# ANALYSIS AND DETERMINATION OF CHEMICAL MECHANICAL PLANARIZATION MECHANISMS

# FOR TUNGSTEN AND COPPER

THESIS

# Presented to the Graduate Council of Southwest Texas State University in Partial Fulfillment of the Requirements

For the Degree

# Master of SCIENCE

By

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by

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This work is dedicated to my parents who raised me to believe I could do anything I want, and to my husband who has helped me achieve it.

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## CHAPTER 1

#### INTRODUCTION

Integrated circuits have become widely used in our society. Initially, all electronics were composed of separate elements such as resistors, capacitors, and transistors, all wired together. An integrated circuit is a large number of elements in a package that is less than a cubic centimeter. They are used in computers, cellular phones, television sets, radios, and essentially any electronic device produced.

These devices are much smaller than older transistors and vacuum tubes and have the ability to process more information at a much higher speed while being manufactured in large quantities at a very low cost. These days a state of the art microprocessor contains millions of transistors.

The construction of integrated circuits has required engineers to develop new manufacturing processes to create these small devices. In manufacturing an integrated circuit, or semiconductor device, silicon disks called wafers are run through a variety of processes designed to control the way electrical signals move through them.

Chemical Mechanical Planarization (CMP) is a process used in the semiconductor industry to remove excess material and reduce the

roughness of the surface of a wafer between the deposition of layers on a device. The CMP process is relatively new in the production of semiconductor devices coming into use throughout the industry in 1995.<sup>1</sup> It was developed to facilitate the decreasing feature size as the number of devices increased. As engineers worked on putting more function into a smaller area and making more devices per wafer, they found that the largest obstacle to overcome was the roughness of the surface on the layers. This was a problem because it limited the use of photolithography in the production of these devices.

The lithography system most commonly used today is refraction projection. In this system, light pulses through a mask and then through a high-resolution lens. The result is an image, four times smaller than the mask, being brought into focus on the surface of the wafer. This image can be repeated over and over on different positions on the wafer. A refraction projection system capable of producing multiple images in this manner is often referred to as an optical stepper. The depth of focus (DOF) of such systems, is<sup>2</sup>  $\leq$  0.5 µm<sup>2</sup>, and so the surface of the wafer must be at this focal point to produce the intended dimensions for the device. If a rough surface is present from previous processes, then various points on the surface may be outside of the focal plane of the stepper as shown in figure 1.1.



Figure 1.1 Depth of focus problems on a non-planarized surface.

If this is true, then some parts of the image may be in focus while others could be larger or smaller than the designer had intended. This may not have been a problem in the early days of semiconductor manufacturing when the transistors had features on the order of  $3-5 \mu m$ , but with features of less than  $0.25 \mu m$ , the regions masked by the photolithography process must be exact. Any distortion of the image could lead to improper placement of ion implantation, etching of an incorrect area, or masking the wrong portion of the oxide during another process. All of these problems could potentially cause device failure. In order to avoid failure at smaller dimensions, developing a way to achieve a smooth surface for photolithography became important. Thus various planarization methods were developed to level the surface of the wafer between all of the layers.

In the future, other methods of lithography may replace refraction projection as the dominant process, but the lifetime of this and other

optical techniques has been extended by CMP and other methods will still require a relatively controlled topography. Thus, CMP has become an important process for extending the capabilities of current technologies and will blend in well with future technologies as they are developed.

There are four different categories of planarization that need to be considered when discussing the results of any planarization method: smoothing, partial planarization, local planarization, and global planarization. <u>Smoothing</u> refers to the individual raised features on the surface of the wafer. In this aspect of planarization, the corners of the feature are rounded and the vertical walls become sloped, but the height of the feature remains relatively unchanged. In <u>partial planarization</u>, there is a significant height reduction of the feature, as well as the corner rounding and wall sloping seen in smoothing.

Local planarization is used to describe a procedure where the smaller gaps are filled, but the height of larger gaps is not significantly reduced. The final form of planarization, <u>global planarization</u>, is what is usually sought for processes in the semiconductor industry. In global planarization, the small gaps are filled, as in local planarization, but the total height of the step is also reduced to the height of the larger gaps so that the surface is all one height.

An alternative planarization method to CMP was the etchback planarization method. In this method, a thick dielectric layer is deposited over existing metal wiring and then coated with a sacrificial planarizing

material. A photoresist is often used as the sacrificial layer, and is then etched back by chemical means. The wafer is then etched by reactive ion etching to a relatively uniform thickness of the interlayer dielectric material.

The problem with etchback planarization is that it is local only. In order to produce global results, dummy masks or plugs must be used in conjunction with the process. A dummy mask uses a blank space in the lithography process during etching so that more material will be left at certain places on the wafer. A dummy plug is when a metal plug that is not connected to the rest of the metal contacts is placed in the wafer to allow the planarization to be more global. Thus, instead of having a hill where there is a metal plug and a valley where there is no metal, the topography of the wafer has the appearance of smoothness that would be created by having non-active metal plugs throughout the wafer.

The production of dummy plugs is time consuming and also adds unneeded components to the chip. CMP does not require the use of dummy plugs to produce global planarization and is therefore more widely used since global planarization is required for most processes.

As suggested by the name, chemical mechanical planarization involves chemical processes as well as mechanical. The combination of a chemical slurry, along with the mechanical force applied during the polishing, have combined to create the most overall global planarization seen in the industry.

The basic equipment used in most current fabs is to place the wafer into a rotating carrier and then use a polishing pad on a rotating platen with a slurry applied in between the wafer and the pad. A schematic of this set up can be seen in Figure  $1.2^3$ .



Figure 1.2 Basic Chemical Mechanical Polishing system

Looking first at the mechanical aspects, there are several factors, which must be taken into account when polishing a wafer. First of all, in order to get a uniform polish across the entire wafer, the spinning of the wafer holder and the platen must be carefully controlled. Based on past experiments, it has been determined that if the radius from the center of the platen to the edge of the wafer is known, then rotational speeds of the wafer and the platen can be chosen so that all parts of the wafer are polished equally<sup>3</sup>. See figure  $1.3^3$  for clarification.



**Figure 1.3** Mathematical relationship of wafer and platen speeds The wafer holder consists of a solid chuck and a flexible material between the chuck and the wafer called a backing film. (Figure 1.4<sup>3</sup>) The backing film is very important because it allows some give to the system to accomodate any defects present in the wafer, such as bowing or variable thickness. The result of a rigid backing to the wafer is shown in figure 1.5<sup>3</sup>.



Figure 1.4 Edge on view of chuck and platen



Figure 1.5 Result of rigid backing

Finally, the rigidity of the pad must be considered. In CMP a pad that is too soft will not planarize the wafer at all. The soft pad tends to conform to the wafer surface and removes atoms from all points at an equal rate as in figure 1.6 (a)<sup>3</sup>. A pad with the right amount of rigidity planarizes the high points on the wafer while leaving the lower points alone as in figure 1.6(b). In both pictures, the dashed line represents the final surface after polishing.



Figure 1.6 (a) A Pad that is too soft does not planarize the oxide shown. (b) The pad with the right amount of stiffness polishes the high points.

