Investigation of novel alumina nanoabrasive and the interactions with basic chemical components in copper chemical mechanical planarization (CMP) slurries

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Investigation of Novel Alumina Nanoabrasive and the Interactions with Basic Chemical Components in Copper Chemical Mechanical Planarization (CMP) Slurries

by

Shravanthi Lakshmi Manikonda

A Dissertation
Submitted to the University at Albany, State University of New York
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Investigation of Novel Alumina Nanoabrasive and the Interactions with Basic Chemical Components in Copper Chemical Mechanical Planarization (CMP) Slurries

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ABSTRACT

Chemical mechanical planarization (CMP) is an enabling process technology for IC fabrication to maintain global planarity across the wafer to satisfy lithographic depth of focus constraints. It also enables integration of materials that cannot be anisotropically etched, such as Cu. CMP utilizes nanoparticle abrasives in aqueous slurry to aid in planarization.

Commercially available copper CMP slurries contain four basic components, in addition to propriety chemical compounds which aid in the removal process. But, reduction of on-chip feature sizes demands high planarity performance with reduced levels of defectivity. This calls for more understanding of the role of each basic component as well as less chemically aggressive slurries. Also, the utilization of smaller nanoabrasive particles in slurries is being investigated as a pathway for extendability of CMP processing to smaller integrated feature sizes.

In this work, the use of novel nanoabrasives for the development of copper CMP slurries for 300mm wafer processing is investigated by engineering and developing copper CMP slurries based on novel single component nanoabrasives. Abrasives are alumina nanoabrasives substantially smaller than used in conventional commercial slurries (approximately 40-50nm in size) that have been manufactured using a novel propriety process that promotes their suspension in solution without the use of additional chemical components. The experimental slurry formulations were comprised of the four basic
components - abrasives, oxidizer, passivating agent, complexing agent. In this work, 200mm Cu blanket wafers, 300mm Cu blanket wafers, and 300mm M1-patterned, Cu wafers were used to develop and evaluate slurry formulations for optimal performance. The absence of additional chemical components in the experimental slurries enables a direct correlation between the individual slurry components and their effects on the Cu polishing performance.

Investigation of the interplay between the nanoabrasives, the slurry chemical components and the efficacy of the CMP process are discussed in terms of the physical effects of slurry composition on 300mm Cu CMP performance and in relationship to post-CMP electrical characterization of patterned interconnect test structures. In addition, initial processing work on 200m blanket Cu wafers is discussed with respect to developing initial slurry formulations with the novel nanoabrasive particles.
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To my parents

Mr. Manikonda Ramana Murty

and

Mrs. Manikonda Bala Tripura Sundari

“God couldn’t be everywhere, so he created parents”
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CHAPTER 1

INTRODUCTION

1.1 History of semiconductors

The overall processing performance of integrated circuits (ICs) has continued increasing in approximate accordance with Moore’s Law. With ever continuing reduction in the critical feature sizes of silicon-based logic and memory devices, now reaching < 28 nm as outlined in The International Technology Roadmap for Semiconductors [1], new materials and processes continue to be introduced in both front-end-of-line (FEOL) and back-end-of-line (BEOL) semiconductor processing as shown in Table 1.1. All these components need to be electrically interconnected for achieving full functionality, a task that requires multiple levels of wiring. Hence, the fabrication of inexpensive, reliable and ultra-fast, multilayer interconnections (which now exceeds 10 layers in some cases), between the individual devices in the chip has become a critical enabling technology in the integrated circuit production process [2].

1.1.1 Multilevel Metallization and Copper Interconnects

Metallization is the process that provides interconnections between the devices and the outside world and between the devices themselves by means of metal wires to form circuits. These metal wires are necessary for a circuit to function. With the increase in the device density, the complexity of the interconnections also increases. Fig 1.1 shows IBM’s 0.09 μm [3] chip interconnect technology using copper as the interconnect material.
However, with the reduction in the dimensions of the devices on the chip, the dimensions of the interconnect wires also have to decrease. Unlike the intrinsic gate delay, the interconnect delay increases with decrease in the dimensions (Fig 1.2a) and becomes
more significant at device dimensions below 0.045 µm. Apart from this, the problem of
device failure associated with electromigration, due to the increased current density in the
metal interconnects also becomes significant.

Figure 1.1 IBM’s 90nm interconnect technology using chip’s copper wires, as seen in
this electron micrograph. (Courtesy: IBM)

Figure 1.2 (a) Dimensions Vs transistor delay (b) dimensions of interconnect structures.

The “RC” product is widely used as the measure of the interconnect delay [4] where, R is
the resistance of the metal interconnect and C is the capacitance of the interlayer
dielectric (ILD) (Fig 1.2b). The RC time delay associated with a metal line is given by

\[
\text{Interconnect delay} = \frac{\rho \epsilon_{\text{ILD}} t^2}{t^*d}
\]

Where, \(\rho\) is the resistivity of the metal
\( \varepsilon \) is the permittivity of the ILD

\( l \) is the length of the metal line

\( d \) is the thickness of the metal line

\( t \) is the thickness of the ILD

Figure 1.3 **Scanning electron microscope image of IBM’s six-level copper interconnect technology.** SEM image of CMOS 7S copper process, showing the six copper levels used for chip wiring and one tungsten level for local interconnect (Courtesy: IBM)

The replacement of Al wiring by copper interconnects was seen as a way to enhance IC performance and reliability. Copper is advantageous because of its higher conductance as compared to aluminum (Al) and tungsten (W) metals that had typically been used for interconnects in microelectronics. Fig 1.3 shows the SEM images of IBM’s six level copper interconnect technology. Copper not only served to reduce the resistance-capacitance (RC) interconnect delay but also increased the circuit reliability due to its higher electromigration resistance. However, copper does not form a volatile compound at low enough temperatures [5,6] to make use of plasma etching/RIE as a feasible means of patterning interconnect lines. Consequently, an inlaid wiring or ‘damascene’ process
was developed. This entailed the development of copper CMP as a means to remove excess copper following interconnect inlay within an ILD. Currently, CMP-based damascene processing as shown in Fig 1.4 is now the most practical technique [7] for patterning of copper interconnects structures for on-chip applications.

