FUNDAMENTAL STUDIES OF CHEMICAL MECHANICAL PLANARIZATION (CMP) PROCESSES OF TUNGSTEN AND COPPER.

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CHAPTER 1

INTRODUCTION

1.1 Tribology and nanotribology

Tribology is defined as the science and technology of two interacting surfaces in relative motion, such as friction, wear, adhesion and lubrication. The word tribology was first introduced by Jost in 1960’s. Tribos is a Greek word meaning “rubbing”, so tribology means literally the “science of rubbing”. Even though tribology has drawn people’s attention quite recently due to its importance in modern life, its record in history dates back to the ancient Egyptian period as early as BC 1880. They knew how to lubricate the wooden tracks below a sledge with water to reduce friction when they moved large stone building blocks or statues. People knew already from ancient times that reducing friction results in a lower consumption of time and manpower. Leonardo da Vinci (1452 – 1519) first introduced the concept of the coefficient of friction (µ) as the ratio of friction force (F_f) to normal load (L). In 1699, Amonton established Amonton’s law, which states that the friction force is proportional to the normal load and independent of the apparent area of contact (A) of macroscopic contacts. Coulomb verified these observations in 1781, and made a clear distinction between static friction (F_s) and kinetic friction (F_k). The force required to initiate the sliding of one body over the other is defined as static friction and the force required to maintain the sliding is defined as kinetic friction. The coefficient of static friction (µ_s) is greater than that of kinetic friction (µ_k).
We are exposed to the realm of tribology in our daily lives even if we don’t fully realize the practical importance of it. We may want strong tribological effects in some cases or weak effects in others. For example, friction with less wear is desired in car brakes, and tires. Friction with wear is desirable in writing with a pencil, machining, and polishing. Friction and wear is undesirable in engines, gears, and bearings. Lubrication of car engines and joints of dynamic components is desired and crucial to increase their efficiency and lifetimes by reducing friction and wear at the interface. People recently recognized the significance of tribology within industry because of economic reasons. Losses up to 6 % of gross national products, or several hundreds of billion dollars in the United States, result annually because of energy loss and wear associated with tribological events. Research in tribology can lead to greater device performance, fewer breakdowns and significant economic savings.

Tribology related matters have been addressed to date on a macroscopic scale due to their significance to engineering applications. However, the continuing desire of miniaturizing devices moves conventional tribology to an ultra small scale, referred to as nanotribology. Nanotribology is the science and technology of two interacting surfaces in relative motion on an atomic or molecular scale. A few examples of its application are magnetic storage devices such as computer hard disk drives, microelectromechanical systems (MEMS), and chemical mechanical planarization (CMP) process in semiconductor fabrication.

First, in the magnetic storage devices, as the physical dimensions of a rigid disk and a slider head in a magnetic storage system shrink, the distance between the disk surface and the slider is reduced in order to increase the storage density. Accordingly,
the thickness of solid coatings and the protecting lubricant layer must be reduced to a molecular scale with good lubricating ability. The development and application of such coating and lubricant materials is essential for the protection of stored data and the elimination of disk surface damage by contact with the head slider. Second, microelectromechanical systems such as microengines have a lot of advantages over the counterparts of macro scale mechanical systems because of lower power consumption and reduced volumes. However, MEMS are yet to be realized in practical applications due to the serious problems caused by friction, wear, and stiction.\textsuperscript{11} Reduction of friction and wear, and the prevention of stiction between ultra small moving components generally made of polysilicon films is crucial for high-speed performance and the prolonged life time of MEMS. Molecularly thin lubricants are needed on the surfaces of microscopic moving components; therefore extensive studies are underway to find effective lubricating materials.\textsuperscript{12,13} Third, the reduction of feature size in integrated circuits requires a decreasing margin of error of the geometry. Chemical mechanical planarization is a recently developed technology of planarizing wafer surfaces by both chemical etching and mechanical abrasion. This process is essential for realizing the sub-0.5 \textmu m technology in the current semiconductor industry. A fundamental knowledge regarding the role of each slurry component on the planarization process is needed to produce wafer products of higher quality with reduced cost. The advent of the atomic force microscope (AFM),\textsuperscript{14,15} quartz-crystal microbalance (QCM)\textsuperscript{16–19} and surface force apparatus (SFA)\textsuperscript{20} has enabled us to probe the properties of buried interface on an atomic or molecular scale and to address fundamental questions regarding nanotribology as in the applications described above.
The transition from tribology to nanotribology does not simply involve a re-scaling from a macroscopic to a nanoscopic length scale. There are two notable distinctions between tribology and nanotribology. First, Amonton’s law \( F = \mu L \), which states that friction is proportional to the applied load in a linear fashion and is independent of the area of contact, is no longer true in the realm of nanotribology. The area of contact that Amonton was dealing with was the apparent area of contact in a practical sense, not the real area of contact. The real area of contact is always much less than the apparent area of contact because two bodies in relative motion contact each other through many microasperities. Friction force is proportional to the real area of contact between two bodies in single microasperity contact. Figure 1.1 shows two bodies in sliding contact with same amount of load exerted where the apparent area of contact is greater in (a) than in (b). The pressure (force per unit area) exerted by the moving body in (b) is much larger than that in (a) because the area of contact in (b) is smaller than in (a). The total microscopic area of contact in both cases is not much different, even though the apparent area of contact in (b) is larger than that in (a). Accordingly, it results in the same amount of friction force in both cases as Amonton had observed. Second, the area of contact formed by a single microasperity increases non-linearly with increasing load due to the details of microscopic contact mechanics.\(^{21-24}\) As a consequence, friction depends on load in a non-linear fashion. Linear dependence of friction on load in macroscopic regime results from the contacts of multiple asperities on both surfaces.

Nanotribology is a newly emerging area of science. It is not just a field of tribology that simply verifies previous tribological principles in nanoscopic regime. In it, the laws and forces characterizing nanometer scale contacts are being
Figure 1.1 Two bodies are in relative motion. The apparent area of contact is bigger in (a) than in (b), while the real area of contact is not much different in both cases due to different amount of pressure exerted.
rediscovered and newly established. The task of bridging the gap between tribology and nanotribology also remains.

1.2 Atomic force microscopy (AFM)

The invention of the scanning tunneling microscope (STM) opened a new era of science and allowed the realization of atomic resolution images of surfaces for the first time in history.\textsuperscript{25} Since STM utilizes tunneling current for a data signal, it has an intrinsic limitation of its own in that it can only image conductors or low band gap semiconductors free of insulating contaminants on their surfaces. Insulators have not been studied with STM-related techniques for that reason. In 1986, Gerd Binnig, the former inventor of STM announced that he and his colleagues had constructed an atomic force microscope (AFM),\textsuperscript{26} a derivative of the STM. Instead of using tunneling current signal between sample and tip, AFM utilizes the force acting on the tip. As a consequence, the conductivity of the sample is not required to image the surface. AFM produces images of a sample surface by scanning a sharp tip mounted on a flexible cantilever, having a spring constant typically between 0.1 and 100 N/m, over the sample surface. In 1987, Mate et al. from IBM observed atomically periodic stick-slip events on a crystalline graphite surface.\textsuperscript{15} They also observed a frictional dependence on load and the actual area of contact between the tip and the graphite surface. Their discovery proved AFM to be a very powerful tool in nanotribology\textsuperscript{27–28} and resulted in the development of the friction force microscope (FFM) or the lateral force microscope (LFM).

In the study of tribological contacts friction force and normal load need to be measured independently and simultaneously in order to probe the frictional dependence
of load. There are several suggested detection methods of cantilever deflection.\textsuperscript{29–30} The optical method\textsuperscript{9,31–35} has been widely used because of its relative simplicity and convenience. In this method laser light is reflected from the back of a gold-coated cantilever onto a four-quadrant position-sensitive photo detector or PSPD (Figure 1.2 (a)). The signals from normal and lateral deflections of cantilever are monitored and recorded independently and simultaneously from the photo detector. The magnitude of each signal from the four individual sectors (A1, A2, B1, and B2) of the quadrant photo detector is summed or subtracted electronically to produce normal and lateral force signals (Figure 1.2 (b) and (c)). The normal force signal is calculated as follows:

$$\text{Normal force} = \Sigma \{\text{PSPD(Top) - PSPD(Bottom)}\} = \Sigma \{(A1 + A2) - (B1 + B2)\}.$$  

In a similar way, the lateral force signal is calculated through the equation:

$$\text{Lateral force} = \Sigma \{\text{PSPD(Left) - PSPD(Right)}\} = \Sigma \{(A1 + B1) - (A2 + B2)\}.$$  

When the tip is far away from the sample surface, the laser light reflected from the back of cantilever hits the center or equilibrium position of photo detector. As a consequence,

$$\text{Normal force} = \text{Lateral force} = 0$$  

Contact of the tip with the sample surface causes the cantilever to deflect normally or laterally, which generates non-zero values of normal or lateral force.

$$\text{Normal force, Lateral force} \neq 0$$  

The advent of AFM has brought not only the visualization of materials on an atomic resolution (regardless of conductivity) but also the opportunity to explore atomic scale friction, wear, and lubrication. The atomic force microscope has unique advantages over other techniques. First, it ideally emulates single microasperity contacts with a sharp AFM tip having a radius typically of 200–300 Å. So, it provides directly
Figure 1.2 (a) The geometry of the components of optical beam deflection AFM. Normal or lateral deflection of cantilever during scanning is recorded from the laser light reflected onto the four-quadrant position-sensitive photodetector (PSPD). (b) The tip does not interact with the sample surface when it is positioned far away from the sample and normal and lateral forces are defined as being zero. (c) When the tip contacts and interacts with the sample surface, normal and lateral forces are recorded as non-zero values.
nanotribological information of bare or lubricated sample surfaces. Second, the diversity of operating conditions is quite unique. It can be operated in air, in controlled relative humidity,\textsuperscript{36} and in liquid environments\textsuperscript{9,37–38} to probe a wide range of materials. It can also be operated in ultra-high vacuum environment\textsuperscript{39} to provide fundamental information of clean and systematically prepared surfaces. Third, AFM allows simultaneous measurements of surface morphology and frictional properties, which makes it possible to correlate directly one with the other. These advantages make AFM both a suitable and indispensable tool in nanotribology.

In spite of these unique advantages, AFM itself also has limitations. First, the contact geometry formed between an AFM tip and sample surface is not defined if the tip shape is not known. Interfacial friction and adhesion is affected by the contact geometry of the tip and sample surface.\textsuperscript{40} For example, the area of contact formed by a dull or blunt tip is bigger than that formed by a sharp tip over the same surface, which results in a substantial difference in friction and adhesion. Variations of the shape and size of the probe apex also influence significantly the image resolution, which can give rise to misinterpretation of surface topography. For example, a blunt tip does not resolve the detail or the fine structure of a surface while a sharp tip does. Also, double tip geometries produce double-shaped images. Sheiko \textit{et al.} proposed that the stepped SrTiO$_3$(305) surface, which is also known commercially as a Mesoscale, can be used to evaluate the profile of AFM probes.\textsuperscript{41} With this approach the curvature of the AFM probe is convoluted into the step and terrace structure of the SrTiO$_3$(305) surface. Geometric deconvolution of the SrTiO$_3$(305) can be used to reveal the tip radius.\textsuperscript{9,40}
Second, the chemical composition of the tip is known to influence the interaction of the tip and sample. It has been reported that altering the chemical nature of the tip changes the interfacial friction and adhesion. However, it is not easy to determine chemical nature or chemical composition of the tip because of the possible contamination of the tip. The chemical composition of the tip may be changed by oxidation of its surface, by picking up materials from the substrate, or by being contaminated by the impurities from its environment. Since the tip makes up one half of the interface, it is crucial to determine the chemical nature of the tip to understand the measured properties of the interface.

Third, fundamental understanding of nanotribological phenomena requires a quantitative analysis of data. However, calibration of forces is difficult because the force constants of micron-size cantilever are usually unknown due to the unknown chemical composition, dimensions and the relevant elastic moduli of the cantilever.

Finally, materials for AFM tips are very limited because of the difficulty associated with the microfabrication process of the tips. As a consequence, the possibility of modeling all tribological contacts is limited. Commercially available tips are typically made of silicon or silicon nitride. Tip materials other than silicon and silicon nitride are dependent on coating or deposition processes onto the silicon-based tips.

The intrinsic limitations of AFM must be understood in order for it to be a useful tool for the study of nanotribology.
1.3 Chemical mechanical planarization (CMP)

The continuing desire to miniaturize device dimensions and the related need to interconnect and embed an increasing number of functional components on a single chip gives rise to the construction of multilevel interconnections on planarized levels in the integrated circuit fabrication process.\(^{44}\) Increased density and reduced feature size on a chip requires greater planarity of the wafer surface due to the high tolerance of feature geometry. Conventional mechanical planarization techniques do not meet the required specifications of wafer planarity. The chemical mechanical planarization (CMP) process was invented to fulfill such needs.

Historically, CMP processes have been employed for a long period of time to polish a variety of materials and provide mirror-like finishes. Nature also runs its own CMP process to produce beautifully finished stones and rocks. Recently CMP was identified as a crucial process in integrated circuit (IC) fabrication. The unique difference between ‘historical’ CMP process and the one used in Si IC fabrication lies in the amount of materials removed. Very thin layers of materials (typically less than 0.5 \(\mu\text{m}\)) are removed with precise control in the CMP process of Si IC fabrication involving embedded metals and dielectric surfaces. Maintaining precise control of film thickness is very important to device performance and requires a sophisticated approach; it has been a challenge to both engineers and scientists since its introduction.

CMP is a process designed to planarize a rough surface by the chemical and mechanical actions of slurry. High points of the surface are subject to mechanical abrasion and chemical etching and are gradually removed. At the same time, low points of the surface are protected from mechanical contact with abrasives and from chemical
etching through the presence of a surface oxide or passivating agent until high points of the surface can be removed (Figure 1.3).

The chemical action of CMP alone can not achieve planarization because its action/reaction is isotropic all over the surface. Mechanical action alone is also undesirable because of the extensive mechanical damage to the surface of thin layers. However, the appropriate combination of these two effects may achieve desired planarity of surface (the balance depending upon the type of materials). Mechanical effects are more important on hard materials such as tungsten and tantalum while chemical effects are more important on soft materials such as aluminum and copper. As device size continues to shrink, the control of slurry chemistry plays a more important role in CMP process. Slight changes of chemical conditions in the slurry can substantially influence the success or failure of planarization processes.

One of the most important factors in CMP process is the polish rate (units of nm/min or µm/min) because it is the decisive factor which determines the throughput of wafer processing. Polish rate is defined as the film thickness removed by the polish time.\(^{(1)}\) Preston empirically modeled the polish rate dependence on pressure and velocity of the pad in the Preston Equation;\(^{(2)}\)

\[
Polish\ Rate = \frac{\Delta H}{\Delta t} = K_p \times P \times \left( \frac{\Delta s}{\Delta t} \right) = K_p \times \left( \frac{L}{A} \right) \times \left( \frac{\Delta s}{\Delta t} \right)
\]

where \(\Delta H\) is the thickness of material removed, \(\Delta t\) is the elapsed time, \(P\) is the pressure, \(\Delta s/\Delta t\) is the linear velocity of the pad relative to the wafer carrier, \(L\) is the load, \(A\) is the area of contact, and \(K_p\) is the Preston coefficient. The Preston equation states that polish
Figure 1.3 As CMP process progresses, high features are removed by slurry and other CMP variables while low features are remained intact.
rate is proportional to the applied pressure and relative velocity between the polish pad
and the wafer for a given pad and slurry. The Preston coefficient empirically includes the
effect of slurry composition and chemistry. From this equation, we anticipate that polish
rate is governed not only by external variables such as pressure and linear velocity of pad,
but also by slurry chemistry. In this dissertation, I focus mainly on the influence of
chemical components of the CMP slurry on the polish rate with other external variables
fixed.