Although the mechanical role of the polishing pad in CMP has been established, the role of the chemicals and abrasive particles in the slurry still needs to be clarified. A chemical slurry is introduced to the system to induce chemical reactions, while abrasive particles suspended in the liquid help to break up the material being removed. The solution and concentration of the particles can be varied depending on what substance requires planarization. Even though using this type of slurry in conjunction with mechanical polishing works, the model for understanding how it works on a microscopic scale tends to vary between substances.

For oxide removal, the following process is believed to be true by most scientists working in the field. The first stage is the formation of hydrogen bonds. In this stage, hydrogen molecules from water molecules in the slurry bond with oxygen molecules on the surface of the wafer and with the solid particles in the slurry. Next, the hydrogen atoms which are attached to the slurry molecules and the wafer form H-H bonds, linking the wafer and the slurry together. In the third stage, a water molecule is removed from the connection leaving the slurry directly connected to the oxygen molecule on the wafer. The final stage is when the slurry molecule breaks the oxide molecule away from the surface of the wafer.

Mechanisms for metal removal are still being determined. Although the process has been optimized in industry for some metals, the understanding of the science behind these processes has not yet been

proven. There are questions as to how much of the removal is due to chemical interactions with the metal surface and how much is due to adhesion with the abrasive particles in the slurry. Each metal has different problems with the planarization process, which may hint towards individual mechanisms for each material used.

Tungsten is a relatively hard metal, which has been used for plugs in semiconductor devices since the early 1990s. Plugs are shafts of metal placed in a layer of dielectric to connect the wiring pattern on different layers. There are currently two different proposed mechanisms for tungsten CMP regarding the role of its oxidation, and it is a long term goal of this research project to prove which is correct. These mechanisms will be reviewed in Chapter 2 of this thesis, which will cover experiments relating to tungsten CMP.

Copper CMP presents different challenges because it is a much softer metal. Industry use of copper CMP has shown contamination of the oxide layers between the copper wiring pattern, as well as dishing and pitting of the copper<sup>4,5</sup>. A greater understanding of the removal mechanism for copper would help to prevent contamination and control the removal during CMP. Thus the need to understand the mechanism behind copper CMP is great. Little work has been published about copper CMP studies, and therefore leaves a wide gap open for new research. To examine the mechanism, various chemical treatments of copper films will be studied to find their effects on the roughness and removal rates.

Peroxide solutions will be looked at first as they are used in several commercial copper slurries <sup>6</sup>. Removal rates of copper will also be tested in a table top sized commercial polishing system. The removal rates will be measured using patterned copper wafers and a stylus profilometer to measure the heights of features on the wafer before and after polishing.

To create patterns in the copper films a combination of photolithography and etching of the copper will be used. This method will also be used in conjunction with the profilometer to measure the thickness of the "as received" copper film.

# CHAPTER 2

#### TUNGSTEN EXPERIMENTS

# 2.1 CURRENT THEORY

The work in this chapter has attempted to determine the mechanism for tungsten CMP. There has been no conclusive work performed to show the importance of an oxide layer, and there has even been recent research claiming that no oxide is present on the tungsten surface during polishing.<sup>7-10</sup> Experiments performed for this thesis attempt to prove which view of tungsten CMP is valid.

Kaufman, *et al*, <sup>11</sup> published the first proposed mechanism about tungsten CMP in 1991, stating that a passive oxide layer was formed on the surface of the tungsten during polishing. Kaufman proposed that this layer protected lower parts of the surface while the higher points were planarized, and that the oxide served as a limiting step to the planarization process by preventing etching of the lower regions. This mechanism also stated that the oxide layer needed to be present on the surface in order for CMP of tungsten to occur. The group used a potassium ferricyanide based slurry for their experiments and proposed

competing oxidation and etching reactions as seen in the following equations:

W + 6Fe(CN)<sub>6</sub> -<sup>3</sup> + 4H<sub>2</sub>O → WO<sub>4</sub> -<sup>2</sup> + 6Fe(CN)<sub>6</sub> -<sup>4</sup> + 8H<sup>+</sup> (etching) (2.1) W + 6Fe(CN)<sub>6</sub> -<sup>3</sup> + 3H<sub>2</sub>O → WO<sub>3</sub> + 6Fe(CN)<sub>6</sub> -<sup>4</sup> + 6H<sup>+</sup> (passivation) (2.2)

In 1996, Kneer, *et al*  $^{12}$ ,  $^{13}$  began looking at the electrochemistry of these reactions and determined that the passivation/dissolution process was not the dominant mechanism in the removal of tungsten during CMP. The group proposed that tungsten removal might be more related to corrosion assisted fracture of the grains. This conclusion was given after polished samples were examined by atomic force microscopy and potential locations for "missing" grains were noticed. However, this work was not performed with the AFM *in situ*. None of the slurry constituents used were present on the surface of the tungsten film during the scans taken.

More recent work by Stein, *et al*  $^{7-10}$  proposes that there is no oxide present on the surface of the tungsten during the polishing process. Although they witnessed oxide growth on the tungsten when placed into various species of chemicals, the group claimed that the absence of oxide on the tungsten surface could be proven through electrochemical measurements. This statement is contrary to all of the previous work and theory of tungsten CMP, which says that an oxide needs to be formed for the process to occur. With such opposing points

of view on the subject of tungsten CMP, it is obvious that more study is needed.

# 2.2 CHEMICAL EXPERIMENTS

Four chemical treatments, which have been used in industry or research experiments, were tested for their effects on the physical and chemical aspects of the tungsten surface. Two of the treatments were selected for their history of use as cleaning agents.<sup>14</sup> The solutions used for these treatments were a solution of NH<sub>4</sub>OH (.0040 M) + H<sub>2</sub>O<sub>2</sub> (.0988 M) and a solution of HCl (.0032 M) + H<sub>2</sub>O<sub>2</sub> (.0988 M). Two other treatments tested have been used as etches on tungsten in the past. These treatments were solutions of KOH (0.1 M)<sup>15</sup> and KIO<sub>3</sub> (0.1M) + NaOH (1.0M)<sup>7</sup>.

The tungsten films used for these experiments were CVD grown as follows by Lucent Technologies.  $WF_6 + SiH_4 + H_2 + Ar$  is reacted to establish the initial seed layer of 500 Å of deposited W. The final W layer is deposited through the reaction of  $WF_6 + H_2 + Ar$  and is a thickness of approximately 4000 Å. The temperature for these reactions is 425° C and the chamber where they are deposited is held at a pressure of 40 torr. The thickness of the tungsten film "as received" was verified by cross sectional examination on the scanning electron microscope (SEM), and the films were found to be approximately 4500 Å thick.

Four pieces from the same wafer used for the thickness measurements were treated with the chemical solutions listed above.

Three of the solutions were used to treat individual pieces for five minute trials, while the  $KIO_3$  (0.1M) + NaOH (1.0M) solution was used to treat a sample of tungsten film for only one minute. Once the treatments had been performed, they were analyzed by X-ray Photoelectron Spectroscopy (XPS) for information about the elements on the surface, by a four-point probe to find the resistance of the film for use in calculating the thickness, and by Atomic Force Microscopy (AFM) for roughness changes.

