CHEMICAL MECHANICAL POLISHING OF GOLD

A Thesis

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by

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To my mother, for everything she has done…
CONTENTS

FIGURES ........................................................................................................................................... v

ACKNOWLEDGMENTS .......................................................................................................................... vii

CHAPTER 1 INTRODUCTION TO CHEMICAL MECHANICAL POLISHING (CMP) ................................................................. 1
1.1 Why CMP? ......................................................................................................................................... 1
1.2 CMP Process, Consumables, Inputs, and Outputs ................................................................. 5
1.2.1 Pressure ..................................................................................................................................... 6
1.2.2 Pad and Wafer Rotation Velocity ......................................................................................... 8
1.2.3 Retaining Ring and Wafer Protrusion .................................................................................. 10
1.2.4 Pad ........................................................................................................................................ 13
1.2.5 Pad Conditioning ..................................................................................................................... 14
1.2.6 Slurry ...................................................................................................................................... 17
1.2.7 pH Adjusters, Oxidizers, and Complexing Agents .......................................................... 18
1.2.8 Surfactants ............................................................................................................................. 23
1.3 Output Variables of CMP ............................................................................................................. 26
1.3.1 Removal Rate and Preston Equation ............................................................................... 26
1.3.2 Selectivity, Dishing, and Erosion ....................................................................................... 29
1.3.3 Planarization Rate .................................................................................................................. 31
1.3.4 Coefficient of Friction ........................................................................................................... 32

CHAPTER 2 EXPERIMENTAL RESULTS ......................................................................................... 36
2.1 Sample Preparation and Process Parameters ........................................................................... 36
2.2 Pad Preparation and Conditioning ......................................................................................... 38
2.3 Post CMP Wafer Cleaning ........................................................................................................ 39
2.4 Slurry ........................................................................................................................................... 39
2.4.1 Metal Contact Recess and Severe Dishing ...................................................................... 41
2.4.2 Dielectric Erosion and Incomplete Removal Of The Adhesion Layer Overlay ............ 45
2.4.3 Particle Redeposition and Unstable Slurry ........................................................................ 49
2.5 Coefficient Of Friction and End Point Detection .................................................................... 58
FIGURES

Figure 1.1 Device fabricated with and without interlayer dielectric CMP [3]. .................3

Figure 1.2 Schematics of a basic rotary type CMP system [9].........................................6

Figure 1.3 Schematic diagram illustrating the geometry of the polisher [12]. .................9

Figure 1.4 stress distribution on the wafer surface in the interface [14]..........................11

Figure 1.5 Pad deformation at the carrier head periphery [15]......................................12

Figure 1.6 Height distribution of pad asperities as a function of conditioning aggressiveness [18].....................................................................................16

Figure 1.7 Pourbaix diagram for Cu-water system indicating the corrosion behavior of copper in water. The right diagram is the simplified pourbaix diagram [22].......21

Figure 1.8 Schematic illustration of hydrogen peroxide concentration effect on material removal rate of copper [23].............................................................................22

Figure 1.9 The structure of sodium dodecyl sulfate (sds), an anionic surfactant and a cationic surfactant, dodecyl trimethyl ammonium bromide [26]..........................24

Figure 1.10 The configuration of surfactant molecules in different concentrations [27].25

Figure 1.11 Dishing and erosion in metal polishing......................................................29

Figure 1.12 The stribeck curve and three modes of contact [43]..................................34

Figure 2.1 Schematic of a gold CMP sample before polishing......................................36

Figure 2.2 CMP result when Ti was used as the adhesion layer, and 30% hydrogen peroxide solution added to ultra-sol a20 in 1:1 ratio was used as the slurry. High static etch rate of gold, and the long time required to polish the Ti overlay resulted in significant gold recess.................................................................43
Figure 2.3 The metal recess starting from the outer edges of the metal array caused mainly by high static etch rate of the metal, and severe erosion of dielectric in the middle of the array. ................................................................................................44

Figure 2.4 Au/ Cr metal layer polished with ultra-sol a20: H₂O₂ in a 1:1 ratio. The results were the protrusion of gold from the dielectric, significant erosion of the dielectric between the pads, and incomplete removal of the adhesion layer. ...........46

Figure 2.5 Au/ Cr Metal layer polished with 0.8 % Wt of PVP added to Ultrasol A20: H₂O₂ in 1:1 ratio. Gold did not protrude the dielectric, and no dielectric erosion was observed.................................................................48

Figure 2.6 The mechanism of high-ionic-strength slurry stabilization by the synergistic mixture of anionic and nonionic surfactants [46]. ..................................................51

Figure 2.7 Au/ Cr metal layer polished with 30 ml tween 80 and 6 ml capstone added to 1600 ml of UltraSol A20: H₂O₂ in 1:1 ratio. The agglomerated abrasives result in re-deposition of relatively large (up to 100µm in size) pieces of gold debris. .....54

Figure 2.8 CMP result using 4.14 grams of SDS with 3.5 ml of tween 80 added to 1200 ml of Ultra-Sol A20: H₂O₂ in 1:1 ratio. This combination resulted in a stable slurry with 45 nm of dishing across a 10 µm wide contact pad........................55

Figure 2.9 Wafer polished with slurry consisting 4 grams of sds and 0.1 grams of PVP added to 900 ml of Ultra-Sol A20 and 300 ml of hydrogen peroxide. This combination resulted in a stable slurry with 37 nm of dishing across a 150 µm wide contact pad.................................................................57

Figure 2.10 Evolution of COF with time for the case when a) Au/Ni layer over sin is polished: coefficient of friction decreases as the gold overlay is being removed and the underlying dielectric is exposed. As the over polishing proceeds, the pad contact with the wafer decreases due to metal recess and increasing topography. This results in reducing the value of COF. .................................................................60

Figure 2.11 Patterned sin is polished without any metal layer deposited. In this case, there is almost no change in COF due to the minimal change in the topography. In both (a) and (b), the initial zero value for COF is for the time that the wafer has not landed on the pad. As the polishing starts, the value for COF abruptly increases.61
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CHAPTER 1
INTRODUCTION TO CHEMICAL MECHANICAL POLISHING (CMP)

1.1 Why CMP?

Polishing has been widely used for centuries in glass mirror and lens manufacturing, as well as by the semiconductor industry to produce single crystal wafers for a few decades. In all of those applications, polishing is used to finish the bulk material surface [1]. On the other hand, the use of chemical mechanical polishing in integrated circuit industry is still very new, and many questions about the nature of this process remain to be answered. Advances in integrated circuit technology necessitate precisely controllable removal of very thin, down to a few atomic layer, films of metal, dielectric, or semiconductor. Chemical mechanical polishing (CMP), which takes advantage of the synergy between chemical and mechanical material removal, is the ultimate solution when the material being processed cannot be removed effectively with other conventional patterning methods. Chemical mechanical polishing is widely used in the semiconductor industry to planarize metals, dielectrics, and also polysilicon.

In 1965, Gordon Moore, Fairchild semiconductor director of R&D, predicted that the number of components per chip doubles every two years [2]. Moore’s famous chart reaches until 1975, but carries the notion that there is no visible end, and the density of
the active and passive devices in integrated circuits is still increasing. This raises the need for an efficient interconnecting system. One possible approach is to use multilevel wiring over the devices [3]. Multilevel interconnect technology, in which the metal lines in different levels are isolated from one another by an insulator layer and are connected through vertical vias in the dielectric, decreases the length of the metal lines and allows them to be scaled down less aggressively than the gate length [4]. The surface topography, which builds up as the number of interconnect levels increases, poses challenges on the main steps in fabricating the multilevel interconnects; contact lithography, dielectric etching, and metal polishing [3]. In photolithography, for instance, the intended pattern is first transferred from a photomask to a photosensitive polymer known as photoresist, and then from this polymer to the materials underneath. In this technique, polymer chains are chemically modified by being exposed to a beam of photons. Depth of field (DOF) is the length along the exposure axis in which the photon beam still has an acceptable diameter. Critical dimension (CD) is the smallest feature size that needs to be patterned on the surface, and is the most important figure of merit in ic manufacturing. DOF has a great impact on the feature dimensions, and if the surface morphology of the device dictates that the resist to be exposed is not planar, then the DOF must be large enough so that all regions in the photoresist are properly illuminated. However, since the DOF is always a finite value, the surface topography should be such that the critical dimension is achieved. Therefore, chemical mechanical polishing, which is a technique used to reduce the surface topography, is an approach to tackle this
Although the device speed increases as dimensions shrink, the RC delay in interconnects deteriorates such that in today’s technology, the total delay of a circuit is determined by the interconnects [4]. Using metals with lower resistivity and low-k dielectrics are among the solutions to this RC delay increase. Low-k dielectrics, which are commonly porous, have poor mechanical properties, imposing challenges in their polish process due to the fact that CMP inherently involves mechanical stress and shear force [3].