CMP has advantages over other old planarization methods. It provides not only
local planarity but also global planarity of the surface that is crucial in achieving sub-0.5
µm geometries and in building multilevel interconnects. Conventional planarization
methods such as plasma etching and reactive ion etching planarize the wafer surface
locally, not globally. The CMP process is also applicable to most materials; however
successful planarization requires significant optimization of the process. The materials
commonly subject to CMP and their applications in silicon integrated circuit (Si IC)
fabrication are shown in Table 1.1.45

As the capabilities of the CMP process are realized, its market grows rapidly. The
market showed an average growth rate of over 30 % annually for several years before the
downturn in the semiconductor industry in 1998.47 It is estimated that one CMP machine
with a wafer production rate of 40 wafer/hr and operating at 65 % of capacity would
consume $275,000 per year only in CMP slurry without considering additional costs for
the disposal of toxic slurry wastes, and deionized water needed for cleaning the processed
wafers. These economic aspects emphasize the need for fundamental investigations of
the CMP process. Most CMP recipes have been developed empirically with a lack of
Table 1.1 Materials to be planarized and possible applications

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applications</th>
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<tbody>
<tr>
<td>Metal</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Interconnection</td>
</tr>
<tr>
<td>Cu</td>
<td>Interconnection</td>
</tr>
<tr>
<td>Ta</td>
<td>DB/AP</td>
</tr>
<tr>
<td>Ti</td>
<td>DB/AP</td>
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<tr>
<td>TiN, TiN_xC_y</td>
<td>DB/AP</td>
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<td>W</td>
<td>Interconnection</td>
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<td>Cu-Alloys</td>
<td>Interconnection</td>
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<tr>
<td>Al-Alloys</td>
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<td>Polysilicon</td>
<td>Gate/Interconnection</td>
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<td>SiO_2</td>
<td>ILD b</td>
</tr>
<tr>
<td>BPSG c</td>
<td>ILD</td>
</tr>
<tr>
<td>PSG d</td>
<td>ILD</td>
</tr>
<tr>
<td>Polymers</td>
<td>ILD</td>
</tr>
<tr>
<td>Si_3N_4 or SiO_xN_y</td>
<td>Passivation/Hard CMP</td>
</tr>
<tr>
<td></td>
<td>Stop Layer</td>
</tr>
</tbody>
</table>

\(^{a}\) DP/AP = Diffusion Barrier/Adhesion Barrier  
\(^{b}\) ILD = Interlayer Dielectric  
\(^{c}\) BPSG = Borophosphosilicate Glass  
\(^{d}\) PSG = Phosphosilicate Glass
fundamental understanding of their details. A fundamental knowledge will serve to optimize the process, ultimately reduce the cost of ownership, and result in a greater quantity of wafer products of good quality and a reduced quantity of slurry waste.

1.4 Subjects to be addressed

This dissertation reports on the investigation of fundamental chemical mechanical planarization (CMP) processes of tungsten and copper surfaces, and focuses on the influence of slurry chemistry. Atomic force microscopy, incorporating an optical beam deflection method, was used to investigate the tribological and morphological properties of tungsten and copper surface in situ in a variety of aqueous conditions. A small AFM tip (silicon nitride, or alumina coated silicon nitride) was used to simulate a single microasperity contact with the tungsten or copper surface. Chapter 3 describes the influence of solution pH on the interfacial friction. Interfacial friction and adhesion between tungsten surfaces and bare or alumina-coated silicon nitride ($\text{Si}_3\text{N}_4$) tips have been measured in solution pHs ranging from 2.2 to 8.2. The concentration of electrostatic charges on both surfaces of tip and tungsten varies under these conditions and gives rise to variations in interfacial friction and adhesion, depending on solution pH and isoelectric points (IEP’s) of the contacting surfaces. Every measurement has been carried out in the absence of significant mechanical wear and chemical dissolution of the surface.

Chapter 4 explores the influence of the chemical composition of the solution on the composition and friction of tungsten surfaces. Interfacial friction between tungsten and a $\text{Si}_3\text{N}_4$ tip has been measured in situ with AFM in different types and concentrations
of oxidizing agents. Three different oxidizing agents (KNO₃, KClO₃, and KIO₃) have been investigated in the same concentration environment (0.01 M). Studies of KIO₃ have been performed as well over a range of concentrations (0.005, 0.01, and 0.02 M). The chemical composition of the tungsten surface has been measured ex situ with XPS following solution exposure to these conditions. Variations in interfacial friction are correlated with changes in the dissolution rate and composition of tungsten surface. Surface topography measured in situ in each chemical condition is presented to support the interpretation of the observed frictional behavior.

In Chapter 5, the interfacial friction of copper surface measured in situ in the presence or absence of benzotriazole (BTA), a corrosion inhibitor, is described. In this study, the influence of adsorbed BTA layer on the interfacial friction and its protective behavior of copper surface have been investigated. Measurements have been carried out in both highly acidic (pH 1.2) and neutral conditions (pH 6.7). Three solutions of 0.10 M HNO₃ (pH 1.2), 0.01 M BTA (pH 6.7) and 0.10 M HNO₃+ 0.01 M BTA (pH 1.3) have been used for this purpose. The surface topography of copper surface has been measured in situ to monitor any morphological change. The thickness of the copper films also has been measured ex situ using a stylus profilometer before and after one hour’s incubation of copper films in the same solutions in order to estimate material removal rates.
1.5 References


35. Ascoli, C.; Dinelli, F.; Frediani, C.; Petracchi, D.; Salerno, M.; Labardi, M.; Allegrini,
    (19), 11226.
    14 (2), 1289.
    1993, 48, 5675.
    8 (4), 3386.
44. Gelatos, A. V.; Nguyen, B. –Y.; Perry, K.; Marsh, R.; Peschke, J.; Filipiak, S.; Travis,


CHAPTER 2

EXPERIMENTAL METHODS

2.1 Introduction

In this chapter, experimental details regarding the friction measurements of copper and tungsten in various aqueous conditions are discussed. This includes the overall description of the microscope, partial modification of an ambient AFM to allow for the measurement in liquid, calibration of the piezo scan tube, force calibration of the cantilever, characterization of tip radius, newly designed sample holder, brief description of the design of fluid cell purchased from a commercial vendor, operational modes, data processing, and sample preparation.

2.2 Instrumentation

Modification of an existing microscope gave rise to a dual mode AFM, operational in both an ambient mode and a liquid mode. Swapping between modes can be done simply by changing upper plates without further change of any other mechanical parts or electronics. The layouts of the modified upper plate and newly designed sample holder are shown in the Appendix. The following sections describe the functional aspects of the microscope as they relate to the experiments described in the following chapters.
2.2.1 Microscope

The microscope used in the course of this dissertation is illustrated in Figure 2.1. It is composed of several components which were either purchased directly from manufacturers or made in the machine shop, Department of Chemistry, University of Houston. The microscope was assembled and tested by a former colleague, Dr. H. I. Kim, and was further modified to be adequate for the liquid environmental experiments.

The main components of the microscope include a laser diode, photo detector, fluid cell, piezoelectric scanner, sample holder, tip/cantilever assembly, and a first stage signal preamplifier. The piezoelectric scanner, sample holder, and upper plate (Figure A.1 in Appendix) were modified for liquid environment experiments. Further details regarding modification of these components of the microscope will be discussed in the following sections.

The laser diode (Toshiba, TOLD9221M) is placed above the cantilever. Light from the laser diode is focused with an optical lense (Melles Griot, 01 LAO 001) and goes through the transparent fluid cell. It is then reflected from the back of the gold coated cantilever which is fixed underneath the fluid cell. The sample is placed on top of the piezoelectric scanner and is in contact with the tip. The light from the back of cantilever is reflected on to a four-quadrant position-sensitive photo detector (UDT Sensors Inc., Pinspot 4D, 11-04-02) and changes to voltage signal. This signal contains the information of normal and lateral deflections of the cantilever which are dependent upon the topographical and frictional properties of the surface. The signal is amplified through the first stage (F in Figure 2.1, RHK PCB # 14-1099-01) of signal pre-amplifiers.
Figure 2.1 An atomic force microscope utilizing an optical beam deflection detection method. A: laser diode, B: fluid cell, C: PZT scan tube, D: position sensitive photo detector. E: upper plate, F: laser power supply, G: first stage pre-amplifier
and further amplified through the second stage (not shown in Figure 2.1, AFM 100 PREAMP PN 14-1098-90, RHK Technology, Inc., Troy, MI). The first stage of the signal amplifier is attached directly to the microscope to improve the signal to noise ratio by minimizing the distance between the photo detector and the amplifier electronics.

2.2.2 Control electronics

RHK AFM 100/RHK STM 1000 control electronics (version 5, enhanced feedback) and software (version 2001) were used for data collection and process. The operation of the laser diode and the photo detector is controlled by the RHK AFM 100 electronics and the movement of the piezoelectric scan tube is controlled by the RHK STM 1000 electronics. The jumper settings of the RHK STM 1000 electronics for the operation of this microscope are summarized in Table 2.1.

2.2.3 Piezo scan tube

The piezoelectric scan tube (1” long, 0.5” OD, 0.02” wall thickness) is made of lead-zirconate-titinate (PZT) ceramic material and is coated with nickel. The un-sectioned PZT tube (Staveley Sensors Inc., East Hartford, CT) was sectioned electrochemically to nine nickel electrode sectors (eight outside and one inside the tube), electrically isolated from one another (Figure 2.2). The sectored scan tube was coated with a lacquer to protect against etching in case of unintended overflow of the liquid during AFM experiments. The scan tube was then wired afterwards. The etching, coating, and wiring processes are dealt in detail in the next sub-sections. This piezoelectric scan
Table 2.1 The jumper settings of the RHK STM 1000 for the operation of this microscope.

<table>
<thead>
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<th></th>
<th>Scan board (#1)</th>
<th>Offset board (#2)</th>
<th>Interface board (#3)</th>
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<td>1 &amp; 2</td>
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</tr>
<tr>
<td>SW3</td>
<td>2 &amp; 3</td>
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Figure 2.2 A schematic of the piezo scan tube. The nickel coating (darkly shaded areas) of the tube is sectioned to nine sectors, eight outside and one inside. The top four sectors outside the tube are assigned for scan motion, and the bottom four sectors are assigned for offset motion. A single sector inside the tube is assigned for Z-offset. The sum of all scan sectors is used for Z-scan.
tube controlled the three-dimensional movement with angstrom precision by applying appropriate voltages. It provides a maximum lateral scan range of $1.5 \mu m \times 1.5 \mu m$.

**CAUTION:** Turn off electronics and disconnect the head whenever working with the piezo; ±130 V signals are present on the piezo surface.

**2.2.3.1 Etching and coating**

Microshield Stop-off Lacquer (Tolber division, Hope, Arkansas) was used for a protective coating material in the selective etching of the nickel plating on the PZT tube. A lacquer solution was made by mixing lacquer with acetone at a volume ratio of 2:1.

The inside and outside walls of the tube were pre-coated with nickel (Figure 2.3 (a)). The tube was rolled over the lacquer solution while maintaining an even coating on the outside wall until the desired lacquer thickness was reached (Figure 2.3 (b)). The coated tube was dried in the air for ~1 hour. After drying the etch lines (line width: 0.5 ~ 0.8 mm) were engraved on it with a sharply tipped blade (Figure 2.3 (c)). The coated tube should not be dried too long in the air because it’s not easy to engrave etch lines when the coated lacquer has hardened too much. Lacquer solution was again applied to the inside of the tube in preparation for the inside sector (not shown in Figure 2.3). Caution should be made for the lacquer solution not to contact the outside wall previously coated and engraved with etch lines. The tube was dried in the air for another hour and engraved with etch lines which electrically isolate the inner electrode from the outside wall. After all of the steps above were done, the tube was further dried in the air overnight so that the coating would be completely hardened before the etching procedure (Figure 2.3 (d)).
The etching solution was made by mixing \( \text{H}_2\text{O} \), concentrated \( \text{H}_2\text{SO}_4 \), and concentrated \( \text{HNO}_3 \) at a volume ratio of 2:1:1. The tube was dipped into the acid solution for \( \sim 5 \) minutes until exposed nickel lines were etched away (Figure 2.3 (e)). It is noted that the etching solution needs to be cooled to slightly above room temperature before use, in order to avoid vigorous etching far inside the boundary lines between the coating and exposed nickel lines. Failing to do so results in irregular and broad etch lines. The tube was then drawn out from the acid solution and rinsed with water. Residual lacquer on the tube was removed by acetone (Figure 2.3 (f)).

*CAUTION: Etching solution is very corrosive. Always wear latex gloves, lab coat, and fully-covering shoes when handling an etching solution. DO NOT use metallic tweezers in holding the PZT tube in the solution. Always use a Teflon tweezer.*

A leak-proof coating process was applied to the outside wall of the tube using the same lacquer solution (Figure 2.3 (g)). It is the same procedure as Figure 2.3 (b). The tube was allowed to be dried in the air overnight (Figure 2.3 (h)).

### 2.2.3.2. Assembling piezo tube compartments

A sample mounting plate and a scan tube mounting plate were attached to the scan tube which was previously sectored and coated with lacquer (Figure 2.4). A small cylindrical magnet was placed underneath the sample mounting plate to hold magnetic sample holders (made of ferrous metals). Non-conductive epoxy (Epo-Tek H61, Epoxy Technology Inc., Billerica, MA) was applied to the joints between the components. The scan tube assembly was then cured in the oven at 60 ~ 80 °C for one hour.
2.2.3.3 Wiring of piezo tube

After the protective coating and assembly of the flanges were accompanied, each sector of the tube was wired (Figure 2.5). A small circular space (~1.5 mm dia.) was taken out from the center of each lacquer-coated sector using a sharply tipped blade, thus exposing a nickel surface to which the lead wires are soldering (Figure 2.5 (a)). Each sector was wired (Figure 2.5 (b) and (c)) separately to the exposed nickel surface. A solder wire (Rosin core, Alpha metals Inc., Jersey City, NJ), and a soldering station (Model: WTCPL, Wassco, Los Angeles, CA) was used. The soldered areas (exposed metallic surfaces) were re-coated with a lacquer solution using a paint brush (Figure 2.5 (d)). The tube was allowed to dry in air overnight (Figure 2.5 (e)). After the tube dried completely, it was dipped into water and the electrical resistance between wire connections was measured (Figure 2.5 (f)). The wires should be electrically isolated from one another. In the case that a finite resistance between the wires is observed, the specific solder area(s) is (are) retouched with another layer of coating. Steps (d), (e), and (f) should be repeated until an infinite resistance is recorded.