#### 2.2.1 XPS ANALYSIS AND RESULTS

XPS involves using collimated x-rays to excite the electrons in the sample and reading the photons that are released as the electrons drop back into their normal states. The x-rays penetrate deeply into the sample, but the electrons produced are low energy. Thus, only electrons from  $\leq 1-2$  nm near the surface can escape to be detected. XPS can be used to gain information about the elements present on the surface of a sample as well as the ionization state of those elements. Tungsten oxide can exist as WO<sub>2</sub> and WO<sub>3</sub>. Tungsten atoms bound to oxygen atoms are detected by XPS as W<sup>+4</sup> and W<sup>+6</sup> ions respectively as compared to tungsten metal atoms.

XPS measurements and analysis were performed by members of Dr. Scott Perry's group in the chemistry department at the University of Houston. To perform the measurements on our samples a PHI 5700 ESCA system with a standard Al X-ray source was used. The surface was

not pre-sputtered, but an ion gun was used as a charge neutralizer during scans. Once the scans were finished a more detailed evaluation of the data was performed by curve fits, giving the following results.

Measurements of an "as received" piece of the tungsten film show an oxide layer present as compared to the expected W and tungsten oxide energies  $^{16}$  shown in Table 2.1. The difference in energy between the  $4f_{5/2}$  and  $4f_{7/2}$  peaks is 2.18 eV.

**Table 2.1** XPS Binding energy of tungsten  $4f_{7/2}$  peaks in different valence states.

Elements	WO <sub>3</sub> (W <sup>6+</sup> )	WO <sub>5/2</sub> (W <sup>5+</sup> )	WO <sub>2</sub> (W <sup>4+</sup> )	W metal (W <sup>o</sup> )
Binding	$256 \pm 0.1$	220 245	$225 \pm 0.1$	$214 \pm 01$
energy (eV) of	$55.0 \pm 0.1$	33.9 - 34.3	$52.5 \pm 0.1$	$51.4 \pm 0.1$
W 4f7/2				

When broken down into percentages the surface shows a substantial amount of carbon in the "as received" sample along with the tungsten and oxygen atoms. Table 2.2 shows these percentages as well as the changes caused by the various chemical treatments.

 Table 2.2 Composition of tungsten films following different chemical treatments

Sample	C (%)	O (%)	W (%)
As Received	43.9	38.0	18.1
$HCl + H_2O_2$	35.3	35.3	29.4
$NH_4OH + H_2O_2$	27.1	42.0	30.9
KIO <sub>3</sub> + NaOH	44.5	34.2	21.3
КОН	44.0	27.3	28.7

There is a noticeable drop in the carbon percentages for the samples treated with the HCl +  $H_2O_2$  solution and the NH<sub>4</sub>OH +  $H_2O_2$  solution. At first look, this seems to show that the solutions are effective cleaning solutions for a tungsten surface, but carbon contamination is common in tungsten films grown by CVD. As some of these treatments remove significant material but leave carbon behind, it is difficult to determine the cleaning effects of the treatments using XPS.

The remaining two solutions show no relevant change in the carbon concentration. This tends to suggest either that the films are contaminated by carbon, or that the solutions were not effective at cleaning. Again, this is difficult to determine with XPS results.

Sample	Wº (%)	W <sup>4+</sup> (%)	W <sup>6+</sup> (%)
As Received	55.5	6.3	38.2
$HC1 + H_2O_2$	64.2	18.4	17.4
$NH_4OH + H_2O_2$	59.7	21.9	18.4
KIO₃ + NaOH	55.2	23.4	21.4
КОН	71.3	15.3	13.4

 Table 2.3 Composition of tungsten oxide components following different chemical treatments

Table 2.3 shows that compared to the "as received" sample, most of the samples show an increase in tungsten metal with the exception of the sample treated in the  $KIO_3$  + NaOH solution, which maintained the same percentage of tungsten metal. What is most interesting to note is that for all samples, there is an increase in the percentage of  $W^{4+}$  atoms and a decrease in the percentage of  $W^{6+}$  atoms. This indicates that although the "as received" sample has a combination of WO<sub>2</sub> and WO<sub>3</sub> present, it has a substantial amount more WO<sub>3</sub> and all of the chemical treatments cause the oxide present to be reduced to WO<sub>2</sub>. Thus, for any of the chemical treatments used on tungsten, a substantial amount of WO<sub>2</sub> is produced.

# 2.2.2 THICKNESS AND MATERIAL REMOVAL RATES

A four-point probe was used to measure the thickness of each sample after treatment. The capabilities of the four-point probe are needed to determine the resistance of the thin film.

A four-point probe uses four contact points, all in a line and at equal distances on the film. The outer two probes are used to pass a known current through the film, which is controlled by having a known resistance in the system and setting a known potential. Then the inner two probes, which are attached to a lock in amplifier, can be used to measure the potential drop as the known current passes between the probes. The contact resistances are not important in the four-point probe technique in a first order approximation, allowing the resistance value for the film alone to be obtained.

To determine the thickness of the treated samples, first resistivity measurements were taken on an "as received" piece of tungsten for comparison purposes. The thickness of the sample was measured from

scanning electron microscope images provided by Lucent Technologies through examining a cross section of the sample with the SEM. With a known thickness value, the measured sheet resistance of the film could be used to find the resistivity of a tungsten thin film through equation 2.3,<sup>17</sup> where F is the correction factor for the sample size as compared to the distance between the electrodes.

$$\rho_{s} = (\rho/t) = F(V/I) \tag{2.3}$$

The resistivity ( $\rho$ ) of the "as received" tungsten film was found to be 98.4  $\mu\Omega$  cm as compared to 5.6  $\mu\Omega$  cm for bulk tungsten. Thin metallic films typically have higher resistivities than in the bulk. This information, along with the sample size of each sample, allows for the measured voltage and the current to be used for calculation of the film thickness. The film thickness was used to determine how much material is removed during the chemical treatments.

After all of the samples were tested, the results showed that the  $NH_4OH + H_2O_2$  solution removed the most material, as shown in table 2.4. This solution was also the one to show the most carbon removal through XPS results. Suspected carbon contamination of the tungsten, however, suspends any correlation between the etch rate of the film and carbon removal noticed. The HCl +  $H_2O_2$  solution also showed a significant etch rate, and showed a noticeable carbon removal from the "as received" sample, but results are inconclusive about whether the two are related.

Sample	Carbon Removal	Material Removal
	(Compared to as	Rate
	received %)	(Å/min.)
$\rm NH_4OH$ + $\rm H_2O_2$	16.8	361.6
$HC1 + H_2O_2$	8.6	89.2
KIO3 + NaOH	0	32.0
КОН	0	18.4

Table 2.4 Carbon removal percentages shown against removal rates.

The solutions which showed no carbon removal,  $KIO_3 + NaOH$  and KOH, had low etch rates. The results seem to suggest that the solutions used for etching do not etch very much and do not remove the carbon from the surface. The  $KIO_3 + NaOH$  and KOH solutions are only useful for producing WO<sub>2</sub> on the surface of the sample as seen in section 2.2.1. The solutions used as cleans, however, are most useful as etches. They remove the carbon present, but they also alter the surface of the film by removing the significant amounts of surface material.

## 2.2.3 AFM RESULTS

An atomic force microscope was used to image the surface of the treated samples and to find changes in the surface roughness as compared to an untreated tungsten film. The AFM was used in contact mode, where a very small cantilever is used to make contact with the surface of the sample. Once in contact, the tip of the cantilever is moved across the surface and moves up and down as it is dragged across the features present.

