and systems has always been a pursuit for researchers and industries since it has great potential to increase performance and reduce cost due to the advantages of batch fabrication. Micro-electromechanical systems (MEMS) represent the technology of miniaturization of coupled mechanical and electrical devices and systems by employing batch fabrication process which has been successfully used in the IC industry. MEMS have many applications, including pressure sensors [4], accelerometers [5], gyroscopes [6], inkjet printers [7], etc. The market for MEMS chips has doubled from the year 2004 to 2012, and it is expect to have a steady growth \ (~13\% \) through 2018 to create a $22.5 billion industry in 2018 [8]. In addition, new types of MEMS sensors and actuators are emerging every year because of the development and emergence of smart devices.

![Figure 1.1: (a): Scanning electron microscope (SEM) image of a micro mirror; (b): SEM image of contact of two intermeshing gears in a micro mirror MEMS (courtesy of Sandia National Laboratories, SUMMiTTM Technologies, www.mems.sandia.gov) [1].](image)

Although MEMS have many applications in industries such as automotive and health care, most
MEMS devices have been designed with some basic components, including cantilever beams, thin membranes, hinges, springs, etc [9]. Figure 1.1(a) and (b) shows a typical MEMS called a micro mirror used in projection systems and a zoom in image of transmission gears in contact of the micro mirror MEMS. From Figure 1.1(a), it can be seen that there is a hinge and some cantilever beams in the micro mirror MEMS system. Figure 1.1(b) clearly shows how linear movement is converted to rotational movement, and this conversion is achieved with gears intermeshed against each other in the system. Likewise the contact between different components makes functionalities of MEMS possible.

MEMS have played a pivotal role in various applications, which require high reliability of the devices. The achievement of high reliability of MEMS devices is dependent on materials properties, micro fabrication processes and working environment. Reliability of MEMS becomes increasingly important as the size of MEMS devices shrink in that surface forces (capillary forces, electrostatic forces, etc.) become dominant over body forces (gravity force, etc.) [9]. These surface forces can render parts in MEMS device to adhere together during intentional or unintentional contact and cause possible failures such as stiction as shown in the Figure 1.2 below in the case of micro cantilevers. The investigation of the contact behavior in MEMS devices is a necessity to understand failure mechanisms and prevent failure induced by contacts. The contact at a macroscale usually involved millions of asperities in touch. The contact in MEMS, however, usually features only a few asperities in touch.

![Figure 1.2: SEM images of stiction of microcantilevers to substrate (excerpted from [2]).](image)

There are several major failure mechanisms in MEMS devices, including stiction, wear, fracture, etc. Stiction as seen in Figure 1.2 is the adhesion of contacting surfaces due to surface forces (mainly capillary force, van der Waals molecular forces, Casimir forces, hydrogen bridging and electrostatic forces.). Wear occurs when material is removed from a solid surface as a result of mechanical action of the opposite surface [10]. The effects of adhesion, friction and wear have been challenging issues in the development of sophisticated and miniaturized devices due to the increasing dominance of surface forces over body forces as devices are scaled down.

To reduce the failure of MEMS devices, the primary concern is to reduce friction and adhesion. Conventional liquid lubricants are not as effective at resolving the tribological problems in MEMS since high viscosity of liquid in confined MEMS channels would cause high energy dissipation. Recently, a great deal of research has been conducted on using various surface modifications techniques for friction and adhesion reduction, including surface roughening [11] and coatings [12].
Adhesion is mainly from two processes: the release process and operation duration of the MEMS device, known as “release adhesion” and “in use adhesion” respectively [2]. This “release adhesion” can be reduced via freeze drying or supercritical drying during the last step of MEMS fabrication. “In use adhesion” problems occur as movable components in MEMS make contact. One approach to reduce the adhesion between silicon surfaces is to reduce the contact area by roughening the surface [11]. Another approach involves using organic coating to render silicon surface hydrophobic, which can prevent water condensation and reduce capillary induced adhesion [12].

Organic coatings can also reduce the friction and wear to a certain degree since they reduce adhesion. However practical application of organic coating as lubricants is limited because of their poor durability during operating cycles [13, 14]. Another method is to apply a hard coating (such as diamond-like carbon, ultrananocrystalline diamond) with high modulus and high wear resistance onto silicon surfaces [15]. The main challenge of this approach is achieving a uniform coating for complicated structures in MEMS. Lubricants such as organic coatings and hard coatings have been extensively investigated, but each coating has its own limitations as has been discussed above.

It has been widely known that bulk graphite has good lubricating properties on the macroscale, however it could not be applied as a solid lubricant in MEMS because of the large size of bulk graphite flakes compared to the confined regions of MEMS. In 2004, Geim and and Novosolov discovered a single atomic layer of graphite, known as “graphene”, with the simple “scotch tape” method [16]. Graphene consists of an one-atom-thick layer of carbon atoms arranged in two-dimensional hexagons, and is the thinnest as well as one of the strongest and stiffest materials in the world till now. The high strength (~100GPa) of graphene also makes it highly wear resistant [17]. Previous studies have shown that it can be used to reduce friction between silicon-silicon sliding contacts by one order of magnitude and thus it has great potential for application as a solid lubricant for MEMS devices [18]. Graphene oxide (GO), the oxidized product of graphene, has also attracted great attention of researchers recently because of its unique mechanical [19] and chemical properties [20] due to the oxygenal functional groups on the ultrathin film. GO maintains some of the properties of graphene suggesting that it could also act as lubricant for MEMS surfaces. As a solid lubricant, it has advantages over graphene in two primary aspects: ultrathin GO film is approximately 50 times lower as compared to ultrathin graphene film [21] and graphene oxide allows for tunable friction properties due to the presence of functional groups [22]. GO can be produced using the well-established and commercially scalable Hummer’s method [23] directly from bulk graphite which is a very low cost and highly available natural resource used in many industrial applications, whereas graphene produced from bulk graphite has been demonstrated by the non-scalable mechanical exfoliation technique. Other methods of graphene synthesis, such as CVD or epitaxial growth onto the substrate [24] require expensive equipment. In addition, application of graphene as a lubricant often involves expensive equipment . While GO is hydrophilic, and this makes GO readily dissolved into a wide range of solvents [25]. This makes the coating application of GO as a lubricant much cheaper as compared to graphene. Friction of GO has been qualitatively investigated by previous studies [26], while quantitative friction and wear behavior of GO has not been determined. As discussed above for the application of lubricant in MEMS, wear is also a very important issue. GO can also be reduced such that the GO plane would become more graphitic and its properties tend to be more graphene like. As a result, friction of reduced GO is predicted to become smaller as compared to GO. This may allow for tunable friction of GO, which could be highly beneficial for the application of designing solid lubricant for MEMS. ased on the above mentioned motivation, the friction and wear of graphene, GO and reduced
GO have been comprehensively investigated in this thesis.

### 1.2 Objectives

#### 1.2.1 Short term

- Quantitatively understand tribological properties of ultrathin films in ambient conditions;
- Investigate the effect of chemical structure on the friction and wear properties of GO;
- Investigate the effect of environment (humidity) on the friction and wear properties of GO.

#### 1.2.2 Long term

- Map the carbon to oxygen ratios of GO with its friction and wear properties, which can allows for coatings with tunable properties;
- Develop GO based composite or sensors with an understanding of the interaction of water molecules with GO;
- Develop practical deposition process of coating these ultrathin films onto MEMS surfaces.

### 1.3 Preview of Chapters

In this thesis, friction and wear properties of ultrathin films of graphene and graphene oxide on silicon dioxide substrates were investigated for application as solid lubricant layers for MEMS lubrication. These properties were probed at a nanoscale by using atomic force microscope (AFM).

Chapter 2 presents a detailed review of the different solid lubricants that have been previously investigated for use in MEMS and then a brief review of previous tribological studies of graphene and GO as well as thermal and chemical reduction of graphene oxide.

In Chapter 3, first a general description of AFM principles are introduced. Then surface forces related to AFM imaging are discussed to give background knowledge with regard to AFM imaging. Finally friction force microscopy (FFM) is discussed including details of FFM friction and wear measurements, as well as models for characterizing contact mechanics behaviors that we used in FFM analysis. The experiment setup of AFM used for friction and wear tests of ultrathin films and thermal reduction of ultrathin films are outlined respectively.

In Chapter 4, friction and wear measurements of ultrathin graphene and graphene oxide films using FFM are presented. Graphene is found to have $\sim$6 times lower friction as compared to SiO$_2$, which could be excellent solid lubricant for MEMS while its application is limited by its high cost. Graphene oxide ultrathin films are also found to reduce friction on SiO$_2$ surface by 1.9-2.3 times, but is found to be easily worn under small normal loads, limiting its effectiveness as tribological coating.

In Chapter 5, the effect of structure and environment on the friction, adhesion and wear properties of GO is investigated using FFM. Friction and wear behavior of thermally reduced GO is characterized using FFM. The effect of relative humidity on the adhesion properties of films and SiO$_2$ surfaces are investigated within an humidity sensing cell in AFM. It is found that adhesion properties of both films and SiO$_2$ surface increase with elevated relative humidity, and a steep increase is identified in adhesion when the relative humidity exceed $\sim$70%.
Finally, Chapter 6 presents conclusions on the tribological properties of graphene, GO and reduced GO as well as discusses future steps for the development of ultrathin tribological coatings with tunable properties for MEMS.
Chapter 2

Introduction

2.1 MEMS reliability

MEMS refer to miniaturized devices which are typically made up of a combination of mechanical and electrical components ranging from 1 to 100 μm in size [27]. At this size scale, physical properties are very different from its counterparts at the macroscale. For example as devices are shrunk from 10 mm to 10 μm, the surface area decreases by a factor of 1 million while the volume decreases by a factor of 1 billion. Surface forces such as adhesion and friction which are proportional to the area therefore can become one thousand times larger than inertial forces resulting in surface forces that are comparable to the driving forces in MEMS devices. Components in MEMS usually involved in various relative motions, exhibit both intended and unintended contact. These contacts in MEMS can render the MEMS components vulnerable due to high resistance forces from those surface forces. To improve the reliability of MEMS, there is a need to understand the surface forces involved in contacts as well as develop lubricants and wear resistant coatings for MEMS. MEMS lubrication cannot be simply resolved by using liquid lubricants that have been proved to be effective at the macro scale. When MEMS components make movements, the high viscosity of liquid lubricants will cause high energy dissipation. Thus boundary lubrication instead of fluid film lubrication is more generally adopted for MEMS lubricating applications. Interactions between the two surfaces are featured by asperities colliding with each other under boundary lubrication conditions [28]. Boundary films are coated onto target surfaces to reduced the energy dissipated during the collision and they are typically formed by physisorption, chemisorption and chemical reaction. Physisorption is formed with van der Waals forces between two surfaces while chemisorption forms covalent bonds such that it involves in electron interchange between the solid surface and chemisorbed species. Physisorption and chemisorption are subcategories of adsorption that atoms or molecules are adhered to surface, which are different from chemical reaction that transforms one set of chemical substances to another [29]. Good candidate of MEMS lubricants typically have these properties: low surface tension, are easily applied to the substrate and are strong bonded to the substrate, chemical and thermal stability which makes it insensitive to environment [9]. To this end, various thin solid lubricants with application for MEMS have been investigated, including perfluropolyether (PFPE) [30, 31], self-assembled monolayers (SAMs) [32, 33, 34], hard coatings (diamond like carbon, etc.) [35, 36, 37, 38] and ultrathin graphene based films [26, 39].
2.2 Traditional boundary lubricants

2.2.1 Perfluoropolyether

Perfluoropolyether (PFPE) has been successfully applied as a lubricant to reduce friction and wear in magnetic storage media due to its various beneficial physical properties, including low surface tension, good chemical and thermal stability, and molecular scale thickness [40, 41]. Recent studies indicate that PFPE may also be a good candidate for MEMS lubrication [30, 31]. Bhushan et al. [31] investigated tribological properties of a chemically bonded PFPE (Z-DOL) as compared to silicon (100) using Si$_3$N$_4$ tips with an AFM, and found that the coefficient of friction of Si and Z-DOL are 0.07 and 0.04 respectively and adhesion forces are found to be 52 nN and 34 nN respectively. This work also indicated that environmental such as temperature and relative humidity have strong effects on the friction and adhesion properties of these two materials, which should be taken into consideration when applying PFPE lubricants into MEMS. Other PFFE such as mobile PFPE (Z-15) has lower durability than Z-DOL and practical application of PFFE for MEMS coatings needs further investigation to enhance its durability.

2.2.2 Self-assembled monolayers

In addition to PFPE, organized layers of long-chain molecules have been investigated to lubricate MEMS surfaces mainly due to their hydrophobicity. These organic layers render silicon surfaces hydrophobic and thus reduce capillary induced adhesion and friction. Techniques of producing molecular scale organized layers include Langmuir-Blodgett (L-B) and self-assembled monolayers (SAMs) processes. In the L-B process, monolayer or multilayers of organic molecules are first organized at the air-liquid interface and then physisorbed onto solid surfaces [42]. While in the SAMs process, molecules are spontaneously formed onto a solid surface by chemisorption to form ordered, robust and dense monolayers [43]. The weak adhesion between the L-B films and the solid surface due to the physical absorption restrict life time of the films whereas SAMs can be much more durable because of the chemical bonding. Here we focus on the introduction of SAMs as a lubricant in MEMS.

![Figure 2.1: Schematic of self-assembled monolayers on a substrate](image)

As shown in Figure 2.1, SAMs consists of three building groups: a hydrophilic head group that attached strongly to the substrate surface, a hydrophobic tail group that made up the outer surface and a spacer chain that connect the head group and the tail group [44]. To date, tribological properties of various SAMs structures have been investigated, including alkanethiol, biphenylihol, alkylsilane and
perfluoroalkylsilane SAMs [45, 46]. These organic layers can reduce capillary force induced stiction during the operation process of devices due to the hydrophobicity of the coatings from their tail group.

Alley et al. [32] applied octadecyltrichlorosilane (OTS) SAMs onto polysilicon structures for adhesion reduction and qualitatively suggested great potential of OTS as a lubricant for anti-stiction during post-release process. Further study of tribological properties of OTS SAMs by Deng et al. [33] indicated that OTS SAMs could not only reduce friction and adhesion to some degree, but also enhance the anti-wear properties of the polysilicon micromotor. Besides OTS SAMs, other SAMs such as dichlorodimethylsilane (DDMS), perfluoroalkylsilane (PTFS) have also indicated beneficial tribological properties as lubricants. Ashurst et al. [34] shown that DDMS might not be better at reducing friction of silicon surfaces as compared to OTS, but DDMS is more wear resistant and less vulnerable to be degraded under high temperature. Maboudian et al. [46] found the adhesion of FDTS(2H-perfluorodecyltrichlorosilane)-coated and OTS-coated polysilicon cantilever beams are four and three times smaller respectively as compared to the standard oxidized coating. It could also be seen that different SAMs possess different tribological properties, which could be influenced by functional groups, chain length, etc. Thus the practical application of SAMs as a lubricant in MEMS requires careful preparation to meet specific needs. Another disadvantage limiting application of the SAMs as lubricant is that they can be irreversibly worn off under small critical loads [47].