CAUTION: The soldering temperature should not exceed the Curie temperature of the PZT (lead-zirconate-titanate), which is at the range of 150-300 °C. If it exceeds this temperature range, the PZT tube loses its piezoelectricity due to the depolarization of the pre-aligned dipoles.
Figure 2.3 Piezo scan tube fabrication and coating procedure. (a) Unsectioned tube. Walls inside and outside the tube are pre-coated with nickel. (b) Coating the tube with stop-off lacquer. (c) Engraving the etch line inside and outside the coated tube after one hour’s drying in air. (d) Drying the tube overnight (e) Etching process in etchant. (f) Removing the residual lacquer coating with acetone. (g) Re-coating the segmented tube with stop-off lacquer. (h) Drying the tube overnight
Figure 2.4 The piezo scan tube, previously sectored and coated to prevent corrosion, was assembled with sample mounting plate and scan tube mounting plate.
Figure 2.5 Wiring procedure of the piezo tube. (a) Making a circular space and exposing a metallic area for soldering on each sector. (b and c) Soldering a wire on each nickel-exposed area. (d) Covering soldered areas with lacquer. (e) Drying the piezo tube overnight. (f) The tube is dipped up side down in water. The conductivity between wires is checked to ensure that each sector is electrically isolated from one another.
2.2.3.4 Calibration

Piezo scan tubes must be calibrated with standards such as highly oriented pyrolytic graphite (HOPG), mica, or gold, of which atomic lattice spacings (2.5, 5.4 and 2.8 Å respectively) are well-known. The scan tube assembly was installed into the microscope and calibrated with HOPG. The x/y scans and offsets were calibrated by collecting a series of atomic lattice images (50 Å × 50 Å) from the lateral force channel by systematically varying the input voltages to x and y scan piezo sectors until the desired lattice spacing of HOPG (2.5 Å) was obtained (Figure 2.6 (a)). Feedback control was minimized by minimizing gain and maximizing time constant. The scan speed was set to between 30 – 50 lines/sec. Two–dimensional fast Fourier transform (2D-FFT) plots were obtained from the collected lattice images (Figure 2.6 (b)), and used to calculate the averaged lattice spacing (d) and the standard deviation (σ) or error of the calibration (Figure (2.5 (c)).

\[ d = a^{-1}, \quad \sigma = \frac{s_1^{-1} - s_2^{-1}}{2} \]  \hspace{1cm} (2.1)

The calculated lattice spacing of HOPG after calibration was 2.5 ± 0.1 Å. Z scan and Z offset were calibrated in the topographic mode by imaging single atomic steps of HOPG surface (3.4 Å).

2.2.4 Tip-cantilever assembly

Silicon nitride AFM probes were purchased from a commercial supplier (Digital Instruments, Santa Barbara, CA). The square pyramidal Si₃N₄ tip is mounted on a flexible, gold-coated cantilever (Figure 2.7). The spring constant of the cantilever
Figure 2.6 Scan piezo calibration procedures. (a) Atomic lattice image of HOPG was obtained from lateral force imaging. (b) 2-D FFT of the lattice image. (c) Cross-sectional plot of the 2-D FFT (white solid line). Calculated lattice space of HOPG is $d \pm \sigma$, where $d = a^{-1}$ and $\sigma = (s_1^{-1} - s_2^{-1})/2$. 
Figure 2.7 A schematic of a silicon nitride probe. There are four tip-cantilever assemblies on a single chip. The spring constant of each cantilever is indicated in units of N/m.
specified by the manufacturer was used for force calibration of the silicon nitride tips. Tips were used either as received or after further process of coating them with alumina for certain experiments.5–6

2.2.4.1 Force calibration

Force calibration is required for the quantitative analysis of interfacial forces. Force calibration addressed both normal and lateral forces. Since forces acting on the tip are dependent on the distance of tip displacement (Hook’s law), accurate calibration of the piezoelectric scan tube should be done prior to the force calibration of cantilevers.

\[ F_N = k_N \cdot \Delta z \]  

(Hook’s law)  

(2.2)

The normal force response was calibrated by collecting and manipulating a series of force-distance curves. Force-distance curves were obtained by gradually moving the sample toward or from the tip and monitoring the resultant signals from the normal deflection of the cantilever (Figure 2.8).

When the tip approaches the sample, it begins to experience attractive forces (i). When the tip is close enough to the sample and its spring constant is exceeded by the attractive force gradient between the tip and sample, it causes the tip to snap into contact with the sample surface (ii). As the sample is advanced, the normal deflection of the cantilever continues (iii). Upon retraction the load applied to the tip is removed (iv). Due to the adhesion that exists between the tip and sample, the tip does not separate from the sample surface at a load of 0 nN. Instead, adhesion extends to a range of negative loads or normal forces (v). The trace of the unloading curve deviates from that of the loading curve because of this adhesion. The difference in the curves is referred to as adhesion
hysteresis. When the spring constant of tip exceeds the adhesion or pull-off force gradient, the tip snaps off the sample surface (vi).

Due to the difficulty in calibrating lateral forces, raw voltage signals from the photo detector were used without calibration. The normal force of the cantilever was calibrated to obtain the normal force conversion factor ($\beta_N$; unit: N/V) before the friction measurements. Unit conversion from volts (V) to nN was accomplished by applying the normal force conversion factor. The slope of the loading range in Figure 2.8 (iii) was measured and denoted as $S_N$ (unit: V/m). The spring constant of the cantilever is denoted as $k_N$ (unit: N/m). In turn, the normal force conversion factor is calculated as:

$$\beta_N = \frac{k_N}{S_N} \quad (2.3)$$

For the collection of force-distance curves and friction measurements, microlever D ($k_N = 0.58$ N/m) was used. The normal force calibration of this assembly using $\beta_N$ was obtained using the procedure described above.

Figure 2.9 (a) is a force-distance curve obtained in air from a tungsten surface. Here, the value of $x$ denotes the adhesive or pull-off force. Figure 2.9 (b) is a force-distance curve obtained in liquid from same tungsten surface.

2.2.4.2 Tip radius characterization

Resolution of the surface topography and friction is known to be greatly influenced by the shape and sharpness of the probing tip.\textsuperscript{7–10} Artifacts in topographic images are generally caused by ill-shaped tips. Interfacial friction and adhesion are also known to be significantly influenced by the tip radius as well. This implies that the tip radius should be characterized before and after each set of measurements. Sheiko \textit{et al.}
Figure 2.8 Force-distance curves were obtained in air before normal forces were calibrated. As the sample approaches the tip, a long range attraction is usually experienced, followed by repulsive contact (i → ii → iii). As the sample is retracted from the tip, the tip is gradually released from the applied load (iv → v → vi) and finally snaps off from the sample. Due to the existence of adhesion between the tip and sample surface, the trace of the unloading curve (iv) differs from the loading curve (iii). This difference is known as adhesion hysteresis.
Figure 2.9 Two force-distance curves were obtained in (a) air and (b) liquid.
has published a scheme to evaluate tip radius and shape using a reconstructed SrTiO$_3$(305) surface (commercially known as Mesoscale; Witec, Hövelsinger, Ulm, Germany).\textsuperscript{11}

The surface of SrTiO$_3$(305) reconstructs when annealed for 20 hours at 1100 °C in flowing oxygen. The reconstructed surface consists of alternating (101) and (103) crystal planes. These alternating planes are inclined at angles of +14° and −11.6° with respect to the (305) surface plane and form a series of long and sharp ridges.\textsuperscript{11}

Topographic imaging of the reconstructed ridges results in the convolution of the tip shape and surface ridge structure (geometry). Figure 2.10 displays two topographic images and the associated cross-sectional profiles of the Mesoscale taken with (a) a sharp tip and (b) a blunt tip. It is evident that the shapes of the ridges are greatly influenced by the sharpness of the tip.

The tip radius was estimated from the parabolic profiles of the ridges. The radius was approximated from a Taylor expansion of a second degree polynomial describing a parabola ($y_1(x) = C_0 + C_1x + C_2x^2$) and hemi-circle equation ($y_2(x) = r - \sqrt{(r^2 - x^2)}$).

The parabola represents a tip profile.\textsuperscript{12} Given that the apices of the parabola and the hemi-circle intersect at the origin (Figure 2.11), $y_2(x)$ can be re-written using the Taylor polynomial expansion

\begin{equation}
y_2(x) = y_2(0) + y_2^{(i)}(0) \cdot x + \frac{y_2^{(2)}(0)}{2!} x^2 + \cdots \tag{2.4}
\end{equation}

where, $y_2(0) = 0$, $y_2^{(i)}(0) = 0$, $y_2^{(2)}(0) = \frac{1}{r}$. Thus, $y_2(x) \approx \frac{1}{2r} x^2$. Since $y_1(x) = y_2(x)$ at the origin or tip apex, $C_0 + C_1x + C_2x^2 \approx \frac{1}{2r} x^2$. From this, the tip radius ($r$)
Figure 2.10 A mesoscopic standard or a Mesoscale (reconstructed SrTiO$_3$(305)) was imaged with (a) a sharp tip and (b) a blunt tip. The line profiles were obtained by taking a cross-section of the topographic images (white solid lines).
Figure 2.11 A parabola and a hemi-circle (radius: $r$) intersect at the origin of the model used for fitting the tip radius.
can be approximated by \( r = \frac{1}{2C_2} \).

Figure 2.12 shows an example of calculating a tip radius from a parabolic ridge profile of a SrTiO\(_3\)(305) or Mesoscale surface. The tip radius is estimated statistically from more than 30 parabolic ridge profiles.

Care must be taken in using this method to estimate tip radii for two reasons. First, the radius of a blunt tip (\( r > 1000 \) Å) is often overestimated because fitting the hemi-circle to the tip profile is usually no longer valid as blunt tips, often resulting from wear. Second, the sharpness of the ridges of SrTiO\(_3\)(305) can degrade over time in the air. The ideal geometry can be recovered regularly by annealing the oxide surface in oxygen at 1100 °C as Sheiko et al. suggested.\(^{11}\)

2.2.5. Fluid cell

A fluid cell was purchased from Digital Instruments (Santa Barbara, CA). The cell was made of a transparent glass so that laser light could pass trough to the underside of the cell and hit the back of cantilever affixed with a cantilever clip (Figure 2.13). The bottom of the cell was coated with a thin film of an anti-reflection coating material to reduce unwanted light scattering. The circular trench on the bottom of the cell was initially intended by the manufacturer for a silicon rubber o-ring to hold liquid inside. However, the liquid trapped inside the o-ring usually slipped out due to gravity when it was replaced with new liquid. This problem was resolved simply by developing a new sample holder (Figure A.2 in Appendix). It will be discussed in more detail in the following section.
Care must be taken in working with the fluid cell. First, a highly alkaline solution (usually pH > 10) can cause unwanted dissolution of the cell surface in contact with the liquid because the fluid cell is made of glass (or silicate). This dissolution can induce roughness of the cell surface and reduce the intensity of the laser light.

Second, the fluid cell should be cleaned after it has been exposed to a liquid other than clean water. For all experiments in the course of this dissertation, the liquid channels inside the cell, where liquids flow in and out during experiments, were cleaned by flowing deionized water into them ten or twelve times with a 5 ml syringe. The manufacturer suggests sonivating the cell with deionized water (not with corrosive cleaners) in Teflon or other soft containers. They also suggest placing the cell with the bottom side up so as to not damage the cell during the ultrasonic procedure.

Third, the body of the fluid cell, especially the areas where light travels in and out, should not be handled with bare hands in order to prevent grease or other impurities from being deposited. Wearing powder free latex gloves is highly recommended in handling the fluid cell.

2.2.6. Sample holder

A silicon rubber o-ring was initially intended to be placed on the bottom of fluid cell to hold liquid inside. However, in common practice the liquid usually leaked out due to gravity (Figure 2.14 (a)). A newly designed sample holder was made to resolve this problem (Figure 2.14 (b)). A circular trench of the size of the original o-ring was made on the sample holder. In this design the o-ring is now placed inside the trench on the sample holder and liquid does not leak out from the liquid region (Figure 2.14 (c)).
\[
y = C_0 + C_1x + C_2x^2
\]

\[
C_0 = -4.7 \times 10^3, \quad C_1 = 4.0, \quad C_2 = -8.3 \times 10^{-4}
\]

\[
\therefore r = \frac{1}{|2 \cdot C_2|} = 602.4 \text{ Å}
\]

Figure 2.12 An example of calculating a tip radius from a parabolic ridge of a SrTiO$_3$(305) or Mesoscale surface profile.
Figure 2.13 Schematic of a fluid cell and syringe assembly. The cantilever/tip assembly is placed underneath the transparent cell. Two syringes are used to transfer liquid into or out of the region of sample–tip contact.
The sample holder is made of ferrous metals such that it is magnetically held in place by the magnet located underneath the sample mounting plate. It was coated with the chemically inert stop-off lacquer to be protected from corrosive solutions and to prevent unwanted chemical reactions with the solutions. The coating procedure is depicted in Figure 2.15.

The sample holder was machined as designed (Figure 2.15 (a)). The details of its design are shown in Figure A.2 of Appendix. The sample holder was coated evenly with stop-off lacquer solution (volume ratio of lacquer to acetone is 2:1). The dipping process was carried out three or four times until the desired coating thickness (dark red) was reached (Figure 2.15 (b)). The evenly coated sample holder was dried overnight in the air (Figure 2.15 (c)).

Samples were attached to a coated sample holder with a Duro Supper Glue (Manco, Inc., Avon, Ohio). The sample, attached to its holder, was left in air for about an hour so that the adhesive was hardened completely. It was then mounted in the microscope for measurement.

2.3 Operational modes

Contact mode atomic force microscope has been used throughout the course of this dissertation to obtain information of the topographic and frictional properties of surfaces. Figure 2.16 shows how the normal and lateral signals are generated and processed to provide frictional and topographic information of surface. The following sub-sections will describe the details of the operational modes in terms of the acquisition of surface topography and friction.
Figure 2.14 (a) Manufacturer’s intended engagement of sample holder and fluid cell. In this arrangement, the liquid usually leaks due to gravity. (b) A newly designed sample holder. (c) New sample holder engaged with fluid cell.
Figure 2.15 Coating procedure of sample holder. (a) Un-coated sample holder. (b) Coating sample holder with stop-off lacquer solution. (c) Drying coated sample holder overnight in air.
2.3.1 Topography

In contact mode AFM, surface topography is obtained by maintaining a constant normal force acting on the tip while scanning the sample in the \( x \) and \( y \) directions. RHK STM 1000 electronics generate a feedback signal (Figure 2.16).

\[
S_F = \varepsilon = (S_{set} - S_N) \quad (2.5)
\]

where \( S_F \) is the feedback signal, \( \varepsilon \) is the error, \( S_N \) is the processed signal arising from the normal deflection of cantilever, and \( S_{set} \) is an electronic set point. This feedback signal is applied to the piezoelectric scan tube to maintain the constant normal force between the tip and the sample. The laser diode and the photodiode are operated by RHK AFM 100 electronics. The sample movements, i.e. piezoelectric tube movements, are controlled by RHK STM 1000 electronics. The RHK SPM32 software generates topographic images by displaying a feedback signal as a function of tip position. The set point of the feedback loop was always set to zero during the surface topography acquisition in this dissertation. The roughness of the surface was obtained from a topographic image by calculating the rms (root-mean-square) error of the heights of image pixels with respect to a best fit plane down through the image surface.

2.3.2 Force-distance curve and friction-load plot

Surface topography should be characterized before friction measurements because surface topography can influence the friction.\textsuperscript{13–14} After topographic images were collected, force-distance curves were obtained over the same area. Prior to the friction measurements, the normal force was calibrated using these force-distance curves and the
Figure 2.16 A schematic showing how the normal and lateral signals are generated and processed to provide frictional and topographic information of the surface.
spring constant of the cantilever suggested by the manufacturer. The details of the force calibration procedure were discussed in a previous section. The force-distance measurements also allow the detection of coupling between lateral and normal motions of the cantilever due to the incorrect alignment of the tip or sample plane with respect to each other. If the sample plane and the tip are aligned correctly, then the lateral force signal should not change during the force-distance measurements. If change is observed, the lateral force signal can be decoupled from the normal force signal by using decouple knob on the AFM 100. Adhesion between the tip and the sample surface was obtained additionally from the force-distance curves. Adhesion or the pull-off force is the force required to separate the tip completely from the sample surface after contact.\textsuperscript{15}

Immediate snap-in and snap-out points in the force-distance curves are barely detected in the aqueous solutions, yet the repulsive regime is still useful for calibration purposes (Figure 2.9 (b)). The reasons for this phenomenon can be explained in two aspects. First, the interaction forces between the tip and sample are quenched in the liquid media.\textsuperscript{16, 17} Long range van der Waals forces are significantly reduced and only short-range repulsive interactions remain in liquid. Second, high meniscus force between the tip and sample surface usually existed in air is not present in liquid.\textsuperscript{18} The presence of snap-in point and big pull-off force (10 – 50 nN) in air is partly due to the meniscus force that is formed by the organic contaminants picked up from the air. Since the sample surface was cleaned by either etching (in case of tungsten sample) or rinsing with organic solvents (in case of copper sample) prior to the force-distance measurement, organic contaminant film would barely be present on the sample surface, which eliminates the meniscus force.
After the topography acquisition and force calibration were completed, friction measurements were performed over the same area, more specifically speaking over the on-top-sites of relatively flat grains. In these measurements a voltage ramp was applied to the piezoelectric Z scan sector to load/unload the sample during friction measurements. These measurements were performed with the feedback control turned off. Signals from both normal and lateral deflections of the cantilever were obtained simultaneously during scanning. SPM 32 software generates two pairs of images. There are the forward (right-to-left) and backward (left-to-right) scan images of both normal and lateral force channels (Figure 2.17 (a) and (b)).