As the tip moves across the surface of the sample, a laser is reflected off the top of the cantilever and into a photodiode. The up and down motion of the tip of the cantilever as it moves across the surface, is detected when the laser is deflected and the photodiode picks up the changes in position. The signal from the laser is then applied to the piezo and used to move the sample so that the deflection of the laser can be kept constant, and to account for the effects of thermal drift. The data recorded by the system to give a surface profile is how much the sample must be moved in order to keep the cantilever deflection constant.

The scan results are then processed to remove low frequency noise by using a second order curve fit to flatten the image line by line. Then the image is analyzed to find the RMS roughness of the selected region. The RMS roughness value is used comparatively with other scans performed by the same tip. All scans of the treated tungsten were compared with scans of "as received" tungsten made with the same tip under the same force and gain conditions. This was done because tips of different sizes can show the surface features of the same sample to be slightly different sizes. A scan of the same sample with multiple tips can produce different roughness values. Therefore, scans of the treated films must be compared with scans of "as received" films with the same tip.

Results from the scans show no noticeable difference in the RMS roughness for any of the solutions. This seems reasonable for the  $KIO_3$  + NaOH and KOH solutions because not much material is removed by

these treatments. For the NH4OH + H2O2 solution this is surprising because 361.6 Å of material were removed per minute, but does not seem to roughen or smooth the film much, despite the fact that the grain structure of the tungsten shows change. (See figures 2.1 (a.)and (b.))



(a.)



**Figure 2.1** (a.) Untreated tungsten film (b.) Film treated in NH<sub>4</sub>OH solution. Both images are 3 μm x 3 μm scans taken with the same tip and shown in the same color scale.

The HCl + H<sub>2</sub>O<sub>2</sub> solution does not show much roughness change with the removal rate of 89.1 Å per minute although slightly more than the faster etching solution. This suggests that the rate of chemical removal of material from a tungsten film does not directly relate to increased roughness.

# 2.3 POLISHING EXPERIMENTS ON TUNGSTEN FILMS

A lab scale polishing system was used to run experiments on tungsten films with different slurries at pH values of 2 and 4. The system used was a Buehler Phoenix Beta polisher with a single sample holder with a diameter of 1" as seen in figure 2.2.



Figure 2.2 Buehler Phoenix Beta Polisher and Metlap 2000 Fluid Dispenser used in all polishing experiments.

The platen and the head of the polisher were set to rotate in complimentary rotation at 30 rpm, the force applied to the sample was 3.8 psi, the slurry was dispensed continuously by a Metlap 2000 fluid dispenser, and all samples were polished for 2 minutes. A time interval of two minutes was chosen in reflection of similar experiments performed on tungsten films. It was also decided not to increase this time interval due to the initial thickness of the "as received" tungsten film and a desire to only remove a portion of the film from the wafer.

The samples were each polished with a different slurry and the machinery was rinsed with de-ionized water between experiments. Two of the slurries used were peroxide slurries, one buffered with acetic acid to pH 4 and one buffered to pH 2, each with 5% by weight 0.05  $\mu$ m alumina abrasive particles. The other two slurries were KIO<sub>3</sub> (0.1 M) with 5% by weight 0.05  $\mu$ m alumina abrasive particles, one buffered to pH 4 and one buffered to pH 2 with acetic acid. These slurries and polisher settings

were chosen based on similar polishing experiments done on tungsten.<sup>18-21</sup>

AFM results of the polished samples showed that there was a decreased RMS roughness value in all samples as compared to the "as received" tungsten sample. This is expected since these slurries are typical for what is generally used for tungsten CMP in industry<sup>7-</sup>10,12,13. Table 2.5 shows the decrease in roughness for each sample at different scan sizes as compared to the untreated sample. The roughness readings are different for different scan sizes because each scan takes the same number of data points to produce a scan, yet for the 1 µm scan, the points are closer together on the surface of the sample and get more detail about smaller features. Larger scans take less detail of a larger area, but show more features and greater differences in the heights between them. These data suggest a need for future experiments.

Chemical	5 μm	3 μm	1 μm
Treatement			
H <sub>2</sub> O <sub>2</sub> @ pH 4	85 Å	87 Å	26 Å
H <sub>2</sub> O <sub>2</sub> @ pH 2	112 Å	103 Å	48 Å
KIO <sub>3</sub> @ pH 4	78 Å	35 Å	-
KIO <sub>3</sub> @ pH 2	88 Å	42 Å	-

Table 2.5 Decrease in roughness after polishing.

The results displayed in this table show that the slurries at a lower pH produce a more planar surface over the same time period. When comparing the  $H_2O_2$  and  $KIO_3$  slurries at the same pH values, it is shown that the  $H_2O_2$  slurry planarizes the surface of the tungsten more than the  $KIO_3$  slurry. Thus, AFM results show that  $H_2O_2$  makes a better slurry for tungsten planarization than  $KIO_3$ .

Removal rates on the sample from the four-point probe were inconclusive. While most of the samples showed material removal, one sample showed an increase in thickness. This may be due to epoxy on the edges of the sample or to alumina particles agglomerated to the surface, which would affect the results from all of the samples. The samples were mounted by pressing them into the base of a cup form while epoxy was poured on top and left to harden. Some of the epoxy hardened on the edges of the tungsten film and may have been smeared across the surface of the film during the polishing step. Further tests need to be done on differently mounted samples to eliminate the possible effects of the epoxy. Longer polishing times allow for more material to be removed and may be important in measuring removal rates. Examining patterned features before and after polishing will also make measuring removal rates possible.

The next analysis for the polished samples will be to examine them by the energy dispersive x-ray spectroscopy (EDS) system on the scanning electron microscope. EDS is used to gain elemental information about a sample. When the electron beam from the SEM energizes the electrons in a sample and they produce x-rays to return to ground state in the atom. These x-rays are analyzed and give qualitative and quantitative elemental information. The x-rays produced can come from

several nanometers within the sample and tend to give information about the material in the bulk of the sample. Thus, the information about the surface of the sample is just a small percentage of the information given.

For these experiments EDS is needed to estimate the concentration of oxide present on the surface of the sample after polishing. Along with the polished samples, a piece of "as received" tungsten and an oven grown oxide sample should be examined to use as a comparison. XPS analysis would give more conclusive information about these samples, as it is better at looking at just the surface of a sample, but EDS can be used as a first look to determine if there is a reason for further analysis.

#### CHAPTER 3

#### COPPER ANALYSIS

## **3.1 CHEMICAL TREATMENTS**

Since there has been less research done on copper CMP, even the simplest results of material removal by the chemicals used in the slurry have not been determined or published. The first goal of this research in copper CMP is thus to show the effects a specific slurry chemical on a set of copper films.

A solution of 3.3% H<sub>2</sub>O<sub>2</sub> was chosen as the basis for these trials as a recent study refers to H<sub>2</sub>O<sub>2</sub> based slurries being used in research<sup>6</sup> and due to their use in industry. Studies were done with the peroxide at different pH values since copper reacts with peroxide under acidic conditions as shown in the following equation<sup>22</sup>:

$$Cu^{\circ} + 2H_2O_2 + 2H^+ \rightarrow Cu^{+2} + 2H_2O$$
 (3.1)

Corrosion inhibitors were also examined since copper corrosion is a concern for producing a planarized surface in industry. Some research has been done with the corrosion inhibitor known as benzotriazole  $(BTA)^{23,24}$ , but a new product known as halogen resistive azole (HRA)

has been untested for thin film applications and may prove to be useful in the industry as it has fewer requirements for waste processing.