CMP of metals is the critical technology that enabled the transition from aluminum to copper interconnects. Copper has higher conductivity, which decreases the
RC delay, and also is more resistant to electromigration. Electromigration, a critical reliability issue for high current densities, decays exponentially with the activation energy of atom diffusion [5]. Due to the higher activation energy in copper, it’s more resistant to electromigration than aluminum. On the other hand, patterning the copper interconnects is not via leith plasma etching at temperatures elo C. The reason is that chloride byproducts formed by the introduced chlorine etchant are not volatile, thereby they inhibit the proceeding of the etch process. Chemical mechanical polishing, used in the so-called damascene process, is the approach proposed by IBM to fabricate copper interconnects. The name of the process comes from metal inlay techniques used in the middle east since the middle ages [6].

Chemical mechanical polishing plays an important role in fabrication of microelectromechanical systems (MEMS). It is important to mention that the MEMS industry does not benefit from CMP in the same way as the IC fabrication industry; the feature sizes in the MEMS devices are several orders of magnitude larger than the gate length in IC devices, and the materials to be polished in the MEMS industry, polysilicon for instance, are not the target materials in the IC fabrication CMP [7].

Although replacing aluminum with copper in interconnects could reduce the RC delay, it is still not the best approach in high frequency applications. For instance, the resistance of metal interconnects increases at millimeter wave frequencies due to a phenomenon known as “skin effect”. Skin effect is defined as the confinement of current to a thin layer close to the surface of the transmission line. The surface of copper is
modified by its surface oxide, and this results in higher electrical resistance of copper interconnects at high frequencies. Gold, on the other hand, is a very promising replacement for copper due to its low resistivity and high chemical stability [8]. The high chemical stability of gold, however, poses challenges for its CMP process owing to the fact that CMP of metals is mainly based on chemical modification of the metal surface.

This thesis presents a set of experiments dedicated to finding a reliable gold CMP process with satisfactory and reproducible results.

1.2 CMP Process, Consumables, Inputs, and Outputs

During CMP, a wafer, placed into a rotating carrier head, is pressed against a rotating pad while slurry is dispensed on the pad. The slurry is distributed across the pad surface due to the centripetal force of the rotating pad. Moreover, there are large machined grooves on the surface of the pad which facilitates slurry transport across the polishing pad. In addition to the rotational motion, the wafer is swept across the pad in a radial direction to slow down the wear process of the pad. Figure 1.2 illustrates a basic rotary type CMP system.
Figure 1.2 Schematics of a basic rotary type CMP system [9].

Clearly from the brief description above, there are many variables in the CMP process that can affect the outcome. Typical polishing variables are the applied pressure, pad and wafer rotation speed, slurry type and flow rate, wafer curvature and its protrusion from the retaining ring, and the pad characteristics. Each of these parameters is briefly explained.

1.2.1 Pressure

The pressure is defined as the load applied to the wafer divided by the wafer area. This is a rough estimate due to the fact that the protruding areas are much smaller than the wafer area, and therefore the actual pressure on these parts is higher than the nominal pressure applied on the wafer. Pound per square inch, psi, and kilopascals, kPa, are the common units for pressure in CMP. In the Logitech Orbis CMP, pneumatic pressure is applied through a membrane to evenly distribute the down pressure.
Zhao et al. introduced “active” abrasives as the ones trapped between the pad asperities and the wafer. Higher pressure increases the removal rate because it increases the contact area between the pad and wafer, leading to a higher number of trapped particles between these two surfaces. They also claimed that the abrasives are embedded in the pad asperities since the pad is softer than the wafer surface. As a result, the indentation depth of the abrasives into the wafer surface does not change at higher pressure values, and it is a function of pad and wafer elastic moduli. They also mentioned “threshold pressure” which arises from the fact that effective abrasion by the slurry particles happens when the trapped abrasives are dragged against the wafer instead of rolling on the surface [10].

Uniform pressure distribution across the wafer is one of the key components affecting the within wafer nonuniformity (WWNU). Generally, higher pressure results in higher removal rates and can increase the throughput. However, it is important to mention that an increase in the applied pressure results in a thinner layer of slurry between the pad and wafer. With thinning of the slurry intermediate layer, the pressure supported by the slurry also decreases. Therefore, the friction between the pad and the wafer increases which may result in delamination of the material being polished from the substrate. Down pressure exceeding 10 psi should be strictly prohibited to avoid wafer breakage and the resulting damage to the pad and other consumables such as backing films and the carrier retaining ring [11].
1.2.2 Pad and Wafer Rotation Velocity

The relative velocity of the wafer with respect to the pad is among the parameters that play a key role in determining the removal rate and quality of the polish. During the material polish, both pad and wafer are rotating around their own axes. Higher pad and wafer velocity leads to an increase in the mechanical abrasion rate and increases the polish rate. Moreover, higher velocities results in faster transport of polish byproducts as well as new slurry across the pad which can also raise the removal rate. Higher pad velocities result in a thicker intermediate slurry layer between the pad and wafer and reduce the friction between these two solid surfaces, and can alleviate the delamination problems.

As mentioned earlier, the wafer is also swept on the pad radially to evenly distribute the wear of the pad. Patrick et al. stated that the relative velocity of each point of the wafer with respect to the pad center is calculated from Eq. 1.1 [12],

\[
\bar{V} = (\bar{W}_T \times \bar{r}_{CC}) - [\bar{r}_W \times (\bar{W}_w - \bar{W}_T)]
\]  

(1.1)

In which \( V \) is the relative velocity of each point relative to the pad, \( W_T \) and \( W_W \) are the angular velocity of the pad and the wafer respectively, \( r_{CC} \) is the vector connecting the center of the pad to the center of the wafer, \( r_W \) is the vector connecting the center of the wafer to the point of interest on the wafer. Figure 1.3 illustrates this coordination.
Based on this equation, they showed that if the wafer is rotating off the pad axis, then equal pad and wafer rotation speed results in equal velocity at every point on the wafer with respect to the center of the pad [12].

Despite the constant relative velocity, the removal rate is not consistent all over the wafer. Several groups have experienced a higher removal rate at the edge of the wafer, and attributed it to the constant contact of the wafer edge with fresh slurry. For example, Coppeta et al. claimed that the center of the wafer entrains fresh slurry more slowly than the edge of the wafer, and therefore is polished away slower [13]. Different speeds for the wafer and the pad further increase the removal rate at the edge. In our CMP experiments, however, the removal rate of the center is higher than the wafer edge. This can be attributed to the deformation of the pad beneath the wafer, as explained in
detail in the section below. Moreover, we believe that the wafer supported by the napcon pad in the carrier head slips while it is in contact with the rotating pad during the process. Therefore, the actual rotation speed of the wafer is different from the one assigned to the carrier head. As a result, during our experiments, the pad was rotating at 60 rpm, while the rotation speed of the wafer carrier was kept at 45 rpm.

1.2.3 Retaining Ring and Wafer Protrusion

Yun-Biao Xin gave interesting analytical and experimental explanations about the pressure distribution across the wafer which is among the primary factors in determining the thickness uniformity of the layer being polished [14]. The author divided the pressure distribution into 3 regions: region 1 in which the pressure is distributed uniformly, region 2 in which there is an abrupt pressure increase due to the geometry discontinuity at the contact periphery, and region 3 which is the transition region from region 1 to 2, where the pressure is slightly lower than the applied pressure. Figure 1.4 illustrates the stress in these regions. \( S_{11}, S_{12}, \) and \( S_{22} \) are the stresses in \( r, r-z, \) and \( z \) directions respectively: \( r \) is on the pad- wafer contact plane and \( z \) is in the direction normal to that plane. The “von Mises” line is the von Mises stress, which is the combination of these three stresses.
The abrupt pressure increase along with the pad deformation at the wafer periphery is referred to as the “edge effect”. Xin found that harder pads with less deformation cause less “edge effect” than softer ones. Moreover, the author showed that the use of a retaining ring can alleviate the nonuniformity of the pressure distribution, and suggested that the pressure of the retaining ring should be higher than the pressure applied on the wafer to achieve the best results [14]. The main role of the retaining rings is to prevent the wafer from slipping out of the wafer carrier during polishing. However, retaining rings are also a means of virtually extending the edge of the wafer, so that the pad deformation takes place at the edge of the retaining ring instead of the wafer. Figure 1.4 Stress distribution on the wafer surface in the interface [14].
1.5 shows the edge effect at the carrier head periphery which would otherwise occur at the wafer edge.