During scanning, a friction loop is generated. The friction-loop enables a quantitative measurement of frictional force at a specific load. Friction loops are obtained by taking the cross-sectional profile from both forward and backward lateral force images, obtained at a specific load and combining them in a single plot (Figure 2.17 (c)). The portions of steep rise and decrease of the loop are due to the twisting of the tip without sliding, and are defined as the regions of static friction. The kinetic frictional force is obtained by averaging values over the entire sliding distance (between vertical arrows or kinetic friction regime) as well as each sliding direction. This represents the frictional force reported for a specific load.

The microscope used in this dissertation makes it possible to obtain two-dimensional lateral force images where the x-dimension is related to sliding distance and the y-dimension is related to a programmed change in the applied load (Figure 2.17 (a) and (b)). These lateral force images consist of a series of friction-loops, each collected at a different load. Figure 2.17 (d) displays three individual friction-loops collected at the
Figure 2.17 Pairs (right-to-left scan and left-to-right scan) of normal and lateral force images were generated simultaneously and independently. (a) Load images. (b) Lateral force images. (c) Friction-loop taken at the load of 35 nN. (d) Friction-loops at three different load regimes. (i) and (vi): F₃ at L₁, (ii) and (v): F₂ at L₂, and (iii) and (iv): F₁ at L₁ (L₁ = 35 nN, L₂ = 17 nN, and L₃ = 35 nN). (i), (ii), and (iii): right-to-left scan, and (iv), (v), and (vi): left-to-right scan.
corresponding loads (L₁, L₂, and L₃) and displayed in a single plot. Data processing was typically accelerated by taking the average of one of the normal force maps and the difference of the two lateral force maps.

The friction image was obtained by taking a difference between the forward and backward lateral force images (Figure 2.18 (b)). Figure 2.18 (c) and (d) are the three dimensional images. These clearly show the increase and decrease of the applied load and the corresponding frictional response. Instead of taking many individual friction-loops and obtaining the corresponding frictional forces from a single friction image, SPM 32 software simply takes an average of frictional forces (or z values) along the x axis at a certain y value. This averaging process is applied over the entire y range. The average friction forces are plotted in a single plot as a function of y displacement (Figure 2.18 (f)). This is called the ‘y-average’. Only the regime of kinetic friction in the friction image is considered in calculating the y-average (dotted area in Figure 2.18 (b)). The same y-average plots are obtained from a corresponding load image (Figure 2.18 (e)). A friction-load plot is obtained by plotting friction as a function of load (Figure 2.18 (g)). This is made possible only through the common y-displacement axes. Arrows on the 3-D images and y-average plots signify the loading (↑) and unloading (↓) regimes.

2.4 Sample preparation

Tungsten and copper thin films used in these studies were provided by Agere Systems, Allentown, PA. They were grown on silicon wafers through chemical vapor deposition (CVD) by practice common within the microelectronics industry. Because of
Figure 2.18 (a) Normal force image. (b) Friction force image, (c and d) their corresponding 3-D images, and (e and f) y-average plots. (g) Friction-load plot is obtained by plotting friction as a function of load. Arrows, $\rightarrow$ and $\leftarrow$ signify loading and unloading regimes respectively.
the difference of chemical and physical properties between tungsten and copper, the cleaning process prior to the measurements is quite different.

2.4.1 Tungsten films

Tungsten thin films were grown on silicon wafers in a process typical of W film deposition within the microelectronics industry. Initially, a 10,000 Å thick SiO₂ layer on top of the silicon, a 400 Å Ti/TiN layer for adhesion promotion, and a 500 Å tungsten seed layer were deposited. The top layer tungsten thin film was grown by chemical vapor deposition to a thickness of ~4000 Å. For these experiments, small samples (~ 0.5 cm × 0.5 cm for AFM measurements and ~ 1 cm × 1 cm for XPS measurements) were diced from the larger wafers (diameter: 8 inches). The W thin film samples were cleaned for three minutes in HCl (conc.)+ H₂O₂ (30 %) + 6H₂O to remove residual impurities residing on the surface.²¹,²² They were then rinsed thoroughly in deionized water and dried with nitrogen gas.

CAUTION: The etching solution to clean tungsten samples is very corrosive. Always wear latex gloves, lab coat, and fully covering shoes when handling this solution. DO NOT use metallic tweezers in holding a tungsten sample in the cleaning solution. Always use Teflon tweezers.

2.4.2 Copper films

Small samples (~ 0.5 cm × 0.5 cm for AFM measurements and ~ 1 cm × 1 cm for stylus profilometer measurements) were diced from a larger wafer (diameter: 8 inches).
Copper samples were then cleaned with iso-propyl alcohol, ethanol, de-ionized water and dried in nitrogen gas.

Samples for the stylus profilometer measurements were prepared through additional steps. Half of a copper sample was coated with stop-off lacquer and was dipped into the 1 M solution of HNO₃ until the other half was completely etched away. *CAUTION: 1 M HNO₃ solutions are very corrosive. Always wear latex gloves, lab coat, and fully covering shoes when handling this solution. DO NOT use metallic tweezers in the HNO₃ solution. Always use Teflon tweezers.*

The sample taken out from the nitric acid container was rinsed with deionized water. The residual lacquer was removed by acetone. This procedure resulted in half of the silicon substrate being covered with copper while the other half is exposed to the air. These samples were rinsed thoroughly with deionized water and dried in flowing nitrogen gas prior to the profilometry measurements.
2.5 References

1. Bedoya, C.; Muller, Ch.; Baudour, J.-L.; Madigou, V.; Anne, M.; Roubin, M.
   
   Materials Science and Engineering 2000, B75, 43.


5. Wiederhold, K. P.; Yamaguchi, Y.; Ayala, A.; Matheaus, M.; Gutierrez, C. J.;


   173, 183.

8. Lenihan, T. G.; Malshe, A. P.; Brown, W. D.; Schaper, L. W. Thin Solid Films 1995,
   270, 356.


    1993, 48, 5675.


CHAPTER 3

pH-MEDIATED FRICTIONAL FORCES AT TUNGSTEN SURFACES IN AQUEOUS ENVIRONMENTS

3.1 Introduction

CMP slurries are often tailored by adjusting variables such as solution pH, oxidizing agents, concentration, and the size and composition of abrasives. The systematic study of the role of the individual components is discussed in the course of this dissertation. In this chapter, the influence of solution pH and abrasive composition on interfacial friction is discussed.

The shearing of two solid bodies in contact and the magnitude of the resulting frictional forces are topics related to many everyday events and to many industrial applications. In some instances, low friction is desirable, as in the case of lubricated mechanical contacts of machinery. However, in other instances, such as the braking of a device in motion or the polishing of an interface, high friction is considered a desirable property. Interfacial design of applications where friction is to be controlled requires the knowledge of what properties of an interface influence the frictional behavior. Traditionally, fundamental studies of properties affecting interfacial friction have been limited by the buried nature of the sliding interface and the ill-defined nature (composition and geometry) of the contact. Studies performed with the atomic force microscope (AFM)\textsuperscript{1,2} and the surface forces apparatus (SFA)\textsuperscript{3} have begun to address
these limitations and to demonstrate a range of chemical and physical effects associated with interfacial friction.

In the work discussed in this chapter, I have employed the AFM to measure the interfacial forces (load, friction, and adhesion) exhibited for the contact of tungsten surfaces with either silicon nitride or alumina particles. In this work, AFM tips of different compositions have been used to model the interaction of a single particle with the tungsten surface. Furthermore, these measurements have been carried out in aqueous solutions as a function of solution pH. The study of these specific interfaces is relevant to the chemical mechanical planarization (CMP) of tungsten films within the microelectronics industry. In the polishing of advanced materials, the surface is generally subject to both chemical interactions with slurry components and physical interactions with the abrasive particles contained in the slurry. The objective of the process is to produce smooth and evenly polished surfaces. In order to optimize a polishing process, a fundamental understanding of the properties influencing both friction and wear is needed.4–14

The present chapter describes an investigation of the frictional properties of tungsten films as a function of the pH of the surrounding environment. The results presented in the following sections demonstrate a systematic variation in interfacial friction related to the relative charge present on the two contacting surfaces and highlight a fundamental pathway by which interfacial friction can be modified in aqueous solutions.
3.2 Experimental

Tungsten thin films were provided by Agere Systems, Allentown, PA and were grown on silicon wafers. The details on the CVD condition of tungsten film growth and sample preparation procedure were described in Chapter 2.

The AFM was used to probe both friction and adhesion forces at the interface of the tungsten films as described in Chapter 2. Briefly, the AFM used a beam deflection technique where light from a laser diode is reflected from the back of a microfabricated cantilever on to a four-quadrant photo detector. Deflections of the cantilever normal to the surface served to monitor surface topography and interfacial adhesion. Torsion or twisting of the cantilever was indicative of frictional forces at the tip-sample interface. In these experiments, samples mounted on a piezoelectric tube scanner were translated with respect to a fixed tip position. The AFM was equipped with a liquid cell (Digital Instruments, Santa Barbara, CA) and controlled with SPM 1000 electronics and software (RHK Technology, Inc., Troy, MI).

Kinetic friction data were acquired by monitoring the lateral deflection of the cantilever as a function of position across the sample surface and the normal applied load. The kinetic friction force values presented here were averaged over both sliding direction and distance across the surface. For this work, frictional forces are presented in arbitrary units; valid comparisons of friction data are enabled through the use of the same cantilever assembly throughout a set of measurements. A series of topographic imaging procedures of both the sample surface and a mesoscopic standard ensured that substantial interfacial wear or alteration of the probe tip did not occur during the course of the experiments. The absence of significant wear of the substrate was monitored by

68
successively imaging the same area of the surface and qualitatively noting no change in surface topography. Wear of the tip was followed quantitatively by imaging a mesoscopic standard before and after a series of friction measurements. A change in tip radius of ~100-300 Å was observed over the course of several hours in which ~50 friction and topographic measurements were obtained. This represents a modest change to tip radius over the course of the numerous measurements. Furthermore, repeating friction measurements at certain pH values at the end of the series and obtaining identical results verified that changes in tip radius did not contribute to the measured trends.

The AFM measurements were carried out in aqueous solutions with silicon nitride tips (Digital Instruments, Santa Barbara, CA) and with alumina-coated tips prepared by pulsed mode DC magnetron sputtering. No effort was made to remove the native oxide of the silicon nitride tips. The pH environment of the local tip-sample interface was controlled by transferring aliquots of different solutions in and out of the liquid cell through the use of two 5 mL syringes. The solution pH was adjusted using NaCl, NaOH and HCl to minimize the number of ionic species in the solution and to maintain a relatively constant ionic strength. These changes in solution composition are not expected to significantly alter the composition of the surface beyond the protonation/deprotonation steps described below. Solution pH values were measured with a VWR Scientific 8000 pH meter incorporating a Ag/AgCl pH, gel and triode Electrode.

3.3 Results and Discussion

Frictional forces between the tungsten films and a Si₃N₄ or alumina-coated tip have
measured as a function of applied load. Friction measurements have been performed in a reciprocating fashion on a single grain over a 300 Å distance in order to avoid contributions from surface topography. An example of a single friction loop collected at a finite load is shown in Figure 3.1. As described above, the frictional forces plotted as a function of load represent values averaged over sliding distance (Figure 3.1, between vertical arrows) as well as each sliding direction.

Figure 3.2 displays representative friction-load data collected as a function of decreasing load with the silicon nitride tip at three different solution pH values. In these plots, negative loads arise from adhesion between the tip and the sample. Neglecting the slight curvature at the lowest loads, the slope of the friction-load plot is measured and defined as the frictional response. (This approach is analogous to the determination of the coefficient of friction in macroscopic systems).

The frictional responses measured as a function of solution pH are summarized in Figure 3.3 for (a) the silicon nitride tip and (b) the alumina-coated tip. The data for each pH value represent the average of six different measurements; the error bars represent the standard deviation of these measurements. A direct comparison of the friction data collected for the two tips is not possible due to the unknown differences in the relative spring constants of the cantilevers.

Independent of the friction measurements, pull-off forces have been measured as a function of solution pH for each interface according to the procedures described above. Figure 3.4 displays the variation of interfacial adhesion over the range of pH conditions investigated, measured between the tungsten surface and (a) the silicon nitride tip and (b) the alumina-coated tip. Interfacial adhesion is represented by the average pull-off force.
Figure 3.1 A single friction loop resulting from the reciprocal motion of the AFM tip over a 30 nm distance depicts regions of both static and kinetic friction. Kinetic friction values (between the vertical arrows) are measured and averaged over distance and direction as a function of load to produce the friction-load curves shown in Figure 3.2.
Figure 3.2 Friction-load plots measured for decreasing loads at three different solution pH values for the contact of a silicon nitride tip and the oxidized tungsten surface.
Figure 3.3 The frictional responses of the interfaces, defined as the slope of the friction-load plots, exhibit a clear dependence on solution pH. The interface involving (a) the silicon nitride tip possesses the maximum frictional response at 4.7, while that involving (b) the alumina-coated tip exhibits the highest response at 6.6.
Figure 3.4 Independent measurements of interfacial adhesion between the oxidized tungsten surface and (a) the silicon nitride tip and (b) the alumina-coated tip reveal a relationship between adhesive normal forces and pH, correlated to the trends observed for lateral friction forces.
values determined from force-distance curves acquired in multiple regions of the sample. Although with greater statistical spread, a trend similar to the pH dependence of the friction is observed with the maximum interfacial adhesion occurring at pH 4.7 for the silicon nitride tip and pH 6.6 for the alumina-coated tip.

Finally, it is noted that all of these measurements have been performed in the absence of significant interfacial wear. The topography of the tungsten surface was measured prior to the friction measurements obtained at each pH condition. Figure 3.5 displays a number of representative topographic images. Figure 3.5 (a) and (b) represent the topographic images taken with the Si$_3$N$_4$ tip in pH 5.4 and 3.8, respectively, shown together with the corresponding cross-sectional plots. Figure 3.5 (c) and (d) represent topographic images taken with the Al$_2$O$_3$ tip in pH 5.6 and 3.2, respectively, together with the corresponding cross-sectional plots. Both cases support absence of significant interfacial wear during the friction measurements. Small differences in feature heights and shapes in the cross-sectional plots originate from the error in reproducibly locating the same cross-sectional lines in the corresponding images.