### 2.2.3 Hard coatings

Due to the wear and degradation tendency of organic layers and SAMs, various hard coatings such as tungsten, diamond and amorphous carbon (DLC) have been investigated to reduce friction and wear for MEMS. These hard coatings have great potential to be applied as solid lubricants due to their high hardness, low friction and chemical inertness. As MEMS components make contact, high hardness of these hard coatings makes contact area smaller, leading to lower adhesion and friction consequently. Techniques such as chemical vapor deposition (CVD) [35, 36, 37] and atomic layer deposition [48, 49] have been successfully applied to produce conformal hard coatings on MEMS surfaces. Mani et al. [35] selectively coated an MEMS device with conformal tungsten using a CVD process and coated MEMS structure shown much less likelihood of adhesion failure as compared to as-released structure from electrical tests. Diamond as hard coatings has very poor adhesion to other surfaces, which reduce friction and wear consequently. Heating during the sliding could be quickly dissipated due to its high thermal conductivity. The application of diamond as lubricants for MEMS is mainly limited by the fact that diamond is very expensive and therefore it generally only applied to components with very extreme anti-wear requirement in MEMS.

Another interesting material as a lubricant in MEMS is diamond-like-carbon (DLC), which can be manufactured more economically than diamond. DLC distinguishes itself from natural or synthetic diamond with respect to its chemical structure, while it has the good properties of high hardness and excellent tribological properties shown for diamond (Amorphous DLC coatings can result in materials that have no long-range crystalline order, so there is no brittle plane. This makes DLC flexible and conformal to the underlying shape being coated, while still being nearly as hard as diamond.) [50]. DLC has favorable low friction and high wear resistant properties [38]. Applications of DLC typically utilize the ability of DLC to reduce abrasive wear. Examples of these applications include: coatings for hard-disk read heads and MEMS devices, as well as medical application due to its biocompatibility. Smallwood et al. [51] indicated that DLC coated MEMS (electrostatic lateral output motor) showed three
hundred times increase in performance from cycling test over the uncoated ones in vacuum. Apart from these advantages of DLC as a lubricant, researches have indicated that deposition methods [52, 53, 54] and environmental factors especially relative humidity [54, 55] have great effect on their tribological properties. For example, unhydrogenated DLC coating in dry air or vacuum exhibited wear rate of two orders of magnitude of that for sliding in humid air [54]. Thus careful considerations should be taken before applying DLC as a lubricant onto target sample surfaces. These issues of DLC may limit the real application as solid lubricant in MEMS surfaces.

2.3 Ultrathin graphene based films

2.3.1 Graphene

Besides PFPE, SAMs and hard coatings, novel emerging nano materials as alternative coatings show great potential as lubricants for MEMS. Ultrathin films stand out among these materials. Ultrathin films of thickness less than 100 nm have been extensively investigated in recent years due to their various unique physical properties as compared to their bulk counterpart. Among these ultrathin films, graphene is the most studied in recent years since its discovery in 2004. Single layer graphene is one of the thinnest freestanding materials (0.33 nm) in the world till now and it exhibits various extraordinary properties. This one atomic thin sheet is the strongest material (~100 GPa) in the world [17], and it also has excellent electronic transport [16] and thermal conductivity properties [56]. The bulk counterpart of graphene is graphite, which means to write in terms of its Greek origin [57]. Graphite has been observed to be easily transferred to the substrate with a gentle rub and it has been investigated as a good solid lubricant for many decades [57]. Graphene maintains the beneficial friction behavior of graphite while it also exhibits various other excellent in plane physical properties.

Friction of single layer graphene was first investigated by Filleter et al. [39] in 2009 and they reported that friction on SiC was reduced by an order of magnitude by a single layer of graphene and reduced by another factor of two on bilayer graphene. From this study, it could be seen that friction of graphene is dependent on its thickness. The study of thickness dependent of friction in graphene was further investigated by Lee et al. [58] and the friction measurements of few layer graphene down to single atomic sheets revealed that friction monotonically increases as the number of layers decrease. Notably four layers of graphene was found to exhibit similar friction as bulk graphite. In addition friction tests show no difference in friction between suspended and substrate-supported graphene [58].

Lin et al. [59] investigated the friction and wear properties of multilayer graphene with a silicon tip by AFM and they found that friction of graphene is much lower as compared to silicon. Wear was detected under a high normal load of 5 μN after 100 cycles and the wear mechanism of graphene was proposed to be due to breakage of in-plane bonds between carbon atoms and shearing at the interface of graphene layers. The measured ultralow friction as well as high anti-wear property of graphene on silicon makes it a good candidate for MEMS lubricant. Friction and adhesion of graphene was further investigated by Cannara et al. [18] and the effect of tip-surface van der Waals interactions on nanoscale friction and adhesion of suspended and supported graphene on a silicon dioxide substrate was studied. Friction of single layer graphene was found to be around one magnitude lower than that of silicon dioxide. Adhesion shows no layer dependence on supported graphene while it exhibits an increase with increasing thickness of suspended graphene. This investigation of interfacial friction and adhesion extends the understanding
of graphene behavior at nano scale.

These fundamental studies of pristine graphene and MEMS substrates (i.e. silicon, silicon dioxide, and silicon carbide) indicate that graphene has favorable tribological properties. However, graphene has poor solubility in typical commercial available solvents and deposition of graphene onto substrates usually involves in CVD or other high cost process. Further research in either coating techniques or graphene solvents are needed for practical application of graphene as a solid lubricant.

2.3.2 Graphene nanocomposite and functionalized graphene

In view of the excellent mechanical properties and ultra-low friction of graphene, extensive efforts have been made towards nanocomposite ultrathin films where graphene act as the load carrying material. Organic thin films such as multiply-alkylated cyclopentane and ionic liquid ultrathin film show desirable tribological properties, but their application as solid lubricant for MEMS is limited due to the fact that they could be easily worn under small normal load. Organic thin film based nanocomposites with graphene have been designed and the nanocomposites show much higher anti-wear property as well as lower friction resistance [60, 61].

In addition to the research into pristine graphene and graphene nanocomposites, emerging research has investigated the properties of graphene after being chemically functionalized. The modulation of properties of graphene by chemical functionalization proved to be a scalable and inexpensive method. For example, graphene itself has zero band gap, which limits its application in the large field of semiconductors and sensors. After the functionalization, graphene could open its band gap and thus the scope that graphene applications would be larger. Extensive research into chemically functionalized graphene indicate that it has potential application in polymer nanocomposite design, solar cells, chemical and biosensors, etc. Mechanical as well as tribological properties of graphene could also be modified after chemically functionalization [62]. The products of chemical functionalization of graphene mainly include hydrogenated graphene, fluorinated graphene and GO [63].

Adsorbed chemical elements such as hydrogen or fluorine on graphene surface can form covalent bonds with the carbon atoms and thus create hydrogenated graphene or fluorinated graphene. This chemisorption process have been found to modulate mechanical as well as tribological properties of graphene [64, 65] which is important for applying a lubricant with tunable properties as well as novel design of graphene based devices. Graphite fluorinate as a bulk solid lubricant has been investigated as a lubricant long time ago [66] and nanoscale research has been conducted to investigate the friction of fluorinated graphene most recently [65].

Park et al. [65] indicated that nanoscale friction on the graphene surface increases by a factor of 6 after fluorination of the surface, while the adhesion force is slightly reduced. Simulation showed that the fluorinated graphene exhibits more friction because of the increased out-of-plane bending stiffness of fluorinated graphene. Meyer at al. [67] compared friction of pristine and hydrogenated graphene and results showed friction on pristine graphene is 1/4 of hydrogenated graphene. It can be seen that tribological properties of graphene could be modified with hydrogenation or fluorination. This modulation due to chemical functionalization could better fit the application which requires specific needs.
2.3.3 Graphene oxide

Graphene oxide (GO) is the oxidized product of graphene and GO is formed when oxygen functional groups such as carboxyl, hydroxyl and epoxy group are chemically bonded to the sp$^2$ hybridized network of graphene sheets. GO has been an attractive area of research recently not only due to its various chemical and physical properties, but also because GO could serve as precursor to produce manufacturing scale graphene [68, 69, 70, 19]. Initial studies have shown that GO has beneficial tribological properties and could be potentially applied as a lubricant in MEMS [26]. In addition, GO can readily be formed into a colloid suspension in water and other common commercial available solvents [25] due to its hydrophilic functional groups, which makes application of GO as a lubricant much easier as compared to graphene. GO can also be reduced by removing oxygenal functional groups to emulate the properties of pristine graphene, this reduction process can be achieved by either chemical or thermal method [71, 72]. Although GO can be reduced, it should be noted that high resolution transmission electron microscope images indicated that graphene from GO reduction exhibits a number of defects such as holes in its plane [73], which are not generally found in pristine graphene.

Chemical reduction is the most common method for reducing GO and the mechanism is based on the reaction with chemical reagents. Chemical reduction process can be achieved in room temperature with no special and expensive equipment. The first idea of reduction of GO came from the reduction of its bulk counterpart, graphite oxide. Graphite oxide has been found to be reduced by hydrazine by Fendler et al. [74]. This inspired the work of chemical reduction of GO by Stankovich et al. [71, 75] and hydrazine has been widely used as reagents for chemical reduction of GO ever since. Apart from hydrazine and its derivatives, other strong reduction reagents such as NaBH$_4$ and hydroiodic acid [76, 77] have also been reported to be effective to reduce GO. Concerned with the potential hazard of hydrazine, Vitamin C has been proved to be a good reduction reagent for GO and could be a potential replacement of hydrazine [78].

In addition to the chemical method of GO reduction, thermal annealing is also an effective and efficient method. GO reduced with the thermal method is achieved with only thermal treatment in either vacuum or an inert gas environment. The high temperature makes the oxygen-containing functional groups in the GO plane decompose into gases and this make GO into graphene [79]. Although the thermal method might be more expensive than the chemical method, it is simple and precludes those hazardous reagents involved in the chemical method. Another beneficial characteristic of the thermal method is that the tunable mechanical or electrical properties of GO, correspond to the reduction rate, could be quantitatively controlled by annealing temperature [22, 72]. This is very beneficial for the design of solid lubricant with different specifications in MEMS.

Friction of reduced GO at different annealing temperature were measured with AFM by Riedo et al. [22] and the result showed a monotonically trend of decreasing friction with increasing temperature. Friction properties GO and reduced GO was then qualitatively investigated by Yang et al. [26] and they showed that friction of GO is around 2.5 times lower as compared to silicon and reduced GO exhibits lower friction than GO. Ding et al. [80] further compared the friction of graphene and graphene oxide. Zhang et al. [81] used a green electrophoretic deposition approach to coat the silicon surface with GO films and tribological behavior of resulted films was investigated with a micro tribometer.
2.4 Summary

After a thorough literature survey, novelties of research in this thesis are then identified as follows. Wear is an important issue for practical application of GO as a solid lubricant in MEMS, but it has not been addressed for GO at nano scale by previous studies. The basic understanding of wear from a nanoscale perspective is a necessity for applying GO as a lubricant to MEMS surfaces and it will be investigated in this thesis. In addition, since GO can be reduced to achieve better mechanical properties, it is of great interest to understand the friction and wear properties of reduced GO as well. We would like to quantitatively map the friction and wear properties of reduced GO with its chemical structures in the near future. Due to the fact that high humidity might cause adhesion induced failure on MEMS surfaces [82], then our study is extended into the effect of relative humidity on the adhesion property of GO which has not been studied before. These investigations would lead to development of coatings with tunable properties and enhance the reliability for MEMS.
Chapter 3

Background and Experimental Setup

3.1 Atomic force microscope

Atomic force microscope (AFM) has become an emerging tool for the investigation of nanoscience since local experiments at the nanoscale or smaller can be performed with its physical probe that scans the specimen [83]. Before the invention of AFM, scanning tunneling microscope (STM) was first invented in 1982 by Rohrer and Binnig [84] and they were awarded the Nobel Prize in Physics in 1986 for the design of STM. STM captures images using quantum tunneling and it could achieve high resolution of 0.1 nm and 0.01 nm in lateral and normal direction respectively [85], which produces atomic scale topography images. In view of the disadvantage of STM that it can not image insulators with high resolution, a new type of microscope named AFM which is able to image insulator surface at nanoscale was introduced by Gerber et al. [86] in 1986. Unlike STM, AFM does not measure the tunneling current but measures the ultra-small force between the tip and surface. The limit of sensitivity of the AFM that Gerber et al. developed was $10^{-15}$N, which is far less than most of the interacting forces such as ionic bonding or van der Waals forces and thus AFM could measure all the important forces with the sharp tip. AFM captures precise images by moving a nanometer sized tip across the surface of the image, which is applicable both to conductors and insulators. As the AFM probe scans in a raster pattern across the sample surface, it gathers information such as topography and force data from its interaction with the surface. Topography map resolution acquired with an AFM is typically on the order of fractions of a nanometer (as low as 0.1 nm) and AFM has become an emerging tool to image, measure and manipulate at the nanoscale [83, 87].

The measurement of forces between the tip and the sample is achieved with a sharp tip at the end of a cantilever which acts as a force sensor (see Figure 3.1). Most AFMs use micro-fabricated force sensors made from silicon, though piezoelectric quartz sensors are used in some application such as ultra high vacuum and low temperature [88, 89, 90]. Different techniques of detecting the bending of the cantilever have been explored [83], including beam deflection [91, 92], interferometry [93], piezoelectricity [94], etc. The beam deflection method is used in most AFM due to its good reliability and simplicity. Also for the investigation of tribological properties of sample surfaces, the beam deflection method is the only method that can simultaneously measure the normal and lateral force acting between the AFM tip and the sample [95].

Figure 3.1 shows a schematic of the beam deflection method used in most AFM systems. In this
method, the laser beam is reflected off of the backside of the end of the cantilever and onto the position sensitive detector (typically a quadrant photodetector). Normal force induces the normal displacement of the cantilever while lateral force induces the twist of the cantilever. Normal and lateral displacement of the cantilever can then be measured from the intensity of the reflected beam in different quadrants of the quadrant photodetector.