In our Orbis CMP equipment, the retaining ring is rigid, and therefore the operator is not able to adjust the pressure applied on the retaining ring. However, I found that if the pressure applied to the wafer is less than 2 psi, the polish nonuniformity is severe, therefore the pressure has been always kept at 2 psi. Wafer protrusion is also crucial in mitigating the edge effect; if the wafer protrudes too far past the retaining ring, it may slide out of the carrier head, but if it is placed much lower than the retaining ring, while the pressures is kept below 2 psi, the pad is deformed under the wafer carrier such
that more pressure is exerted at the center of the wafer, leading to high removal rate at the center and slow removal at the area between the center and the edge, i.e. about 1cm away from both the edge and the center. Therefore, and optimum protrusion is required. The operator can adjust the height of the wafer in the carrier head by placing mylar shims with different thicknesses underneath the wafer in the template. In my experiments, wafer protruded the carrier head by approximately 150 µm. In the Logitech Orbis CMP system, the wafer curvature is adjusted through pneumatic pressure. The back pressure and down force are independently applied on the wafer. A back pressure of 25 psi maintains a flat surface on the puck, thus ensuring even download force across the whole sample. Values towards 0 psi produce a concave puck shape and values towards 50 psi produce convex surface shape.

1.2.4 Pad

The pad used in CMP is responsible for the transport of fresh slurry and polish byproducts. The pores and grooves in the pad are used to meet this requirement. The pad also transmits the normal and tangential force to the wafer. Due to the nature of CMP, which involves both chemical and mechanical removal, a polishing pad is constantly exposed to reactive chemicals, extreme pH variations, and mechanical stress. As a result, a reliable pad should be both chemically and mechanically stable. Polyurethane is among the polymers that satisfy these two conditions when used in pads. This polymer has two segments: Isocyanate (rigid) and Polyol (flexible). These “hard” and “soft” segments
have different properties, which lead to different polishing pad characteristics [16]. Hardness is among the physical properties that are determined by the ratio of polyurethanes hard-to-soft segments and affects the CMP performance. Hardness of the pad indicates the ability of the pad to conform to wafer topology, and is related to the pad’s elastic properties. Harder pads lead to higher removal rates, less dishing in the polished material, and better planarization, but they also result in micro-defects and poor wafer uniformity due to their difficulty in conforming to wafer surface variations [17].

1.2.5 Pad Conditioning

Pad conditioning is the process of dressing the pad with an abrasive medium like a diamond disk. The surface of an unconditioned pad wets poorly and is not suitable for slurry transport beneath the wafer. Therefore, pad conditioning is crucial to maintain a consistent polishing surface during the life of the pad. During the wafer polish, the cells of the polyurethane pad get clogged, but they open up during the pad conditioning. Pad conditioning removes a thin layer of the pad, and gradually makes the pad thinner. It can also result in a gradual change in the groove dimensions. The cutting rate of the diamond disk is a function of the conditioning aggressiveness which depends on the size and design of the diamonds, pressure applied on the diamond disk, and rotation speed of the pad and abrasive block during conditioning. During the CMP process, the coefficient of friction of the previously conditioned pad gradually decreases due to the wear from the wafer being pressed on the pad. In general, aggressive conditioning, and low applied
pressure during wafer polishing result in less friction variation during the CMP, and therefore improves the uniformity and polish rate consistency. If the cut rate of the diamond disk is much less than the wear rate of the pad, the pad is prone to glazing effect. Pad glazing refers to a reduction in the pad surface roughness and removal rate. It also aggravates the within wafer non-uniformity. On the other hand, higher cut rate than the wear rate result in pad lifetime reduction which leads to a higher cost in CMP consumables. Choi et al. investigated the effect of the pressure applied on the conditioning disk and its rotational speed on the height of the pad asperities. They observed that using low pressure and rotational speed, the height distribution is not much different from a fresh pad. A fresh unconditioned pad has a sharp height distribution with a peak near the mean value. However, as the speed and pressure increase, the distribution becomes closer to a normal distribution [18]. Figure 1.6 shows the effect of conditioning aggressiveness on the height distribution of pad asperities which have been measured by white light interferometer. It is important to mention that in this paper, the aggressiveness of the conditioning is determined by the pressure applied on the diamond block and the rotation speed of the block.
In Figure 1.5, recipe 4 is a combination of low conditioner down force and low rotation speed of this block. In recipe 3, the conditioner rotation speed was increased, whereas the down force applied on the conditioner was increased in recipe 2. Both the down force and the rotation speed were increased in recipe 1. Based on this experiment, low applied pressure on the conditioning disk results in more truncated asperities, whereas more aggressive conditioning results in high aspect ratio asperities. Less
aggressive conditioning increases the planarizing ability of the pad since the pad asperities are shorter and therefore are preferentially in contact with the higher parts of the wafer [19].

1.2.6 Slurry

Slurries are aqueous solutions with abrasive particles and chemical additives. Abrasive particles, which are mainly responsible for the mechanical aspect of CMP, get trapped between the pad asperities and the wafer, and enhance the mechanical strength of the pad, resulting in an increase in the polish rate. These particles also play a role in the chemical aspect of CMP. For instance, abrasive particles made out of cerium oxide, ceria, were observed to chemically react with a silicon dioxide layer [20]. Higher concentration of abrasives in slurry, usually defined in weight percent, generally results in higher removal rates. Hardness of the abrasives determines the effectiveness of the abrasion such that harder abrasives result in higher removal rates. On the other hand, harder abrasives may also cause defects in the material being polished. The effect of the abrasive size is in the same direction as its hardness, and control of the abrasive size distribution is important for damage free CMP. Density of the abrasive particles is among the other properties which can affect the behavior of the slurries. In general, abrasives with higher densities are more probable to sediment and agglomerate, which makes the slurry unstable [21]. Zeta potential as well as the isoelectric point of the abrasive particles and other materials in contact with the slurry is of great importance. Zeta potential is the
charge associated with a particle in an aqueous solution and is used as a criterion to determine the stability of particles in a colloidal system. A system in which the absolute value of the particles zeta potential is over 3 mV is considered as “stable”, meaning that the electrical repulsion of the particles is stronger than the van der waals force which draws colloidal particles towards one another. In addition to the system stability, zeta potential of the abrasive particles and polished materials can play an important role in the polish rate of the material. The same sign of zeta potential decreases the polish rate, while different sign between the polished material and abrasives increases this parameter. Ph of the aqueous system is a key parameter in determining the zeta potential of the particles in the system. Generally, particles in a highly alkaline system have negative zeta potential, while this parameter is positive in a strongly acidic environment.

The isoelectric point is the pH value at which the zeta potential of the particle is zero. The pH of a useable slurry is usually far from this point to ensure the stability of the aqueous system.

1.2.7 pH Adjusters, Oxidizers, and Complexing Agents

Complexing agents, also known as “chelating” agents, improve the solubility of the material being polished in the slurry solution. Using these chemicals, one can adjust the effectiveness of the chemical aspect of the CMP process. While high dissolution rate leads to isotropic material removal, which is unfavorable in CMP, very low dissolution rate of the abraded materials in the slurry results in particle redeposition [4].
pH is defined as the negative logarithm of the hydrogen ion concentration, and has a great impact on the polish result and slurry behavior. This parameter affects the dissolution rate, solubility, and redox potential of the material or its modified surface. As mentioned before, it determines the stability of the slurry by changing the zeta potential of the colloidal particles. The pH of a slurry is drawn towards neutral when the slurry is diluted with deionized (DI) water. This pH change has a great effect on the stability of the slurry. To counteract this effect, the pH can be adjusted back to its initial value by pH adjusters such as ammonium hydroxide and hydrochloric acid.