Special care has been taken in limiting the applied load in the systems in order to avoid creating wear scars on the surface or altering the tip geometry. The absence of interfacial wear has been verified by carefully probing the topography of the regions of the friction measurements, nearby regions of the surface with high aspect ratios (particularly sensitive to tip shape), and the structure of a mesoscopic standard from which the actual tip radius can be determined.$^{15}$ Furthermore, data from initial pH conditions were re-measured and validated at the end of each experimental run (series of
Figure 3.5 Selected topographic images and their corresponding cross-sectional profiles (white solid lines on the images) of the tungsten surface were taken at different pH conditions. There is no evidence of surface deformation in either the images or cross-sectional profiles. Small differences in feature heights and shapes between the profiles originate from the error in locating the cross-sectional lines. (a) and (b): Topography of tungsten surface taken with Si$_3$N$_4$ tip. (c) and (d): Topography of tungsten surface taken with Al$_2$O$_3$ tip.
pH changes) to ensure that systematic errors were avoided. The small changes measured in tip radius over the course of many measurements represented a minor effect in light of the reproducibility of the friction results and the drastic changes in surface topography that has been observed for more aggressive solution compositions.

The adhesion and friction data presented above, dependent upon solution pH and tip composition, are interpreted in terms of the electrostatic interaction between two surfaces having different isoelectric points (IEP’s). An isoelectric point is the pH at which a material immersed in the solution has zero net charge. Below the isoelectric point, a surface is more fully protonated and is described as being positively charged. Conversely, the surface is deprotonated at a pH above the isoelectric point so that it is negatively charged. These changes are reversible with changes in solution composition and are schematically represented in Figure 3.6.

The isoelectric points of tungsten oxide, silicon nitride and alumina are summarized in Table 3.1. Although no in situ measurements of surface composition have been performed in this work, other studies have determined that WO₃ and Al₂O₃ are the expected compositions under the measurement conditions presented here. Previous determinations of the IEP of silicon nitride have made no attempts to remove the native oxide and the cited values therefore reflect its presence.

For the interface between two materials of significantly different isoelectric points, the interfacial interaction will be determined by the relative charge on the two surfaces, interacting strongly when oppositely charged and weakly when similarly charged. For the interface of tungsten oxide and silicon nitride, the surfaces will be similarly charged under two sets of pH conditions: positively charged at a pH below 0.5 and negatively...
Figure 3.6 A schematic model of the tip-sample interface indicating the relative changes in surface charging as a function of pH. The isoelectric points (IEP’s) of the different surfaces describe the pH conditions under which the surface will have no net charge. Maximum interfacial forces are encountered at pH values intermediate to the IEP’s of the two contacting surfaces.
Table 3.1 Literature values of isoelectric points.

<table>
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<tr>
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<th>Isoelectric point (pH)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>6.0 ± 0.4</td>
<td>18, 19, 22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.5, 9.0-9.4</td>
<td>10, 20</td>
</tr>
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charged above \(~6.0\). For the interface of tungsten oxide and alumina, the surfaces will be positively charged at pH values below 0.5 and negatively charged above \(~9.0\). For both interfaces, opposite net charges will exist on the tip and the surface at pH values located between the isoelectric points of the two contacting materials. It is at this point that the greatest electrostatic attraction is experienced, thereby resulting in maximum friction and adhesion. As the protonation/deprotonation of the surface is an equilibrium process dependent upon solution concentrations, surface charge is expected to smoothly vary at intermediate pH values. The results presented in Figures 3.3 and 3.4 agree completely with this model. The maximum interfacial forces occur at pH 4.7 for the tungsten-silicon nitride interface and pH 6.6 for the tungsten-alumina interface and systematically fall to lower values as pH is varied from this point. For these data, the maximum interfacial force is skewed toward the higher IEP. This slight effect is thought to arise from either local variations in the surface charge or specifics of the sample or tip preparation.

Prior studies of interfacial forces in solution have also discussed the atomic-scale nature of interactions in terms of isoelectric points.\(^{18–20,22}\) These studies have demonstrated a similar pH-dependent behavior for a range of materials and solution compositions and have addressed both adhesion and interfacial friction. In particular, the work of Marti et al. investigated the friction and adhesion between an oxidized silicon surface and a silicon nitride tip.\(^{18,19}\) They discussed their results in terms of a contact area model set forth by Israelachvili et al. in which friction will scale with the degree of adhesion hysteresis (dissipated energy) and with surface topography. For systems in which the interface is very smooth, this model suggests that the frictional behavior will be most heavily influenced by the nature of interfacial adhesion. This is the case for the
interfaces investigated in the work presented here (little topographic effect), and indeed a strong correlation between adhesion and friction is observed. (The low magnitude of forces in the present study prevented the integrated measurement of adhesion hysteresis.) However, friction is proportional to both the area of interfacial contact (A) and the shear strength of the interface (τ) \( (F \sim A \tau) \), and we find that the shear strength term also must be considered. This observation is based upon the shape of the friction-load curves shown in Figure 2. In these data measured as a function of decreasing load, the adhesive interaction between the tip and the sample can be estimated from the lowest load at which friction is measured (before the tip snaps off the surface). If interfacial adhesion were the predominant effect responsible for the frictional differences and acted by effectively modifying the area of contact, different pull-off forces and parallel friction-load curves would be expected. This type of effect has been observed in the work by Marti et al.,\textsuperscript{18} in AFM investigations of humidity-dependent friction,\textsuperscript{24,25} and in AFM measurements of a platinum-mica interface.\textsuperscript{26} In this work, the friction-load curves for decreasing load exhibit very similar pull-off forces (Figure 3.2) and yet significantly different slopes (Figure 3.3). As a result, it is proposed that the frictional variations measured here are heavily influenced by a change in interfacial shear strength, which results from the systematic protonation/deprotonation of the contacting surfaces. Of course these variations will accompany small changes in relative areas of contact (indicated by changes in adhesion, Figure 3.4) that result from the electrostatic nature of the interface.

The primary conclusion drawn from these data relates to the modification of frictional forces with changes in solution composition. While interfacial friction is known to be mediated by the presence of third bodies such as lubricants, the fundamental
results presented here (for single asperity contacts, of known composition, independent of significant material removal) indicate that the frictional response of an interface embodied in an acidic or basic environment is influenced by chemical changes related to the protonation/deprotonation of the contacting surfaces, specifically through modifications of the interfacial shear strength. For applications such as CMP, these results indicate that variations in interfacial forces with changing solution conditions may also play a role in addition to more dramatic changes such as chemical oxidation or dissolution. Increases in interfacial friction and adhesion represent a fundamental pathway by which interfacial wear can be enhanced. In fact, this effect has been used by Chen, et al. to explain the removal rates of low-k polymer materials in CMP processes.\textsuperscript{27,28} The significant change in friction over the range of pH conditions investigated here indicates that any complete model of the CMP process should consider changes in atomic-scale interfacial forces as an underlying phenomenon to broader chemical and mechanical issues. For example, changes in interfacial forces of the scale reported here are entirely consistent with the observations of Stein, et al. that show polishing rates of tungsten depend on both pH and the composition of the colloidal species.\textsuperscript{29}

The data presented in this chapter show that friction forces at tungsten surfaces vary with solution pH and reach a maximum value at pH intermediate to the IEP of tungsten and silicon nitride. Within the CMP literature, it has been reported that low pH environments (below 4) stabilize tungsten oxide on the surface and prevent the agglomeration of abrasive particles through electrostatic repulsive interactions. The results presented here indicate that future modifications of tungsten CMP processes, as
well as the development of CMP processes for other materials, must also account for modified interfacial forces when altering the slurry pH. Specifically, these studies have shown that material removal can be enhanced through increased friction at pH values between the IEP of the surface and abrasive particle.

3.4 Conclusion

In this chapter, the frictional properties of tungsten films in solution have been measured \textit{in situ} with AFM as a function of tip composition and solution. Silicon nitride and alumina-coated tips have been used as models of single abrasive particles in solutions ranging in pH from 2.2 to 8.2. In these studies, the frictional responses and adhesion forces are observed to reach a maximum value at a pH value intermediate to the isoelectric points of the tip and sample surface. Systematically lower values are measured as the pH is varied from these intermediate points in either direction. The concept of isoelectric point is useful in describing the electrostatic character of the interfaces contained in solutions of varying acid-base character. The variation in the magnitude and sign of surface charge results from the protonation/deprotonation of the surfaces and leads to changes in effective area of contact and interfacial shear strength. For the atomic-scale contact of silicon nitride and alumina surfaces with the native oxide of tungsten, frictional properties appear to be most strongly influenced by pH-dependent changes to the interfacial shear strength. This work demonstrates the nature in which interfacial friction is influenced by the pH of the solution and the composition of the contacting surface. These findings further depict an atomic-scale change that must be
considered when describing the fundamental nature of interacting surfaces contained in an aqueous media.
3.5 References


CHAPTER 4

INFLUENCE OF METAL DISSOLUTION ON THE FRICTIONAL FORCES AT TUNGSTEN SURFACES: ATOMIC-LEVEL INSIGHT INTO CHEMICAL MECHANICAL PLANARIZATION PROCESSES

4.1 Introduction

Over the last decade, chemical mechanical planarization (CMP) has become firmly established as the method for planarizing multilevel metal layers within microelectronic systems. Metal CMP processes are of increasing importance as further advances demand the fabrication of smaller devices with more complex processes and new materials. Current microelectronics designs are heavily dependent on tungsten as a stable interconnect material for the first layer of connections to the transistors. When a blanket film of tungsten is deposited by chemical vapor deposition onto a patterned surface, tungsten CMP is used to remove excess material.1-2 Similar processes are used in creating Cu lines in a damascene process as well as in planarizing inter-level dielectrics.3

Although tungsten CMP has been widely investigated, uncertainty regarding the chemical nature of the interface in the presence of the polishing slurry remains.4-11 A number of studies have addressed the issue of a surface oxide layer and its role in the CMP process.7-9,12-13 Kaufmann, et al. introduced a model of tungsten CMP in 1991 based on the sequential formation of a chemically passivating barrier layer, the mechanical removal by abrasion and the chemical removal by dissolution of the abraded surface.7 Kneer et al. questioned this proposal, observing that the dissolution rate of chemically
vapor deposited (CVD) tungsten or metal tungsten is not fast enough to account for the total tungsten removal rate. Instead, they proposed a model of transgranular fracture where corrosion takes place predominantly at grain boundaries. In yet another model, Osseo-Asare and Kahn proposed that chemically-based adhesion between tungsten oxide surface species and the alumina abrasive particle surface contributes to metal removal and polishing during CMP. These widely ranging views of the tungsten removal mechanism emphasize the need for further fundamental studies of the CMP process.

In the tungsten CMP process, the surface of the metal is subject to both chemical interactions with slurry components and physical interactions with the abrasive particles contained in the slurry. Although both chemical and mechanical effects are known to be active in CMP, it has been historically difficult to discern the relative contribution of the effects without a fundamental understanding of discreet mechanisms. In an attempt to investigate the fundamental interactions within CMP, the probe tip of an atomic force microscope has been used to simulate the interaction of a single abrasive particle with the tungsten surface and measurements in different solutions have been performed to explore the influence of their respective chemistries. In this chapter, I have performed in situ measurements of friction and RMS roughness using atomic force microscopy (AFM) in 0.01 M aqueous solutions of KNO₃, KClO₃, and KIO₃ and 0.005 M, 0.01 M, and 0.02 M aqueous solutions of KIO₃. Standard silicon nitride AFM tips have been used as a model of the silica abrasives common in the CMP processes throughout the microelectronics industry. X-ray photoelectron spectroscopy (XPS) also has been used to perform the ex-situ measurements of the composition of surfaces prepared in the same chemical solutions. The experimental approach in this chapter has aimed to reduce the complexity
of actual CMP processes to the interaction of a single abrasive particle and the tungsten surface in controlled chemical conditions and to investigate the chemical aspects of the CMP process in the presence of interfacial wear.

In recent work, it has been demonstrated that a significant oxide layer exists at the tungsten-solution interface for a range of solutions and pH values. Thus, it is the influence of solution chemistry on the interaction of an amorphous tungsten oxide film with an abrasive particle that is considered in the present work. While direct information regarding the exact chemical or physical nature of the interface in solution is not accessible on the nanometer scale, the measurements presented in this study demonstrate a systematic interfacial response related to the dissolution of the tungsten surface. The present chapter also provides new microscopic insight into fundamental interactions influencing tungsten removal in CMP environments.

4.2 Experimental

All friction measurements and topographic images presented in this study were collected in an aqueous environment through use of the AFM liquid cell (Digital Instruments, Santa Barbara, CA). Interfacial friction measurements between CVD tungsten films and Si$_3$N$_4$ tips (Digital Instruments, Santa Barbara, CA) were performed in situ in 0.01 M aqueous solutions of KNO$_3$, KClO$_3$, and KIO$_3$ and 0.005 M, 0.01 M, and 0.02 M aqueous solutions of KIO$_3$. All solutions were buffered with CH$_3$CO$_2$H (0.5 M) and KCH$_3$CO$_2$ (1.74 mM) to pH 2.3. Minimal variations in ionic strength were present under these conditions. The ionic strengths of the 0.005 M, 0.01 M, and 0.02 M solutions of KIO$_3$ were calculated as 0.507 M, 0.512 M, and 0.522 M, respectively, while those of
the 0.01 M solutions of KNO₃, KClO₃, and KIO₃ were all 0.512 M. All solution pH values were measured with a VWR Scientific 8000 pH meter incorporating a Ag/AgCl pH, gel and triode electrode. Friction was plotted as a function of the applied load and the frictional response, or slope of each curve in the friction-load plot was plotted with respect to the order of the measurements.

Topographic changes of the sample surface were monitored in each solution of oxidizing agent, separately from the friction measurements. Images were acquired every 15 – 25 minutes for 250 minutes. Applied loads were minimized during the scanning procedure. After each image was collected, the liquid cell was flushed with a fresh solution of the same chemical composition in order to minimize the potential effect of dissolved tungstate ions. The reported RMS values were calculated as the standard deviation of the surface height from a best fit plane.

Potential changes (wear) in the tip radius were monitored by imaging a SrTiO₃(305) mesoscopic standard (WiTech, Germany) before and after each series of measurements. For all series of measurements, radius changes were limited to less than 6 %. It was also verified that changes in tip radius did not influence the reported frictional behavior by repeating and varying the sequence of measurements. All RMS and friction data presented in a single plot were collected with a single tip, although multiple tips were used throughout the course of study.

The chemical composition of the tungsten surface treated in various solutions was measured ex-situ using XPS. The samples were prepared in the same etching solution as before and were incubated for 1 hour in 0.01 M aqueous solutions of KNO₃, KClO₃, and KIO₃ and 0.005 M, 0.01 M, and 0.02 M aqueous solutions of KIO₃. Upon removal, each
sample was rinsed with deionized water, dried in nitrogen gas and transferred immediately into the vacuum chamber to minimize its exposure time to air (~ 5 minutes). The XPS spectra were collected on a Physical Electronics Model 5700 instrument using a monochromatic Al K$_\alpha$ X-ray (1486.6 eV) source operated at 350 W. The hemispherical analyzer was operated in the fixed retard ratio mode at a pass energy of 11.75 eV throughout. The area analyzed and the collection solid cone were fixed at 1100 µm and 5°, respectively. A resolution of ≤ 0.51 eV full width at half-maximum is attainable under these conditions.

4.3 Results

AFM was used to measure the *in-situ* interfacial friction between a tungsten surface and a silicon nitride tip in 0.01 M aqueous solutions of KNO$_3$, KClO$_3$, and KIO$_3$. Six measurements of friction in each chemical condition were averaged and are plotted as a function of decreasing load in Figure 4.1. The frictional response (slope of the friction load plot) is tabulated in Table 4.1. The interfacial friction at the tungsten surface in the KNO$_3$ and KClO$_3$ solutions is approximately equivalent, but that in the KIO$_3$ solution is greater by factor of two.