## 3.1.1 THICKNESS OF AS RECEIVED COPPER

Before the experiments in chemically treating copper films could be performed, the thickness of the "as received" copper films had to be determined. The measurement of the film was done by two methods to gain an accurate thickness value. First, the SEM was used to look at a cross section of the film on the silicon wafer and found the thickness to be approximately 2.2  $\mu$ m. SEM measurements were performed at Lucent Technologies.

The stylus profilometer was the second instrument used to measure film thickness, but a sample of the copper film had to be etched away so that the tip on the profilometer could measure a height difference between the top of the film and the surface it lays on. In order to etch a trench in the copper for this purpose, the rest of the film had to first be protected from being etched away.

To accomplish this a photoresist was spun onto the surface of the sample and cured by baking<sup>25,26</sup>. The photoresist was then exposed through a photomask with the incandescent light of a microscope to expose a 1.5 mm line of light on the photoresist. The exposed photoresist was then etched away with a weak NaOH solution, leaving a line of

copper exposed. The copper was then etched away with another solution and the remaining photoresist was removed with acetone.

After the photoresist was removed, the sample was analyzed with the profilometer, looking at height differences on both sides of the trench. Measurements were taken at several locations along the trench and the results were averaged for each side. One side of the trench showed an average thickness of  $2.208 \pm .008 \mu m$  for the film while the other side showed an average thickness of  $2.220 \pm .020 \mu m$ . Both measurements concur with the film thickness found using the SEM.

3.1.2 EXPERIMENTAL

Copper samples were treated with 3.3% H<sub>2</sub>O<sub>2</sub> in an unbuffered solution at pH 5, and in solutions buffered to pH 4 and 2. Acetic acid was used to buffer the 3.3% H<sub>2</sub>O<sub>2</sub> for most solutions, but an HCl buffered solution at pH 2 was used to test one sample for a one minute treatment.

The remaining three solutions, consisting of the unbuffered 3.3%  $H_2O_2$  solution, the pH 4 buffered solution and the pH 2 buffered solution, were used to treat samples for one minute, five minute and ten minute trials. All samples were rinsed in de-ionized water after they were removed from the chemical solution. The treated samples were all examined by the four-point probe for thickness analysis and by the AFM for roughness comparisons with an untreated sample.

Results from these tests, shown in sections 3.1.3 and 3.1.4, indicated that corrosion inhibitor test would best be performed using the pH 2 buffered 3.3%  $H_2O_2$  solution because it showed the most material removal over time. This meant that differences between the treatments with the corrosion inhibitor and without it should be easier to detect.

The first corrosion inhibitor tested was the BTA mixed to a 0.01M solution. Different concentrations of this compound were tried in the peroxide solution. 5 ml, 10 ml, and 20 ml amounts of the 0.01M BTA were added to 100 ml of the 3.3% H<sub>2</sub>O<sub>2</sub> solution at pH 2. One sample was treated in each concentration for ten minutes. The samples were then rinsed in de-ionized water and then examined with the four-point probe and the AFM for comparison with the results of the other chemical treatments.

## 3.1.3 RESISTIVITY AND THICKNESS OF TREATED COPPER

The method used for finding the thickness of the copper films is the same as that used for section 2.2.2 of this thesis. Results from the SEM and profilometer showed the "as received" copper film to be approximately 2.2  $\mu$ m thick. Using equation 2.1, the resistivity of the film was calculated to be 14.6  $\mu$ Ω·cm as compared to the bulk thickness value for copper of 1.7  $\mu$ Ω·cm. This value was then used to calculate the thickness of the treated films.

The thickness values for the films without the corrosion inhibitor are listed in table 3.1, and are plotted in figure 3.1 as follows.

Time	Untreated	3.3% H <sub>2</sub> O <sub>2</sub>	$H_2O_2$ @	$H_2O_2$ @	$H_2O_2 + HC1$
(Min.)			pH4	pH 2	
0	2.1702 μm				
1		2.1069 μm	2.1043 μm	2.1679 μm	1.8623 μm
5		2.0977 μm	2.0048 μm	1.7938 μm	
10		2.0781 μm	1.9331 µm	1.6630 µm	

**Table 3.1** Thickness of copper films after chemical treatment.





As can be seen, there is a general trend that the lower the pH of the solution, the more material is removed over time. A notable exception to this trend is the sample treated with the 3.3% H<sub>2</sub>O<sub>2</sub> + HCl solution. This solution removed approximately 0.4 µm of material in one minute. Such a great amount of material removed in a short time can make this a difficult solution to use because it would be difficult to control. Even though one goal of CMP is to remove material, it must be a controlled process to gain a planarized surface. The effects of this solution will be examined again in section 3.1.4 when surface roughness is discussed.

Examining the other solutions used, the removal rate was most noticeable after treatments with the 3.3% H<sub>2</sub>O<sub>2</sub> solution buffered to pH 2, so this solution was chosen to test different concentrations of BTA. Since ten minute trials showed significant material removal, all copper samples tested in different concentrations of BTA were treated for ten minutes.



Figure 3.2 Copper thickness after treatments including BTA.

The data show how as the concentration of BTA in the peroxide solution is increased, the removal rate of the copper decreases. Thus, depending on how much material removal is desired, the removal rate can be controlled through the concentration of corrosion inhibitor. The roughness of these samples will be examined in the next section.

## 3.1.4 ROUGHNESS DATA

The solutions of varied pH, with and without corrosion inhibitors, were examined using the contact mode of the AFM as described in

chapter 2. The results, as shown in table 3.2, for the different solutions showed some interesting results. For the pH 4 setting, the roughness appeared to increase as the time of the treatment increased for the 1  $\mu$ m scans, but decreased as the time of the treatment decreased for the 5  $\mu$ m scan size. The 3  $\mu$ m scans do not show any trend.

The results of this scan may seem inconsistent, but it may have more to do with the idea of global planarization versus local planarization. Following this idea, the roughness decrease at the 5  $\mu$ m scan size would show more global planarization of the sample. The increase in roughness at the 1  $\mu$ m scan size would show that locally, the surface gets rougher while the overall sample is planarized.

The pH 2 solution made with the acetic acid shows definite trends in increasing roughness in all scan sizes with increased time of treatment. When the pH 2 solution, made with hydrochloric acid, is compared to this sample it is obvious that this solution creates a much rougher surface than the other solution. A sample treated with this solution for only one minute is considerably rougher than the sample treated in the acetic acid solution for ten full minutes. It can thus be concluded that hydrochloric acid makes a poor buffer for peroxide solutions used in copper CMP.

Treatment	Time	5 μm	3 μm	1 μm
H <sub>2</sub> O <sub>2</sub> @ pH 4	1	362 Å	109 Å	30.4 Å
	5	342 Å	342 Å	130 Å
	10	298 Å	283 Å	94 Å
H <sub>2</sub> O <sub>2</sub> @ pH 2	1	20.5 Å	9.9 Å	0 Å
	5	248 Å	132 Å	39.8 Å
	10	317 Å	145 Å	62.1 Å
pH 2 w/ HCl	1	550 Å	533 Å	279 Å

Table 3.2 Increase in roughness for samples without different pH values.