Oxidation refers to a reaction in which the reactant, an atom or a molecule, loses one or more electrons, whereas reduction is a reaction in which at least one electron is given to the reactant. Oxidizers are a species that are themselves reduced by accepting the electrons released from the oxidized reactant. In other words, they make the oxidation reaction possible by draining the released electrons. Reaction 1.2 shows the oxidation of copper in which the oxidation state of copper is raised from 0 to +2. Reaction 1.3 shows the reduction of ferricyanide. These two reactions happen at the same time, and can be written as reaction 1.4:

\[
\text{Cu} \leftrightarrow \text{Cu}^{2+} + 2e^- \quad (1.2)
\]

\[
2e^- + 2\text{Fe} (CN)_6^{3-} \leftrightarrow 2\text{Fe} (CN)_6^{4-} \quad (1.3)
\]

\[
\text{Cu} + 2\text{Fe} (CN)_6^{3-} \leftrightarrow \text{Cu}^{2+} + 2\text{Fe} (CN)_6^{4-} \quad (1.4)
\]
This chemically modified layer forms a surface which either dissolves in the slurry or it is porous and can be easily abraded and removed by the abrasive particles. In order for a redox reaction, reaction 1.4 for instance, to be thermodynamically favorable, the net free energy change, which is the sum of the energy change in each of the first two reactions, should be negative. Free energy is usually expressed in terms of electrochemical potentials. The electrochemical potential, $\varepsilon$, and the free energy change are related according to eq. 1.5:

$$\Delta G = -nF\varepsilon$$

(1.5)

Where $\Delta G$ is the free energy, $n$ is the number of electrons, in moles, transferred in the reaction, $F$ is faraday’s constant, i.e. charge per one mole of electrons, and $\varepsilon$ is the electrochemical potential in volts. For a reaction to be thermodynamically favored, the free energy change should be negative, while the electrochemical potential is positive. The relative redox potentials and chemical composition of the film surface under thermodynamic equilibrium can be illustrated by the relevant Pourbaix diagram. The Pourbaix diagram also shows the driving force of different oxidation reactions that a metal can have in an aqueous solution. A simplified Pourbaix diagram indicates regions of "immunity", "corrosion" and "passivation", instead of the stable species. They thus give a guide to the stability of a particular metal in a specific environment. Immunity means that the metal is not attacked, while corrosion indicates the dissolution of the metal in form of ions. Passivation occurs when the metal forms a stable coating of an oxide or other salt on its surface. It’s important to mention that addition of oxidizers, passivating
agents, and chelating agents changes the boundaries of the regions in a potential-pH
diagram, and therefore modifies the dissolution rate of the materials. Figure 1.7 shows the
Pourbaix diagram of the cu-water system.

Figure 1.7  Pourbaix diagram for cu-water system indicating the corrosion behavior of
copper in water. The right diagram is the simplified pourbaix diagram [22].

At low pH, the oxidation of Cu to Cu$^{2+}$ is favored. In near neutral pH, the
formation of cuprous and cupric oxide is thermodynamically favored, and the copper
surface is passivated by the oxide film. At higher pH, copper oxides may be dissolved to
form HCuO$_2^-$ and CuO$_2^{2-}$. Corrosion of a metal film is an isotropic reaction and is not
desirable in the polishing process.
Hydrogen peroxide is among the most common solutions added to the slurry as an oxidizer. It was found that at a proper pH, Cu reacts with $\text{H}_2\text{O}_2$ to form $\text{Cu}_2\text{O}_2$. The film is porous and can be abraded and polished away. At this pH, material removal rate increases as the $\text{H}_2\text{O}_2$ concentration is raised. On the other hand, after adding additional $\text{H}_2\text{O}_2$, a thicker and denser film starts being formed which is strong enough to serve as a passivating layer. Under these conditions, the material removal and static etch rates decreases with increase in hydrogen peroxide concentration. This behavior is illustrated in the Figure 1.8 below:

![Figure 1.8 Schematic illustration of hydrogen peroxide concentration effect on material removal rate of copper](image)

Figure 1.8 Schematic illustration of hydrogen peroxide concentration effect on material removal rate of copper [23].
The removal rate of copper in the so-called “etch region” can be reduced by adding passivating agents such as benzotriazole (BTA), while in the passivation region, the removal rate is increased by introducing complexing agents like glycine. The effect of hydrogen peroxide concentration on the removal rate of tungsten and nickel has been investigated, and gives the same, but not as pronounced, result [21], [24].

1.2.8 Surfactants

Surfactants are amphiphilic molecules, meaning that they have at least one hydrophilic “head” and one hydrophobic end. The main desirable characteristic of surfactants in CMP is their tendency to aggregate at an interface. Surfactants are divided into four major groups based on the charge of their head: anionic, cationic, non-ionic, and zwitterionic. Ionic surfactants dissociate in an aqueous environment to form an electrically charged head and a corresponding counter ion. The head is negatively charged in case of an anionic surfactant and positively charged when the surfactant is cationic. The overall charge of the zwitterionic and non-ionic surfactant head is neutral with the difference that in zwitterionic surfactants, the head contains both positively and negatively charged groups while non-ionic surfactant has no charged groups. Non-ionic surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type [21]. Some zwitterionic, or amphoteric, surfactants are insensitive to pH, whereas others are cationic at low pH and anionic at high pH, with an amphoteric behavior at intermediate pH. Amphoteric surfactants are generally quite expensive and
consequently, their use is limited to very special applications such as cosmetics where their high biological compatibility and low toxicity is of primary importance [25]. Figure 1.9 shows the structure of two common examples of ionic surfactants.

![Figure 1.9 The structure of sodium dodecyl sulfate (sds), an anionic surfactant and a cationic surfactant, dodecyl trimethyl ammonium bromide [26].](image)

Surfactants adsorb on the interface and orient so as to have their polar head groups with water, while projecting the hydrophobic tail into the air, thus forming a single layer of surfactant molecules at the interface. This decreases the surface tension of the solution. The driving force for this phenomenon is the hydrophobic effect as in this way the hydrophobic tails are not in contact with water. The result is increasing the entropy of surfactants. Upon reaching the solubility limit for the surfactant monomers, they start to aggregate, forming structures known as micelles. At this concentration, the decreasing trend of the surface tension stops. Now, hydrophobic parts are hidden inside the micelle core while the micelle surface consists of the hydrophilic parts. This process
is also driven by the hydrophobic effect. Figure 1.10 illustrates the formation of surfactant micelles.

![Surfactant Micelles](image)

**Figure 1.10** The configuration of surfactant molecules in different concentrations [27].

The two main purposes of using surfactants in CMP are slurry stabilization and passivating the surface of the material being polished. In general, there are two ways by which the stability of slurries is enhanced; steric dispersion and charge dispersion. Steric dispersion is based on the fact that the adsorption of non-ionic surfactants on the surface of abrasives prevents these particles from adhering to one another due to the Van der Waals attraction force. In charge dispersion, electrically charged surfactants adsorb on the surface of the abrasives, and ensure their stability by electrostatic repulsion. It is important to mention that adsorption of ionic surfactants on the particle surface alters the zeta potential of the particle and can either improve or undermine the stability of the slurry.
Surfactants can also be used to passivate a layer and change its polish rate. It has been found that by adding sodium dodecyl sulfate (SDS) to silica based slurry, preferential adsorption of SDS on silicon nitride, mainly because of electrostatic effects, results in the formation of a passivation layer on the nitride surface and leads to a higher oxide to nitride polish selectivity in shallow trench isolation (STI) process [28].

It is important to mention that in order for the surfactant to become a good dispersant or passivation layer, there should be enough adhesion between the surfactant and the target surface. The adhesion is a function of the abrasive type and the slurry ph. While most surfactants can be used in alkaline environments, few types of surfactants are compatible with acidic slurries [29].

1.3 Output Variables of CMP

1.3.1 Removal Rate and Preston Equation

Removal rate is defined as the thickness of the material removed per unit time. Higher polish rate shortens the process time and therefore increases the throughput. On the other hand, a very high polish rate may undermine the control on the process. The removal rate of the material being polished during the CMP, was first suggested as following Preston’s equation [30]:

\[
RR = K_p PV
\]

(1.6)
In which RR is the expected removal rate, $K_p$ is the Preston constant, $P$ is the local applied pressure, and $V$ is the relative velocity of a point on the wafer relative to the pad. It is important to note that although this equation gives useful information about the processing start point, there are several CMP experimental results that deviate from this equation. Zhuang et al. along with Katoh et al. attributed this deviation to the additives, especially surfactants, in the slurry which form a passivation layer on the dielectric. When surfactants adsorb on the surface, they require a minimum pressure to be removed [31], [32]. This would result in an offset in removal rate, and make the removal rate equation non-linear.

Additionally, Zhao et al. [10] suggested a threshold pressure which needs to be applied to make the abrasives, trapped between the pad asperities and the wafer, slide on the wafer surface. This pressure is more than that needed to roll the abrasives on the wafer surface. They also claimed that the traditional Preston equation applies to cases in which the pad is harder than the abrasive and the polished material, while the contemporary pad material, polyurethane, is softer than the abrasives. Therefore, they proposed a modified equation for calculating the removal rates as shown below [10]. RR stands for removal rate, $K(V)$ is a function of rotation velocity and other process parameters, and $P$ is the applied pressure on the wafer.

$$RR = K(V)P^{2/3}$$ (1.7)
In addition to this modified equation, there are several modified equations for removal rate calculations in metal and dielectric CMP, each of which has its own limitations and advantages.