![Figure 3.1: Schematic of beam deflection method in AFM.](image)

Normal bending is determined from the difference between the upper and lower quadrants (A-B in Figure 3.1) and the lateral bending from the difference between the left and right quadrants (C-D in Figure 3.1). Normal and lateral bending can then be simultaneously measured using the quadrant photodetector, which is important in particular for friction studies. Conversion of both normal and lateral bending to force will be discussed later in Section 3.6. A piezoelectric scanner as shown in Figure 3.1 is typically used to make displacement of the tip with respect to the sample with sub-nanometer resolution in all three dimensions.

Figure 3.2 shows the Asylum MFP-3D AFM setup used for this thesis in ambient conditions in an acoustic isolation chamber. It mainly consists of a head, scanner and controller. The head mainly includes the Z piezo, Z Linear variable differential transformer (LVDT), optical beam deflection system and cantilever. The optical beam deflection system and the Z piezo in the head monitor and control the deflection of the cantilever. LVDT are position sensors that physically attached to the piezo and thus it could detect the position of respective piezo. Each axis (X, Y and Z) has a position sensor to detect the position of the piezo, which makes a close loop control system. The scanner moves the sample in X and Y direction during the scanning process with the X and Y piezo and the position of the two piezo are detected with the X and Y LVDT. The MFP-3D closed-loop scanner for study in this thesis has a 90 \( \mu m \) scan range and 5 Å resolution in the X and Y directions, and a 15 \( \mu m \) range and 0.6 Å resolution in the Z direction.
3.2 Operation modes in AFM

Modes of operation are based on the characteristics how of the tip interacts with the sample surface and can be divided into static and dynamic modes. Static modes typically feature static bending of a cantilever while dynamic modes record the changes in dynamic properties of a vibrating tip that interacts with a surface [96]. Changes in vibrational properties of the dynamic mode include oscillation frequency, oscillation amplitude and phase. As shown in Figure 3.3, the interaction force between the tip and the sample surface falls either into the repulsive regime, which is considered to be in “contact”, or the attractive regime, which is considered to be in “non-contact”. Thus modes in AFM are also often differentiated from each other with respective to whether the tip is in contact in the surface or not.

Figure 3.3: Tip-surface force vs. tip-surface distance.

Contact mode has been used as a simple method to generate topography images of a sample surface.
In contact mode, the deflection of the cantilever is sensed and maintained at a desired value by the feedback loop of the controller. Topography of the surface is measured by scanning the tip over the surface at a constant normal deflection. The scanner moves the sample in X and Y direction under the cantilever tip to form a raster pattern. Then the topography image of the sample surface is recorded from the Z piezo voltage required to maintain a constant deflection of the cantilever. Since forces between the tip and sample surfaces are relatively high, contact mode is mainly used to measure the topography of hard surfaces because it might damage the soft sample surface such as biological samples during the scanning.

When the tip moves across the surface in contact mode, friction between the tip and the sample will cause a lateral force on the tip. This lateral force then produces a torsional bending of the cantilever, which is measured by the quadrant photodetector of a beam deflection AFM. Consequently, the friction of the tip in contact with the sample surface can be measured with high resolution under various external normal deflections, scanning velocities or environments. This mode, typically referred as friction force microscopy (FFM), can record the topography and lateral force map simultaneously during the scanning. This characteristic of FFM also makes it a good tool to investigate the wear behavior of the surface since it can record subsequent image of the surface after wear initiates in a set of experiments.

The non-contact mode was introduced because tip-surface contact in contact mode might destruct the surface with the small force. In this mode, attractive van der Waals force between the tip and sample are detected and topographic images are recorded by scanning the tip approximately a few nanometers above the surface. Since the attractive force is much smaller as compared to repulsive force in contact mode and thus the tip must be given a small oscillation (typically < 10 nm) [97] so that non-contact modes can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample.

Most sample surfaces develop a meniscus with the AFM tip in ambient environment, which might lead to major problems during imaging caused by the stiction between the tip and sample in contact mode or non-contact dynamic mode. In view of this problem, tapping mode was introduced [98] where the tip oscillates at near its resonate frequency with an amplitude greater than 10 nm (typically ~100 nm). In tapping mode, a cantilever is attached to an actuator, which is often referred as “shake piezo”. The shake piezo converts the voltage input into oscillatory movement that drives the cantilever to oscillate. The cantilever is excited near its fundamental oscillation frequency. The oscillation of the cantilever would cause the oscillation of the deflection signal, and thus the cantilever’s motion could be characterized with amplitude of the deflection signal. As the tip scans over the sample surface, interaction of forces such as van der Waals force and static force with the tip decreases the amplitude of the oscillation and the feedback system controls the height between the tip and sample surface to maintain the amplitude of cantilever oscillation. In this way, the Z piezo moves the cantilever up and down and thus it can record the topography of the sample surface. Tapping mode is also known as intermittent contact mode since the image is produced from the intermittent contacts of the tip with the sample surface [99]. As a result, tapping mode is near to a nondestructive imaging method, it is often used to image a surface before and after mechanical testing.
3.3 Interacting forces in AFM

As it is shown above, different modes in AFM involves in different interacting forces between the tip and the sample surface. The forces that interact at atomic scale can be classified as short- or long-range forces, attractive or repulsive [100]. These interacting forces act on the tip as it is located in the vicinity of a surface. Typical short range forces include chemical binding forces, Pauli exclusion and ionic repulsion forces, which are due to the overlap of electron wave functions and from the repulsion of ionic cores. Long range forces mainly include van der Waals force and electrostatic interaction.

Short range forces play an important role in contact mode while long range forces dominant in non-contact mode. Understanding these forces acting on the tip during scanning is important for the accurate interpretation of the properties investigated by the AFM. For example, one of the most common MEMS failure mechanisms is stiction due to large adhesion, which prevents relative motion between MEMS components. Forces such as chemical, capillary and van der Waals forces all contribute to adhesion between the tip and sample surface and thus should be taken into consideration for the investigation of adhesion [101, 102]. For adhesion measurement in contact mode, as we will discussed later in Section 3.5, various interacting force involved as the tip jump into contact and then pull off from the surface. Besides adhesion, analysis of friction and wear behavior of the surface measured in contact mode requires an in-depth understanding of the interacting forces exerted onto the surface.

3.4 Friction and wear

The investigation of macroscopic friction was first presented by Amonton in 1699, in which he indicated the well-known law that the force of friction is directly proportional to the applied load. Ever since the investigation of friction has been extended to kinetic friction, fluid friction, etc. It has been reported that energy losses due to friction and wear are estimated to be around 6% of the United States’ gross national product [103]. To reduce the energy losses, physical mechanisms behind friction have been extensively investigated by researchers during the last century and it continuously attracts their interests. The development of nanotechnology inspired the research into fundamental understanding of tribology from the macro scale to the micro/nano scale. Micro/nano scale contacts typically consists of a few nanometer-scale asperities that touch, which are intrinsically different from that in the macroscopic case where millions of asperities make contact. In addition, surface forces such as van der Waals and capillary forces, which are negligible in macro scale tribology should be taken into consideration in nanotribology, which make the contact in micro/nano scale behave differently from that in macro scale. The study of friction, adhesion and wear of surfaces at the nanoscale (a few hundred nanometers or less) have been referred to as “nanotribology” [104]. In nanotribology, Amonton’s law no longer generally applies due to the fact that the behavior of single asperity contact dominates over the collective behavior of many contacts. The investigation of nanotribology has been an emerging study due to the rapid development of AFM. The well-defined contact between the sharp AFM and the surface gives quantitative and fundamental understanding of interfaces and surface, and thus the use of AFM for single asperity studies on surfaces have been a useful tool in such studies. The contact between the sharp AFM tip and surface ideally mimic the contact behavior in MEMS and it gives perspective for topography information as well as various properties of lubricants that are applied in MEMS.

Wear is an important issue to be considered when applying a lubricant onto a surface. Wear is
related to interactions between surfaces with relative sliding motion, and more specifically the removal or deformation of material on a surface due to mechanical action of the opposite surface [10]. The wear process involves in complex interaction between two surfaces and it can be divided into subcategories due to different mechanisms, including adhesive wear, abrasive wear, surface fatigue, fretting wear and erosive wear, etc. [105]. The investigation of wear at the macroscopic scale gives the wear rate of the surface (not intrinsic properties of the surface, and it is highly dependent on the material's state [106]), while often a fundamental understanding of the wear behavior related to the interface is missing. While in the case of nanoscale investigation, mechanisms of the wear during the sliding could be investigated with the single asperity contact measurement while simultaneously imaging the surface by AFM. Information of the tip-sample interface could be obtained from adhesion measurement with the AFM as well as from the contact models discussed in Section 3.7.

3.5 **Friction force microscopy**

AFM has been an emerging tool to study the friction properties of sample surfaces. When the tip scans across the sample surface in contact mode, the topography and lateral force information can be measured simultaneously. This technique is known as friction force microscopy (FFM). Frictional force between the AFM tip apex and the surface causes torsional bending of the cantilever, which is measured with the angle changes of the optical beam reflected on the cantilever. The AFM measures the deflection or lateral force in voltage and other constants of the tip or the scanner need to be determined in order to quantify the measured forces. The calibration usually involves the determination of the spring constants of the cantilever and deflection sensitivity of the scanner, which we will discuss later in Section 3.6.

As tip scans across the sample surface, the lateral force between the tip can be measured with resolution as high as a few pico newtons due to the high resolution of the force sensor. Lateral force measured during the forward and backward scan across the same line, known as friction loop, usually exhibit hysteresis with respect to each other due to the opposite direction of the friction force during scanning. The average lateral force, referred as friction force, could be calculated as half the difference between the forward and backward sliding forces. The FFM technique usually records the 2D lateral force map in both forward and backward scanning direction simultaneously with the topography image at a normal deflection. Then the friction force could be calculated for each line in the 2D force map, which gives friction force as well as topography information at each raster point of the image.

The 2D lateral force map only gives the friction force at one normal load. It would be more interesting to know how the friction responses with respect to the changes in normal load. With the FFM technique, ramped deflection signals (i.e. ramped normal load) were applied on the cantilever and a series of friction force vs. normal load could be recorded. The friction vs. normal load plot then could be fitted with a contact model such as the DMT-JKR transition model that we will discuss in Section 3.7 and thus tip-sample interaction information such as interfacial shear strength could be extracted from fitting this model.

The adhesion can be determined from the force required that the AFM tip to pull off from the sample surface. It is calculated from measuring a force vs. distance curve as shown in Figure 3.4 when the tip is approached and retracted from the sample surface. The cantilever exhibits deflection when the tip touches the surface at point A and then the piezo extends until the deflection reaches the preset setpoint value. The piezo then retracts from point B and thus the deflection reaches point C, where
Chapter 3. Background and Experimental Setup

the elastic force of the cantilever equals to the adhesion force between the tip and sample. Point D corresponds to the point where the tip pulls off from the sample. The pull off force can then be obtained by simply multiplying the maximum deflection (C - D) from the force distance curve and the normal spring constant of the cantilever which we have calculated using the Sader method that will be discussed in the next section.

3.6 AFM force calibration

The quantitative measurement of the mechanical and tribological properties with AFM requires force calibration to convert measured voltage signals. Force calibration is critical in FFM, which requires information of both the tip and the photodetector. And this has not been done for some previous studies on GO where only qualitative results were given. As the AFM tip scans laterally across the surface, the normal and lateral forces acting on the tip are given by [83]:

\[
F_N = k_N S_N V_{A-B} \quad (3.1) \\
F_L = \frac{1}{h^2} k_T S_L V_{C-D} \quad (3.2)
\]

Where \( h \) is the tip height, \( k_N \) and \( k_T \) are normal and torsional spring constant, \( S_N \) and \( S_L \) are the normal and lateral deflection sensitivity of the photodetector, \( V_{A-B} \) and \( V_{C-D} \) are the normal and lateral deflection signals (in Volts) measured by the four quadrant photodetector respectively.

From the equations above, it can be seen that the lateral force is proportional to lateral deflection signal. The lateral deflection signal for each raster point is recorded when a tip scan across a surface area and this gives a friction signal (lateral signal) map. However, a friction force map only yields information at one normal load. The normal force could be varied for an entire friction map to measure the load dependence of friction acting on a tip.

To quantify friction force, the lateral spring constant of the cantilever and the deflection sensitivity of photodetector should firstly be measured. In the past years, many methods have been developed for the calibration of spring constants of an AFM cantilever. The Cleveland method, thermal method, and Sader method are common methods used to calculate the spring constant of the cantilever [107, 108, 109].
Among these methods, the Sader method is considered to be easier and more robust as compared to the two other methods. The Sader method measures the damping of the beam in a viscous medium and it determines the spring constants from values of the resonant frequency (ω) and quality factor (Q), together with the cantilever dimensions. Normal and torsional spring constants are then calculated from the following equations [109]:

\[
k_N = 0.1906 \rho b^2 l Q_N \omega_N^2 \Gamma_i(\omega_N)
\]

\[
k_T = 0.1592 \rho b^4 l Q_T \omega_T^2 \Gamma_i(\omega_T)
\]

Where \( \rho \) is the density of the viscous medium (in our case air), \( b \) and \( l \) are the width and length of the cantilever and \( \Gamma_i \) is the imaginary part of the hydrodynamic function for a rectangular beam.

Both the normal and torsional spring constants require the value of the resonant frequency and quality factor, which are measured from collecting the thermal noise spectra of the cantilever in air. The normal deflection sensitivity of the photodetector is determined from the slope of the bending of a cantilever vs. distance curve. The output of the normal deflection signal is plotted as a function of the Z-displacement when an approach and retract linear ramp is applied to the Z piezo input. The lateral deflection sensitivity of the photodetector, similarly, is determined from lateral deflection signal as a function of lateral displacement. Measurement of lateral deflection sensitivity is typically more difficult than the normal deflection sensitivity because of higher lateral stiffness of the cantilever and possible in-plane bending in addition to the torsional response. Several methods have been developed to measure the lateral deflection sensitivity. In this work we choose to use the test probe method because it has been demonstrated to be both accurate and easy for implementation [110].

![Figure 3.5: (a): SEM image of a glass sphere glued on an integrated cantilever; (b): SEM image of the glass sphere (view from direction as white arrow shows in (a)).](image)

As shown in Figure 3.5, a colloidal glass sphere with a diameter of approximately 70 μm was attached to a silicon cantilever (the same type of cantilever used for FFM measurement) by epoxy with a micromanipulator under optical microscope. The lateral deflection signal versus distance was obtained via pushing the colloidal sphere against a freshly cleaved side wall (100 orientation) of a KBr crystal with an AFM under ambient conditions. The slope of the contact region in the resulting force plot gives the lateral deflection sensitivity \( S_{L,test} \). The lateral deflection sensitivity of the photo detector with
the sharp integrated tips used for FFM measurements \( (S_L) \) was then calculated from \( S_{L,\text{test}} \) considering the differences of the torsional arm length and lateral in-plane bending parameters between the colloid probe and sharp integrated tip. Details of the colloidal probe preparation and this lateral deflection sensitivity conversion can be found in Appendices Section 7.1. The resulted \( S_L \) was then used for the calculation of lateral force from the torsional signals. With the measured spring constants and deflection sensitivities, the friction forces and normal forces could then be quantified from measured voltage signals using Equation 3.3 and 3.4.