Figure 1.4 Schematic process flows for single and dual damascene process
1.2 Fundamentals of Chemical Mechanical Polishing (CMP)

Chemical Mechanical Polishing (CMP) has been used to prepare planar Si and SOI Si wafers for the last 3 decades in the semiconductor industry [8]. It has also been used for glass polishing in the lens manufacturing industry. In the fabrication of ICs, CMP is used as a final step in the preparation of starting wafers. CMP of lens fabrication and wafer preparation differs from IC fabrication in one important aspect. In all three applications, a high degree of planarity or flatness is required, however, for CMP; the same degree of flatness must be achieved with far less material removal. In addition, the tolerances for material removal are much tighter for CMP than any other planarization techniques. Wafer thicknesses, for example, may vary by several mils while ILD thicknesses must vary less than ~100 nm from wafer to wafer. Thus, CMP used for planarization demands much tighter process control as the goal of wafer preparation is local site flatness with specifications adhering to lithographic requirements. A schematic of a typical rotary CMP tool used in this work is shown in the Fig 1.5.

![Schematic of a Chemical-Mechanical polishing tool](image)

Figure 1.5 Schematic of a Chemical-Mechanical polishing tool
A chemical mechanical polishing tool essentially consists of a polishing pad affixed to a circular polishing table, called platen, and a carrier, which holds the wafer against the pad. The carrier and the platen are rotated in the same direction as the wafer is pressed against the pad, while the slurry is delivered on to the pad. The slurry is typically a colloidal suspension of sub micron particles in an aqueous chemical solution with certain pH value. The slurry is transported by a combination of drag and centrifugal forces resulting from the rotation of the pad and also by the pores present in the pad. These forces distribute the slurry across the pad forming a thin sheet of liquid on the pad. Chemicals alone cannot achieve planarization as most of the chemical reactions are isotropic and hence material at the protruding and the recessed regions are equally removed. The key to achieving planarization with CMP is to maintain high removal rates at the high surface features and low removal rates of the low surface features [9]. This difference in removal rates is obtained if the polish pad is rigid and incompressible. The pad exerts force onto the high features, resulting in material removal of the high features. However, because the pad is rigid and incompressible, it does not conform to the wafer surface and therefore does not exert force on the low features. Because the etch rate of the surface is generally negligible in the absence of any applied force, and the removal rate of the low features is very small. The ability of the CMP process to achieve planarization is measured by the planarization rate given by:

\[ \text{Planarization rate} = \text{polish rate of the high features} - \text{polish rate of low features} \]  

(1.2)
1.2.1 Copper CMP

Figure 1.6 shows the Pourbaix potential [10] – pH diagram for copper – water system at room temperature. Copper is a relatively noble metal in the absence of complexing agents. As shown in the equilibrium diagram, copper can be corroded by acidic or strongly alkaline solutions in the presence of oxidizers. Under neutral or slightly alkaline conditions copper oxide is formed. CMP of copper can be performed in acidic, neutral, and alkaline media. Luo et al [11] investigated Copper CMP in the acidic medium (pH 1~2) using ferric nitrate as oxidizer and 1H-benzotriazole (BTA) as inhibitor.

![Figure 1.6 Potential – pH equilibrium diagram for copper – H₂O system at room temperature [10].](image)

They proposed that ferric nitrate oxidized Copper on the film surface to Cu²⁺ ions and that BTA protected the recessed regions by forming a three dimensional complex polymeric layer, in agreement with observations of other researchers. Steigerwald et al. [12] investigated copper CMP using ammonia based slurries and proposed that the removal is primarily effected by the mechanical abrasion by the particles. The chemicals
in the slurry dissolve the abraded copper particles. The higher surface area per unit volume of the abraded copper particles increased their dissolution rates when compared to the surface copper film. By comparing data on polishing of W, they argued that mechanical abrasion was dominant mechanism in this case, while chemical dissolution dominant in Copper CMP.

Luo et al. [11] studied copper CMP in different media and concluded that though the removal is mainly by mechanical abrasion, various chemicals in the slurry certainly play a role in modifying the surface mechanical properties of the film.

CMP of copper in acidic media without any inhibiting agents leads to corrosion problems, while in alkaline media it is faced with ILD erosion due to unfavorable polish selectivity. Thus an intermediate pH range appears to be a suitable choice for copper CMP. Hariharaputhiran et al. [12] studied the effect of hydroxyl radicals on copper CMP using slurries proposed by Hirabayashi et al. [13]. They observed that Cu\(^{2+}\) – amino acid complex (chelate) is an effective catalyst in decomposing H\(_2\)O\(_2\) to yield *OH radicals. They attributed the increase in the removal rates of copper with an addition of glycine in peroxide based slurry to stronger oxidizing nature of *OH radicals. Citric acid is also being investigated by various researchers as an attractive complexing agent in peroxide based slurries.

In summary, slurry chemicals play an important role in copper CMP. The essential requirement of the slurry chemicals is to balance the dissolution and passivation of the film surface to obtain a planar surface after CMP.
1.3 Description and Mathematical Model of the CMP Process

A tribological model, Preston’s equation [14], is the basic model for the CMP process described by Preston in 1927. The Preston model predicts that the volumetric removal rate at a point P is proportional to the normal load and the relative velocity. This is given by

\[
\frac{dh(x)}{dt} = C \frac{dL(x)}{dt} \frac{ds(x)}{dt}
\]

(1.3)

where \(h(x)\) is the depth of the wear, \(A\) is the contact area, \(L(x)\) is the normal load, \(C\) is the Preston’s coefficient, \(s(x)\) is the sliding distance and \(t\) is the processing time. Since the Preston model was developed for glass/optics polishing before the concept of CMP was proposed, it does not include the complicated physical and chemical phenomena. The suitability of the Preston’s equation was examined by Tseng and a modified Preston’s equation was proposed based upon the combined solid and fluid mechanics.

\[
Material \text{ removal rate} = M(P,V) \cdot P^{0.5} \cdot V^{1.2} \]

(1.4)

where \(P\) is the pressure, \(V\) is the velocity and \(M(P,V)\) is a function of \(P\) and \(V\). In the current approach, Chemical Mechanical Polishing takes place where the surface of the wafer to be polished is forced against a polishing pad. The polishing pad is covered with liquid slurry mixture which contains nano-abrasive particles. The wafer is moved relative to the slurry-covered pad and the rate at which material is removed from the wafer is often described by modified Preston’s Law:

\[
\text{MRR} = K_p \cdot P \cdot V \]

(1.5)

where RR – removal rate

\(K_p\) – a constant, Preston’s coefficient
P – local pressure on wafer surface

V – relative velocity of the point on the wafer surface vs. the pad.