The material removal rate may not remain constant throughout the polish time. Kim et al. noticed a rise in the dielectric removal rate and attributed this effect to an increase in the pad temperature as the polishing proceeds [33]. Moreover, Mainka et al. investigated the CMP of iridium and iridium oxide, and stated that the removal rate of iridium oxide increases with time, while it remains constant during the iridium polish. They called this effect “self-polishing mechanism” in polishing iridium oxide, and attributed it to the role of the abraded oxide particles in removal of the remaining unpolished oxide. The authors believe that due to the greater hardness of these particles with respect to the abrasives in the slurry, they have the dominant effect in determining the polish rate, and increase the removal rate as they accumulate while the CMP proceeds. While an increase in the polish rate of iridium oxide was observed, there was no change in the iridium removal rate. They called iridium oxide CMP “mechanical polishing” and iridium CMP “chemical polishing” to emphasize the dominant aspect of CMP in each process [34].
1.3.2 Selectivity, Dishing, and Erosion

Selectivity between two materials is defined as the ratio of their polish rate during CMP. The CMP samples generally consist of a pattern etched into the dielectric. The target material for polishing is then deposited on the whole wafer, and the role of CMP is to remove the material overlay on the dielectric, leaving the trenches filled with the target material. Erosion is localized loss of the oxide level between the patterns with respect to the oxide on the field, while dishing accounts for the localized loss of the target material with respect to the dielectric on the field. It is called dishing because the material loss is highest at the center of the target material, resembling the curvature of a dish. This curvature is due to the finite hardness of the pad, which allows the pad to deform if the recessed region is wide. Erosion and dishing in CMP reduce the thickness of both the dielectric and the target material and result in surface non-planarity. Figure 1.11 illustrates the dishing and erosion in metal CMP.

Figure 1.11 Dishing and erosion in metal polishing.
Dishing is directly related to the selectivity and becomes severe with highly selective slurries. In addition to the selectivity, pad properties have a direct impact on the degree of dishing; softer pads result in more dishing as they can deform and be in contact with the recessed target material and polish them further. By the same token, aggressive pad conditioning which results in high aspect ratio asperities on the pad increase the dishing effect, due to the fact that the asperities can be made tall enough to be in contact with the recessed target material [19]. The size of the features also has a great impact on the severity of dishing. The elastic deformation of the pad is more pronounced at wider recessed areas, and this allows the pad to be in contact with the material in the trench and remove it further.

Erosion dependence on selectivity is not intuitive. While highly selective slurry is commonly used to mitigate the nitride erosion in shallow trench isolation (STI) [35], Tanaka et al. controlled the amount of erosion by reducing the difference between the metal and the dielectric removal rate in metal CMP [36]. When the target features are polished much faster than the oxide between those features, as the over polish proceeds, oxide protrudes in that localized area, and therefore experiences a higher pressure than the rest of the oxide field, and can be polished faster. Due to the fact that the removal rate of oxide is negligible compared to the target material, this layer is not going to be polished away significantly. On the other hand, when the dielectric and the target material are polished at the same rate, there shouldn’t be any protruded area and the polish rate of both materials is very close to the field polish rate. However, despite the
reduced topography, dielectric removal may be significant, and the thickness of the whole dielectric layer is reduced. Although the relation between the selectivity and erosion is not straightforward, it is clear that higher pattern densities results in more severe erosion, due to the fact that at high pattern densities, the density of the protruding oxide features is less which results in higher removal rate in those areas [37]. Due to the fact that the local oxide layer is polished faster at higher densities, it is said that selectivity is also dependent to the pattern density and decreases in denser areas.

It has been reported that in multilayer metal interconnects, erosion is more significant at the device level features where the width of cu interconnects is small. However, dishing is more prominent in top layers of a multilevel damascene structure where copper lines become wider [38].

It’s important to mention that regardless of the relation between erosion and dishing with selectivity and pattern density, over polishing the wafer deteriorates these issues, and therefore a reliable endpoint detection method is very desirable.

1.3.3 Planarization Rate

As it is obvious from the name, one of the main goals of the CMP is to reduce the topography of the wafer. Planarization rate is defined as the step height reduction per unit time. This is especially of great importance in ILD CMP where the main goal is planarization of the dielectric layer. In CMP, the removal rate of the protruded areas is
higher than the field due to their lower density. Boning et al. suggested that the removal rate of protruding areas is inversely proportional to the effective density of the raised topography [39].

Grillaert et al. [40] proposed a model for the evolution of step height reduction versus time. They found that the efficiency of step height reduction depends on the height of the step at each point in time. At the initial stage when the pad is not in contact with the bottom of the step, the height reduction rate is almost constant and inversely proportional to the pattern density. When the CMP proceeds, however, there would be a point when the polishing pad contacts the bottom of the step, and the pad pressure differential decreases with time leading to less efficient reduction of the constantly shrinking step. At this point, both the step height and its reduction rate are exponentially decreasing. The first stage when the pad is not in contact with the lower level of the step is called “incompressible pad model” while the next phase is “compressible pad model”. It is clear that a harder polishing pad would be a more efficient planarizer than a soft and compressible one.

1.3.4 Coefficient of Friction

Coefficient of friction (COF) is among the common metrological factors used in chemical mechanical polishing, defined as the ratio between the shear frictional force and the normal load. COF reveals useful information about the nature of the contact between pad, slurry, and wafer [41]. This parameter depends on the pad characteristics, i.e. its
hardness, the slurry properties, i.e. its viscosity and abrasive concentration, and the process conditions, i.e. applied pressure, temperature, the material being polished, and rotation speed of wafer and pad.

Coefficient of friction is plotted with respect to Sommerfeld number in a curve called the Strubeck curve. The Sommerfeld number depends upon the CMP parameters during the process, and is defined using eq. 1.7 [42]:

\[
S_t = \frac{\mu U}{P\delta_{\text{eff}}}
\]

Where \( \mu \) is viscosity of the slurry, \( u \) is the relative velocity between the pad and the wafer, \( p \) is the applied pressure, and \( \delta_{\text{eff}} \) is the effective fluid thickness which is approximated by the pad surface roughness. The Strubeck curve gives some information about the lubrication regime at the polish interface. In the Strubeck curve, the lubrication regime is divided into three main regions: boundary lubrication, partial lubrication, and hydrodynamic lubrication. Boundary lubrication reflects the direct solid-solid contact between the pad and the wafer. In this region, the polish is mainly based on the surface abrasion. Boundary lubrication results in high shear force between the pad and wafer which can lead to the delamination of the layer being polished. Moreover, the significant thermal energy generation results in non-uniform and non-reproducible polish results. As the Sommerfeld number increases, the polish process enters the partial lubrication region in which the applied pressure is partially supported by the thin slurry film between the
pad and wafer, which alleviates the aggressive abrasion by the pad asperities and reduces surface damage. Hydrodynamic lubrication, also referred to as hydroplaning, reflects the region in which the applied pressure is completely supported by the slurry film between the solid-solid interface, and results in a very low coefficient of friction and a dramatic reduction in the polish rate. Figure 1.12 depicts these three regions.

![Figure 1.12 The stribeck curve and three modes of contact](image)

Although COF has proven to be a useful parameter to monitor during the polishing process, its relation with removal rate is not intuitive, and has not been very well understood. For instance, higher values of the COF do not necessarily lead to a higher removal rate. Philipossian et al. [43], [42] investigated the behavior of COF in response to the abrasive concentration and slurry flow rate. They observed that the reduction of the abrasive concentration leads to an increase in the COF, and justified the result with the fact that abrasive particles in the slurry act like a lubricant during the
polish process and reduce the coefficient of friction. The removal rate, however, decreases with lower abrasive concentrations. Moreover, they found that higher slurry flow rates results in lower coefficient of friction. This COF decrease, however, is not reflected in the removal rate up to a 4 fold increase in the flow rate. Based on this observation, they accentuated weakness of the traditional Stribeck curve due to the absence of slurry flow rate in Sommerfeld number parameters. Zhuang et al. also investigated the impact of abrasive’s shape and density on the coefficient of friction, and found that ceria abrasives that have sharp edges and are denser result in a higher COF than that by silica abrasives that are round [32].

Due to the fact that the materials being polished during the process can modify the COF value, this parameter can be used to detect the end point of CMP, i.e. the point at which metal or dielectric over lay is polished. We investigate this method in the next chapter.
CHAPTER 2

EXPERIMENTAL RESULTS

2.1 Sample Preparation and Process Parameters

The samples for Au CMP were fabricated in the Notre Dame nanofabrication facility (NDNF). 150 nm of SiNₓ was deposited using plasma enhanced chemical vapor deposition (PECVD). A pattern was transferred to the deposited dielectric by photolithography and reactive ion etching (RIE). 15 nm of Cr, Ni, or Ti, that serve as an adhesion promoter, followed by 200 nm of Au, comprise the evaporated metal on the dielectric layer by electron beam evaporation. Figure 2.1 shows the schematics of a gold CMP sample prior to processing. Gray color represents the adhesion promoter layer, while the yellow color represents Au.