The BTA corrosion inhibitor was added to the pH 2  $H_2O_2$  solution as explained in section 3.1.3, and then different concentrations were compared to the pH 2  $H_2O_2$  solution without any BTA added. As can be seen in table 3.3 below, the increase in the roughness of the film, compared to an untreated film, decreases as the concentration of BTA is increased. The concentration of 20 ml of 0.01 M BTA to 100 ml of 3.3%  $H_2O_2$  at pH 2 shows the least amount of roughening of all of the chemical treatments, and is a good candidate to use as a slurry in polishing trials. **Table 3.3** Increase in roughness for HoO at pH 2 with different BTA concentrations as

т е	able 5.5 increase in roughness for 11202 at pri 2 with different DTA concentrations as									
	compared to an untreated film.									
	Treatment	Time	5 um	3m	1 um					

Treatment	Time	5 μm	3 μm	1 µm
H <sub>2</sub> O <sub>2</sub> w/ no BTA	10	317 Å	145 Å	62.1 Å
$H_2O_2 \text{ w/ 5 ml BTA}$	10	313 Å	179 Å	43.6 Å
$H_2O_2 \text{ w}/10 \text{ ml BTA}$	10	153 Å	122 Å	38.7 Å
$H_2O_2 \text{ w}/20 \text{ ml BTA}$	10	24.9 Å	9.6 Å	6.7 Å

## 3.1.5 RECOMMENDATIONS FOR FURTHER CHEMICAL WORK

The work done with the peroxide solutions has given some clues as to how copper reacts with peroxide based slurries, but is difficult to test with *in situ* AFM methods. The bubbles from the peroxide solution make it difficult to reflect the laser off of the cantilever and can move the tip in the solution. For this reason, the design of experiment for the peroxide work may be initially applied to other chemicals used in copper CMP slurries. Some suggestions for further research include sulfuric acid (HNO<sub>3</sub>) or Ammonium Hydroxide (NH<sub>4</sub>OH).<sup>23</sup> These chemicals do not have a tendency to form bubbles and should prove easier to use in the AFM liquid cell.

#### 3.2 ROUGHNESS OF POLISHED SAMPLES

The information from the chemical treatments was used to develop slurries for use in the Buehler polishing system. Two slurries were created using the 3.3% H<sub>2</sub>O<sub>2</sub> buffered with acetic acid. A solution buffered to pH 4 was created along with a pH 2 solution. The abrasive added to these solutions was 0.05 µm alumina particles, and enough were added so that they were 5% of the solution weight.

Two additional slurries were created using the same buffered solutions, but they had 0.01 M BTA added in a concentration of 20 ml of BTA to 100 ml of  $H_2O_2$  solution. Alumina particles of the same size were then added to the solutions so that they made up 5% of the solution weight.

Four copper samples were then mounted on the top of epoxy forms, with another adhesive, for use in the polishing device. The samples were all polished for five minutes in the system at a rotational speed of 35 rpm. The applied force to the samples was 3.8 psi and the slurries were dispensed continuously during the experiments. Each

sample was run with a different slurry, and the polishing device was rinsed out with de-ionized water in between experiments.

Once the samples had been polished, they were examined for roughness comparisons using the AFM. The RMS roughness values were compared with "as received" copper films for a roughness increase or decrease, and then compared to chemical treatments done on copper samples without the polisher. Results, as seen in table 3.4, showed that although the polished samples were rougher than the "as received" copper, the polished samples were less rough than the samples treated chemically, but not polished.

Table	<b>3.4</b> Incre	ease m	roughne	ess of	polished	d and u	unpolisi	hed sam	ples.

Treatment	Time	5 µm	3 µm	1 µm
Unpolished pH 2	5	248 Å	132 Å	39.8 Å
Polished pH 2	5	17.3 Å	17.4 Å	3.8 Å
Polished pH 2 w/ BTA	5	0.6 Å	7.2 Å	2.9 Å
Unpolished pH 4	5	342 Å	342 Å	130 Å
Polished pH 4	5	60.6 Å	44.0 Å	38.1 Å
Polished pH 4 w/ BTA	5	42.2 Å	26.0 Å	1.7 Å

Table 3.4 also shows that the samples polished with the BTA mixtures are less rough than the samples polished without the BTA added into the slurry. In the case of the pH 2 BTA slurry it appears that there is very little difference in roughness between the polished sample and the "as received" copper sample. Thus, this solution has shown it can be used to successfully polish a copper surface.

Four-point probe analyses were attempted on some of the above samples, but were inconclusive as some of the results showed a thicker copper layer than was seen on the "as received" copper samples. The samples were mounted on top of epoxy forms by using another glue compound to attach the back of the sample to the epoxy form. Therefore, the epoxy could not be responsible for skewing the thickness results as was a potential problem in chapter 2 with the tungsten samples.

Elimination of the epoxy contamination could mean that alumina agglomeration on the surface of the sample is more likely to be the cause of the problems with thickness measurements after polishing. Another possibility is that not enough material is being removed from the samples to allow an accurate measurement. A possible method of examining these ideas is to use the EDS function of the SEM to look for alumina on the surface of the samples. If alumina is found on the samples, then it is the likely problem. No alumina on the surface would suggest limited material removal. Longer polishing times on the films should also be tested to make material removal rates easier to measure.

## 3.3 POLISHING WITH PATTERNED COPPER

The results of the four-point probe analysis are inconclusive, so another method for measuring polish rates must be developed. The easiest method would be to polish features large enough to be measured on the stylus profilometer. Since the technology now exists in this department<sup>25,26</sup> to etch trenches in copper films, this seems to be the easiest way to measure the amount of copper etched off the sample. Once the films are developed, the tests performed on the blanket copper films can be repeated and examined by profilometry for polish rates.

#### CHAPTER 4

#### MACROSCOPIC REACTION CHAMBER

## 4.1 THEORY

A macroscopic reaction chamber was designed and built to study the electrochemical reactions of metal films with the slurries used in CMP. Specifically, the chamber is designed to show the oxidation effect of the CMP slurries used on metals. Since oxidation is potentially an important step in CMP, because it allows for metallic atoms to bond with oxygen atoms, the electrochemical effects of the slurry on a metal sample are worth studying.

Electrochemistry is the study of the oxidation and reduction reactions of metals. As metals are oxidized they give off electrons. When a metallic ion gains electrons it is reduced. When electrons are transferred from one metal to another in an electrochemical cell, a potential drop can be read, and information about the energy of the oxidized metal can be gained.

The simplest explanation of an electrochemical cell for studying these reactions is a divided cell with two electrodes. A salt bridge connects the two sections of the cell. This allows ions to travel back and

forth across the bridge without the solutions contained within them to mix. A set up for a simple electrochemical reaction using a zinc electrode and a copper electrode is shown in figure 4.1.



Salt Bridge

Figure 4.1 Zinc/Copper galvanic electrochemical cell.

As can be seen in the above figure, the zinc electrode acts as an anode and the copper electrode acts as the cathode of the system. As electrons flow from the anode to the cathode, the copper ions in solution are attracted to the cathode and are reduced to copper metal. The negative ions in the copper solution attract positive ions from the salt bridge, leaving only negative ions in the barrier.