In most abrasive CMP processes, the Preston equation is a sufficient model of the relationship between the material removal rate, pressure and pad-wafer velocity. This equation states that there is an increase in the amount of material removed as the pressure increases or as the pad-wafer velocity increases. Thus there is a direct relationship that exists between these physical parameters and the surface material removed. This relationship can be seen graphically in Figure 1.7.

Changes to the Preston equation have occurred such that other mechanical effects can be accounted for. Among these changes includes the introduction of friction into the equation. During the planarization process the surface of the wafer comes into contact with the pad, thereby creating friction between the two. It is believed that the coefficient of the friction present between the wafer and the pad has a direct effect on the material removal rate.

Therefore, a revised Preston equation has been formulated in which the coefficient of friction ($\mu$) is included. This revision can be seen in equation 1.6.

$$RR = Kp \times (\mu \times P) \times V$$  \hspace{1cm} (1.6)
Figure 1.7 Prestonian relationship that exists in abrasive CMP [15].

Through modeling this revised Preston equation, it is believed that smaller coefficient of friction result in decreased delamination as well as less heat generation. The generation of heat is not desirable even though it results in increased material removal rates. The production of heat through friction has proven to be extremely difficult to control and often leads to unfavorable surface quality that can be detrimental to the wafer during planarization. The Preston equation as well as variations to this equation has been shown experimentally to accurately represent abrasive systems.

CMP is a complex process and a complete fundamental understanding of the chemomechanical phenomena between the pad and the wafer is still lacking. This complexity arises because of the large number of variables and their interactions involved in the CMP process. Table 1.2 lists some of the variables involved in the CMP process.
Table 1.2 Input and Output variable involved in a CMP process.

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<td>Spindle oscillation</td>
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<tr>
<td>Abrasive Particles</td>
<td>Size(primary particle size, aggregate size), Shape, Hardness,</td>
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<tr>
<td></td>
<td>Concentration</td>
</tr>
<tr>
<td>Slurry Chemicals</td>
<td>Oxidizer, Complexing agent, Surfactant</td>
</tr>
<tr>
<td>Substrate Variables</td>
<td>Wafer curvature, Film stress and hardness, Pattern geometries</td>
</tr>
<tr>
<td>Polishing Pad</td>
<td>Hardness, Roughness, Pore size, Compressibility, Thickness,</td>
</tr>
<tr>
<td></td>
<td>Elastic modulus, Conditioning</td>
</tr>
<tr>
<td>OUTPUT</td>
<td>Polish rate, Planarization rate, Within Wafer Uniformity,</td>
</tr>
<tr>
<td>PARAMETERS</td>
<td>Wafer to Wafer Uniformity, Surface defects</td>
</tr>
</tbody>
</table>

1.4 Chemical Mechanical Planarization consumables

CMP is a complex process that depends on numerous variables such as CMP tool process parameters, surfaces (wafers) to be polished, slurries, pads, and pad conditioner [16] protocols as shown in Table 1.3. It combines chemical and mechanical interactions to polish (smooth) and planarize surfaces. Typically, CMP slurries are composed of aqueous-based chemical solutions and nanoabrasives (in suspension form).
Table 1.3 Main and primary input variables for CMP process.

<table>
<thead>
<tr>
<th>Primary CMP Process Parameters</th>
<th>Main CMP consumables</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Down force</td>
<td>• Polishing Pad</td>
</tr>
<tr>
<td>• Carrier (wafer) angular velocity</td>
<td>• Pad conditioning disk</td>
</tr>
<tr>
<td>• Table (pad) angular velocity</td>
<td>• Slurry</td>
</tr>
<tr>
<td>• Slurry flow rate</td>
<td>• Nanoabrasives</td>
</tr>
<tr>
<td>• Polishing time</td>
<td>• Chemicals</td>
</tr>
<tr>
<td>• Back pressures</td>
<td>1. Oxidizers</td>
</tr>
<tr>
<td></td>
<td>2. Complexing agents</td>
</tr>
<tr>
<td></td>
<td>3. Inhibitors</td>
</tr>
<tr>
<td></td>
<td>4. pH stabilizers</td>
</tr>
<tr>
<td></td>
<td>5. Dispersants</td>
</tr>
<tr>
<td></td>
<td>• Buffing pads</td>
</tr>
<tr>
<td></td>
<td>• Wafer cleaning brushes and chemicals</td>
</tr>
</tbody>
</table>

As most chemical reactions are isotropic, chemistry alone can not achieve planarization. Consequently, pad and abrasive particles are also required to successfully complete a CMP process. Table 1.4 shows the need for such CMP consumables as per the ITRS 2010 [1]. Primary consumables in CMP processing are nanoabrasive slurries, pads and pad conditioning disks. These consumable will be discussed in detail in the following subsections.

1.4.1 CMP Pads

The CMP polishing pad plays a crucial role in CMP processing [16]. It influences key aspects of the CMP process including post-CMP defects counts, material removal rate (MRR), within-wafer nonuniformity (WIWNU), wafer-to-wafer nonuniformity (WTWNU) and step height reduction efficiency (SHRE). The pad delivers the slurry (chemicals and nanoabrasives) to the wafer surface and removes polishing residue from the polishing region to allow new polishing reactions. It also transmits normal and shear forces from the polisher to the wafer.
Table 1.4 CMP consumable needs as per ITRS 2010 [1].