Figure 2.1 Schematic of a gold CMP sample before polishing.

36
Adhesion of a metal layer to its substrate requires a physical interlocking, interdiffusion of the deposited metal or a chemical bonding between the metal and substrate in order to work. Gold is known for its poor adhesion to a silicon substrate due to its chemical inertness. To address this problem, a very thin layer of a metal with good adhesion to both the substrate and gold is always deposited as a first layer. Ti, Cr, and Ni are the common metals used to enhance the adhesion of gold to Si. However, the hardness of these adhesion layers is generally much higher than that for gold. On the Mohs’ scale of hardness, nickel is 4, titanium oxide is 5.5-6.5, chromium (oxide) is 8.5, and gold is between 2.5 to 3. The hardness of materials indicates their resistance to abrasion and therefore a harder material is polished slower. When the adhesion layer is much harder than Au, a long time is spent in CMP to remove the adhesion-promoter overlay on the dielectric. Meanwhile, Au is also being polished in the trenches at a higher rate, resulting in a significant amount of dishing. Among the investigated adhesion-promoters, Ni has the least hardness, and therefore has proven to be the best adhesion layer for our experiments. Different concentrations of abrasives and oxidizer have been tested to find the condition in which Ni polishes faster than Au. This step is crucial to alleviate the dishing of Au interconnects.

The main parameters for the CMP process were determined based on the polishing results of pilot blanket wafers and are listed in Table 2.1.
TABLE 2.1
THE LIST OF THE PROCESS PARAMETERS USED IN OUR EXPERIMENTS

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Applied down load on carrier head</td>
<td>2 psi</td>
</tr>
<tr>
<td>Back pressure</td>
<td>25 psi</td>
</tr>
<tr>
<td>Pad velocity</td>
<td>60 rpm</td>
</tr>
<tr>
<td>Carrier velocity</td>
<td>45 rpm</td>
</tr>
<tr>
<td>Wafer protrusion from the carrier head</td>
<td>150 µm</td>
</tr>
<tr>
<td>Slurry flow rate</td>
<td>100 ml/min</td>
</tr>
</tbody>
</table>

2.2 Pad Preparation and Conditioning

Prior to starting CMP, the pad is conditioned with a rotating diamond disk for 5 minutes, the pressure applied on the diamond disk is 0.4 psi, the rotation speed of both the pad and the disk is 30 rpm, and the flow rate of the deionized water being dispensed on the pad during the conditioning is 75 ml/min. The pad is conditioned between each CMP run to provide a consistent pad surface structure. Due to the existence of mobile potassium ions in the slurry, every time gold CMP is performed, anything that has been in contact with the gold slurry must be rinsed. This includes flushing the slurry delivery line with one gallon of diluted ammonium hydroxide and one gallon of diluted hydrochloric acid both in 1:50 ratio with water. Between these two steps, the delivery line is flushed with
four gallons of di water and the pad is conditioned for five minutes during the flush. $\text{NH}_4\text{OH}$ helps in removing the positive ions remained on the pad and delivery lines by replacing the metal ions with $\text{NH}_4^+$. Hydrochloric acid has also proven to help reduce the metal particle contamination.

2.3 Post CMP Wafer Cleaning

Post CMP process, there may be surfactants, polished materials, and pad debris re-deposited on the wafer surface. As a result, wafers must be cleaned after polishing. In cleaning, we used DuPont EKC 4000™ with a PVC sponge. This proved to be very effective in removing the particles left on the wafer after polishing.

2.4 Slurry

Singh Rajiv gives an excellent explanation of the polishing mechanism of noble metals [44]; the potassium iodide added to the slurry ionizes and produces iodide ions ($I^- \text{.}$). These ions, referred to as “halides” in chemistry, oxidize by an oxidizer, that is hydrogen peroxide in our case, and form iodine ($I_2$). These iodine molecules are referred to as a “halogen” in chemistry and give a light-to-dark yellow color to the slurry depending on their concentration. The remaining iodide ions react with halogens to form a polyhalide ($I_3^-$). Equation 2.1 describes the reactions taking place in the slurry.
Polyhalide reacts with the metal to form a passivation layer which is abraded by the abrasive particles during CMP. An important point to note is that excessive addition of ki increases the chemical dissolution rate of gold in an uncontrollable way, and can result in the complete removal of 200 nm of Au in less than 10 seconds.

Ishii et al. also suggested that an alumina based slurry with added potassium iodate ($\text{KIO}_3$) and hydrogen peroxide at pH=4 results in the removal of gold [8]. They achieved the maximum polish rate of gold, $35 \ \frac{\text{nm}}{\text{min}}$, when 30% $\text{H}_2\text{O}_2$ solution was added to Rodel MSW 2000, a commercially available alumina based slurry with added potassium iodate, in 1:1 ratio.

We started our set of experiments with 30% $\text{H}_2\text{O}_2$ solution added to ultra-sol a20 in a 1:1 ratio. Ultra-sol a20, purchased from Eminess Corp., is an alumina based slurry with added potassium iodide at pH=4. The mean abrasive size in this slurry is 240 nm, and the solid content makes up 15% of the total weight. The exact content of the slurry is unknown as it is proprietary. Using the slurry combination above, we faced several issues in the outcome of the process. These problems and the measures to improve the outcome are explained below in detail:

\[
2I^- \rightarrow I_2 + 2e^- \\
I_2 + I^- \rightarrow I_3^-
\]
2.4.1 Metal Contact Recess and Severe Dishing

The result of the initial experiments showed 50% loss of the metal in the interconnect trenches. To solve this problem, we tried to lower the strength of mechanical abrasion of abrasives and chemical dissolution of gold. I believe that the positive zeta potential of alumina abrasive and negative charge of gold at pH=4 has a negative impact on Au interconnect dishing. This is due to the fact that the electrostatic force between the abrasives and the target material affects the abrasion efficiency of the abrasives. If slurry particles and the target layer are oppositely charged, the removal rate is more than when their charges have the same sign. To achieve a slower removal rate, I tried to alter the surface charge on the alumina abrasive by adding sodium dodecyl sulfate (SDS) which is an anionic surfactant.

The slurry with 50% concentration of hydrogen peroxide results in high static etch rate, i.e. chemical dissolution, of gold, approximately 95 nm/min. This high static etch rate increases edge recess and dishing in the interconnect trench. At 50% concentration of hydrogen peroxide, due to the lower polish rate of the adhesion promoter compared to gold, the main part of the polish time belonged to the removal of the adhesion layer overlay, which was longest for Cr and shortest for Ni due to their different hardness. At this concentration, while the adhesion promoter overlay is being polished on the dielectric, the gold in contacts is being polished at a higher rate. The amount of dishing in metal contact is thus determined by the time it takes the adhesion layer to be removed, and also the relative rate at which the gold is being polished. In order to achieve the least
amount of dishing, we changed the concentration of the oxidizer, hydrogen peroxide, to obtain a lower removal rate of gold. Moreover, we selected Ni as the adhesion layer due to its lower hardness than the other adhesion promoters.

At relatively large, 100 µm wide for instance, trenches in the dielectric that are filled with metal, we noticed the metal recess in the trench starting from the sides with less pattern density in their vicinity. Figure 2.2 illustrates this effect in gold contacts when Ti was used as the adhesion layer. When the high static etch rate of Au results in high selectivity between dielectric and metal, dielectric erosion becomes severe as it is also mentioned in the first chapter. In an array of metal contacts, due to the higher density of the metal pattern in the middle of the array, the dielectric erosion is more severe, and this results in the pad deformation over the array. However, at the array boundaries, the deformed pad cannot fully conform to the pattern geometry, leaving space for slurry to accumulate and chemically etch the metal in the trench. Figure 2.3 illustrates this effect. The recessed area becomes wider as the CMP proceeds. Therefore, by using an adhesion promoter with lower hardness, the process designer can decrease the total polish time, and minimize the metal recess. Moreover, the static etch rate of gold has to be reduced. Lowering the concentration of the oxidizer, we found out that the removal rate of Ni increased while the gold was polished at a lower rate than the previous concentration.
Figure 2.2 CMP result when Ti was used as the adhesion layer, and 30% hydrogen peroxide solution added to ultra-sol a20 in 1:1 ratio was used as the slurry. High static etch rate of gold, and the long time required to polish the Ti overlay resulted in significant gold recess.
Figure 2.3 The metal recess starting from the outer edges of the metal array caused mainly by high static etch rate of the metal, and severe erosion of dielectric in the middle of the array.