The influence of these solutions on the sliding contact of the Si$_3$N$_4$ tip and the tungsten surface was further investigated through time dependent measurements of the surface topography. Topographic images (0.5 µm × 0.5 µm) of the tungsten surface were obtained continuously at an applied of 0 nN for ~ 4 hours in 0.01 M aqueous solutions of KNO$_3$, KClO$_3$, and KIO$_3$. At 15 – 25 minute intervals, the RMS surface roughness was
Figure 4.1 Friction-load plots measured for decreasing loads at 0.01 M aqueous solutions of KNO₃ (□), KClO₃ (Δ), and KIO₃ (○) for the contact of a silicon nitride tip and the tungsten surface.
Figure 4.2 The RMS roughness of the tungsten surfaces was measured from the topographic images (0.5 µm × 0.5 µm) taken in 0.01 M aqueous solutions of KNO₃ (□), KClO₃ (△), and KIO₃ (○) in every 15 – 25 minutes for ~ 4 hours and plotted as a function of time.
Table 4.1 Surface composition, frictional response, and $\Delta$RMS of tungsten films in 0.01M aqueous solutions of KNO$_3$, KClO$_3$, and KIO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Surface composition (%)</th>
<th>Frictional response (a.u)</th>
<th>$\Delta$ RMS over ~ 4 hours (nm)</th>
</tr>
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<tbody>
<tr>
<td>0.01 M KNO$_3$</td>
<td>W 48, WO$_2$ 36, WO$_3$ 16</td>
<td>4.0 ± 0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>0.01 M KClO$_3$</td>
<td>W 56, WO$_2$ 28, WO$_3$ 16</td>
<td>4.1 ± 0.1</td>
<td>1.8</td>
</tr>
<tr>
<td>0.01 M KIO$_3$</td>
<td>W 15, WO$_2$ 16, WO$_3$ 70</td>
<td>8.0 ± 0.3</td>
<td>4.1</td>
</tr>
</tbody>
</table>
measured from an image. The data are plotted as a function of imaging (contact) time in Figure 4.2. The initial RMS values of all of the tungsten samples were approximately the same (22.5 – 23.4 nm). Over time the RMS values of the tungsten surface in KNO₃ and KClO₃ solutions decreased by ~ 10 %, however, the RMS values of the tungsten surface in KIO₃ are reduced by ~ 20 %, indicating a significantly greater change in surface morphology (effective polishing) in KIO₃ as compared to KNO₃ and KClO₃. Absolute changes in the RMS values that occurred over a ~ 4 hour period for surfaces in the different solutions are tabulated in Table 4.1. In all cases, concurrent measurements of the tip radius verified that changes in the properties of the tip did not dominate the observed effects.

Additional evidence for differences in the chemical/mechanical behavior was obtained through comparative analysis of the surface region imaged for the extended times. To accomplish this, the scan area was expanded to a 1 µm × 1 µm area to include the 0.5 µm × 0.5 µm area imaged in the three solutions. Figure 4.3 (a) and (c) displays the larger topographic images of the tungsten surface in KNO₃ and KIO₃ solutions, respectively. The dotted square boxes centered in the images represent the repeatedly scanned areas. Four hours of repetitive scanning in KNO₃ at an applied load of 0 nN did not deform the tungsten surface. This is clearly indicated by the similarities in the cross-sectional plots of surface height collected before and after the time-dependent RMS measurements (Figure 4.3 (b)). Likewise, no substantial change in the tungsten surface topography imaged in KClO₃ solution was observed. However, a significant deformation of the tungsten surface imaged in KIO₃ solution was observed as evidenced by the square hole apparent in the image (Figure 4.3 (c)) and the significant difference in the cross-
Figure 4.3 The scan area was expanded to 1 µm × 1 µm before and after ~ 4 hours repeated scanning of a 0.5 µm × 0.5 µm area of the tungsten surfaces in 0.01 M aqueous solutions of KNO₃, KClO₃, and KIO₃. Two vertical arrows in each profile indicate the traveling range of tip during the repeated scanning. (a) An expanded topographic image (1 µm × 1 µm) taken of the tungsten surface after repeated scanning in 0.01 M KNO₃ and (b) a cross-sectional profile from the corresponding white cross-sectional line on the image. (c) An expanded topographic image (1 µm × 1 µm) taken of the tungsten surface after corresponding repeated scanning in 0.01 M KIO₃ and (d) a cross-sectional profile from the corresponding white cross-sectional line on the image. The two vertical arrows in the profiles of (b) and (d) indicate the traveling range of the tip during the 0.5 µm repeated scanning. The dotted and solid lines denote, respectively, the cross-sectional profiles obtained from the topographic images before and after the repeated scan.
sectional profile (Figure 4.3 (d)). Two vertical arrows in each profile indicate the traveling range of tip during the repeated scanning. Again, the AFM data depict a greater degree of material removal occurs in KIO3 solution as compared to KNO3 and KClO3 solutions.

XPS spectra were acquired ex-situ of tungsten films incubated for 1 hour in 0.01 M aqueous solutions of KNO3, KClO3, and KIO3 in order to observe compositional changes of the tungsten surface treated with a range of oxidizing agents (Figure 4.4). The detailed chemical composition of the surface region was assessed by deconvolution and integration of the XPS spectra. For samples removed from 0.01 M solutions of KNO3, and KClO3, tungsten 4f7/2 peaks were observed at 31.4, 33.6 and 35.6 eV and assigned to W, WO2 (W4+), and WO3 (W6+). These features correspond well with literature values.16 For samples incubated in 0.01 M KIO3 solution, tungsten 4f7/2 peaks were observed at 31.4 and 33.6 eV as before and similarly assigned. However, the 4f7/2 peak position of WO3 (W6+) was observed at 36.0 eV, shifted by 0.4 eV in comparison to the samples treated in KNO3 and KClO3. In all cases, the corresponding 4f5/2 peak was observed with a 2.0 eV energy splitting. Integrated peak intensities of the different tungsten states allowed the calculation of the relative surface composition of each sample. These values are reported in Table 4.1. These data clearly indicate a greater degree of surface oxidation through the greater presence of WO3, at the surface treated in the KIO3 solution.

The influence of solution composition was further investigated through in-situ AFM measurements of interfacial friction between a tungsten surface and silicon nitride tip in 0.005 M, 0.01 M and 0.02 M KIO3 solutions. As before six measurements of friction in each chemical condition were averaged and plotted as a function of decreasing
Figure 4.4 (a) XPS spectra (W$_{4f}$ region) obtained from tungsten surfaces following 1 hour incubation in 0.01 M aqueous solutions of (a) KNO$_3$, (b) KClO$_3$, and (c) KIO$_3$. 
Figure 4.5  Friction-load plots measured in 0.005 M (□), 0.010 M (△), and 0.020 M KIO₃ (○) solutions. Data represent the frictional response of a contact between a silicon nitride tip and the tungsten surface, measured as a function decreasing load. Note that different tips were used for the measurements of data presented in Figure 4.1 and 4.5 and thus prevent a direct comparison of the values.
Table 4.2 Surface composition, frictional response, and $\Delta$RMS of tungsten films in 0.005 M, 0.01M, and 0.02 M aqueous solutions of KIO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Surface composition (%)</th>
<th>Frictional response (a.u)</th>
<th>$\Delta$ RMS over ~ 4 hours (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W</td>
<td>WO$_2$</td>
<td>WO$_3$</td>
</tr>
<tr>
<td>0.005 M KIO$_3$</td>
<td>17</td>
<td>21</td>
<td>62</td>
</tr>
<tr>
<td>0.01 M KIO$_3$</td>
<td>18</td>
<td>19</td>
<td>64</td>
</tr>
<tr>
<td>0.02 M KIO$_3$</td>
<td>21</td>
<td>21</td>
<td>58</td>
</tr>
</tbody>
</table>
load (Figure 4.5). The slope of each data set in Figure 4.5 was calculated and tabulated as an average frictional response in Table 4.2. The frictional response increases gradually with increasing concentration of KIO$_3$. The difference in absolute interfacial friction is only evident at the higher applied loads.

The surface topography (0.5 µm × 0.5 µm) was recorded in-situ at 15 – 25 minute intervals over a ~ 4 hour period for tungsten samples immersed in 0.005 M, 0.01 M and 0.02 M aqueous solutions of KIO$_3$. The RMS roughness was calculated from these images, and plotted as a function of time (Figure 4.6). For all concentrations of KIO$_3$, RMS values decrease with increasing scan time, however a greater reduction in roughness (effective polishing) is observed for the tungsten sample in the 0.02 M KIO$_3$ solution. From the experimental results presented in Figure 4.5, this reduction in roughness is understood to occur through a tip mediated dissolution mechanism where only the region being scanned undergoes a change. Absolute changes in the RMS values that occurred over a ~ 4 hour period for surfaces in the different solutions are tabulated in Table 4.2.

XPS spectra acquired ex situ for the tungsten surfaces immersed in 0.005 M, 0.01 M and 0.02 M solutions of KIO$_3$ for 1 hour (Figure 4.7 (a)) revealed a small amount of carbon (non-carbidic) on each tungsten surface. This is believed to arise through the sample transfer process and does not adversely affect the quantitative assessment of tungsten species present. The percent composition of the tungsten region was again evaluated through the deconvolution of the tungsten 4f regions. The results of this analysis are presented in Table 4.2 and indicate that the small variation in KIO$_3$ concentration leading to the observed changes in frictional response and tip mediated
Figure 4.6 The RMS roughness of the tungsten surfaces was measured from the topographic images (0.5 µm × 0.5 µm) acquired in 0.005 M (□), 0.01 M (△), and 0.02 M (○) KIO$_3$ at 15 ~ 25 minute intervals over a period of for ~ 4 hours.
Figure 4.7 XPS spectra ($W_{4f}$ region) obtained from tungsten surfaces after one hour incubation in (a) 0.005 M, (b) 0.01 M, and (c) 0.02 M KIO$_3$. 
dissolution do not produce a large compositional difference in the surfaces, as observed for the case of different oxidants. This indicates that the degree of surface oxidation is constant over the narrow range of KIO₃ concentrations investigated here. It is believed that the difference in compositions reported for the two tungsten surfaces processed in 0.01 M KIO₃ (Tables 4.1 and 4.2) represents simple run-to-run variations in processing and deconvolution procedures and does not detract from the reported trends.

4.4 Discussion

The results presented in the previous section agree well with a number of observations made from macroscopic polishing studies of tungsten surfaces. First, the oxidation strength of KIO₃ is known to be greater than KNO₃ or KClO₃. The use of different oxidants in CMP slurries has been long known to dramatically influence the success of the polishing process. For example, the dissolution rate of tungsten films has been reported to be approximately ten times faster in KIO₃ than in KNO₃. The microscopic results presented in Figures 4.2 and 4.3, and tabulated in Table 4.1, agree with this trend. Second, the dissolution rate of various metals is known to be proportional to the concentration of oxidants. More specifically, Stein et al have reported variations in tungsten removal rates in macroscopic CMP studies with changes in KIO₃ concentrations. They observed that the polish rate of tungsten film increased with increasing concentrations of KIO₃ over the range of 0 – 0.15 M and suggested that the concentration of KIO₃ is one of the primary parameters affecting the polish rate of tungsten. In the present study, the concentration range has been limited to 0.005-0.02 M in order to minimize the variation of ionic strength among the three solutions. Yet, even
over this limited concentration range, measurable changes in the RMS values have been detected (Figure 4.6, Table 4.2).

While the present studies have not been performed under conditions exactly replicating a CMP process (low loads, slow sliding speeds, simplified slurry conditions, low concentration ranges) it is believed that the correlated use of scanning probe microscopy and surface chemical analysis provide new microscopic-level insight into CMP processes. It was observed from the XPS data that the type of oxidant used in solution heavily influences the degree of surface oxidation. In solutions of KNO₃ and KClO₃, the predominant species at the surface is WO₂ while WO₃ species dominate the surface treated in KIO₃ solutions. (Metallic tungsten detected in the XPS measurements presumable arises from the bulk metal underlying the thin oxide layer). Coupled with the RMS and in situ surface topography measurements, it is concluded that the dissolution (polishing) rate of tungsten surfaces is enhanced through a greater extent of surface oxidation and the formation of surface WO₃ species.

With respect to solution concentrations, the XPS data revealed no significant differences in the degree of surface oxidation for the tungsten samples treated in KIO₃ solutions ranging from 0.005 to 0.02 M. And yet, a measurable difference in the interfacial friction and the rate of RMS reduction is observed. Together, these results suggest a kinetic origin to the microscopic observations made from the AFM data. As described in the previous section, the dissolution of the tungsten surface, under the reported conditions, is only observed in the region of tip-surface contact (Figure 4.3). Thus it is concluded that the difference in the rate of tungsten removal (RMS reduction) in solutions of varying KIO₃ concentrations is related to the rate of surface re-oxidation,
as material is removed under the influence of the scanning tip. This rate of re-oxidation is in turn proportional to the concentration of KIO₃ in solution. This mechanism, as well as the frictional difference observed in Figure 4.5, is consistent with the model presented above relating the rate of tungsten removal to the extent of surface oxidation.

Finally, the role of interfacial friction in these processes is considered. Clearly, changes in solution conditions (composition and concentration of the oxidant) lead to variations in the interfacial friction. In the regime of wearless friction, typically that accessed through most AFM studies, frictional differences are ascribed to differences in the interfacial shear strength.²⁰⁻²¹ However, in the present study, two details point to a different mechanism through which the friction may vary. The first is the similar composition of the surface region. Although no detailed information exists regarding the fundamental shear strengths of WO₂ and WO₃, it is believed that the materials should possess similar properties simply from our observations of the similarity in the frictional properties of metal oxides of more widely varying composition. The second aspect that points to a different mechanism relates to the presence of wear in these studies. From a fundamental point of view, friction can be described as dissipative energy losses.²⁰ In the wearless regime, friction largely arises from the excitation of surface and bulk phonons that are dissipated from the contact region in the form of heat.²⁰⁻²² However in regime of wear, energy can also be accommodated through chemical action or the breaking of bonds.²⁰ It is believed that the data presented in this chapter collectively support this as the dominant mechanism leading to frictional differences. In terms of the process of tungsten removal, the greater extent of RMS reduction and localized topographic change can be correlated to the greater presence of WO₃. In turn, it is concluded that the tip-
mediated dissolution of WO$_3$ is greater than that of WO$_2$ and leads to the reported frictional variations in the different oxidizing environments.

This experimental results presented in this chapter demonstrate the complex tribochemical role of solution oxidants within CMP processes. For tungsten surfaces, it has been demonstrated that the production of WO$_3$ at the tungsten solution interface, in contrast to partial oxidation to WO$_2$, is required for localized material removal. While only a mild dependence on oxidant concentration has been observed, these studies clearly indicate that the identity of the oxidant is critical. Any future modifications of the tungsten CMP processes must include a species of oxidizing the tungsten surface to WO$_3$ in order to provide sufficient material removal rates.