The CMP polishing pad must have sufficient mechanical reliability and chemical resistance to survive the mechanical stresses (applied downforce and polishing-induced friction force) and aggressive slurry chemistries. Additionally CMP pads must be sufficiently hydrophilic. Polishing pads are generally made of polymeric materials (polycarbonates, nylons, polysulfones, and polyurethanes). CMP pads made with polyurethane are the most commonly used. They have balanced mechanical properties (strength, hardness and modulus) and excellent chemical stability. Additionally, polyurethane pads are able to transport and deliver aqueous slurry on its surface more uniformly and effectively as they have the highest critical surface tension values compared with the aforementioned polymeric materials. The pad can be made with a wide range of microstructures, textures and fillers. In CMP processing, surface roughness, viscoelastic properties, thickness, and pore size also play very important roles. Fig 1.18 shows the role of CMP pad grooves and their texture role in slurry flow and
transport. For better polishing, multilayer or stacked pads are normally used which are comprised of a stiff/hard top layer and a soft/flexible substrate. Top pad (IC 1000) hardness allows the material to planarize across wide areas with minimal dishing and good planarity. The bottom pad (Suba IV) improves the resilience and compressibility of the staked pad and enhances the global uniformity in the polish rate. Pad surface texture and grooves have vital roles in the fluid mechanics of the polishing slurry. Therefore, rigorous surface texture characterization and elucidation of transport kinetics at length scales below that of the groove dimensions is required for complete optimization of pad microstructure.

1.4.2 Pad conditioning disks

Pad conditioning greatly influences the removal rate, planarization performance and hydrodynamic effects. No conditioning or insufficient conditioning during polishing leads to ‘glazing’ of the pad surface, wherein particles build up and clog the pad surface pores. This alteration of the pad surface morphology also depends on the type of slurry solution used. Fig 1.18 shows the role of CMP pad grooves [17] and texture role in slurry flow and transport. The copper material removal rate also declines for a CMP process without conditioning. This also results mainly from changes in pad surface morphology. This leads to lower removal rates and higher wafer-level defectivity. In a state of the art CMP process pad conditioning is performed through contact between the CMP pad surface and
Figure 1.8 Schematic diagram show role of CMP pad grooves and texture role in slurry flow and transport (Courtesy: Dow Advanced Materials).

A diamond abrasive disc or wheel as illustrated in Fig 1.9. Abrasive pad conditioning using diamond-impregnated disks has been found to be the most effective method.

Figure 1.9 Illustration of polishing pad and conditioner geometry as well as the interaction between pad and conditioner surfaces.

The surface of the diamond conditioner disc is coated with a distribution of diamond grains to enable restoration of CMP pad morphology and removal of residues from the filled surface pores of the pad. During pad conditioning, the diamond disk conditioner is swept back and forth radially across the pad surface either during (in-situ) or after (ex-situ) the polishing step. Preferential radial conditioning has been proposed in combination
with circular grooves. This may also serve to reduce wafer nanotopography (groove pattern transfer on wafer due to grooved-scale slurry transport) as observed with radial grooves. After the installation of each new CMP pad, the conditioner is also used for the ‘break-in’ process of the pad. Such a process may last as long as 20-30 minutes. The purpose of the break-in process is to open up the closed pores (cells) on the pad surface. Overall pad-wafer contact area reaches a minimum value at an intermediate pad conditioning time and contact distribution improves significantly at longer times for hard pads. Many factors will influence pad conditioning effectiveness. Key conditioning parameters includes conditioner down force, pad and conditioner rotation speeds, conditioner sweep speed, and the conditioning time.

1.4.3 CMP Slurries and Slurry Transport

CMP slurries for copper consist of sub-micron and/or nanosized abrasive particles, like alumina, silica, abrasives, coated polymer particles etc. These abrasive particles are dispersed in DI water containing dissolved chemicals such as oxidizers, complexing agents, corrosion inhibitors, surfactants, buffering agents, etc. Some of the commonly used slurry additives for copper CMP are listed in Table 1.5. These chemicals may modify the copper surface that comes in contact with the slurry and the abrasives present in the slurry abrade this modified film as shown in Fig 1.10. Thus, the chemical processes, passivation and etching of copper metal, and the mechanical action (abrasion) of the abrasives act synergistically in the slurry to contribute towards enhancing and controlling the material removal rates.
Table 1.5 *Slurry additives for a Copper CMP process.*

<table>
<thead>
<tr>
<th>Oxidizing agents</th>
<th>Complexing agents</th>
<th>Inhibitors</th>
<th>Surfactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric nitrate</td>
<td>Glycine</td>
<td>Benzotriazole</td>
<td>Triton-X</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Citric acid</td>
<td>Benzimidizole</td>
<td>DOWFAX</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>Ethylenediamine</td>
<td>Poly triazole</td>
<td>Arabic gum</td>
</tr>
<tr>
<td>Ammonium persulphate</td>
<td>Ammonium hydroxide</td>
<td>Phenyl triazol thion</td>
<td>Brij series</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The role of slurry additives used in the Copper CMP process is dealt in detail in the following subsections.
1.5 Role of chemical components in Copper CMP slurries

The roles of various chemical components that were used in copper CMP slurries are discussed in this chapter. Typical CMP slurries involve four types of chemical components – (i) Oxidizing agent (ii) Complexing agent (iii) Passivating agent and (iv) pH of the slurry.

In this work, hydrogen peroxide is used as an oxidizing agent, glycine is used as a complexing agent and BTA is used as a passivating agent. These chemical components were suspended in DI water making it CMP slurry. The role of pH of the CMP slurry is also discussed.