### 3.7 Contact models

Researchers have used theories of continuum mechanics to investigate the parameters of interest at nanoscale contact. Atomistic simulations are used to test continuum contact mechanics at nano scale since continuum contact mechanics might break down \[111\]. Contact mechanics is based on continuum mechanics and it investigated the deformation of solids that touch each other at one or more points \[112\]. Contact behavior of two spheres was solved by Heinrich Hertz in 1880 with the famous Hertz model, which eliminate any surface interactive forces such as van der Waals and adhesive interactions between the two surfaces. These surface interactive forces could be neglected at some macro scale studies, but they could not be eliminated at the micro or nano scale since their values are comparable to body or external forces. In 1970s, Johnson, Kendall, and Roberts presented an improved model, known as the JKR model, which considers adhesion only inside the area of contact. As an alternative model for the JKR model, the Derjaguin-Muller-Toporov (DMT) model assumes that the contact profile remains the same as in Hertzian contact but with additional adhesive interactions outside the area of contact \[113\]. This contradiction between the JKR and DMT theory was resolved later with the Maugis-Dugdale model (referred as “DMT-JKR transition” model in this thesis) \[114\] since they could be considered as two extreme limits of a single theory with a new parameter. The Maugis-Dugdale model provides an analytical solution for the contact radius, but the calculation is complicated and Carpick et al. \[115\] simplify the process by approximating the analytical solution with a Carpick-Ogletree-Salmeron method.

The differences between the Hertz, JKR, DMT, and DMT-JKR transition model are compared in Figure 3.6 as shown below. The “DMT-JKR transition model” has been a well recognized model for the contact mechanics study at the nano scale and it has been adopted by a lot of literature studies \[18, 116, 117\]. In this thesis, the “DMT-JKR transition” model is used to model the contact behaviors for friction studies. This method simply calculates a “transition parameter” \( \alpha \) from Equation 3.1 with an easy curve fitting routine and then researchers could easily compare the model with experimental data from AFM measurements.

\[
a = a_{0(\alpha)} \left( \frac{\alpha + \sqrt{1 - L/L_{c(\alpha)}}}{1 + \alpha} \right)^{2/3} \tag{3.5}
\]

Where \( a \) is contact radius and \( L \) is applied normal load, \( a_{0(\alpha)} \) is contact radius when normal load is zero, \( \alpha \) is transition factor with range from 0 to 1 (where \( \alpha = 1 \) corresponds exactly to the JKR case, and \( \alpha = 0 \) corresponds exactly to the DMT case), and \( L_{c(\alpha)} \) is the pull-off force. \( \alpha \), \( a_{0(\alpha)} \) and \( L_{c(\alpha)} \) are considered to be free parameters during in the fitting procedure.

Friction is assumed to be proportional directly to the contact area for single asperity contact \( \left( F_f = \tau \pi a^2 \right) \), where \( \tau \) is the interfacial shear strength of the contact \[118, 119\]. Then the relationship between
friction force and normal force is given by the following Equation 3.2:

\[ F = F_0(\alpha) \left( \frac{\alpha + \sqrt{1 - L/L_{c(\alpha)}}}{1 + \alpha} \right)^{4/3} \]  

(3.6)

Where \( F \) is measured friction and \( L \) is applied normal load, \( F_0 \) is friction force when normal load is zero, \( \alpha \) is transition factor with range from 0 to 1 as described above, and \( L_{c(\alpha)} \) is the pull-off force.

Using this equation, the experiment data of friction force and normal force can be fitted to obtain the fitting parameters. The calculation then gives the adhesion energy and interfacial shear strength, which is beneficial for the understanding of friction and wear mechanisms in subsequent data analysis in Chapter 4. Detailed Matlab code of the fitting procedure could be found in Appendices Section 7.2.

### 3.8 Humidity sensing cell

To control the environment during scanning, an environment control cell was used as an extension of the AFM to control the relative humidity during AFM scanning (details will be discussed in Section 5.3). Relative humidity has been reported to have a great effect on the tribological properties of the sample surface [82]. To study the effect of relative humidity of the tribological properties, a humidity sensing cell was introduced to interface with the AFM system. Figure 3.7 shows the schematic of a humidity sensing cell, which controls and measures humidity conditions with external gas flow system and a sensor located within a sealed sample cell respectively. The humidity level in the humidity cell can be changed by increasing and decreasing the flow rates of the gas flow system.
3.9 Chemical characterization and thermal reduction

Chemical analysis of the sample surface is essential for the understanding of tribological behaviors of materials. Methods of characterization used in this thesis includes Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) [120]. Raman spectroscopy has been widely used in material science for materials identification due to the fact that it could easily provide “finger print” information. Raman measures the molecular vibration in a sample system in ambient by detecting the scattered light (photons) after a laser source was projected onto the sample. The energy of laser photons would be shifted after interacting with excitations such as molecular vibrations in the system, which gives information about the vibrational modes in the system [121].

Raman spectroscopy has been a simple and easy method for characterization since it requires little sample preparation and measurement is very fast. So it is usually used for materials identification before measuring properties. But it is inherently not sensitive (need \(\sim\) 1 million incident photons to generate 1 Raman scattered photon) and fluorescence may interfere with the Raman data, which makes Raman generally difficult to provide quantitative results. Thus although Raman could detect the surface changes in the sample surface, no quantitative information of materials composition could be extracted from the spectra. To determine the quantitative elemental composition of sample surface, elemental analyzer or X-ray photoelectron spectroscopy (XPS) is typically used. Here we will focus on XPS since it not only gives the elemental composition parts per thousand range, but also give the percentages of difference chemical functional groups in the materials system. And as XPS was chosen for the chemical analysis of graphene oxide in this thesis. In addition, compared to Raman spectroscopy, XPS analysis is a non-destructive method since Raman spectroscopy could destruct the sample surface through excess local heating due to strong laser energy applied on the surface.

XPS spectra are obtained by irradiating a sample surface with an X-ray beam while measuring the kinetic energy and number of electrons that emitted from the top 10 nm of the surface being analyzed. Given the energy of the X-ray and the kinetic energy of the emitted photons, the binding energy of each element was then determined using the theorem of energy conservation. Then XPS spectra was
produced by plotting the number of electrons detected versus the binding energy. Since electron counting detectors in XPS instruments are typically a meter long away from sample surface, which would need low pressure (usually high vacuum or ultra-high vacuum (UHV)) in the system to eliminate any errors caused in the long detection path.

Another advantage of XPS is that it not only could probe surface chemistry of materials as received, but also for materials after certain treatment such as exposure to heating or ultraviolet light. XPS usually has heating component within its vacuum chamber and thus analysis of the surface chemistry could be conducted with an *in situ* approach, which accurately determines the effect of heating on sample composition. This capability of XPS is highly beneficial for analysis of thermal treatment on materials in UHV and it gives excellent condition needed for graphene oxide thermal reduction as we discussed in Chapter 2.

Thermo Scientific Theta Probe (as shown in Figure 3.8(a)) is an XPS instrument which can do XPS at certain temperature in either UHV environment and it was used for both thermal annealing and XPS characterization of graphene oxide. Figure 3.8(b) shows the experiment stage set up of thermal annealing of graphene oxide within the XPS chamber. It has an ion beam heater for sample heating, thermo coupler for temperature measurement, and clamp for sample fixture. The thermo coupler was placed between the sample surface and the clamp since it could best measure the temperature on the sample surface in this way. The ion beam heat the sample from the bottom of the substrate and then the temperature was measured with the thermo coupler. Details of the thermal annealing experiment and corresponding FFM measurement are presented in Chapter 5.
Chapter 4

Friction and Wear of Ultrathin Graphene and Graphene Oxide Films

This Chapter has been peer reviewed by the journal ACS Applied Materials & Interfaces and it is currently in the final stages of revision for publication. The applicant was the first author on the paper and played the primary role in experiment design, execution, data analysis and paper writing. Changhong Cao is gratefully recognized for assistance in conducting Raman spectroscopy. The efforts of corresponding author Tobin Filleter are gratefully acknowledged for useful suggestions and reviews.

4.1 Introduction

As discussed in Chapter 2, surface forces dominate over body forces as the size of devices shrink to micro and nano scales. This is particularly critical in Micro/Nano-electro-mechanical systems (MEMS/NEMS) devices. Consequently devices will have an increased likelihood of failure due to tribological issue such as adhesion, friction, and wear when two components in the MEMS/NEMS make intentional and unintentional contact. Channel gaps between MEMS/NEMS surface to contact range from 1 μm to 100 nm, thus traditional lubrication and wear mitigation methods are ineffective due to their small size [122]. In particular, liquid based lubrication approaches fail due to high viscosity under such confined geometries. Correspondingly, novel nano-engineering approaches have begun to be explored to address tribology reduction of MEMS/NEMS surfaces [15].

Graphene, a 2D sheet of carbon atoms, has attracted a great deal of interest by scientists most recently for its exceptional properties including: high electric conductivity and beneficial mechanical properties such as ultrahigh strength [17, 123, 124]. Additionally, recent research indicates that graphene also exhibits ultralow friction properties. Filleter et al. demonstrated that a single layer of graphene can reduce friction on a silicon carbide surface by approximately 10 times [39]. Lee et al. also observed that friction of graphene reduces as its layers increase to a saturation level similar to that of bulk graphite at a layer thickness of 4 atomic layers [58]. Besides ultralow friction properties, graphene also exhibits very beneficial adhesion properties. Bunch et al. showed that the adhesion energy of monolayer and
multilayer graphene in contact with a silicon dioxide substrate is larger than the adhesion energies of typical micromechanical structures, which makes graphene easily adhered to MEMS/NEMS substrates [125].

Graphene films, however, have a very high cost which may limit its application to lubricate real systems [21]. As a lubricant, GO has some advantages over graphene including a lower cost of mass production, and the potential to allow for tunable friction properties through controlled surface functionalization [126]. In addition, GO can be chemically and thermally reduced to allow for tunable electronic and mechanical properties [22, 127]. This has motivated initial studies of using GO as a lubricant layer. Ou et al. covalently deposited GO onto a silicon substrate and investigated the friction properties of GO using AFM and showed the relative friction coefficient was reduced by 20% and 70% respectively after coating silicon with GO and reduced GO [26]. Friction of reduced GO was further investigated by thermal reduction from about 100 °C to 700 °C and they show that the friction difference of GO exhibits almost a linear trend with increasing temperature [22]. These initial studies have demonstrated a friction signal difference, however, a quantitative study of friction force, adhesion force and wear of GO at the nanoscale has not yet been comprehensively investigated. In particular, previous studies have only focused on thick GO films, and have not measured local friction differences between few layer GO using the same scanning friction force microscopy (FFM) tip. This is critical for accurate interpretation of friction reductions due to the ultrathin layers that are proposed as coatings for MEMS devices. Also the difference of the friction and adhesion properties between GO and modified silicon surfaces have not been investigated. In many MEMS applications, surface treatments are used in the fabrication process which can influence their tribological properties. For example, the surface of silicon can be modified from hydrophobic to hydrophilic during the MEMS fabrication process by wet etching with potassium hydroxide solution [128].

Here we have investigated the friction, adhesion and wear properties of silicon/silicon dioxide, graphene, and GO at a nanoscale using FFM. We have also explored silicon dioxide surfaces that have been treated with potassium hydroxide to get a better understanding of their tribological properties. This basic research will lead to a comprehensive understanding of the friction, adhesion, and wear of graphene based ultrathin films and could be potentially applied for MEMS/NEMS lubrication and a better understanding of graphene based devices.

4.2 Experimental section

4.2.1 Materials and sample preparation

Graphene and graphene oxide (GO) films were prepared on silicon substrates for FFM tribology experiments. The silicon wafers (N-doped, 100 orientation, 285 nm SiO₂ thickness) were first cleaned for 10 min in acetone followed by a 10 min cleaning in methanol using an ultrasonic bath. The silicon wafer was then blown dry with nitrogen gas. Graphene was deposited onto silicon substrates by mechanically exfoliating highly oriented pyrolytic graphite (HOPG) (SPI Supplies) onto the substrate via the scotch tape method [129].

An ultrathin GO aqueous solution was obtained by dissolving 1.0 mg of single layer graphene oxide flake (ACS Materials LLC) prepared by the modified Hummers method [23, 130] into 20 mL of deionized water (DI) (resistivity>18 MΩ cm, MP Biomedicals, LLC) by sonication for 1 h in an ultrasonic bath.
Chapter 4. Friction and Wear of Ultrathin Graphene and Graphene Oxide Films

(Branson, model 1800, Danbury, CT). The as-prepared light brown solution was then diluted to 0.01 mg/ml. The obtained solution was then centrifuged at 4000rpm for 30min to remove unexfoliated graphite oxide using an Eppendorf MiniSpin centrifuge to produce the supernatant. Thick GO aqueous solutions were prepared by dissolving 1.0 mg of GO flake into 20 mL of DI water by slow stirring for one day with a magnetic stirrer. The solution was then sedimented and the supernatant was used for thick GO sample preparation on the silicon substrate.

Poor deposition coverage of GO on the silicon substrate was observed in the absence of a surface treatment. Consequently, the silicon wafer was treated with aqueous potassium hydroxide solution (weight concentration: 50%) for 15 min to make the silicon more hydrophilic. Then the silicon wafer was cleaned with the same method of substrate cleaning describe previously for the graphene sample preparation. To prepare sample for FFM measurements the GO solution (8 μL) was drop casted onto the silicon wafer with a micropipette and afterwards the solution was dried in air.

4.2.2 Film structure characterization and friction force microscopy

Thin films of graphene deposited on Si substrates with a SiO$_2$ surface oxide layer were identified via an optical microscope (Zeiss, Germany) [131]. Raman spectroscopy (Renishaw, 532 nm laser excitation) was performed to characterize the microstructure of the graphene and GO samples, and the surface morphologies of graphene and GO samples were observed by an atomic force microscope (Asylum MFP3D) in tapping mode.