The negative charge in the salt bridge causes it to attract the positive zinc ions from solution into the salt bridge and leaves the zinc solution negatively unbalanced. Thus, the zinc metal on the anode is oxidized, creating more positive zinc ions in solution and creating electrons to react with the cathode. A voltmeter placed in the system can be used to measure the potential difference between the two electrodes. This value can be compared to standard potentials for oxidized metals to determine the activity of the anode in solution. Since this cell can produce electrical energy, it is referred to as a galvanic  $cell^{27}$ .

If a power source is added to the system, along with a third electrode, the system becomes an electrolytic cell, with a working electrode, a counter electrode and a reference electrode. The electrode where the voltage is applied and controlled is the working electrode with the current moving from it to the counter electrode. The reference electrode is then used to measure the overvoltage of the solution by comparing it to the potential at the working electrode<sup>28</sup>.

The overvoltage is the additional amount of voltage that is applied to a system to maintain a desired current flow. Thus, the overvoltage can be used to show the resistance of the electrode in solution. Significant overvoltages can be a clue that oxide is present on the surface of the working  $electrode^{29}$ .

The model of the electrolytic electrochemical cell is what was chosen for experimental work at this institution. An AgCl/Ag double junction reference probe was chosen as the reference probe for the cell, while platinum wires would be used for the counter electrode and as the wire attached to the sample for the working electrode. A similar set up was constructed by Kneer, *et al*<sup>13</sup> for studying electrochemical reactions while polishing a tungsten sample. Stein, *et al*<sup>7</sup> also used an electrochemical cell for studying reactions during polish, but used a

saturated calomel electrode as a reference probe, a copper strip as the working electrode, and platinum mesh as the counter electrode.

#### 4.2 CHAMBER CONSTRUCTION

A chamber for the previously described reactions needed to be constructed. To produce the required conditions, an airtight chamber with a gas inlet and outlet had to be designed. This allows nitrogen to be bubbled through a solution to remove dissolved oxygen. There was also a need for platinum wires, used as a working electrode and a counter electrode, and a double junction reference electrode to be introduced into the system. The chamber also needed to be able to be opened and resealed in order to allow for changes of solution between experiments.

A 2000-ml beaker was chosen as the main vessel for the chamber, and a lid was designed that could be resealed. Teflon was chosen for the material for the lid and it was then designed to have a notch in it to hold an O-ring. The O-ring was then used to seal the gaps between the lid and the beaker. See figure 4.2 for clarification.



Figure 4.2 Chamber Plan Sketch

In order to make a notch large enough to hold the O-ring, two pieces of Teflon were cut, notched on one edge, and then bolted together with stainless steel screws and nuts. The assembled lid was then drilled with appropriate sized drill bits for the gas inlet and outlet tubing, the platinum wires, and the wire for the reference probe. These holes were then sealed with Teflon tape once the wires and tubing were inserted.

With the chamber put together and the gas lines and wiring installed, the chamber was ready to be used in conjunction with the bipotentiostat to find the overvoltage of a system as the potential and current were applied.

#### 4.3 PROJECTED USAGE

The system should first be used to look at tungsten samples with various slurries to find the overvoltage of the tungsten with only the chemical portion of the CMP system present and no polishing apparatus. Slurries should be tested with and without abrasive particles to determine if the abrasive particles have much effect on the overvoltage readings of the tungsten.

Once the non-polishing experiments are complete, the electrolytic cell should be modified to accommodate a polishing device as was devised by Kneer, *et al*<sup>13</sup> or Stein, *et al*<sup>7</sup>. The overvoltage of the tungsten in polishing conditions can then be compared to the results found with chemical reactions only.

Studies performed on tungsten films can later be used to design a set of experiments for copper films. Copper overvoltage can also be tested in chemical conditions without abrasives or with abrasives, and then with a polishing apparatus introduced into the cell. The results should show whether oxide is present on the surface of these metals during polishing.

## **CHAPTER 5**

## CONCLUSIONS

## 5.1 TUNGSTEN

Tungsten thin films have been studied for the effects of four different chemical solutions on material removal, roughness of the film and changes in oxidation. The solutions containing NH<sub>4</sub>OH and HCl show the highest material removal rate of while the KOH and KIO<sub>3</sub> solutions showing virtually no material removal. None of the solutions showed large changes in roughness as compared to the "as received" tungsten film, but they all showed a reduction from the W<sup>6+</sup> oxidation state to the W<sup>4+</sup> oxidation state.

The films were also tested in the table top polishing system with four different slurries. All of the slurries used reduced the roughness of the tungsten as compared to the as received sample. When comparing the four slurries, it was shown that the  $H_2O_2$  based slurries produced a smoother surface on the tungsten film than the KIO<sub>3</sub> slurries. Another noticeable trend is that the slurries buffered to pH 2 produced smoother samples than those slurries buffered to pH 4. Thus, the  $H_2O_2$  based slurry buffered to pH 2 is the most effective for tungsten planarization.

## 5.2 COPPER

Peroxide based solutions have been used in the analysis of copper. The solutions were buffered with acetic acid to vary the pH. As the pH of the solution was lowered, the rate of material removal increased. The addition of the corrosion inhibitor BTA to the pH 2 solution slowed the material removal rate considerably. As the concentration of BTA in solution was increased, the removal rate decreased.

For the pH 2 solution the roughness of the copper sample increases over time. Experiments with the pH 4 solution seem to vary depending on scan size, which could mean that globally the sample becomes smoother while it becomes locally rougher. The experiments performed with BTA at pH 2, however, show that the copper surface becomes less rough with increasing concentration. Even though all of the surfaces of the treated copper are rougher than the "as received" copper, the strongest concentration tested of BTA in solution produced a sample closest to the roughness of the original film.

Samples tested in the polishing system with peroxide slurries buffered to pH 2 and pH 4 were compared to unpolished samples and samples polished with slurries containing BTA. The polished samples were all less rough than the unpolished samples exposed to chemicals for the same amount of time. Again the samples that had BTA in the slurry showed to be less rough than the solutions that did not contain BTA. The solutions buffered to pH 2 produced less rough samples than

the pH 4 solutions did. The smoothest sample produced by this method was a sample run with a pH 2 slurry that contained the most concentrated amount of BTA used in earlier tests. AFM scans of the sample showed that it was only marginally rougher than the original untreated copper sample.

Thickness measurements of the polished samples were inconclusive. In order to measure polish rates, a series of patterned copper samples must be used. The patterns in the copper must be large enough to be read with the profilometer. Then the patterns can be measured before and after polishing to see how much material is removed.

## 5.3 FUTURE WORK

Work on the copper that should be continued includes testing the samples with HRA solutions. Peroxide solutions with the same concentration of HRA as was used in the BTA tests should be used to see if HRA is as effective in reducing material removal and roughness of copper films. HRA solutions should then be used in the polisher to see the effects of HRA in polishing conditions.

The patterned copper experiments can be performed as soon as the copper samples are patterned through lithography methods or patterned samples are acquired from another source. Samples should be tested for buffered peroxide solutions without corrosion inhibitors, with BTA and with HRA.

Once the method for measuring removal rates is established, the experiments described in this thesis for copper films need to be repeated with different slurries such as nitric acid or ammonium hydroxide. Although the peroxide slurries are most commonly used for copper CMP, studies with these other slurries may yield more information about the removal mechanism. These other slurries also have the advantage of not producing many bubbles, which would affect the workings of the AFM liquid cell.