1.5.1 Role of hydrogen peroxide as an oxidizing agent

H₂O₂ is one of the most powerful and widely used oxidizers in present-day industrial CMP slurries. Hirabayashi et al [13] were among the first to describe copper CMP slurry that contains hydrogen peroxide, glycine, and silica particles. It was proposed that, at proper pH, a Cu₂O layer is formed by H₂O₂ oxidation. In the presence of an effective complexing agent such as glycine and at low concentration of hydrogen peroxide, the film is porous and easy to be removed with mechanical abrasion. As shown in Fig 1.11, under these conditions, the material removal rate increases with the increase in hydrogen peroxide concentration (<1 wt %). At higher pH or higher hydrogen peroxide concentration, the film becomes thicker and denser.
The film is strong enough to serve as a passivating layer. Under these conditions, the material removal and static etch rates, thus, decrease with the increase in hydrogen peroxide concentration. Such a dual effect of hydrogen peroxide concentration on MRR is schematically illustrated in Fig 1.12. As shown in the figure, in the so-called etching region, addition of extra effective complexing agent will increase the MRR and reach a peak MRR sooner with lower hydrogen peroxide concentration. Similarly, addition of a passivating agent such as BTA should cause a decrease in MRR and a delay in reaching its peak at a higher peroxide concentration. In the passivation region, an addition of complexing agent will slow down the decreasing trend in MRR. Most copper CMP slurries are formulated with a hydrogen peroxide concentration in the passivation region.
Figure 1.12 A schematic illustration of hydrogen peroxide concentration effect on material removal rate of copper with the addition of complexing agent such as glycine and passivating agent such as BTA.

There have been numerous publications dealing with the mechanism of reaction between hydrogen peroxide and copper film. The electrochemical data generated by Brusic et al. [19] suggested that H$_2$O$_2$ and glycine promote the formation and removal of a Cu (II) oxide film. The formation of the Cu–glycine complex and its effect on the copper film removal rate and static state dissolution rate was also studied. It was concluded that the Cu–glycine complex formed during CMP enhanced the decomposition of H$_2$O$_2$ to give hydroxyl radical (*OH).

Table 1.6 Oxidation Potential for Various Oxidizers.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidative Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.0</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>2.8</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.8</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>1.7</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>1.5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1.4</td>
</tr>
</tbody>
</table>
As shown in Table 1.6, hydroxyl radical is a stronger oxidizer than hydrogen peroxide itself. The formation of such a strong oxidizer leads to a significant increase in both copper removal rate and static etch rate. During copper CMP, the catalytic reactions that lead to hydroxyl radicals involve the Cu(I) and Cu(II) pair as given by equations:

\[
\begin{align*}
M^{2+} + H_2O_2 &\rightarrow M^{3+} + OH^- + \cdot OH \\
M^{3+} + H_2O_2 &\rightarrow M^{2+} + \cdot OO H + H^+
\end{align*}
\]

As a transient species, hydroxyl radical can react with various components in the slurry. \(H_2O_2\) yields these hydroxyl radicals which increases these copper dissolution rates. Increasing \(H_2O_2\) concentration can also decrease copper dissolution rate via oxide passivation.

The passivating film formed by the hydrogen peroxide is abraded by the nanoabrasives particles, exposing a fresh surface Cu(I) surface for dissolution. The practical implication of these radical reactions in copper CMP is multifaceted. First, the presence of any metal impurities can significantly lower the pot lifetime of the slurry. The pot lifetime is often defined as the lifetime of slurry after hydrogen peroxide is added. The second option is to add a stabilizer into the slurry. Some of the hydrogen peroxide sources may already contain stabilizer. The function of these stabilizers is to sequest the metal ions and prevents them from directly interacting with hydrogen peroxide. The third implication of metal ion mediated formation of radicals is that the metal ions introduced during metal CMP changes the chemical composition of the fluid at the interface between the pad and the wafer. The newly introduced ions may play a significant role in determining the effectiveness of all key components in the original CMP slurry.
1.5.2 Role of Glycine as complexing agent

Although the function of hydrogen peroxide as an oxidizer is well known, the role of glycine in copper CMP was somewhat less clear. One commonly used copper CMP model slurry can be traced back to the formulation reported by Hirabayashi et al. [13] in which hydrogen peroxide, glycine, and abrasive particles were used.

![Figure 1.13](image)

**Figure 1.13** Bond structure formations with copper when the slurry additive glycine is mixed.

The main role of glycine as a complexing agent to form a complex with the Cu$^{2+}$ ions generated during the polishing process as shown in Fig 1.13. The complex can catalyze the decomposition of hydrogen peroxide leading to the formation of hydroxyl radicals (*OH). A hydroxyl radical is a much stronger oxidizing agent than hydrogen peroxide itself and thus causes a significant increase in the static etch and material removal rates. The static etch (dissolution) rate of copper was found to be closely correlated with the steady-state *OH concentration. Similarly, the formation kinetics of *OH has also been shown to have a direct correlation with the material removal rate of Copper during the polishing process. Upon the addition of excess Cu$^{2+}$ in the form of Cu(NO$_3$)$_2$, the material removal rate was further increased as the concentration of *OH was elevated.
Other amino acids such as serine, and cysteine were used to deconvolute the specific impact of pH on hydroxyl radical formation since the addition of copper ions causes a decrease in the slurry pH. It was found that the dissolution and polish rates with and without copper ions at pH = 4 are essentially the same, suggesting that the amino acid–copper complex may have minimal impact on the formation of hydroxyl radicals or the hydroxyl radicals have negligible impact on the dissolution and removal rate. Considering the fact that, at pH = 4, the majority of the amino acid is pronated and unable to form copper–amino acid complex, it is possible that the amount of hydroxyl radicals formed under this condition is essentially unaffected by the presence of extra copper ions.

The study does show that, at pH = 8, the dissolution and removal rates increase linearly with the increase in copper ions added to glycine-based copper CMP slurry. At such a high pH, the formation of amino acid–copper complex shall be efficient and so will be its impact on the formation of hydroxyl radicals. For glycine-based slurry, the removal rate
is high throughout the entire pH between 2 and 10. This is a result of a large formation constant for the glycine–copper complex. The impact of complexing agents on a metal system in the presence of an oxidizer under various pH conditions can be described in a quantitative format such as a Pourbaix diagram. Fig 1.14 shows a typical shift in Cu–H$_2$O Pourbaix diagram [21] in terms of the stability and the composition of the species due to the presence of a complexing agent. The presence of an effective complexing agent significantly extended the soluble regions for copper species to a much higher pH.