The nanotribological properties of graphene and GO samples were measured using an AFM (Asylum MFP3D) in friction force microscopy (FFM) mode using rectangular cantilevers (Nanoworld FMR10, Normal spring constant: \( \sim 1.3 \) nN/nm) in ambient conditions of 25 °C and 45% relative humidity. For each FFM measurement first the adhesion force between AFM tip and film was measured by taking a force distance curve and measuring the adhesion force as the maximum force required to pull the AFM tip out of contact with the surface. The error of the adhesion force was calculated as the standard deviation of several (minimum of 10 measurements) pull-off force measurements recorded on different regions of the surface in the near vicinity of the area used for friction measurements. Adhesion forces measured for different samples were measured under the same ambient condition to minimize any influence on changes in the meniscus [132]. FFM was used to measure lateral force signals simultaneously over surface regions containing two surfaces within the same scan line (either SiO$_2$ and Graphene, or SiO$_2$ and GO) to make a direct comparison of lateral force differences of two surfaces. As the AFM tip was scanned laterally across a surface, lateral force signals in both forward scan and backward scan directions were recorded while sliding. The friction force was then calculated as half the difference between the forward and backward sliding force. Details of adhesion and friction force calibration could be found in Section 3.5 and 3.6 respectively.

4.3 Result and discussion

Thin films of graphene deposited on Si substrates with a SiO$_2$ surface oxide layer were identified via an optical microscope [131] (see Figure 4.1(a)) and the thickness of graphene was characterized using AFM in tapping mode (see Figure 4.1(c) and line profile in Figure 4.1(e)). From the AFM topography image, we observed multilayer graphene with a thickness of approximately 2.9 nm. A similar approach was used to observe, and measure the thickness of GO films (see Figure 4.1(d) and line profile in Figure
4.1(f)) which were dropped cast onto SiO$_2$/Si (see Figure 4.1(b) which shows a GO aqua-solution in centrifuge tube after centrifuge). The presence of graphene and GO were then verified using Raman spectroscopy [133, 134] as shown in Figure 4.2. The Raman spectrum of graphene indicates the G peak located at 1582 cm$^{-1}$ and 2D peak at 2675 cm$^{-1}$, which are signatures of the in-plane vibration and second-order zone boundary phonons respectively. The absence of D peak in the Raman spectrum of graphene indicates that the exfoliated graphene in this study has a low defect density. The Raman spectra of the GO shows a prominent peak at 1347 cm$^{-1}$ with intensity comparable to the G peak at 1599 cm$^{-1}$, which is characteristic of GO, and is indicative of significant structural disorder due to the defects in the GO plane. The thickness of single layer GO was found to vary from 0.6 to 1.2 nm, which is in agreement with literature values, and can be understood by its hygroscopic nature [71]. Thicker GO films were also observed. For example, the GO flake in Figure 4.1(d) has thickness of ~3.30 nm and thus it has a thickness of three to four layers.

![Figure 4.1: (a): Optical image of exfoliated graphene on a SiO$_2$/Si substrate (white arrow identifies the graphene films); (b): GO aqua-solution in centrifuge tube after centrifuge (precipitates are below the red dashed line and black arrow identifies the precipitates); (c): AFM tapping mode image of multilayer graphene film on a SiO$_2$/Si substrate and corresponding line profile (e) along the black dashed line showing a multilayer graphene flake on SiO$_2$/Si substrate; (d): AFM tapping mode image of GO film on SiO$_2$/Si substrate and corresponding line profile (f) showing a multilayer graphene oxide flake on SiO$_2$/Si substrate.](image-url)
Figure 4.2: (a): Raman spectrum of exfoliated graphene on a SiO$_2$/Si substrate: G peak at 1582 cm$^{-1}$ and 2D peak at 2675 cm$^{-1}$; (b): Raman spectrum of GO films on a SiO$_2$/Si substrate: D peak at 1347 cm$^{-1}$ and G peak at 1599 cm$^{-1}$ (The Raman spectra of graphene and GO were both taken at a laser wavelength of 532 nm).

Figure 4.3: (a): AFM height topography (contact mode) image and corresponding line profile (c) along the white dashed line showing a 4 layer graphene film on a SiO$_2$/Si substrate; (b): Lateral force map of forward scan and corresponding lateral force line profile (d) of both forward and backward scan along the same line.

#### 4.3.1 Friction of graphene on SiO$_2$/Si

Figure 4.3 shows the height topography and lateral force map of graphene on a SiO$_2$/Si surface, and Figure 4.4 shows friction vs. normal force curves of graphene on a SiO$_2$/Si surface. Friction on the multilayer graphene (4 layers) is found to be much lower than that of silicon dioxide, as shown in Figure 4.4, where friction of graphene is $\sim$6 times lower than SiO$_2$ under a normal load condition of $\sim$200 nN. Root mean square (RMS) roughness of 1.5 nm graphene and silicon dioxide is 0.39 ± 0.07 nm and
0.22 ± 0.03 nm respectively. It can be seen that graphene has larger RMS roughness than SiO₂, which suggests that the lower friction of graphene as compared to SiO₂ is not due to its roughness. Despite the large friction difference, the force of adhesion (pull-off force between tip and sample) of graphene and untreated SiO₂/Si was found to be 25 ± 1 nN and 27.1 ± 0.9 nN respectively, suggesting that the friction difference is an intrinsic difference in the energy difference due to sliding. This is in agreement with the observation of a change in the slope of the friction vs. normal force curves in Figure 4.4.

![Figure 4.4: Friction force vs. normal force of silicon dioxide and graphene (4 layers) on a SiO₂/Si substrate. The solid black and red lines are fits using the DMT-JKR transition model.](image)

In order to estimate the interfacial shear strength between the two contacts under study, we have fit the friction vs. normal load curves using the generalized Maugis-Dugdale model [115], which allows determination of the interfaces contact behavior which is intermediate between the DerjaguinMueller-Toporov (DMT) assumption of a hard contact to the JohnsonKendallRoberts (JKR) assumption of a soft contact. The generalized Maugis-Dugdale model has been referred to as DMT-JKR transition model in this study. The friction force vs. normal force was fit with the DMT-JKR transition model with a curve fitting optimization routine and the fitting gives the interfacial shear strength. The Young’s modulus and Poisson’s ratio of 70 GPa and 0.17 [135] were used in the model for silicon dioxide (both silicon dioxide substrate and silicon dioxide tip) and graphene sample. The tip radius was assumed to be 15 nm in this model, it should be noted that while this is an estimate of the tip radius the same tip was used for simultaneous measurements on the graphene and silicon dioxide surfaces. From the fits we found that the interfacial shear strength between the silicon tip and graphene was 173 ± 13 MPa, and it was 1800 ± 44 MPa between the silicon tip and silicon dioxide. This measured interfacial shear strength between the tip and the silicon dioxide surface is on the same order of magnitude as compared to that reported in previous literature with a similar contact system [18]. This again confirms that the difference in friction behaviour is due to different interfacial shear strength but not any significant difference in adhesion. The observed friction difference between graphene and silicon dioxide is also in agreement with previous reported result in the literature [18] where friction forces were found to decrease by 90% on the supported monolayer graphene relative to SiO₂.
4.3.2 Friction of GO

Friction of GO on untreated SiO$_2$/Si

Figure 4.5: (a): AFM Height topography image (contact mode) of GO on untreated silicon dioxide substrate under normal force of -32.8 nN; (b): lateral force map of forward scan; (c): AFM Height topography image (contact mode) of GO on untreated silicon wafer under normal force of -3.8 nN; (d): line profile along the black dashed line in (a); (e) Lateral force of forward scan and backward scan along the black dashed line in (b); (f): line profile along the black dashed line in (c). White dashed circle indicates wear of GO flake in comparison with (a) and (c).

Figure 4.5 shows the height topography of multilayer GO films (~3 nm and ~5 nm) on an untreated silicon dioxide surface. Similar to Figure 4.3 of graphene on SiO$_2$ surface, the topography and friction of GO on untreated silicon dioxide surface were measured simultaneously with FFM. For simplicity, we just show the lateral force map of the surface before wear as shown in Figure 4.5(b). It can be seen from comparing the forward and backward lateral force traces in Figure 4.5(c) that friction measured on the ~3 nm (3-5 layers) and ~5 nm (4-8 layers) thick GO is quite similar, whereas a change in friction is only observed when the tip scans over the substrate surface. This is consistent with previous measurements on other ultrathin films, such as graphene, which demonstrated that friction reaches a value comparable with bulk graphite at an approximate layer thickness of 4 layers [58]. In contrast, friction of the untreated SiO$_2$/Si was found to be 1.8 times higher than on the multilayer GO films. The force of adhesion (pull-off force) for the untreated SiO$_2$ and multilayer GO (~5 nm) was found to be 27 ± 2 nN and 21.2 ± 0.8 nN respectively. This difference in adhesion between the film and substrate is similar to the result reported earlier for SiO$_2$ and graphene (27.1 ± 0.9 nN and 25 ± 1 nN respectively) and indicates that while GO does exhibit a slightly lower adhesion, the GO layers do not have a significantly lower adhesion than graphene films despite a significant difference in the two atomic structures. It is also interesting to note that GO does exhibit a slightly lower adhesion than the silicon dioxide surface.

A major difference was, however, observed in the wear of the GO films on the SiO$_2$/Si surfaces as compared to graphene. While graphene was found to adhere well to the surfaces and exhibit good wear
resistance, GO was found to adhere poorly, and exhibit low wear resistance as compared to graphene films. A comparison of Figure 4.5(a) & (c) shows that a GO film that was found to wear at very low normal loads (a few nN). The white circle in the figure shows a region of the GO film that was completely worn away from the substrate surface after scanning. The local region of the initially continuous GO film layer was found to both become separated from the adjacent region of the GO flake and removed from the surface. This behaviour was found to be consistent for many thin GO films deposited on the untreated SiO$_2$/Si substrates.

**Friction of GO on KOH treated SiO$_2$/Si**

![Image](image_url)

Figure 4.6: (a): AFM height topography image (contact mode) under normal force of -13.8 nN; (b): Line profile along the black dashed line in the topography (a) showing a $\sim$1.2 nm GO film a SiO$_2$/Si substrate; (c): Lateral force of both forward and backward scan along the same black dashed line in (a); (d): Zoom out image (tapping mode) of the FFM scan area (black dashed rectangle area corresponds to the area of image (a) scanned in FFM mode) and the red dashed rectangle indicates the worn area of GO during FFM scanning; (e): Friction force vs. normal force of SiO$_2$ surface area, worn GO surface area and unworn GO surface area.

Figure 4.6(a) shows the height topography of a 1-2 layer GO film ($\sim$1.2 nm) on a silicon dioxide surface treated with KOH. After this surface treatment the GO films were found to be more uniformly coated on the surface. This improved coating is in part a result of the reduction of the contact angle of the solution deposited on the treated silicon wafer [136]. In order to first understand the role of KOH treatment on the silicon wafer, we have compared the friction of untreated SiO$_2$/Si and KOH treated
SiO\textsubscript{2}/Si using the same tip. RMS roughness of silicon of these three scan are 0.12 ± 0.02 nm, 0.14 ± 0.03 nm and 0.12 ± 0.03 nm respectively. From Figure 4.7, it can be seen that friction of untreated Si before and after scanning KOH treated SiO\textsubscript{2}/Si remains almost the same at small normal force. The higher friction of the KOH treated SiO\textsubscript{2}/Si may be attributed to its slightly larger RMS roughness, however, this cannot be confirmed given that the measured difference falls within the experimental error. Therefore the KOH treatment has the beneficial effect of improving the uniformity of coating the GO films, however there is a resulting increase in the intrinsic friction of sliding on the SiO\textsubscript{2}/Si surface which becomes more apparent at higher normal loads.

Figure 4.6(c) shows the lateral force of the forward and backward scan along the black dashed line in Figure 4.6(a) at a normal load of -13.8 nN. From Figure 4.6(c) it can be seen that friction on the KOH treated SiO\textsubscript{2}/Si surface is approximately 2.3 times larger than on the 1-2 layer GO film at a normal force of -13.8 nN. This demonstrates that, as is also true for graphene films, just one or two atomic layers of GO is effective at reducing friction on the surface.

If we compare the results found on GO to graphene, we find that friction of 1-2 layer GO is approximately 3 times higher. Considering that the relative adhesion for GO and graphene and the substrate is similar, this suggests a higher interfacial shear strength between GO and silicon dioxide than that between graphene and silicon dioxide. This is likely due to the presence of the dangling functional groups and higher defect density in the 2D GO plane as revealed by high resolution TEM studies [73]. This is consistent with molecular dynamics simulation which predicted that functional groups such as epoxide and hydroxyl groups on the GO plane increase the shear strength as compared to pristine graphene [137].

Figure 4.6(d) shows the zoom out AFM topography image of the FFM scan area, which indicates that some of the GO area has been worn out (e.g. the red dashed rectangle area in Figure 4.6(d)) while some other areas are still effectively lubricating the SiO\textsubscript{2} surface. In addition, worn GO particles were found to be piled up in the edge of the scan area after the FFM scan as shown in Figure 4.6(d). In order to correlate this wear behavior with friction force, friction vs. normal load curves for FFM scans...
on GO (both on the worn area and unworn area) and the KOH treated SiO$_2$/Si surface were plotted in Figure 4.6(e) to give a direct comparison between the three surface areas. From Figure 4.6(e), there is an indication that the GO films started to wear when normal force is higher than $\sim 0$ nN. The onset of wear can be identified by the discontinuous jump in the friction vs. normal load curve [138]. From the different friction and wear behaviour on these areas it is clear that some area of the GO flake are able to resist wear at relatively higher normal load. This behaviour can be attributed to the heterogeneous nature of the GO surface [73] which will be discussed in detail later in the context of the proposed wear mechanism for thin GO films.

Figure 4.8: (a): AFM contact mode topography image (normal force of -3.6 nN) and line profile along the black dashed line in the topography showing multilayer GO a SiO$_2$/Si substrate as shown in (c); (b): Lateral forward scan signal force map and line profile of lateral force signal along the same line as shown in (d); (e): AFM contact mode topography (normal force of $\sim 21.4$ nN) of partially worn multilayer GO and corresponding line profile.

Figure 4.9: AFM contact mode topography images of GO on a SiO$_2$ surface at normal force of -3.6 nN (a), 10.8 nN (b) and 21.6 nN (c) respectively.