Future research with tungsten depends on determining a method for etching tungsten in a lithography process without etching away the protective photoresist. Once this is accomplished, polishing rates for KIO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> solutions can be determined in the same manner described for patterned copper wafers. This will yield more accurate results as well as allowing measurements on patterned samples.

SEM analysis of polished tungsten films can also be used to measure the oxide present on the wafer after the polish step as compared to untreated samples. This method can also be used to determine if further XPS analysis would be useful, as XPS provides a more detailed surface view.

# Appendix A

# Mounting Samples for the Buehler Polisher

This is the procedure used for mounting samples on epoxy forms so that they can be polished on the Buehler table top polishing system. This method mounts the samples on the already prepared epoxy forms to prevent epoxy contamination of the sample during polishing. Standard mounting embeds the smaples.

- 1. Use the Buehler SAMPLE-KWIK epoxy mix to make forms for samples to be mounted on. The epoxy mix consists of two components, a powder resin, and a liquid hardener. To mix the epoxy, use 2 times as much resin by weight as hardener. For a 1" sample mount, use approximately 5 grams of hardener and 10 grams of resin.
- 2. When mixing, add powder into hardener and stir rapidly.
- 3. Pour epoxy into the form immediately after mixing, it will solidify in approximately 8 minutes.
- 4. Remove cured epoxy from forms.
- 5. Apply super glue to back of sample.
- 6. Place sample back down on top of mount and press down with tweezers.
- 7. Allow sample to dry for a few hours as glue instructs.

# Appendix B

# Mixing Slurries for the Polisher

The following instructions are designed to explain how to add the abrasive particles necessary for a chemical slurry to be used in the polisher. Usually, the pH of the slurry is determined by previous chemical tests on the film. The researcher tests the effects of the chemical component of the slurry on the film, and uses the information gained to determine what solution should be tested in the polisher. At this point, slurries of pH 2 and 4 have been used in the polishing system without any noticeable degradation.

- 1. Mix solutions as done for chemical treatments. (See Appendix C.)
- 2. Weigh a clean dry graduated cylinder and use to tare the electronic balance.
- 3. Pour 20 ml of solution into cylinder and weigh.
- 4. Calculate the number of grams per ml of the solution. (I always calculated the number of ml necessary to equal 95 grams of solution.)
- 5. Re-tare balance using a clean dry beaker.
- 6. Weigh out an amount of alumina or silica particles in beaker. (I weigh out the abrasive particles in 5 gram increments to make the math easier to calculate a 5% by weight solution. For every 5 grams of abrasive particle, add 95 grams of solution.)
- 7. Add the appropriate amount of liquid solution to the beaker. (For use in the polisher, approximately 300 grams of the solution will last about 5 minutes.)
- 8. Stir solution with metal spatula until alumina particles have been mixed fully into solution.
- 9. Pour solution into one of the glass bottles provided for the fluid dispenser.
- 10. Cap and mark bottle as to contents.

# Appendix C

# **Creating Buffered Peroxide Solutions**

The solutions made for my research were mainly peroxide based and the steps below describe how to obtain different pH peroxide solutions. For my work, acetic acid was used as the buffer solution.

- 1. To get a 3.3% peroxide solution using 30% peroxide, mix 3.3 ml of 30% peroxide to 96.7 ml of de-ionized water.
- 2. For adjusting the pH of the peroxide, add an acid such as acetic acid or nitric acid to the peroxide a few milliliters at a time while checking the pH with either pH paper testers or using the electronic pH meter.
- 3. If you are testing tungsten or copper in the solution, DO NOT USE HCL TO BUFFER THE pH. These metals are eaten quickly by HCl and become extremely rough on the surface.
- 4. If you are planning to compare the peroxide solution to a nitric acid solution in your experiments, do not use the nitric acid as your buffer acid.
- 5. Once the solution has been made, store it in an appropriate container and label it for contents and date.

# Appendix D

# Using the Buehler Polishing System

The Buehler Phoenix Beta polisher with a Vector Force Head was used for all of the polishing experiments in this thesis. A Metlap fluid dispenser was used to deliver slurry into the system during the polishing cycle. The following instructions are a description of how to set up the polishing system for experimental use.

- 1. For metallic film samples, use a black chemical polishing cloth on the platen. Make sure the cloth is securely attached and that the platen is stable. You may need to press down on the platen to ensure that is secure and will not wobble. (When using diamond lapping films, use double stick tape to attach the film to the platen. Water does not hold the film in place.)
- 2. Make sure the sample holder is set to move in the direction you require (complimentary or contrary). To do this, unscrew both of the tightening rings above the sample holder and then lift the collar to release the holder. (See following figure.) Check to see that the pin is in the correct position for the direction you require. Metallic films should be polished with the complimentary direction. (Spherical lenses should be ground using the contrary mode.)



- 3. Replace the sample holder in the force head and tighten the two tightening rings by hand. DO NOT USE ANY TOOLS TO TIGHTEN THE RINGS. These rings should be checked for tightness before any polishing experiment is run.
- 4. Turn on the force head by the switch in the back and press the select button to activate the display. Refer to the manual for a list of what the settings are for. Make sure you select complimentary or contrary motion, set the time for the experiment and set the force on the sample in pounds. (2 lbs. = 2.5 psi, 3 lbs. = 3.8 psi) BE SURE TO TURN ON THE WATER. Turn on the fluid dispenser if you are planning to use a slurry.

- 5. On the polishing platen, turn the speed to the appropriate rpm for your experiment.
- 6. Turn on the fluid dispenser, and check the panel to see if one or two bottles are lighted. If you wish to change the set up, turn the power switch off and flip the other switch in the back to change the configuration. Turn the dispenser back on.
- 7. Once the dispenser is on select the correct location of the slurry bottle and place the tube for that location into the slurry. Be sure to watch the end of this tube during the procedure to make sure it stays in the solution.
- 8. Press the purge button on the dispenser to purge the water from it. Continue purging until the slurry starts to come out of the dispenser.
- 9. Once the line for the slurry is purged, set the dispenser to automatic mode, and set the duration to 4.9 seconds and the frequency to 5.0 seconds for continuous flow.
- 10. Place the sample(s) in the sample holder with the o-ring on top of the holder, holding the sample in place.
- 11. Press the green buttons on the force head simultaneously, and hold them until the head is lowered. Check to make sure that your samples are touching the surface of the pad before you proceed. If not, press the stop button to raise the head and reposition your samples.
- 12. If the samples are in the correct position, press and hold the green buttons again until the system begins to spin.
- 13. KEEP AN EYE ON THE BUCKET DURING THE CYCLE TO MAKE SURE IT DOESN'T OVERFLOW.
- 14. When the cycle ends, remove the sample and rinse it with de-ionized water. Rinse the polisher with de-ionized water between sample runs and empty the bucket if necessary.
- 15. If additional samples are run, refer back to step 7 and repeat.
- 16. When you are done using the polishing system, place the tubes from the fluid dispenser in a beaker of de-ionized water and purge them of the slurries inside them. Then rinse the polishing platen and sample holder again.
- 17. Finally, cap all slurries and shut off the fluid dispenser and force head. Cover the polisher with the splash shield and get rid of any waste. (Water from copper samples must be treated with ammonium hydroxide before it can be disposed.)

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