1.5.3 Role of BTA as a passivating agent

Passivating agents or corrosion inhibitors hold an important position in copper CMP slurry design as they provide the necessary passivation for the low-lying regions. The most commonly used inhibitor in copper CMP slurries is Benzo-Tri-Azole commonly known as BTA. The structure of BTA [22] is shown in Fig 1.15.

![Structure of Benzo-tri-azole](image)

Figure 1.15 *Structure of Benzo-tri-azole.*

In a BTA based copper slurry, the formation of the hydrophobic Cu(I)–BTA surface complex functions as a physical boundary between the slurry and the oxidized surface, thereby preventing any unwanted dissolution. Many commercial and developmental copper CMP slurries contain BTA as a corrosion inhibitor. In copper CMP slurry, a combination of hydrogen peroxide (H$_2$O$_2$) and a complexing agent is used to oxidize and
soften the copper surface. Without any passivating agent, such a solution can give high copper removal regardless of the involvement of any abrasive particles. The material removal using such a solution is, however, mostly isotropic. In other words, the step height reduction efficiency is practically zero when using such a polishing solution because the softened copper surface can be significantly disrupted or removed even with the weakest mechanical force including the shear force impinged by the fluid flow. In the presence of a dedicated passivating agent such as BTA, the softened film is somewhat protected and hardened. The art of slurry formulation is to balance the need for protection in the lower lying areas and the need for removal at higher or protruded areas. More specifically, a proper combination of BTA as passivating agent and a complexing agent can balance the need to have low static etch rate (in the absence of mechanical abrasion) and a high polishing rate (in the presence of mechanical abrasion). For a CMP solution containing glycine and hydrogen peroxide, addition of BTA results in a significant reduction in the copper removal rate because of the formation of Copper–BTA complex on the copper surface. BTA can also act as corrosion inhibitor and decreased the dissolution rate. They also showed that the inhibition efficiency of BTA was enhanced by an increase in BTA concentration as well as the presence of hydrogen peroxide. Fig 1.16 shows the bond structure formation when BTA is mixed with copper in the presence of hydrogen peroxide.
Figure 1.16 Bond structure formations with copper when the slurry additive BTA is mixed in the presence of hydrogen peroxide.

This is consistent with the fact that the passivation film has two key components. The first is a complex layer between BTA and oxidized copper. The second is a hydrophobic layer stacked with BTA molecules as shown in Fig 1.17.

Figure 1.17 Schematic representation of a BTA passivating layer formed on copper [23].

At low BTA concentration (about 0.001 mol/dm$^3$) and moderate oxidizer concentration (about 0.05 mol/dm$^3$ of Fe(NO$_3$)$_3$) the Copper–BTA film may not be strong enough to withstand shear stress during polishing either mechanically or hydrodynamically, leading to insufficient protection. For a slurry that contains higher concentration of BTA ($>$0.005 mol/dm$^3$), the passivating efficiency is significantly improved, which leads to a lower copper dishing value. It was also shown that corrosion rate in a solution of 5 wt% of HNO$_3$ declined by two orders of magnitude after the addition of 0.1 wt% of BTA. Addition of corrosion inhibitor also improves the surface roughness of copper surface as
the inhibitor reduces the copper corrosion such as pitting corrosion that takes place on the surface. As a copper oxide film is never fully developed under the conditions described above using nitric acid and ferric nitrate as oxidizers, BTA must form the first complex layer with an oxidized surface that is rich in copper ions.

BTA exhibits the highest inhibition efficiency at pH=6. This is consistent with the fact that, to form both complexing and multilayer effectively, the BTA molecules must be neutral. BTA would not be effective if the molecules are protonated (under acidic condition) or deprotonated (under extreme basic condition). BTA protects and hardens the copper film which has been chemically softened by the oxidizer and complexing agent, thereby reducing the static etch rate.

### 1.5.4 Role of pH

The static etch rate (SER) and material removal rate (MRR) of copper as a function of slurry pH was studied using figures 1.18 [24] and 1.19 [25].

![Figure 1.18](image)

**Figure 1.18** Effect of CMP solution pH on the copper SER in CMP slurry containing 1 wt% of glycine, 3 wt% of H$_2$O$^+$, 3 wt% of SiO$_2$, and 1 mM of BTA [24].
Figure 1.19 Effect of CMP solution pH on the MRR of copper in CMP slurry containing 1 wt% of glycine, 3wt% of H₂O₂, 3 wt% of SiO₂, and 1 mM of BTA [25].

The static etch and material removal rates of copper are lower at higher pH. There are two synergistic effects that lead to such a trend. At higher pH the copper oxide formed under oxidizing condition is stronger and provides stronger passivating effect. This is consistent with the thermodynamic property of copper as indicated by Pourbaix diagram. At the same time, BTA is less protonated at higher pH. In another words, at acidic pH the formation of Copper–BTA passivation film is less effective because of increased water solubility of protonated BTA. This is a key reason why many copper CMP slurries are formulated at pH 5 or above. It is important to point out that there is a trade-off for high pH slurry as BTA and BTA–copper clusters have low solubility in water. It often leads to the formation of large particles that may cause scratches during polishing and leave organic residues that are difficult to clean. It is also worthwhile to mention that the copper static etch rate obtained on slurry prior to polishing may not reflect the true picture for the copper surface during polishing. As soon as the polishing starts, copper ions are introduced into the solution. During the polishing, the local concentration of copper ions can be extremely high. Such a high concentration of copper ions can lower
the pH to below 3. At such a low pH, the effectiveness of BTA as a passivating agent can be severely diminished.