A similar transition in the friction vs normal load curves that identifies the onset of wear was also observed for multilayer GO films. Figure 4.8(a) and Figure 4.8(b) shows the height topography and lateral force map of a multilayer GO film ($\sim$3 nm) on a silicon dioxide surface. From Figure 4.8, it could
be seen that the friction of KOH treated SiO$_2$/Si is about 1.9 times higher than that of multilayer GO at the normal force of -3.6 nN. Adhesion between the silicon tip and silicon dioxide, silicon tip and GO here are 4.4 ± 0.3 nN and 4.1 ± 0.2 nN respectively. It should be noted that the RMS roughness of the GO film covered areas was measured using AFM to be the same as the uncoated SiO$_2$ areas within measurement error, which rules out the possibility of differences in RMS roughness as the dominant mechanism for the observed friction difference between GO and SiO$_2$. From Figure 4.8(C) a discontinuity in the friction force was observed when the normal force is higher than ~9 nN. This was confirmed to correlate to the onset of wear by looking at topography images of the GO flake at varying normal loads. From Figure 4.9(a-c), it can be observed that the GO flake becomes smaller and smaller with increasing normal load during the FFM scan. This onset of wear was found to initiate at a normal load of ~10 nN which is consistent with the discontinuity observed in the friction force plot. GO appears to be suddenly displaced in the lateral direction resulting in a jump in friction force and subsequently removed gradually from the substrate, potentially arising from plastic deformation. Repetition of the experiment with another GO flake under the same conditions exhibited worn GO particles accumulated at the edge of the scan area. Such discontinuities in friction, which we have been shown to indicate the first stages of wear, are likely to initiate at lower normal loads that for graphene due to differences in the local shear strength at different locations on the GO surface with different functional groups [137] and at defects in GO plane which act as nucleation sites for wear to initiate. Wang et al. have shown through DFT calculations that epoxide and hydroxyl functional groups that exist in GO lead to a local higher energy corrugation and shear strength for sliding between small flakes of graphene oxide as compared to graphene [137]. Microscopic GO films, such as those that are under investigation here, have a different structure than the small flakes studied in the DFT calculations. Larger experimental GO flakes are instead composed of a mixture of non-homogenous regions of pristine graphene-like and functionalized GO-like patches. This has been nicely demonstrated recently through high resolution TEM imaging of GO surfaces [73]. Therefore we expect that there will be local differences in the shear strength between the sliding tip and the GO surface on these different surface regions. XPS experiments conducted on the GO samples show the presence of ~19 atomic % of epoxide, ~28 atomic % of hydroxyl, and ~8 atomic % of carboxyl groups that make up these functionalized regions of the surface. We believe it is at these local regions on the GO surface with higher shear strength that wear initiates when the normal force reaches a critical level and the in plane stress is such that the fracture strength of the GO films is reached. Wear then progresses in the form of the local fracture and removal of small regions of the GO films. Both the added energy required to wear the GO films, as well as sliding on areas of the exposed substrate surface, leads to the higher friction forces measured during scanning. This can explain the shape of the friction vs normal load curves show in Figure 4.6 (c) in which the friction smoothly increases with normal force until the onset of wear at which point a discontinuity is observe when portions of the GO flake are worn away. At higher loads the friction signal also becomes more noisy as wear is continuously occurring and reducing the size of the GO flake as can be seen in Figure 4.9. In addition the non-homogenous nature of the GO surface can explain why some regions wear at lower normal loads than others, as was observed in Figure 4.6. This is significantly different behavior than that observed for graphene films which exhibited wear free sliding for normal forces of ~200 nN, almost two orders of magnitude higher (see Figure 4.4). This points to a major limitation in using GO as a solid lubricant under larger applied stress, as it contains surface regions that tend to wear much more easily than graphene.

Similar to the transition fit used for friction load curves of graphene data, we selected the friction vs.
normal load curves of GO before wear occurred and fit them into the DMT-JKR transition model. The Young’s modulus and Poisson’s ratio of 70 GPa and 0.17 [135] are used for silicon dioxide (both silicon dioxide substrate and silicon dioxide tip) and GO sample. The tip radius was also assumed to be 15 nm in the transition model. We found that the interfacial shear strength between silicon tip and GO was 1220 ± 180, and it was 1930 ± 282 MPa between the silicon tip and silicon dioxide surface.

Friction of thick GO films

Figure 4.10: (a): AFM topography image (contact mode) of thick GO film on treated SiO$_2$/Si substrate; (b): Height topography profile of line 1; (c): Height topography profile of line 2; (d): Friction force vs. normal force of treated SiO$_2$/Si, GO films (∼40 nm and ∼120 nm) with the same AFM tip.

After a thorough investigation of friction of atomically thin GO sheets, we now extend our research to frictional properties of relatively thicker GO films (>40 nm). Figure 4.10(a) shows the height topography of the thick GO film, from which we could observe that the roughness of thick GO films is quite high. Friction vs. load measurement of silicon and thick GO films (both ∼40 nm and ∼120 nm GO) using the same AFM tip (Figure 4.10(b)). The adhesion force recorded for SiO$_2$/Si, ∼40 nm GO film, and ∼120 nm GO film was 39 ± 3 nN, 28 ± 3 nN and 29 ± 2 nN respectively.

A clear transition in the friction force error could be observed in the GO plot as the normal force reaches higher than ∼60 nN. It should be noted that we observed a transition in friction force error for other thick GO films as well, with the transition normal force varying for each case in the range of 10s of nN. This transition could be attributed to the propagation of the local wear during the FFM scan [139]. This signature of the onset of wear is different from that observed for the thin GO samples as now clear discontinuity in the friction vs normal load curve was observed. While some local wear of individual GO flakes may occur before the transition, a transition to a regime of large-scale wear was found to occur when the normal force exceeded ∼60 nN. For these thicker GO (40 nm and 120 nm) films, when the top films are worn away there are still many layers of GO remaining underneath. In this case the trend of the friction vs load plot is not found to change abruptly, but the additional edges induced from the top layers wearing, as well as the local wear occurrence at different layers likely contribute to higher scatter in the friction measurement and the large error measured in friction. This can be thought of as the thick film friction response being a convolution of many layers of the thin layer friction response.

From Figure 4.10(b), it can be seen that friction of ∼40 nm GO film is almost the same as that of ∼120 nm GO film and friction of both GO films are ∼2 times smaller than that of Si. For example, the
friction force for SiO$_2$/Si, $\sim$40 nm GO and $\sim$120 nm GO at a normal force of 104 nN are 153.7 nN, 84.6 nN and 84.7 nN respectively. From linear fits to both the SiO$_2$/Si and GO plots before the transition to large-scale wear the friction coefficient of GO was found to be $\sim$1.4 times lower than that of SiO$_2$/Si. It should be noted that this is similar to that reported earlier for few layers GO demonstrating that ultrathin layers of GO are as effective at reducing friction as thick layers. measured RMS roughness measurements of thick GO films in Figure 4.10(a) were approximately ten times higher than that for SiO$_2$, which again suggest that the reduced friction on the thick GO and SiO$_2$ is not primarily due to a lower RMS roughness although the roughness would likely have a contribution to the absolute friction measurements.

The friction difference between GO and Si reported here is slightly lower as compared to that previously reported by Ou et al. ($\sim$2-3 times) [26]. This difference may be attributed to the fact that the silicon wafer studied by Ou et al. were treated with pirahna which may increase the roughness of the silicon surface resulting higher friction in the absence of the GO film. In addition, previous studies of thick GO films ($\sim$50-400 nm) by Liang et al. [81] exhibit the same general finding of reduced friction on the GO surfaces as compared to Si as reported here, although it is difficult to quantitatively compare the studies which utilize very different contact sizes and loading conditions. One major difference between the findings reported here are that Liang et al. found that the thick GO films exhibited an increasing trend between film thickness and friction coefficient for their micro-tribometer experiments of thick GO films on Si that was attributed to differences in film roughness [81]. Here we have found instead that thick GO films do not exhibit significantly higher friction differences from SiO$_2$/Si as compared to the few layer GO films.

4.4 Conclusion

The tribological properties of untreated SiO$_2$/Si, KOH treated SiO$_2$/Si, graphene and GO were investigated using FFM. Several different length scales in thickness of the GO films were investigated from single atomic layers up to $\sim$120 nm thick films. Friction of few-layer graphene was found to be approximately 6 times lower than that of untreated SiO$_2$/Si, which could be attributed to lower interfacial shear strength between graphene and silicon dioxide. In contrast friction of 1-2 layer, few-layer (3-4 layers), and thick GO films were found to range between 1.9-2.3 times lower than that of SiO$_2$/Si under similar normal loading conditions with no significant dependence on film thickness, suggesting that ultrathin GO layers are as effective as thick films at reducing friction.

A major difference in the wear behavior was observed between graphene and GO films. Graphene could resist wear with normal loads of up to $\sim$200 nN. In contrast, atomic thin GO sheet tend to wear easily under normal loads of a few nN with the onset of wear that is attributed to higher local shear strengths of the non-homogeneous surface regions on the GO films as compared to graphene. The wear behaviour of GO is also found to be spatially dependant on the non-homogeneous surface regions. These findings indicate the great importance of the local surface structures of GO films on their tribological behaviour, and motivate future studies which focus on how variations in this surface structure may lead to tunable approaches for lubricating and wear resistance coatings. Thick ($\sim$40 nm and $\sim$120 nm) GO films exhibited a transition to large-scale wear at normal load of up to $\sim$60nN revealing a limitation in applying GO under high contact stress conditions. While the lower friction of GO as compared to SiO$_2$/Si makes it a potential economical coating for M/NEMS devices to extend the lifetime of devices.
and reduce energy dissipation, its higher propensity for wear as compared to graphene must be considered when applying it as a solid lubricant.
Chapter 5

Effect of Structure and Environment on Tribology of Graphene Oxide

5.1 Introduction

GO has been an interesting material for researchers recently due to the fact that its properties can be tuned along with its chemical structures, namely by modifying the carbon to oxygen ratio of GO [22]. This tunability is usually achieved by reduction either with a thermal or a chemical method. GO can be reduced to be more graphitic, achieving better electrical and mechanical properties as well as potentially beneficial friction and wear properties. This might also make reduced GO exhibit the anti-wear properties shown in graphene and thus overcome the issue of poor wear resistance as observed in Chapter 4. To this end, friction and wear behavior of thermally reduced GO was also investigated.

In Chapter 4, the friction, adhesion and wear properties of graphene and GO under ambient conditions have been extensively investigated. Environmental factors such as temperature [140] and relative humidity [2, 141] induced stiction has been a big issue for MEMS reliability since they can greatly influence the friction and adhesion properties of MEMS surfaces. The effect of relative humidity on the adhesion properties of GO is particularly interesting in that GO has super sensitivity for water [142], which indicates the strong interaction between GO and water molecules. This interaction is of great interest for its application as a solid lubricant for MEMS because water could potentially increase the adhesion induced failure in MEMS. Therefore, there is a need to understand the effect of relative humidity on the tribological properties of GO.

In this Chapter, we first measured friction and wear behavior of thermally reduced GO using FFM. Then the effect of relative humidity on the adhesion properties of GO was presented.

5.2 Nanoscale friction and wear of reduced graphene oxide films

5.2.1 Introduction

In Chapter 4 GO was found to exhibit lower friction as compared to silicon dioxide surfaces, however it was also found to be easily worn under a few nano newtons normal load. Graphene, however, was found to resist wear under normal loads of up to several hundred nano newtons. As a precursor of graphene,
graphene oxide can be reduced into graphene as discussed in Chapter 3. Namely, GO can be reduced to achieve which has the potential to achieve more beneficial friction and wear properties as were found in graphene. Methods of this reduction process typically include chemical and thermal reduction. As compared to chemical reduction, thermal method proved to be more advantageous for this study in that tunable frictional of GO could be quantitatively controlled by annealing temperature [22].

As we’ve discussed in Section 2.3.3, friction of reduced GO at different annealing temperature were measured with AFM by Riedo et al. and the result showed a monotonically trend of decreasing friction with increasing temperature [22]. Friction properties GO and reduced GO was then qualitatively investigated by Yang et al. and they showed that friction of GO is around 2.5 times lower as compared to silicon and reduced GO exhibits lower friction than GO [26]. These studies indicated reduced GO has lower friction than GO, but the wear behavior of reduced GO at nanoscale has not been addressed. Since GO has been observed to be easily worn while graphene was highly wear resistant in our studies (see Chapter 4), there is a need to know what reduction rate of GO would be appropriate to achieve beneficial wear resistant property.

In this subsection, we first compared the wear of GO with different carbon to oxygen ratios to “mimic” the effect of thermally reduced GO samples. Then reduction process and chemical characterization results of thermally reduced GO were presented in Section 5.2.3.

5.2.2 Experimental section

Materials

Two samples of single layer graphene oxide was obtained from ACS Material LLC and CheapTubes Inc prepared by the modified Hummers method [23, 130]. N-type silicon wafers (100) was purchased from Graphene Supermarket. Si$_3$N$_4$ film (LPCVD, 300 nm) on silicon wafer was purchased from MTI Corp. Potassium hydroxide was obtained from Bioshop and deionized (DI) water (resistivity > 18MΩ cm) was purchased from MP Biomedicals.

Graphene oxide sample preparation

A GO aqueous solution was obtained by dissolving 1.0 mg of GO flake into 20 mL of DI water (MP Biomedicals, LLC) by sonication for 1 h in an ultrasonic bath (Branson, model 1800, Danbury, CT). The as-prepared light brown solution was then diluted to 0.01 mg/ml. The obtained solution was then centrifuged at 4000 rpm for 30 min to remove unexfoliated graphite oxide with an Eppendorf MiniSpin centrifuge to produce supernatant for drop casting.

Thermal reduction of graphene oxide

GO as received from ACS Materials LLC was used for thermal reduction in the XPS chamber. Silicon dioxide wafer has oxygen groups on its surface, which would contribute to oxygen signals collected during XPS measurement. As a consequence, measured C/O ratio for GO could not accurately represent the sample. In view of this problem, both Si$_3$N$_4$ and SiO$_2$ substrate were used in this study. GO on Si$_3$N$_4$ substrate was used for XPS analysis while GO on SiO$_2$ was used for FFM measurements. Firstly, both SiO$_2$ and Si$_3$N$_4$ wafer were cleaned for 10 min in acetone followed by 10 min clean in methanol using an ultrasonic bath. The water were then blown dry with nitrogen gas. Then GO solution (5μL) was drop casted onto the silicon and silicon nitride wafer with a micropipette and afterwards the solution dried in
air. After the two samples have been dried, friction and wear behavior of GO on silicon dioxide substrate were measured using FFM. After FFM measurement, both samples were simultaneously put into the XPS chamber for thermal annealing to make sure GO sample on both substrate undergo same thermal treatment. The base pressure of the UHV chamber was $1 \times 10^{-7}$ Torr. XPS data was measured on the GO on Si$_3$N$_4$ sample before and after thermal annealing. The annealing rate was around 20 °C/min and the chamber was maintained at 100 °C for 15 min. Then the heater shut down and the chamber started to cool down to room temperature, which typically would need several hours due to high vacuum. Samples were left in the vacuum chamber for one night and taken out to do another FFM measurement afterwards. With the same procedures of thermal reduction described above, GO was reduced at 150 °C, 200 °C, 300 °C and 500 °C respectively. And friction and wear of GO reduced at these temperature were measured with FFM.