My experiments showed that changing the ratio between hydrogen peroxide and ultra-sol A20 concentration, i.e. $\text{H}_2\text{O}_2 : \text{Ultrasol A20}$, from 1:1 to 1:3 reduces the polish time three times. Although the chemical etch rate of gold dropped from $90 \frac{\text{nm}}{\text{min}}$ to $30 \frac{\text{nm}}{\text{min}}$, the total polish time also decreased from 3 minutes to 1 minute. This is mainly due to the higher adhesion layer removal rate that results from reducing the oxidizer concentration. At this concentration, the polish selectivity between Ni and Au using this slurry was about 3, the removal rate of Ni being three times higher than that of Au.

In reducing the oxidizer concentration while keeping the surfactant concentration constant, it was observed that the polish result is more reproducible when 1 part of $\text{H}_2\text{O}_2$ is added to 3 parts of Ultra-Sol A20, i.e. $\text{H}_2\text{O}_2 : \text{ultra-sol a20}$ 1:3, instead of the case when one part of slurry is replaced by DI water, i.e. 1:1:2 $\text{H}_2\text{O}_2 : \text{DI water} : \text{ultra-sol a20}$. The reason may be explained as follows: when di water is added, the concentration of abrasives and also other additives in the final slurry will be less than the case where no di
water is added. This would modify the amount of surfactants that adsorb on the abrasives surface as well as the surfactant micelle concentration, and therefore may alter the slurry behavior. Moreover, when di water is added, the pH of the slurry will increase towards neutral and this may result in the change of the CMP kinetics.

2.4.2 Dielectric Erosion and Incomplete Removal Of The Adhesion Layer Overlay

The outcome of the initial experiments showed adhesion layer residues on the dielectric as well as a significant color variation in the dielectric at the contact-dielectric interface which showed the thickness variation of dielectric at this region. Figure 2.4 shows the result of the wafer polish using 30% H$_2$O$_2$ solution added to Ultra-Sol A20 in a 1:1 ratio. Additionally, the gold contacts protruded the dielectric. These protruded contacts are good anchors for particles and slurry residues.
Figure 2.4 Au/ Cr metal layer polished with ultra-sol a20: H₂O₂ in a 1:1 ratio. The results were the protrusion of gold from the dielectric, significant erosion of the dielectric between the pads, and incomplete removal of the adhesion layer.

According to Cho et al., abrasive particles get trapped at the interface between dielectric and metal. The trapped abrasives are considered “inactive” and don’t take part in the polishing process, however, they widen the trench in which there are trapped as the polishing proceeds [45]. This behavior results in non-uniform polish by the slurry. Adding Poly(vinyl pyrrolidone) (PVP), a polymeric surfactant, in a proper concentration,
can alleviate this issue in two ways: first, adsorption of PVP molecules on the abrasives results in the steric dispersion of these particles. Steric dispersion allows fewer large particles to be formed. Choi et al. observed that below 0.8 wt % of PVP, the effective abrasive size decreases by adding the PVP, and it increases above this concentration, likely due to the formation of PVP double layer on the abrasives surface. Smaller particles are more likely to escape the trench and take part in the polishing process. Second, these polymers also adsorb on the wafer surface, and fill the trenches formed at the metal-dielectric interface. This results in smoother corners and less sharp trenches, and also alleviates the issue of the abrasives trapped in the trenches. The added PVP provided a passivation layer for the dielectric, and therefore increased the selectivity between metal and dielectric polish. Figure 2.5 shows the image of a wafer polished with an alumina based slurry with added peroxide and PVP. In addition to PVP, my experiments show that tween 80 also has the passivation effect and can improve the dielectric erosion.

When the adhesion promoter was changed from Cr and Ti to a softer metal, Ni, the incomplete removal of the adhesion layer overlay was resolved.
Figure 2.5 Au/ Cr Metal layer polished with 0.8 \% Wt of PVP added to Ultrasol A20: H\textsubscript{2}O\textsubscript{2} in 1:1 ratio. Gold did not protrude the dielectric, and no dielectric erosion was observed.
2.4.3 Particle Redeposition and Unstable Slurry

Particle redeposition and scratches on the wafer surface are indicators of agglomerated abrasives and unstable slurries [46]. When the abrasive particles agglomerate, they form larger particles. Large abrasives increase the mechanical removal, and result in higher removal rates and larger debris from the material being polished. The larger pieces of debris are attracted to the wafer surface by Van der Waals force and therefore re-deposit on the surface. CMP results using unstable slurries are not reproducible, and therefore are not reliable.

Based on the high ionic strength of the slurry, the charge on the surface of the alumina abrasives are shielded by the ions in the slurry. This undermines the effect of electrostatic dispersion, and results in sedimentation and agglomeration of the alumina particles. Therefore, a proper stabilization of the slurry is achieved when a combination of ionic and non-ionic surfactants are used to provide both electrostatic and steric dispersion at the same time. The ionic surfactant adsorbs on the surface of the abrasives mainly due to the electrostatic attraction. When a non-ionic surfactant is added, the surfactant molecules penetrate the film of ionic surfactant around the abrasives due to hydrocarbon chain interaction of the ionic and non-ionic surfactant molecules. The adsorption of the non-ionic surfactant on the abrasives surface enhances the stability of the slurry by steric dispersion of the abrasive particles [47]. This idea is depicted in the Figure 2.6 below. It is important to mention that when more than one surfactant is added to the slurry, the process designer should consider the compatibility between different
types of surfactants. In some cases, the combined surfactants will not interact with each other well and that will result in the slurry instability. The concentration of surfactants is also among the main points the process designer should consider. Although adding surfactants in the proper concentration results in stable slurry, adding too much of a surfactant will lead to significant amount of foam and instability in the slurry. The effect of different surfactants on the stability of the slurry and their impact on CMP outcome a s investigated, and it’s summarized in Table 2.2.
Figure 2.6 The mechanism of high-ionic-strength slurry stabilization by the synergistic mixture of anionic and nonionic surfactants [46].
**TABLE 2.2**

**SUMMARY OF THE INVESTIGATED SURFACTANT COMBINATIONS AND THEIR EFFECT ON THE SLURRY STABILITY**

<table>
<thead>
<tr>
<th>Surfactant combination</th>
<th>Concentration</th>
<th>Abrasives agglomeration</th>
<th>Stable Slurry</th>
<th>Removal Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>0.8% wt</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVP Capstone FS 63</td>
<td>0.8% weight PVP 0.4% volume capstone</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tween 80 Capstone FS 63</td>
<td>2% volume tween 80 0.4% volume capstone</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDS Tween 80</td>
<td>0.34% weight SDS 0.26% volume tween 80</td>
<td>X</td>
<td>In 1:3 $\text{H}_2\text{O}_2 : \text{A}_20$ 110 nm/min</td>
<td></td>
</tr>
<tr>
<td>SDS PVP</td>
<td>0.34% weight SDS 0.08% weight PVP</td>
<td>X</td>
<td>In 1:3 $\text{H}_2\text{O}_2 : \text{A}_20$ 200 nm/min</td>
<td></td>
</tr>
</tbody>
</table>
Our experiments showed that capstone FS 63, an ionic surfactant, when used with PVP, did not improve the stability of the slurry. Simultaneous addition of tween 80, a non-ionic surfactant, and capstone FS 63 also resulted in an unstable slurry. Figure 2.7 shows the CMP result from an unstable slurry prepared by adding capstone and relatively high concentration of tween 80, 1.85% volume. Palla et al. observed that high concentration of non-ionic surfactant could have like a “glue”, entangling several abrasive particles, and resulting in unstable slurry [47]. As mentioned earlier, redeposited particles can be as large as 100µm in size and result in local deformation of the pad and non-uniform polishing in their vicinity.
Figure 2.7 Au/ Cr metal layer polished with 30 ml tween 80 and 6 ml capstone added to 1600 ml of UltraSol A20: \( \text{H}_2\text{O}_2 \) in 1:1 ratio. The agglomerated abrasives result in re-deposition of relatively large (up to 100\( \mu \text{m} \) in size) pieces of gold debris.

Simultaneous addition of SDS, an ionic surfactant, and tween 80 lead to a relatively stable slurry. Figure 2.8 shows the CMP result using 4.14 grams of SDS with 3.5 ml of tween 80 added to 1200 ml of Ultra-Sol A20: \( \text{H}_2\text{O}_2 \) in 1:1 ratio.
Figure 2.8 CMP result using 4.14 grams of SDS with 3.5 ml of tween 80 added to 1200 ml of Ultra-Sol A20: H$_2$O$_2$ in 1:1 ratio. This combination resulted in a stable slurry with 45 nm of dishing across a 10 µm wide contact pad.