4.5 Conclusion

In the context of CMP processes, the surface properties of tungsten films treated in aqueous solutions of KNO$_3$, KClO$_3$, and KIO$_3$ have been measured ex situ with XPS and in situ with AFM. Measurements of the surface composition reveal, through the greater presence of WO$_3$, a greater extent of surface oxidation in solutions of KIO$_3$ in comparison to the other solutions. No significant differences in surface composition were observed over the narrow range of KIO$_3$ concentrations investigated here. Increases in the degree of surface oxidation have been correlated on a microscopic scale to an increased rate of tungsten removal. This material removal process has been characterized as tip-mediated dissolution that occurs to a greater extent for WO$_3$ as compared to WO$_2$. Collectively, these measurements identify a fundamental pathway of material removal in tungsten CMP processes and highlight the complimentary roles of
chemical and mechanical action. It is noted, however, that additional mechanisms may also exist under more mechanically extreme conditions.
4.6 References


CHAPTER 5

MICROSCOPIC STUDIES OF FRICTION AND WEAR AT THE 
BENZOTRIAZOLE/COPPER INTERFACE

5.1 Introduction

The continual reduction of feature size within the microelectronics industry has required the development of processing steps of higher spatial precision with reduced tolerances.\(^1\) One such process involves the creation of metallic vias, leads, and passivation barriers. In production, metal layers are typically deposited onto the wafer surface by chemical vapor deposition.\(^2\) A final step in this process involves the removal of excess metal and planarization of the resulting patterned surface, and employs a complex polishing process known as chemical mechanical planarization (CMP).\(^{1-2}\) The CMP process, as the name implies, involves both chemical and mechanical action at the interface, in the form of etching and abrasion, respectively. CMP processes have been developed for tungsten,\(^3\)\(^-4\) copper,\(^2\)\(^-5\) aluminum,\(^6\) and silicon oxide\(^7\)\(^-8\) depositions and involve a wide range of parameters including oxidants,\(^9\) solution pH,\(^10\) abrasive composition and size,\(^11\)\(^-12\) and corrosion inhibitors.\(^13\)

Copper is widely used in device fabrication for interconnects due to its superior conductance and resistance to electromigration.\(^14\) However, copper has proven to be difficult to process because of its softness, causing serious problems associated with dishing, oxide erosion and surface defects in the form of scratches.\(^15\) In addition, copper is easily corroded by even mild chemical solutions. As a result, slight changes in the
chemical conditions of copper CMP slurries can drastically impact the overall success of
the intended process. A fundamental understanding of the interrelated steps in this
complex process is needed to further optimize the process with respect to cost, precision,
and environmental concerns.

Copper CMP is typically performed in acidic solutions with the support of
corrosion inhibitor such as benzotriazole (BTA or BTAH)\textsuperscript{13-14} and in neutral/alkaline
solutions without corrosion inhibitor.\textsuperscript{14,16} BTA has been used for several decades as a
corrosion inhibitor in the processing of copper and copper alloys. CMP processing of
copper under acidic conditions with BTA additives provides highly selective polishing of
copper with respect to silicon dioxide and excellent protection by the BTA layer from
isotropic etching. Copper oxide is known to be stable in neutral and alkaline media and
to protect bulk copper from dissolution.\textsuperscript{17}

The nature of the BTA layer formed over
the copper surface has been studied previously in
liquid, air and ultra-high vacuum (UHV)
environments with a range of experimental
techniques.\textsuperscript{18-23} Cho et al. employed UHV
scanning tunneling microscopy (STM) to
demonstrate that BTA molecules react with copper to form a Cu-BTA complex. They
obtained real space molecular images of a BTA layer chemisorbed on Cu(110)\textsuperscript{18} and
observed the formation of well-ordered c(4×2) superstructures consisting of planar
structures on the clean surface and cluster-like structures in regions of surface oxidation.
Vogt et al. obtained molecular STM images of BTA chemisorbed on Cu(100) surface in
aqueous environments.\textsuperscript{19} They observed an ordered BTA adlayer in H\textsubscript{2}SO\textsubscript{4} solutions, commensurate with the substrate lattice, and consisting of chain-like structures. They also observed that the BTA layer limited the dissolution of copper surfaces under the acidic conditions employed in their study. Early infrared studies by Poling of the BTA/copper complex formed upon adsorption revealed that copper is coordinated to nitrogens of 2 BTA molecules, thus forming an extended complex or polymeric structure.\textsuperscript{23}

Although the structural and chemical nature of the BTA layer on copper surface has been studied, efforts to relate these properties to real CMP processes have been limited. In actual CMP processes, the existence of an irregular copper surface and the presence of interfacial friction and wear contribute to the overall process. In the present study, atomic force microscopy (AFM) has been employed to investigate the BTA/copper interface in aqueous solutions, thus emulating slurry conditions. With this approach, the mechanical processing of a copper surface has been modeled by simulating the action of a single abrasive particle with the AFM tip. The native oxide of a Si\textsubscript{3}N\textsubscript{4} tip is taken to loosely model that of silica abrasives used in the CMP processing of copper. In addition, this approach has provided microscopic insight into the cooperative influence of chemical and mechanical action. Parallel measurements performed \textit{ex situ} with stylus profilometry following treatment of the copper films in identical solutions have been used to determine the relative changes in the copper film thickness. In these studies, we have observed that BTA protects copper surfaces from dissolution under acidic conditions, that unprotected copper surfaces undergo etching under acidic conditions in an isotropic fashion, and that mechanical action within the BTA/copper complex overlayer provides a pathway for localized material removal.
5.2 Experimental

An atomic force microscope (AFM) fitted with a liquid cell has been used to measure the frictional properties and topography of the copper films. The AFM was controlled with RHK Technology (Rochester Hills, MI) SPM1000 electronics and software. The frictional properties of a given interface have been evaluated by measuring the frictional force as a function of applied normal load. In this procedure, friction is reported as a value averaged over sliding distance (30 nm), direction, and physical location on the sample surface. The slope of the plot of friction versus load is reported as the frictional response of a surface. Effort was made to perform the friction measurement on top of the grains (50 – 100 nm in width).

Copper samples have been provided by Agere Systems, Allentown, PA. The thin copper films were deposited on 8.0 inch silicon wafers by CVD. Smaller samples (0.5mm x 0.5 mm) were sectioned from the larger wafer for the measurements described here. Prior to being mounted in the microscope, the copper films were cleaned with isopropyl alcohol, ethanol, de-ionized water and dried in nitrogen gas.

Interfacial friction and topography were measured in situ with a Si$_3$N$_4$ tip (Digital Instruments, Santa Barbara, CA) in solutions of 0.10 M HNO$_3$ (pH 1.2), 0.01 M BTA (pH 6.7) and 0.10 M HNO$_3$ + 0.01 M BTA (pH 1.3). No effort was made to remove the native oxide from the tip. Nitric acid solutions were prepared from conc. HNO$_3$ (68.0 – 70.0 %, EM Science, Gibbstown, NJ). Benzotriazole was obtained from Acros Organics, New Jersey and used without further purification. Solution pH values were measured with a VWR Scientific 8000 pH meter incorporating an Ag/AgCl pH, gel and triode
electrode. In order to avoid uncontrolled changes in the surface region, measurements were made sequentially in the different solutions without removing the copper film from solution. Each solution was transferred directly into and out of the tip-sample interface and the liquid cell was flushed with deionized water for 30-45 minutes before introducing a new solution composition.

All AFM measurements have been repeated with a different sequence and different tip. No significant differences for those reported here were observed. Furthermore, tip-effects in the form of changes in the radius of curvature were excluded by before and after imaging of a SrTiO$_3$ (305) standard (Wltech, Germany). For the measurements reported here, the tip radius was estimated as $728.5 \pm 135.0$ Å before measurements, and $810.8 \pm 135.4$ Å after measurements. We do not believe that this modest change (~10%) over the course of numerous measurements has significantly contributed to the observed changes in friction and experience.

Surface topography ($0.5 \mu m \times 0.5 \mu m$) was collected every 3 – 5 minute for about 100 minutes in 0.10 M HNO$_3$ and 0.10 M HNO$_3$ + 0.01 M BTA independently from friction measurements. An expanded image ($1 \mu m \times 1 \mu m$) was also collected before and after the repeated scans of smaller area. Right after an image was obtained, the solution was replaced with a new solution to further simulate continuous addition of slurry onto the wafer surface in real CMP process. No external load (0 nN) was applied during topography acquisition.

A Dektak IIA stylus profilometer (Sloan Technology Corporation, Santa Barbara, CA) was used to monitor changes in copper film thickness before and after 1.0 hour incubation in the various solutions investigated. To prepare for these measurements, a set
of samples was generated in which the thin copper film was removed from one half of the surface. This was accomplished by coating one half of the surface with stop-off lacquer, which in turn was air-dried for an hour. These films were incubated in 1.0 M HNO₃ solution until the uncoated portion of the copper film was removed, exposing the underlying silicon surface. These samples were rinsed thoroughly with deionized water, treated with acetone to remove the stop-off lacquer, and then rinsed again with deionized water. Step profiles were measured by profilometry on these samples following treatment in the solutions described above. The reported changes in the film are entirely representative of five separate profilometer measurements made across the length of the copper step.

5.3 Results

The interfacial friction between a silicon nitride tip and the CVD copper surface immersed in 0.10 M HNO₃, 0.01 M BTA and 0.10 M HNO₃ + 0.01 M BTA was measured on a microscopic scale in the absence of substantial changes to the tip. Friction was measured as a function of both increasing and decreasing load. By performing the series of measurements with the identical tip, we are able to directly compare the frictional responses as function of solution composition. Figure 5.1 displays the average of six measurements of friction at different surface locations in each solution. Data for decreasing loads are shown here and do not significantly differ from that collected for increasing loads. The slope of each curve in Figure 5.1 is defined as the frictional response and is tabulated in Table 5.1. Several comparisons are evident from this data.
Figure 5.1 Interfacial friction of copper surface was measured *in-situ* with AFM in (○) 0.1 M HNO₃ (pH 1.2) (●) 0.1 M HNO₃ + 0.01 M BTA (pH 1.3) (■) 0.01M BTA (pH 6.7). All friction measurements have been repeated with a different sequence and no significant differences for the frictional trend reported here were observed.
Table 6.1 The change of film thickness, frictional response, and surface topography of copper surface in 0.1 M HNO₃, 0.1 M HNO₃ + 0.01 M BTA, and 0.01 M BTA.

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>Film thickness (µm)</th>
<th>Frictional response (a.u.)</th>
<th>Topography</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HNO₃ (pH 1.2)</td>
<td>Before: 2.43 ± 0.05</td>
<td>1.43 ± 0.10</td>
<td>No significant change</td>
</tr>
<tr>
<td></td>
<td>After: 1.69 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01 M BTA (pH 6.7)</td>
<td>Before: 2.40 ± 0.02</td>
<td>2.16 ± 0.09</td>
<td>Formation of a shallow square hole</td>
</tr>
<tr>
<td></td>
<td>After: 2.43 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M HNO₃ + 0.01 M BTA (pH 1.3)</td>
<td>Before: 2.42 ± 0.03</td>
<td>7.64 ± 0.25</td>
<td>Formation of a deep square hole</td>
</tr>
<tr>
<td></td>
<td>After: 2.65 ± 0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
First, the frictional response of the copper surface immersed in 0.01 M BTA is slightly higher than that measured at copper surfaces immersed in 0.1 M HNO₃. Second, the frictional response of the copper surface immersed in an acidic solution of BTA (0.1 M HNO₃ + 0.01 M BTA, pH 1.2) is approximately four fold greater than that of the surface immersed in BTA alone. While the frictional differences can be clearly correlated to changes in solution conditions, greater insight into the specific origin of the frictional differences required a more complete understanding of the interface in the different solutions.

To this end, the surface topography of the copper films was monitored as a function of time under the different solution conditions described above. In these experiments, the tip was placed in contact with the sample surface with an applied load set point of 0 nN (a small adhesive force between the tip and the sample provided a stable contact during scanning). Over the period of one hour, ~20 topographic images of a 0.5 µm × 0.5 µm area were collected. The absence of drift allowed the identical region to be continuously imaged. Before and after the one-hour period, topographic images of a larger 1 µm × 1 µm area, encompassing the smaller area, were collected. In each of these images (Figures 5.2 – 5.4), the dotted box represents the region of the smaller scan area and the solid line represents the location of the corresponding cross sectional plot of topographic height shown to the right. The arrows in the cross sectional plots indicate the width and relative proximity of the smaller scan region. Before (upper) and after (lower) images of the copper surfaces immersed in 0.10 M HNO₃, 0.01 M BTA, and 0.10 M HNO₃ + 0.01 M BTA are shown in Figures 5.2 – 5.4, respectively.

In Figure 5.2, the grain structure of the copper surface is apparent and is relatively
Figure 5.2 Surface topography of copper film (scan size: 0.5 µm × 0.5 µm) was taken in every 3 – 5 minute intervals for about an hour in 0.1 M HNO₃ (pH 1.2). The area of scan was expended to 1 µm × 1 µm and scanned (a) before and (b) after one hour’s repeated scanning of a smaller area (0.5 µm × 0.5 µm). The dotted square boxes in the images and the vertical arrows in the cross-sectional profiles denote the smaller topographic images (0.5 µm × 0.5 µm) obtained before and after the repeated scan and the corresponding trajectories that the tip moved along with.
unchanged by the one-hour incubation in 0.10 M HNO₃. In contrast to the surface in the acidic solution, the copper surface immersed in 0.01 M BTA exhibited notable changes. In Figure 5.3, the grain structure is less apparent for the copper immersed in 0.01 M BTA, due to the formation of an adsorbate overlayer (see description below). In addition, the smaller region continuously imaged is noticeable in the form of a slight depression and a somewhat blurred feature resolution, as compared to the area immediately outside the smaller scan area. Finally, topographic analysis of the copper surface held in 0.1 M HNO₃ + 0.01 M BTA exhibited drastic changes (Figure 5.4). As evident in both the image and the cross sectional plot, a localized region corresponding to the smaller scan area has been etched under repeated scanning. The depth of the feature was greater than the range of the microscope operating under the imaging conditions employed (>140 nm). As with the weak effect observed in solutions of BTA alone, the localization of the feature highlights the role of tip-surface interactions in the dissolution process. In addition, substantial changes outside this small area were noted in the surface topography of the surface immersed in acidic solutions of BTA. In general, the size of the surface features was observed to increase over time and indicated a significant chemical modification of the copper surface in this solution apart from any mechanical action.

Greater insight into the relative contributions of chemical and mechanical action to the interfacial interactions at the copper surfaces was provided through *ex situ* stylus profilometry measurements. For these studies, the copper film was selectively removed from the silicon substrate by the procedures described above to reveal a step profile with a height equivalent to the thickness of the copper film. Before and after the immersion of the fabricated copper steps in solutions of 0.10 M HNO₃, 0.01 M BTA, and 0.10 M
Figure 5.3 Surface topography of copper film (scan size: 0.5 µm × 0.5 µm) was taken in every 3 – 5 minute intervals for about an hour in 0.01 M BTA (pH 6.7). The area of scan was expended to 1 µm × 1 µm and scanned (a) before and (b) after one hour’s repeated scanning of a smaller area (0.5 µm × 0.5 µm). The dotted square boxes in the images and the vertical arrows in the cross-sectional profiles denote the smaller topographic images (0.5 µm × 0.5 µm) obtained before and after the repeated scan and the corresponding trajectories that the tip moved along with. Formation of the square hole after the repeated scan is indicative of the tip-mediated dissolution of the BTA-Cu layer.
Figure 5.4 Surface topography of copper film (scan size: 0.5 µm × 0.5 µm) was taken in every 3 – 5 minute intervals for about an hour in 0.1 M HNO₃ + 0.01 M BTA (pH 1.3). The area of scan was expended to 1 µm × 1 µm and scanned (a) before and (b) after one hour’s repeated scanning of a smaller area (0.5 µm × 0.5 µm). The dotted square boxes in the images and the vertical arrows in the cross-sectional profiles denote the smaller topographic images (0.5 µm × 0.5 µm) obtained before and after the repeated scan and the corresponding trajectories that the tip moved along with. Formation of the square hole after the repeated scan is indicative of the tip-mediated dissolution of the BTA-Cu layer.
HNO₃ + 0.01 M BTA for 1 hour, the height of the copper edge was measured at more than five different locations along the length of the step profile. The quantitative values of these measurements are listed in Table 5.1. Figure 5.5 displays representative profilometry cross sections of the copper film in the region of the step for the three different solutions. Figure 5.5 (a) clearly illustrates that copper dissolves from the surface in 0.1 M HNO₃ as the step height has been reduced by ~30%. Together with the AFM topography results, we conclude that the copper surface undergoes isotropic etching under these conditions. Figure 5.5 (b) shows little change in the copper surface immersed in BTA alone. In stark contrast to other treatments, immersion in 0.1 M HNO₃ + 0.01 M BTA results in an increase in step height corresponding to ~10% (Figure 5.5 (c)). This increase in film thickness is ascribed to the formation of a reaction film composed of the BTA-copper complex.