![Figure 5.1: (a) Tapping mode image of GO on SiO$_2$ substrate; (b), (c) and (d) are topography images under normal load of 0 nN, 60 nN and 270 nN respectively from FFM scan in the white dashed rectangular area in (a).](image)

5.2.3 Results and discussion

Wear of GO with different C/O ratios

As we’ve discussed in Chapter 4, the GO sample from ACS Materials could be easily worn under small normal load. However, from the investigation of friction and wear properties of the CheapTubes GO sample, we found that the sample was highly wear resistant. It should be noted that the carbon to oxygen ratio of the GO sample can be varied during the sample preparation process with modified Hummer’s method.
Figure 5.1 (a) shows a tapping mode image of GO on SiO$_2$ substrate and it can be seen that lateral size of GO flake from CheapTubes is around 10 nm, which is ten times larger than GO sample from ACS Materials. Friction was measured in the white area in Figure 5.1(a) with normal load from 0 to 270 nN. Friction of GO was found to be 1.2 times lower than silicon dioxide surface at a normal load of 0 nN. From the topography image of Figure 5.1(b), (c) and (d), it can be seen that GO flake could resist wear with normal load up to 270 nN. This high wear resistance is quite different from the easy tendency of wear of GO from ACS Materials. So we first conducted XPS analysis on both sample to see the chemical composition differences.

![XPS spectra of ACS GO (a) and CheapTubes GO (b) sample.](image)

Table 5.1: The values of C1s/O1s (atomic ratios) obtained by XPS survey spectra (excerpted from [143])

<table>
<thead>
<tr>
<th></th>
<th>200 °C</th>
<th>500 °C</th>
<th>700 °C</th>
<th>900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited film</td>
<td>2.8 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat treatment in Ar</td>
<td>3.9 ± 0.1</td>
<td>6.8 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UHV heat treatment</td>
<td>8.9 ± 0.2</td>
<td>13.2 ± 0.3</td>
<td>14.1 ± 0.3</td>
<td></td>
</tr>
</tbody>
</table>

As discussed in Chapter 4, GO ultrathin films (ACS Materials) could be easily worn under normal load of a few nano newtons. The different wear behaviors in these two samples could be due to their different chemical compositions. XPS was used to characterize the effect of chemical composition on wear properties of GO samples. XPS survey data indicated that ACS Materials GO has C/O ratio of 2 while CheapTubes GO has a ratio of 3.7. Difference between the two samples were further investigated with high resolution XPS measurement as shown in Figure 5.2, which indicated different concentrations of oxygen functional groups in the two samples.

XPS results of GO from ACS Materials and CheapTubes Inc with different C/O ratios were compared and mapped with literature (see Table 5.1). It can be seen that C/O ratio of ACS Materials GO is a bit smaller than “As deposited film” in the table, which indicated the ACS GO is more oxidized. While C/O ratio of CheapTubes GO is similar to that of GO reduced at 200 °C. This indicated that CheapTubes GO was “slightly reduced” as compared to ACS Materials GO. Since CheapTubes GO was considered as “slightly reduced”, it would became more “graphitic” and thus it exhibited higher wear resistivity. A study is needed to map the C/O ratio in GO with wear resistivity. To this end, we’ve designed
Chapter 5. Effect of Structure and Environment on Tribology of Graphene Oxide

Figure 5.3: XPS survey spectra of GO (a) and reduced GO at 200 °C (b).

Experiment to reduce the ACS GO for enhancing anti-wear property and measure its friction and wear with FFM techniques.

Friction and wear of thermally reduced graphene oxide films

First we compared chemical structure and friction of GO and reduced GO at 200 °C. XPS survey data as shown in Figure 5.3 indicates that C/O ratio of ACS GO sample was 2.2 in room temperature, while it increased to 3.0 when reduced at 200 °C. It can be seen that GO was in situ reduced in the XPS chamber. Friction and wear of GO reduced at 200 °C, 300 °C and 500 °C will be investigated using FFM and compared with GO in the future. These studies would lead to a comprehensive understanding of the friction and wear properties of reduced GO and provide in-depth insight into the design the GO coatings with tunable properties.

5.3 Effect of relative humidity on adhesion properties of graphene oxide films

For this subsection, the applicant took the primary role in experiment design, implementation and data analysis. Richard Tian (NSERC summer student) is gratefully acknowledged for the work of humidity sensing cell set-up.

5.3.1 Introduction

GO is a derivative of graphene and it has been used as a precursor for graphene preparation via GO reduction. The chemical structure of GO can be viewed as a two-dimension network of sp² hybridized carbon atoms decorated with different oxygen functional groups (hydroxyl, epoxy, carboxyl, etc.) on the basal plane and edges [69]. These functional groups render GO hydrophilic and thus it can be readily be
exfoliated into water and form a stable colloid suspension. GO has attracted the attention of researchers most recently because it has novel properties from those oxygen functional groups while preserving some of the unique properties of graphene. Ruoff et al. showed excellent mechanical properties of GO paper and Compton et al. reported that mechanical properties of GO paper could be tuned via intersheet hydrogen bonding, which indicated that water molecules could influence the mechanical properties of GO [144, 145]. What is more interesting for GO is that water shows super permeability into the GO membrane, which indicated GO could be an excellent candidate for filtration and humidity sensing [146].

Interaction between water molecule and GO ultrathin films is interesting because the hydrophilic oxygen functional groups on the GO plane would influence mechanical and electrical properties of GO as reported in literature study [147, 148]. Yao et al. indicated that GO swells upon exposure to increasing humidity and vice versa and GO-silicon bilayer structures exhibit excellent humidity sensitivity and small humidity hysteresis [147]. Borini et al. recently reported an 15 nm GO ultrathin film based humidity sensor has ultrafast sensitivity, and response and recovery time of this film are almost 10 times faster compared to commercial available humidity sensors [142]. This sensing capability of GO is due to the interaction of water molecules with the GO plane which has greatly influence the electrical properties of GO. Interaction between water molecules and GO surface under controlled relative humidity (RH) can also be quantitatively characterized with surface forces such as adhesion and friction forces, which have not been reported in the literature. Also given that GO can act as a good solid lubricant for MEMS devices in ambient conditions, the investigation of its lubricating properties under various environmental conditions need to be addressed for its adaptation to various applications. Among these working environments, RH in particular plays a big role in reliability of MEMS devices [82, 149]. For silicon surfaces, adhesion increases with RH [150]. The effect of RH on adhesion and friction properties of GO, however, has not been addressed in the literature. In this section of the thesis this has been addressed through, quantitative measurements of adhesion and friction of GO ultrathin film are conducted using an AFM.

We measured adhesion of GO ultrathin films as a function of RH with an AFM. This research contributes to a comprehensive understanding of interfacial phenomena of GO under different RH values and is highly beneficial for GO lubricant application as well as GO based sensor design.

### 5.3.2 Experimental section

Single layer graphene oxide was obtained from CheapTubes Inc prepared by the modified Hummers method [23, 130]. N-type silicon wafers (100) was purchased from Graphene supermarket. Potassium hydroxide was obtained from Bioshop and deionized water (resistivity > 18MΩ cm) was purchased from MP Biomedicals.

A GO aqueous solution was prepared by dissolving 2.0 mg of GO flake into 20 mL of DI water by slow stirring for one week with a magnetic stirrer. The upper portion solution was centrifuged at 3000 rpm for 5 minutes and further centrifuged at 5000 rpm for 5 min with an Eppendorf MiniSpin centrifuge. The precipitate was mixed with DI water and diluted at desired concentration. Before drop casting, the silicon wafer was cleaned for 10 min in acetone followed by 10 min clean in methanol using an ultrasonic bath. The waters were then blown dry with nitrogen gas. Then GO solution (5 μL) was dropped casted onto the silicon wafer with a micropipette and afterwards the solution dried in air. The sample was then ready for chemical characterization and AFM measurement.

The MFP-3D AFM typically works in ambient environment, but can achieve various controlled
environmental conditions with different external accessories. These accessories are commercially available and one of which is the humidity sensing cell. The design of the cell is shown in Figure 5.4. This cell can monitor relative humidity in the cell chamber with an integrated humidity sensor, and control RH with an external gas system piping into the cell. The cantilever holder was placed into the cell chamber and thus the working environment of the cantilever could be monitored and well controlled.

An external gas tubing system was designed to control the RH in the cell chamber. The diagram of the whole system can be found in Section 3.7. Figure 5.4 shows the water bubbler system in the diagram, which was the key component since it is used to control RH in the cell. It can be seen from the figure that pure nitrogen gas was piped into the water bubbler and then mixed with water molecules as it moved along the porous PVC tubing. As a result, a water and nitrogen gas mixture was produced in the right outlet of the water bubbler. The moisture degree of the nitrogen gas from the outlet was empirically determined with tuning the rate of inlet nitrogen flow. As shown in the dashed line, the moisture enriched gas was piped into the humidity sensing cell and RH values in the cell could be controlled in the range between 3%-90%.

Adhesion between the AFM tip and sample surface was measured after RH stabilized in the cell for a range of RH. Adhesion was calculated from force distance curves, which were measured in contact mode with the AFM. Details of calculation and measurement principles could be found in Section 3.5. For adhesion of a surface at one RH, at least 10 force distance curves were collected and then averaged. And all the curves were batch processed with same algorithm in Matlab (code can be found in Section 7.2) to ensure consistent analysis.

5.3.3 Result and discussion

GO ultrathin films on a SiO$_2$ substrate are first identified with Raman spectroscopy and then it was imaged with the AFM in tapping mode as shown in Figure 5.5. The Raman spectrum indicated a D peak at 1350 cm$^{-1}$, G peak at 1600 cm$^{-1}$, and 2D peak at 2680 cm$^{-1}$, which identified the sample to be GO. From Figure 5.5 (b) and (c), the line profile indicated a single layer GO as well as folded multilayer GO on silicon dioxide substrate. From Figure 5.5 (c), it can been seen that thickness of both single layer GO and multilayer GO did not increase as RH went higher. This behavior of GO is different
from that reported in literature in which they observed thickness increase with rising RH [147]. This contradiction may be due to the fact that GO here was ultrathin while GO in literature study was tens of nano meters. When water molecules penetrate into the interlayer of GO, thicker GO accumulated higher total interlayer expansion [147, 151]. Figure 5.5 (d) indicated that adhesion of SiO$_2$ increase with elevated RH and it showed a sharp increase with RH increasing from 58% to 72%. This sharp increase in adhesion was attributed to the condense of water molecules in the tip-surface interface, and RH value where sharp increase occurred was similar to that reported in literature [150]. It should be noted that the error bar in the adhesion data is relative large and this is due to the fact that the tip we used for adhesion measurement has very sharp tip (radius $\sim$15nm). This can be one major source of the measurement error due to the unstability of the interaction between the meniscus and the sharp tip. For future studies, we would like to use a colloidal probe (as shown in Figure 3.5) with micro scale tip radius to investigate the adhesion properties of GO under different relative humidity. The large tip radius will eliminate the large instabilities of adhesion measurement as shown in measurement with a sharp tip. Also the contact between the colloidal probe and the sample surface will be well defined in this way, which is very beneficial for quantitative calculation with contact mechanics models.
5.3.4 Conclusions and future steps

In this Chapter, effect of relative humidity (RH) on the adhesion property of GO and SiO$_2$ were investigated with a humidity sensing cell by FFM technique. Adhesion of GO was smaller than SiO$_2$, and both adhesion of SiO$_2$ and GO increased with elevated RH. A sharp increase in the SiO$_2$ adhesion plot was observed as RH increased from 58% to 72%, while adhesion in GO did not show a steep increase. This sharp increase behavior was attributed to the condensed meniscus between the tip and SiO$_2$ surface. As a solid lubricant, GO can reduce adhesion on SiO$_2$ surface in both ambient and high humidity environment, which might be attributed to its lower tendency of meniscus condensation with increasing RH since water can penetrate into GO sheet. This behavior of GO is very beneficial for the application of GO as solid lubricant in MEMS devices subjected to varying humidity environments.

Interfacial phenomena has always been an interesting topic in the area of nano scale research. Adhesion of GO under different RH has been studied, future steps would be two fold. One part would be investigating friction on GO under different RH, which would give a basic understanding of interfacial shear between tip and GO surface. Another aspect would be the study of adhesion properties of GO as well as other interesting materials with our well established colloid probe techniques. This research would provide quantitative perspectives for interfacial properties from contact models since radius of the colloid probe could be more easily measured.
Chapter 6

Conclusions and Outlook

6.1 Conclusions

This thesis discussed the tribological properties of graphene and GO under ambient as well as controlled environmental conditions. The tribological properties of these films were investigated using an atomic force microscope (AFM) since the sharp tip of the AFM can quantitatively probe the tribological properties between the tip and sample surface. Friction and wear of graphene, GO and reduced GO were investigated at the nano scale. Initial studies focused on the friction and wear of graphene and GO under ambient conditions and subsequent studies extended the work to study the effect of changing the structure of reduced GO as well as the environment in the form of varying relative humidity.

The tribological properties of untreated SiO$_2$/Si, KOH treated SiO$_2$/Si, graphene and GO were first investigated. Friction of few-layer graphene was found to be approximately 6 times lower than that of untreated SiO$_2$/Si, which can be attributed to lower interfacial shear strength between graphene and silicon dioxide. In contrast friction of ultrathin GO films (1-4 layers), and thick GO films were found to range between 1.9-2.3 times lower than that of SiO$_2$/Si under similar normal loading conditions with no significant dependence on film thickness, suggesting that ultrathin GO layers are as effective as thick films at reducing friction.

Graphene can resist wear with normal loads of up to $\sim 200$ nN. In contrast, atomically thin GO sheets tended to wear easily under normal loads of a few nNs with the onset of wear that is attributed to higher local shear strengths of the non-homogeneous surface regions on the GO films as compared to graphene. The heterogeneous nature of GO surface also makes the wear behavior spatially dependent on the GO plane. These findings indicate the effect of the local surface structures of GO films on their tribological behavior, and motivate our further studies which focus on how variations in this surface structure may lead to tunable approaches for lubricating and wear resistance coatings. While the lower friction of GO as compared to SiO$_2$/Si makes it a potential economical coating to reduce energy dissipation and extend the life time of M/NEMS devices, its higher propensity for wear as compared to graphene must be considered when applying it as a solid lubricant.