Another surfactant combination that led to a stable slurry and successful polishing was SDS+PVP. In this slurry, the relative concentration of these two surfactants also played an important role in stability of the slurry. While a single layer adsorption of SDS on alumina abrasives enhances the PVP adsorption on these particles, if a double layer of SDS is formed due to the excess SDS concentration, the adsorption of PVP is
significantly suppressed and the slurry is prone to agglomeration. This phenomenon was confirmed by Esumi et al. and they claimed that SDS concentration above 4 mm resulted in abrupt decrease in the amount of adsorbed PVP [48]. It is important to mention that the critical value for SDS depends on the abrasive concentration, and increases with higher particle concentration in slurry. The order by which the surfactants are added also made a difference meaning that SDS should not be introduced into the slurry before PVP. This confirms our claim about the sequence of surfactant adsorption on the abrasive particles. The SDS/ PVP combination that was successfully used to polish the gold samples was 4 grams of SDS and 0.1 grams of PVP added to 900 ml of ultra-sol a20 and 300 ml of hydrogen peroxide. Figure 2.9 shows the successful result of using this slurry combination.

It is worth mentioning that the polish rate of gold when using SDS-PVP is higher than when SDS-tween 80 is used to stabilize the surfactant. This can be mainly due to the positive surface charge of PVP in acidic environments which attracts the abrasive particles to the negatively charged gold around pH=4 [49].

Another point which is worth mentioning is the fact that it is always preferable not to use the slurry on the bottom 2.3 cm of the container. Large agglomerated particles usually sediment on the bottom of the container, and if used in the CMP, would result in significant amount of scratching on the dielectric and metal layers.
Figure 2.9 Wafer polished with slurry consisting 4 grams of sds and 0.1 grams of PVP added to 900 ml of Ultra-Sol A20 and 300 ml of hydrogen peroxide. This combination resulted in a stable slurry with 37 nm of dishing across a 150 µm wide contact pad.
2.5 Coefficient Of Friction and End Point Detection

As it was explained in chapter one, the coefficient of friction reflects the nature of contact between pad, wafer, and slurry. Moreover, it depends on the materials involved in the process, for instance the size and concentration of abrasives, and also the nature of the materials being polished.

COF is among the waveforms that the operator can choose to be displayed on the screen of our Orbis CMP system. The machine calculates the coefficient of friction by measuring the power of the motor rotating the platen. Having the value for power and the pad rotational speed, the torque of the rotating pad can be readily calculated. Next, the shear frictional force is found by dividing the torque by the radius of the platen. The coefficient of friction is then calculated by dividing this shear force by the cumulative down load force from the carrier heads. The mathematical expressions can be found in eq. 2.2, where \( p \) is the power of the motor rotating the pad, \( \tau \) is the torque of the rotating pad, \( \omega \) is the pad rotational speed, \( F_f \) is the shear frictional on the pad, \( r \) is the pad radius, \( \mu \) is the coefficient of friction, and \( N \) is the normal load applied on the pad.

\[
P = \bar{\tau}, \bar{\omega}
\]

\[
\bar{\tau} = \bar{F}_f \times \bar{r} \Rightarrow \bar{F}_f = \frac{\bar{\tau}}{\bar{r}}
\]

\[
\bar{F}_f = \mu \times \bar{N} \Rightarrow \mu = \frac{\bar{F}_f}{\bar{N}}
\]

During our experiments, we noticed that there is a correlation between the COF variation and the point where the polish should be stopped. Our results show that the
COF when sin is being polished is approximately 0.1 lower than when Au is being removed. Therefore, during the gold polishing, the process should be stopped when the COF parameter drops, since this decrease indicates the complete removal of the metal overlay, and the exposure of the underlying dielectric to the slurry. This variation, although small, can be detected by the operator. After the point where the process should be stopped, the topography of the wafer increases as the over polishing proceeds, and this decreases the coefficient of friction because of the decreasing contact between the pad and the wafer [50]. Figure 2.10 shows the change in COF waveform when Au/Ni layer over SiN is polished, while Figure 2.11 shows the COF waveform when patterned SiN is polished without any metal over layer deposited. As it is shown on this figure, COF average does not change when bare silicon nitride is being polished, and it is mainly due to the minimal polishing of this material. The change in the COF when the metal overlay is polished has been also confirmed in literature [51]. Hardness of materials generally indicates their resistance to deformation, friction, and abrasion. As a result, the coefficient of friction is expected to be lower when a harder material is being polished. In Mohs’ scale, the hardness of chromium and titanium is close to that in silicon nitride, resulting in relatively similar values of COF. Therefore, the change in coefficient of friction when the Cr or Ti overlay is removed is not significant, and this waveform could not be used to detect the polish stop point.
Figure 2.10 Evolution of COF with time for the case when Au/Ni layer over SiN is polished: coefficient of friction decreases as the gold overlay is being removed and the underlying dielectric is exposed. As the over polishing proceeds, the pad contact with the wafer decreases due to metal recess and increasing topography. This results in reducing the value of COF.
Figure 2.11 Patterned sin is polished without any metal layer deposited. In this case, there is almost no change in COF due to the minimal change in the topography. In both Figure 2.10 and Figure 2.11, the initial zero value for COF is for the time that the wafer has not landed on the pad. As the polishing starts, the value for COF abruptly increases.

Additionally, we noticed the correlation of COF with agglomeration of particles. We observed that this parameter increases significantly, by approximately 50%, when there are particle agglomeration and dielectric delamination. In case of agglomeration and delamination, COF evolution cannot be successfully correlated to the CMP process for finding the end point. However, since a high value of the COF indicates the slurry agglomeration, this signal can be used to monitor the behavior of the slurry [52].
CHAPTER 3
CONCLUSION AND FUTURE WORK

3.1 Results and Conclusions

The goal of this project was to develop a recipe for gold chemical mechanical polishing (CMP). The following factors make this process challenging:

1. Gold is known as a “no le” metal, which implies its resistance to chemical reactions. This makes the CMP process design challenging due to the fact that metal polishing in CMP usually involves chemical modification of the metal surface. However, we successfully used the combination of potassium iodide and hydrogen peroxide to passivate the gold surface and polish this metal at a reasonable rate, 200 nm/min. The concentration of the oxidizers should be calculated such that it does not result in high static etch rate of gold, since high chemical dissolution causes significant metal dishing, edge recess, and within wafer nonuniformity.

2. On the Mohs’ scale, the hardness of gold is 3.5, while the hardness of the metals that are generally used to enhance the adhesion of gold to silicon is twice this value. The hardness of materials indicates their resistance to
mechanical abrasion, which is an important component in CMP. These adhesion promoters, as a result, are polished slower than gold. This results in significant thinning in gold patterns. The process designer therefore should choose an adhesion promoter with a relatively low hardness. Moreover, due to the fact that the oxidizer concentration in the slurry determines how dense the oxidized surface of a metal is, one can choose the concentration of the peroxide such that the oxidized gold is denser than that the oxidized layer of adhesion promoter, thus it is polished at a slower rate. We have shown that by changing the concentration of the oxidizer from 50% to 25% the removal rate of Ni becomes 3 times higher than gold.

3. The slurries for metal CMP are not as stable as the slurries used for dielectric polishing. This is due to the higher density of the alumina with respect to silica and ceria that are used in dielectric CMP slurries. Moreover, high ionic strength of the metal CMP slurries usually undermines the electrostatic dispersion of the particles, due to the fact that ions in the slurry screen the surface charge of the abrasives. The stability of the slurry has a great impact on the outcome of the CMP process. Therefore, a significant amount of effort went into improving the stability of the slurry. Our experiments show that simultaneous use of an anionic surfactant and a polymer or a non-ionic surfactant can stabilize the slurry. It’s important to note that the stability of the slurry depends on the interaction between those two types of surfactants, and
this can range from very strong interaction to no apparent interaction. The mechanism for this interaction is usually either electrostatic interactions (if the surfactants are oppositely charged) or hydrophobic interactions (between the hydrophobic parts of surfactants). As a consequence, it’s clear that the compatibility of the surfactants is among the main points to consider. We successfully used SDS-PVP and SDS-tween 80 to stabilize the slurry.

3.2 Future Work

In our experiments, the adhesion promoter and gold were both polished in one step using one slurry. As a result, the slurry had to be modified such that it polished gold at a satisfactory rate, while polishing the adhesion promoter faster. This requires a relatively soft adhesion layer, Ni for instance. On the other hand, one can design a two-step polishing process, such that the first slurry polishes gold without removing the adhesion promoter, and the second slurry removes the adhesion promoter in the second step. If the second step is designed such that the gold is polished minimally during the removal of the adhesion promoter overlay, dishing would be minimized. This two-step process allows a broader choice for the adhesion promoter, since it is removed independently.

We monitored the coefficient of friction to detect the end point in the CMP process. This method, although it seems promising to avoid over polishing, is susceptible to particle agglomeration, dielectric delamination, and therefore is not widely used for
this purpose. Further investigations should be done find a more robust method by which
the stop point is detected.
REFERENCE