5.4 Discussion

The experimental results described above, together with information of the composition of the interface available from other studies, provide a microscopic picture of copper CMP and identify the role of the corrosion inhibitor in the planarization process. With respect to surface composition, previous studies have indicated that copper oxide (Cu₂O) at the copper surface is unstable and dissolves under in highly acidic conditions while it is stable and persists over the pH range 6.0 to 12.0.¹⁷,²⁰ Furthermore, as shown through the profilometry studies above as well as through other investigations,²⁵ low pH solutions also act to dissolve or etch the bare copper surface. Under neutral conditions containing the corrosion inhibitor BTA, we find little change to the copper film thickness;
Figure 5.5 Step profiles of the copper films on silicon surfaces were obtained with a stylus profilometer. Film thickness was measured before and after each sample was treated for 1 hour in (a) 0.1 M HNO₃ (pH 1.2) (b) 0.01M BTA (pH 6.7) (c) 0.1 M HNO₃ + 0.01 M BTA (pH 1.3), respectively.
however, a thick overlayer is formed when the copper film is immersed in acidified solutions of BTA (Figure 5c). A number of techniques have been employed to measure the dependence of BTA film growth on solution pH. Xu, et al measured the thickness of BTA films formed on copper surfaces in BTA solutions with pH values ranging from 2.0 to 12.0 with using ultraviolet spectroscopy. They observed that the film thickness increased dramatically as the pH was lowered from 7.0 to 2.0. No substantial film growth was observed at pH values above 7.0. The formation of a dense overlayer film has also been detected under acidic conditions by Cohen, et al, Poling, et al, and Mansfeld, et al using XPS, IR spectroscopy, and ellipsometry. Most notably, the XPS studies indicated that a thick BTA-copper complex film grown at pH 2 contained the Cu$^+$ ion with a 1:1 BTA to Cu$^+$ ratio. From these studies, we understand the AFM tip in our studies of the 0.10 M HNO$_3$, 0.01 M BTA, and 0.10 M HNO$_3$ + 0.01 M BTA solutions to be in contact with metallic copper, a thin layer of chemisorbed BTA, and a thick interfacial layer of a BTA-copper complex, respectively.

The microscopic picture of copper planarization is completed by coupling this understanding to the measurements of topography and interfacial friction in the different solutions. AFM measurements in solutions of 0.1 M HNO$_3$ revealed little localized change to the surface morphology under the action of the tip (again, modeling the action of a single abrasive particle). Coupled with the profilometry measurements, we conclude that copper surfaces in highly acidic conditions undergo isotropic dissolution or etching, a process that does not serve to planarize the surface because it is not a localized effect. In solutions of 0.01M BTA alone, only a very slight topographic effect was noted in the AFM measurements with no change in film thickness indicated in the step profile
measurements. This result highlights that mechanical action (albeit at very low loads in this model study) is not sufficient to alter the copper surface and that there exists the need for significant chemical action as well. The absence of significant reactivity in 0.01 M BTA solutions is ascribed to the rate limiting production of Cu$^+$ ions under neutral conditions.

In contrast to these two solutions, the treatment of copper in acidified solutions of the corrosion inhibitor BTA resulted in both significant chemical action as well as localized mechanical action. As described before, and as indicated in the profilometry data of this study, copper surfaces undergo reaction in 0.1 M HNO$_3$ + 0.01 M BTA solutions to form a substantial (~230 nm) reaction overlayer composed of a BTA-copper complex. While we have not determined the growth rate of the overlayer film nor its thickness limit, we believe that its thickness will be ultimately limited due to kinetically limited diffusion of Cu$^+$ and H$^+$ through the film. The formation of this film resulted in the presence of significantly higher interfacial friction than either of the other two surfaces (Figure 5.1). On a microscopic scale, we attribute the higher friction predominantly to an increase in energy dissipation at the sliding interface (Figure 5.6). This model is strongly supported by the AFM topographic measurements that reveal the presence of substantial interface deformation under prolonged scanning and indicate that energy is dissipated through the localized dissolution of the BTA-copper complex film (Figure 5.4).

From a CMP perspective, the combined influence of interfacial film formation and film removal under mechanical action serve to planarize the copper in the following way. Under polishing conditions, the interfacial reaction film will be formed across the
Figure 5.6 A schematic of energy dissipation through the dissolution process of BTA-Cu polymeric layer.
entire copper surface. The microscopic theory of interfacial contact dictates that the most protruding features of copper surface (asperities) will experience the greatest mechanical interaction with the abrasive particles found within the slurry. Under this mechanical action, the BTA copper complex film will be removed in this localized region, which will in turn undergo further reaction with the $0.1 \text{ M } \text{HNO}_3 + 0.01 \text{ M BTA}$ solution, effectively removing copper from the surface. The continuation of this process at the high points across the surface, while low points remain relatively protected by the film formed by reaction with the BTA (corrosion inhibition) provides the pathway to copper planarization.

Within the CMP community, soft materials have been notoriously difficult to process. For copper surfaces, the incorporation of BTA as a corrosion inhibitor has proven to provide highly planar surfaces. The microscopic studies presented in this chapter demonstrate the complex role that BTA plays in the overall process, far in excess of the simple prevention of isotropic etching. The formation of an interfacial reaction layer composed of a BTA-Cu complex provides a mechanism of localized material removal through mechanical action. This mechanism is related to the mechanical properties and relative solubility of the reaction layer, as evidenced through enhanced friction and material removal under appropriate solution conditions. These studies suggest that CMP processing of other soft materials may also benefit from significant interfacial reaction film formation, which likewise serves multiple roles in the overall process.
5.5 Conclusion

In this study, interfacial friction and microscopic changes in surface topography have been measured \textit{in situ} with AFM for CVD copper films immersed in nitric acid and in acidic and neutral solutions of benzotriazole (BTA), a known corrosion inhibitor. In addition, changes in the thickness of the copper film have been measured \textit{ex-situ} using stylus profilometry as a function of solution treatment. Together, these studies reveal a process of isotropic dissolution in 0.10 M HNO$_3$ solutions containing no corrosion inhibitor. Little change in the interfacial properties of the copper film has been observed in neutral solutions of BTA. However, the formation of a reaction overlayer, the presence of higher interfacial friction, and the tip-mediated, localized dissolution of copper interface has been observed in acidified solutions of BTA. Collectively these microscopic studies portray the multifunctional role of BTA in the copper CMP process. In regions not experiencing mechanical abrasion, the presence of BTA acts to passivate the surface from isotropic etching by the acid through the formation of a BTA-copper complex. However, at microasperity protrusions, the presence of BTA and the resulting interfacial reaction layer leads to the localized removal of copper through a process of mechanically activated dissolution and the reformation of the reaction layer. These studies further demonstrate the role of microscopic investigations in deciphering the elementary steps of synergistic processes involving tribological interactions.
5.6 References


CHAPTER 6

CONCLUDING DISCUSSION

6.1 Summary of Results

In this dissertation, atomic force microscopy (AFM) has been used to investigate the frictional properties of tungsten and copper surfaces in a variety of aqueous solutions. A small AFM tip has been used to simulate the contact of a single microasperity with tungsten and copper surfaces. These studies have been performed in the context of chemical mechanical planarization (CMP) processes. Following an introduction to CMP in Chapter 1, a description of the novel experimental approach used in these studies is described in Chapter 2.

In Chapter 3, the influence of solution pH and tip composition on the interfacial friction and adhesion of tungsten surfaces is described. Bare or Al₂O₃ coated Si₃N₄ tip have been used to emulate a single abrasive particle in tungsten CMP slurries. The frictional response as well as adhesion force reached a maximum value at the pH located between the isoelectric points of the tungsten and tip surfaces (4.7 in W/Si₃N₄ and 6.6 in W/Al₂O₃). This occurs because the protonation/deprotonation of both surfaces depends on solution pH and leads to the variation in the magnitude and sign of surface charge, which in turn causes changes in the effective area of contact and interfacial shear strength.

In Chapter 4, the surface composition and interfacial friction of tungsten films in aqueous solutions of KNO₃, KClO₃, and KIO₃, investigated ex-situ with XPS and in-situ with AFM, are described. The measurement of the surface composition revealed a
greater degree of surface oxidation (WO$_3$) in KIO$_3$ solutions in comparison with the other solutions. Small variations in the concentration of KIO$_3$ did not change the extent of tungsten oxidation at the surface of tungsten film. The degree of surface oxidation was correlated with a microscopic tungsten removal rate. The increase of material removal rate in KIO$_3$ in comparison with KClO$_3$ and KNO$_3$ solutions is due to the tip-mediated dissolution that occurs to a greater extent for WO$_3$ as compared to WO$_2$. There was a noticeable variation in the material removal rate with changing KIO$_3$ concentrations, despite the same degree of the oxidation of tungsten. This is a kinetic effect due to the relative rates of dissolution and re-oxidation of the tungsten surface. The change of the solution conditions, both the composition and concentration of the oxidant, results in differences in the interfacial friction of the tungsten surface. This frictional variation is due to the energy dissipation associated with the dissolution process of the tungsten oxide.

In Chapter 5, the influence of BTA absorption on the interfacial friction of copper surfaces and the growth mechanism of polymeric BTA film on the copper surface were investigated in-situ with AFM and ex-situ with stylus profilometer. From the step profiles obtained from a stylus profilometry, Cu-BTA polymeric films were observed to grow thicker on the copper surface with decreasing solution pH. This is due to the acid-catalyzed formation of a Cu-BTA complex. Interfacial friction of copper surface exposed to BTA was observed to increase with decreasing solution pH, or increasing the thickness of Cu-BTA film. It is due to the energy dissipation that occurs through the dissolution of the Cu-BTA film. The tip-mediated dissolution of the Cu-BTA film was verified through the observation of square holes in the AFM topographic images of these surfaces subjected to prolonged tip-surface contact. Cu-BTA polymeric films demonstrated the
protection of copper films from dissolution in pH 1 – 7. It is proposed that BTA-Cu films provides an electron-rich environment (lone pair electrons of nitrogens and \( \pi \)-electrons of benzyl rings) and prevents reactive hydrogen ions to reach the copper surface.

From these studies, a microscopic picture of the chemical mechanical planarization of tungsten and copper is generated. High points of the surface are subject to both mechanical abrasion and chemical etching and are gradually removed. At the same time, low points of the surface are protected from both mechanical contact with abrasives and chemical etching through the presence of a passivating layer (i.e. a surface oxide layer in the case of tungsten or a BTA-Cu layer in the case of copper) until the high points of the surface are removed, and reach low points of the surface leading to a reduction in surface roughness (Figure 6.1).

These studies also revealed that the interfacial friction of metal surfaces is substantially influenced by slurry characteristics such as solution pH, the composition and concentration of an oxidizing agent, the presence of a corrosion inhibitor and the composition of the tip. Since interfacial friction is one of the critical factors influencing the efficiency of CMP processes, it must be carefully controlled while minimizing the introduction of surface defects.\(^1\) Caution needs to be exercised in order to prevent the introduction of the unwanted surface defects or contamination of the surface during the planarization process. For example, abrasive particles tend to adhere on the wafer surface at intermediate pH values between the isoelectric points of the abrasives and the wafer due to electrostatic adhesion.\(^2\)\(^3\) These studies demonstrate how these issues can be fundamentally understood as modifications to future CMP processes are introduced.
Figure 6.1 A schematic showing the planarization process of a metallic surface. Interfacial forces at the point of contact are influenced by pH, composition and energy dissipation mechanism.
6.2 The importance of in-situ microscopic studies

There are several unique features of the approach adopted in this dissertation that make it distinct from other CMP studies. First, the interactions between abrasives and the wafer surface in CMP process have been studied by simulating the contact of a single microasperity with the interface of an AFM tip and a model surface. This experimental approach has enabled the investigation of individual slurry characteristics such as solution pH, concentration, corrosion inhibitor, and oxidizers as they relate to the interfacial friction and the polishing process.

Second, every AFM measurement has been performed in solutions emulating CMP conditions. Interfacial friction and adhesion have been measured in the same microscopic area while systematically changing the chemical conditions of the aqueous media. The change of surface morphology at a certain chemical condition of the solution has also been monitored by acquiring surface topography over the same area over extended times. The frictional and morphological information of the surface obtained in a variety of chemical conditions has been related to the chemical influence of the slurry on the CMP process.

Third, the measurement scale was reduced to nanometers (nm) in length and nanonewtons (nN) in force, which enabled atomic level insight into chemical mechanical planarization processing of tungsten and copper surfaces. As wear is minimized on these scales, the chemical influence of the slurry on the planarization process could be investigated in the absence of dominating mechanical effects.

Overall, it has been demonstrated in this dissertation that AFM is a versatile tool in obtaining fundamental insight into dynamic interfacial processes. While other CMP-
related studies have utilized the atomic force microscopy, mainly for the measurements of surface morphology, the studies described in this dissertation have provided fundamental and in-situ tribological information of chemical mechanical process.

6.3 Future directions

This dissertation has focused on solution pH, the composition and concentration of an oxidizing agent, the presence and role of a corrosion inhibitor, and the tip composition and their relation to interfacial friction. These studies have provided the fundamental knowledge needed for the optimization of the CMP process. However, more work is needed to fully understand the fundamentals of the CMP process.

First, little has been done to understand the nature of the abrasives in their mechanical actions. For example, the surface topography of tungsten films has been obtained before and after friction measurements in acidic solutions (pH 2.4) using a bare and an alumina (Al\textsubscript{2}O\textsubscript{3})-coated Si\textsubscript{3}N\textsubscript{4} tips (Figure 6.2). The alumina-coated tip produced plastic deformation in the form of lines having a depth of ~ 3 nm while the bare Si\textsubscript{3}N\textsubscript{4} tip did not produce any trace. The widths of the traces are all about 30 nm and correspond to the line-scan distance applied during the friction measurements. This observation implies that alumina acts to remove more material than silicon nitride does. This observation which agrees with what Stein et al. observed on the macroscopic scale where the choice of colloidal abrasives substantially influenced the polish rate of tungsten.\textsuperscript{4} Specifically, they also found that alumina abrasives remove more material (> 100 times) than yttrium or zirconium abrasives do. These results suggest that mechanical interactions between the wafer surface and abrasive should not be overlooked. The advanced technology of
Figure 6.2 Surface topography of tungsten surface obtained (a and c) before and (b and d) after the friction measurements using (a and b) bare and (c and d) alumina (Al$_2$O$_3$) coated Si$_3$N$_4$ tip in pH 2.4. (e) A cross-sectional profile obtained from the line cross-section, A in (d). The size of all images is 0.5 µm × 0.5 µm.
depositing various materials on AFM tips should be pursued to allow for the model studies of these interactions.

Second, more work needs to be done to clarify the synergistic effects of individual slurry variables on the planarization process. For example, the polishing rate of tungsten is reported to be significantly influenced by the slurry pH, the concentration and composition of oxidizing agent, and the particle size and composition of abrasives. Further polishing efficiency can be realized by optimizing two or more slurry components together, however, little has been done to correlate the influence different variables within the CMP process.
6.4 References


APPENDIX

Figure A.1 Upper plate detail – top view and side view material brass
Figure A.2 Sample holder. Material: ferrous metal.