Motivated by the finding that the local structure of GO can influence its friction and wear properties, subsequent studies were pursued to study samples with different GO compositions. The local structure of GO was modified using GO reduction, which makes GO emulate the good mechanical property of graphene. Friction and wear of sample which “mimic” reduced GO was measured in this thesis providing
proof of principle results that support the tunable properties of reduced GO. While the thermal reduction method is expensive and non-scalable, more scalable method such as chemical reduction should be investigated in near future for the practical application of applying GO/reduced GO as lubricants into MEMS. Recently, graphene and GO has been used as building blocks for M/NEMS. It would be very interesting to develop graphene/GO based devices or graphene based nanocomposite with these findings in the future.

The study of the tribological properties of these films was then extended from ambient condition to controlled environment conditions. Namely, the effect of relative humidity (RH) on the adhesion property of GO and SiO₂ were investigated with a humidity sensing cell with an AFM. Adhesion of GO was smaller than SiO₂, and both adhesion of SiO₂ and GO increased with elevated RH. A sharp increase in SiO₂ adhesion plot was identified to be attributed to the condensed meniscus between the tip and SiO₂ surface, while the steep increase has not been observed in the GO case. As solid lubricant, GO can reduce adhesion on SiO₂ surface in both ambient and high humidity environment in that GO has lower tendency of meniscus condensation with increasing RH. As a solid lubricant, GO can act as coating to protect MEMS surfaces from adhesion induced failure.

6.2 Outlook

The friction and wear properties of GO can be tuned with its carbon to oxygen ratios from our preliminary results. To better understand the tunability in tribological properties of GO, a quantitatively map of carbon to oxygen ratio with its friction and wear properties is necessary and it will be investigated in the future. Ultrathin films of graphene and GO show great potential to be applied as solid lubricant to enhance reliability of MEMS devices. With the knowledge of the tribological properties of these ultrathin films, practical deposition process of coating the MEMS surfaces with these ultrathin films will also be developed.

Another future step involves in the study of tribological properties of GO using the colloidal probe technique. On one hand adhesion contact behavior between the well defined probe and sample can be quantitatively modeled with contact mechanics models. On the other hand, friction of GO under a set of RH would be measured to understand the interfacial shear between the Si tip and GO surface. For the design of composite materials, the interfacial shear is a very important parameter to consider. The quantitative understanding of interfacial shear of GO can contribute to future design of GO based composites. In addition, the knowledge of interaction between the water molecules and GO sheets can provide perspective for water filtration and GO based sensor design.
Chapter 7

Appendices

7.1 Test probe method

7.1.1 Colloid probe preparation

Glass beads (Polysciences, Inc., glass beads, 50-100 μm) were mixed with deionized water and then drop casted onto glass slides. The sample was then dried in air for one hour. Afterwards, a sharp probe was dipped into premixed two part epoxy under optical microscope with an XYZ micro manipulator (Signatone, Model S-926, Gilroy, CA). Then the probe touched the aluminum side of the cantilever and left a layer of epoxy on it. After this step, the probe touched and adhere one bead from the glass slide under microscope. Then the probe that attached with the bead approached the cantilever slowly and touched the cantilever. This would leave the glass bead onto the cantilever since adhesion between the cantilever and the bead was greater than that between the probe and bead. The colloid probe was then fully dried in air for more than 2 hours.

7.1.2 Lateral deflection sensitivity calibration

After the lateral deflection sensitivity has been tested as discussed in Section 3.6, the lateral deflection sensitivity of the integrated cantilever is determined with Equation 7.1 and 7.2 respectively [110].

\[
S_{\text{lat,target}} = S_{\text{lat,test}} \frac{T_{\text{target}}/T_{\text{test}}}{(h_{\text{target}}/h_{\text{test}})(1 + \varepsilon_{\text{test}})(1 + \varepsilon_{\text{target}})} \tag{7.1}
\]

where \( S_{\text{lat,target}} \) and \( S_{\text{lat,test}} \) are lateral deflection sensitivity with an integrated tip and colloid probe respectively, \( T_{\text{target}} \) and \( T_{\text{test}} \) are total signal intensities, \( \varepsilon_{\text{test}} \) and \( \varepsilon_{\text{target}} \) are lateral in-plane bending criterion.

The \( \varepsilon_{\text{test}} \) and \( \varepsilon_{\text{test}} \) can then be calculated from Equation 7.2 with knowledge of the geometrical parameters and spring constants calculated from Sader method as discussed in Section 3.6.

\[
\varepsilon = \frac{k_T}{k_N} \left(\frac{t}{hw}\right)^2 \left(\frac{L'}{L}\right)^2 \tag{7.2}
\]

where \( \varepsilon \) is lateral in-plane bending criterion, \( k_T \) and \( k_N \) are torsional and normal spring constant respectively, \( t \) is cantilever thickness, \( h \) is tip height, \( w \) is cantilever width, \( L' \) is the distance from the base of the cantilever to the tip position and \( L \) is the full length of the cantilever.
7.2 Matlab code

7.2.1 Batch adhesion calculation from force distance curves

```matlab
%-----calculate adhesion from force distance curves.-----

function adhesioncal

clear; clc;

Sn=92; %Normal deflection sensitivity

CurrentFile=dir(fullfile(pwd,'/*.ibw'));
% Read the list of "ibw" files in the current folder
n=length(CurrentFile); %number of iteration
result=[];

for nsp=1:n

% Read "ibw" files with the function IBWread
D = IBWread( CurrentFile(nsp).name);
A=D.y(:,2);
[y1,spl]=max(A);
% Plot the originl data
va=D.y(1:spl,2)';
vr=D.y(spl+1:end,2)';
B=D.y(1:spl,1)';
Br=D.y(spl+1:end,1)';

[minv, i] = min(vr);
% First smooth the data to clean up some noise
Smooth_va = va;
smooth_range = 5;
for ii = 2:spl-1
    if ii - smooth_range < 1
        imin = 1;
        imax = ii + smooth_range;
    elseif ii + smooth_range > spl
        imin = ii - smooth_range;
        imax = spl;
    else
        imin = ii - smooth_range;
        imax = ii + smooth_range;
    end
    p = PolyFitPlus([B(ii+1:imax)', B(ii+1:imax)', [va(ii+1:imax)'; va(ii+1:imax)'], 2);
    Smooth_va(ii) = p(1)*B(ii)ˆ2+p(2)*B(ii)+p(3);
end
va_diff = diff(Smooth_va*100)+ 100;
end_plateau = find(va_diff < 99.95,1); % end_plateau is the va index of the end of the ...
plateau
```
if end_plateau > 1
    end_plateau = end_plateau + 3;
end

clear Smooth_va

plot(B,va,'b','LineWidth',2)
% Approach curve
hold on
plot(Br,vr,'r','LineWidth',2)
% Retract curve
hold on
plot(B(end_plateau),va(end_plateau),'go')
% A green circle is placed at the end of the plateau
set(gca,'XDir','Reverse');
set(gca,'YDir','normal');
legend('approach','retract');
grid on
% Define pull-off voltage as the difference between the minimum PSD voltage
% and the PSD signal at zero deflection.
[minv, i] = min(vr);
Indn=size(Br,2);
zero_polyfit = PolyFitPlus(Br((i+(end-i)/10):int32((Indn+i)/2)), ...
    vr((i+(end-i)/10):int32((Indn+i)/2)),1);
zero_polyfit(1)
zero_defl_val = zero_polyfit(1)*Br(i) + zero_polyfit(2);
Vpo = zero_defl_val-minv;
Slope=polyfit(Br(1:(i-10)), vr(1:(i-10)),1)
plot(Br,zero_polyfit(1)*Br+zero_polyfit(2))
plot(Br(i),vr(i),'ro')
% A red circle is placed at the pull-off point
hold on
plot(Br(i),zero_defl_val,'ko','MarkerSize', 3)
hold on
% A black circle is placed at a pt. that represents out-of-contact (zero deflection)
% Fit line to the contact region of approach trace
slope_fit_end_idx = find(va(end_plateau:spl)<= (va(end_plateau)+zero_defl_val)/2,1) + ...
    end_plateau - 1;
p= PolyFitPlus{ B(end_plateau:slope_fit_end_idx), va(end_plateau:slope_fit_end_idx), ... 
    1}; % Fit a polynomial to the appropriate data range
plot(B(slope_fit_end_idx),va(slope_fit_end_idx),'bo')
% A blue circle is placed at the snap-in point.
hold off
pause(0.1)

if end_plateau > 1
    % If a plateau occurred in the data, extrapolate to find the deflection at max. ...
    extension
    Output = [-p(1)*Vpo*10^9 -Vpo/p(1) -(p(1)*B{1}+p(2)-zero_defl_val)/p(1)];
else
Output = [-p(1)*Vpo*10^9 -Vpo/p(1) -(vr(1)-zero_defl_val)/p(1)];
end
result=[result;Output];
% The output contains:
% [slope of the in-contact line; pull-off voltage; pull-off deflection (nm); max. ...
% in-contact deflection (nm)]
end
% Write data to a file

C={'slope(V/nm) ' 'pull-off(nm) ' 'pull-off(nm) ' 'max_defl(nm)'};
data = num2cell(result');
data1=cat(1,C);
fid = fopen('Force Distance Result_different fit line.xls', 'w');
fprintf(fid, '%s %s %s %s %s', C{:});
fprintf(fid, '%u %u %u %u %u', data{:});
close(fid);
end
%-----end of code calculate adhesion from force distance curves.-----

7.2.2 Fiction force calculation and fitting with contact model

%----- calculate friction force from lateral force map.-----
cic; clear;
format long;
% data for the cantilever
kn=1.38;  % normal constant
kt=2.14e-008;  % torsional constant
s=66.621;  % normal deflection sensitivity (nm/v)
s1=12.138;  % lateral deflection sensitivity (nm/v)
h1=14e-6;  % cantilever arm height (m)
l=225;  % cantilever length (micrometer)

% Read and process data from file
N=45;
for nsp=1:40
  formatSpec = '%2.0f';
namewt{nsp} = ['TraceX', num2str(nsp,formatSpec),'.csv']
namewt{nsp} = ['ReTraceX', num2str(nsp,formatSpec),'.csv'];
[h,m] = csvreadh( namewt{nsp});
[hr,mr] = csvreadh( namewt{nsp});
ma=zeros(1,N);
for i=2:N+1
  for j=1:N
    ma(1,i-1)=ma(1,i-1)+(m(i,j)-mr(i,j))/2;  % get the sum of every row
  end
end
meanl(nsp,1)=mean((ma)/N);
Err(nsp,1)=std(ma/N)
end

%convert voltage signals into forces
setpoint=(-0.20:0.01:0.19)';
fn=kn*s*setpoint;  \( \text{nN} \)
fl=1/(h1^2)*kt*sl*meanl;  \( \text{nN} \)
Err=Err*1/(h1^2)*kt*sl;

%plot the normal vs. lateral
figure(1)
plot(fn,fl,'k*-','linewidth',1);
xlabel('normal force/nN','fontsize',18);
ylabel('lateral force/nN','fontsize',18);
legend('lateral force as a function of normal force',2);
hold on

%write friction and normal load data into excel file
 fid=fopen('friction force table Si.xlsx', 'w');
 fprintf(fid, '%s
', c);
 fprintf(fid, '%u
', data);
 fclose(fid);

% -----calculate transition fit from measured friction and normal load plot.-----
clc; clear;
figure (1)

%calculate and plot transition fit, here are the code for Si and GO
[NUM,TXT,RAW]=xlsread('friction force table Si.xlsx');
x=zeros(10,3);
for i=2:6
 xdata=NUM(1:10,1);
 ydata=NUM(1:10,i);
 [f,y_feval]=transition_fit_function(xdata,ydata);
 x(i-1,:)=f;
 if (i==3)
  xlin=-10:0.1:10;
  y_si=feval(y_feval,xlin);
 end
hold on
end

[NUM,TXT,RAW]=xlsread('friction force table GO.xlsx');
for i=2:6
 xdata=NUM(1:10,1);
 ydata=NUM(1:10,i);
 [f,y_feval]=transition_fit_function(xdata,ydata);
 x(i+4,:)=f;
 if (i==3)
xlin=-10:0.1:10;
y go=feval(y feval, xlin);
end
hold on
end

%write excel datasheet for transition fit parameters result
fid = fopen('transitionfit_result.xls', 'wt');
fprintf(fid,'%s %t %n','Si (1-4)', 'GO (5-8)');
fprintf(fid,'%s %t %n','yo', 'alpha', 'Lc');
m=x(:,1);
x(:,1)=x(:,3);
x(:,3)=m;
fprintf(fid,'%6.2f %t %6.2f %t %6.2f %t %n',x');
close(fid);

fid2 = fopen('transition_line.xls', 'wt');
fprintf(fid2,'%s %t %s %t %n','Fn','Si', 'GO');
x=[xlin; y si; y go];
figure(2)
plot(xlin,y si,xlin,y go)
fprintf(fid2,'%6.4f %t %6.4f %t %6.4f %t %n',x);
close(fid2);

%function for transition fit of friction vs. normal load data
function [f, y feval] = transition_fit_function(xdata, ydata)

func = @(p,xdata)(p(3)*((p(2)+sqrt(1-xdata/p(1)))/(1+p(2))).ˆ(4/3));

lb = [-inf; 0; -inf];
ub = [0 ; 1 ; inf];
x0=[-100;0.5;0.7];

options = optimset('Display', ...
    'iter','TolFun',1e-10,'Algorithm','trust-region-reflective');
[p, resnorm, residual, exitflag] = lsqcurvefit(func, x0, xdata, ydata, lb, ub, options);
f=p;
y feval=@(xdata)(p(3)*((p(2)+sqrt(1-xdata/p(1)))/(1+p(2))).ˆ(4/3)) + y_0*{(a+sqrt(1-x/l))/(1+a))}^-4/3;
linspace=floor(xdata(1))-1:0.1:floor(xdata(end))+2;
y_new=feval(y feval, linspace);
F0=feval(y feval,0); %calculate lateral force at zero normal force

%calculate the transition fit
figure (1)
plot(linspace, y_new,'-',xdata, ydata, 'd', 'LineWidth',2);
axis auto
fprintf('%r y o %t alpha %t L c %t F_0 (nN) %r');
fprintf('%7.3f\t%7.3f\t%7.3f\t%7.3f\t',p(3),p(2),p(1),F0);

%write data into file
data=[p',F0];
fid = fopen('transitionfit_result.txt', 'wt');
fprintf(fid,'%6s %12s %6s %6s\n','yo','alpha','Lc','F(0)');
fprintf(fid,'%6.2f %6.2f %6.2f %6.2f\n',data);
fclose(fid);
end
Bibliography