Owing to the integration of low-k dielectric materials [26], the IC industry is moving toward using acidic CMP slurries for bulk Copper CMP to minimize delamination at the metal–low-k dielectric interface. Copper CMP process is thus becoming more chemically active than mechanically driven processes. BTA, however, as mentioned earlier is known to have poor corrosion inhibiting efficiency under acidic conditions and cause polishing debris aggregation at high pH. A poor inhibition of copper surface may lead to surface defects such as dishing, corrosion, and erosion. Therefore there is a need for identifying a passivating agent that forms effective protective film on copper surface under acidic condition.

1.6 Role of nanoabrasives

In addition to the chemical component described in the previous sections the mechanical forces are primarily provided by the abrasives. The primary function of abrasive particles is to enhance the mechanical strength of the pad and transmit the downforce to the wafer surface, resulting in an increased removal rate. In addition to the mechanical function, the abrasives also serve as adsorption sites to the reaction by-products and polishing debris and assist in their transportation and elimination from the vicinity of the wafer. The debris, if not removed, may lead to unwanted defects such as a scratch or corrosion. Therefore, the role of abrasive particles during polishing is multifaceted and dynamic. As a result, both bulk and surface properties of these particles are important in controlling the polishing characteristics such as removal rate and post-CMP surface quality.
A wide variety of materials have been implemented as abrasive particles in CMP processes. They include alumina, silica, ceria, zirconia, titania, and diamond. The effectiveness and suitability of these particles in CMP with particular applications are greatly influenced by their bulk properties like particle density, hardness, particle size, crystallinity etc.) and the surface properties (surface area, isoelectric electric point (IEP), OH content, etc.). The next two sections will focus on the bulk and surface properties of abrasives used for the CMP of copper.

1.6.1 Abrasive Particle Hardness

Hardness is one of the most influential bulk properties in metal film CMP. To remove material from a surface the abrasive particle must be harder than the substrate. The difference in hardness values between the abrasives and the modified substrate film may determine the removal rate during a CMP process. The hardness of the modified layer that is in direct contact with the abrasive particles is important as it may be significantly different from its bulk film hardness. The modification can be accomplished by the oxidizer added into the slurry or the native oxygen in the atmosphere. The hardness of a material is determined by Mohs’ scale that consists of a qualitative hardness index scheme ranging from extremely soft materials (value of 1 Moh) to very hard materials such as diamond (10 Moh). Quantitative methods such as nanoindentation [27] have been developed recently. This technique applies a small and a controllable load on to the substrate with a probe.
Li et al. [28] investigated the relative importance of abrasive hardness and functional group on the particles for copper using alumina, silica and diamond particles. For copper CMP, the abrasive hardness played a significant role in determining the material removal rate. For metal CMP, the material removal rate is not the only requirement as the final surface quality of a polished substrate is as important as removal rate. Therefore, when considering the hardness of abrasive particles, one must not trade surface quality for material removal rate where the mechanism of material removal can alter from abrasion to indentation. The transition from abrasion to indentation depends on the relative hardness of the abrasive and the substrate. In the case of small particles, less than 50 µm in diameter, the primary force is dominated by Van der Waals forces.

1.6.2 Bulk Particle Density

Density of a particle may be defined as the weight of the abrasive particle per unit volume. In principle, the bulk density of agglomerated particles in the slurry can offer an indirect measurement of the abrasive particle hardness. The bulk density of the particle can be calculated by using eqn 1.8, where \( \rho \) stands for the specific gravity of the slurry measured using a pycnometer.

\[
\text{Bulk density} = \frac{\text{Solids (wt \%)} \times 100}{\rho - (100 - \rho)}
\]  

(1.8)

Babu et al [29] established that the abrasive particle density offered a means for characterizing the hardness of submicron abrasive particles based on the material removal rates. The polishing rates of both Cu were measured for slurries of submicron-sized
alumina particles with varying bulk densities ranging from 3.2 to 3.8 g/cm$^3$, dispersed in DI water. It was found that the polishing rate increased significantly when the dry powder bulk density exceeded a threshold value. The bulk density of abrasives also has a direct impact on the slurry dispersion stability. The weight of the abrasives might overcome the repulsive forces among particles required for the stability of the slurry system. For example, the particle settling issue is much more severe for alumina-based slurry than that for silica because of the difference in particle density.

1.6.3 Abrasive Particle Crystallinity and Shapes

Particle crystallinity is another physical property that can be related to particle hardness. Another important factor which is important as the hardness of an abrasive particle is its shape due to the effectiveness of creating indentation on the substrate. In principle, irregular and sharp edges of the particle could lead to high local pressures causing scratches on the surface. Particle shape has both positive and negative effects on CMP performance. It is desirable to have some degree of sharpness to ensure the material removal rate but a balance needs to be achieved in order to avoid additional defects. Li et al. investigated the use of plate-like boron nitride particles for metal CMP that provide high surface contact area between the abrasive particles and the substrate film and low scratching frequency caused by sharp edges.

Silica can exist in many crystalline forms such as quartz, cristobalite, and tridymite. Fumed silica on the contrary tends to be amorphous, which could be attributed to the fabrication process of the abrasive. Colloidal silica synthesized via wet chemical methods
is also amorphous. Also colloidal silica particles are spherical and hydrated in nature which makes them far less likely to cause scratches on metal substrate surface.

1.6.4 Abrasive Particle Size

In addition to the hardness and shape, particle size is another important property for an abrasive. Three relevant parameters that characterize CMP slurry are mean particle size, particle-size distribution and oversized particle count. The particle size modulates the material removal rate, WIWNU, and surface quality for both metal and nonmetal CMP. There are two CMP mechanisms that describe the relationship between particle size and removal rate. For slurry containing extremely large particles, the indentation mechanism may dominate as the material removal rate depends on the indentation volume. In other words, the volume of material removal per particle is directly proportional to the particle size. The net effect is that an increase in particle size leads to an increase in material removal rate. Slurry containing smaller particles will follow the contact-area mechanism where the material removal is determined by the contact area of the particles with the substrate. The contact area increases with the increase in the particle concentration and reduction in the particle size. At a fixed concentration the number of particles increases with the reduction in the particle size. Mahajan et al. [30] studied the impact of abrasive size at different particle concentrations on the oxide removal rate. It was found that the removal rate was a direct function of the particle concentration for mono-size abrasives of size 0.2 mm, thereby supporting the contact-area mechanism. The mechanism shifted to indentation at 1.5 mm resulting in reduced removal rates.
Particle-size distribution has an equally important effect as the particle size. A larger number of oversized particles in the distribution also cause a shift in the mechanism of material removal. Mahajan et al. [30] conducted studies to evaluate the impact of size distribution on oxide removal rates. Baseline commercial slurry was spiked with different concentrations of impurities in the range of 0.5–1.5 mm. The size at different concentrations resulted in removal rates lower than the original slurry. Slurry spiked with 1.1% of 1.5mm particles resulted in a removal rate equal to the baseline slurry, suggesting the predominance of indentation mechanism. Slurries spiked with other concentrations and sizes resulted in a decrease in the removal rate explained by the reduction in the contact area of the abrasives with the oxide substrate.

The behavior of abrasive particles during polishing can be described as an indentation process. Cook et al. [31] developed a model for polishing and according to this model, the penetration depth \( h \) is given by

\[
h = \frac{3}{4} \left[ \frac{P}{2KE} \right]^{\frac{2}{3}} \phi
\]

and the removal rate \( RR \) is

\[
R = \frac{\Delta H}{\Delta t} = \frac{1}{2E} P \frac{\Delta S}{\Delta t}
\]

where \( \phi \) is the diameter of the particle, \( K \) is the particle fill fraction which is unity for a fully filled closed packing and \( E \) is Young’s modulus. The term, \( \frac{\Delta \phi}{\Delta t} \), represents the relative velocity between the particle and the substrate. Figure 1.20 shows the contact mechanics between the particle and the substrate.
The impact of particle size in metal CMP was studied by Lu et al. [32]. It was observed that the material removal rate increased with the increase in the specific surface area of the abrasives in the slurry. The slurry particle size can have a dramatic impact on the surface quality of the polished surface. A large number of so-called oversized particles tend to give high scratch counts on the polished wafers. The particles that are > 1.0 mm will scratch most surfaces close to 100% while the particles that are > 0.5 mm can cause scratch-related defects. Remsen et al [33] studied the impact of oversized particles on fumed silica slurries and their correlation with scratches on silicon dioxide films. It was found that the count had a direct correlation with the number of scratches observed on the substrate.
1.6.5 Abrasive Particle Preparation

Abrasive particle properties are attributed to the method or process used to generate the particles. The surface properties can be altered or modified by varying the physical conditions (temperature, pressure, time) or chemical composition of the initial reactants. This section will survey the various preparation techniques for silica and alumina.

Fumed silica is produced by vapor phase hydrolysis of silicon tetrachloride in a hydrogen–oxygen flame. Equation 1.11 shows the reaction sequence for this process. The combustion process creates silicon dioxide primary particles that condense to form the aggregates which have a length of 0.2–0.3 mm after sintering. These aggregates become entangled to form larger agglomerates.

Unlike fumed silica, colloidal silica is produced by a wet method. Colloidal silica can also be produced in spherical shape with uniform size distribution. Stober et al [34] developed a system where the hydrolysis of alkyl silicates and the condensation of silicic acid in alcohol solution with an ammonia catalyst were used to control the morphology and growth. This method produces uniform spheres of 0.05 to 2 mm in diameter. Tabatabei et al. [35] showed that the size and morphology can also be controlled by the reaction kinetics and also the molar ratio of the reagents. The design and fabrication of microfluidic chemical reactors for the synthesis of colloidal silica particles were reported by Khan et al [36], in which different reactor configurations and flow types were employed to yield varying sizes of the colloidal silica particles.

Alumina is traditionally formed via thermal dehydration of aluminum hydroxides where the final size and crystallinity of the alumina abrasives largely depend on the temperature and time of the process. The total conversion occurs at a temperature of 1500 K.
Technical grades of calcined alumina are also used for smelting, ceramics, and abrasive particles. Other forms of alumina produced are fused and white tabular alumina. Fused alumina is produced by melting calcined alumina at a high-temperature furnace for extended time periods.

\[
\begin{align*}
2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} \\
\text{SiCl}_4 + 2\text{H}_2\text{O} & \rightarrow \text{SiO}_2 + 4\text{HCl} \\
\text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 & \overset{1800^\circ\text{C}}{\rightarrow} \text{SiO}_2 + 4\text{HCl}
\end{align*}
\]

White tabular alumina is composed of large well-developed crystals of \(\alpha\)-alumina, which is generally produced in high-temperature furnaces. By elevating the temperature of dehydrated alumina, the system reaches a temperature close to fusion. The formation of alumina via furnace heating methods has been shown to be the most successful for both small-scale and industrial-scale applications.

### 1.6.6 Abrasive Particle Surface Properties

The abrasive content is usually defined by weight percentage. At a constant weight percentage of the abrasives, smaller particle size translates to larger total surface area. At a certain point, the surface property of a particle competes with bulk properties in influencing the application outcome. For CMP slurries, as the abrasive particles are \(\leq 100\) nm, the surface properties influence the CMP performance. In some cases, they may exert more influence on the CMP outcome than their bulk properties. Relevant surface properties include charge and functionalities on the abrasive surface.
The nature of the charges developed on abrasive surface when introduced into solutions depends upon the solution pH, ionic strength, and the surface functionalities of the abrasive. In the case of silica and alumina, the amount of negative or positive charge depends on the relative number of hydroxyl groups on the surface. Surface charge of abrasive governs the interactions among the abrasives and also between the particles and the substrate. The interactions among the abrasives determine the stability of the dispersion as explained in the earlier section.

The interaction between the abrasive and the surface functionality plays an important role in determining the removal rate and also plays a role in forming or eliminating surface defects. In CMP slurry, all chemical additives reach an adsorption–desorption equilibrium with abrasive surface. During polishing, the slurry is in direct contact with the wafer and the polishing by-products. The added surface adsorption onto wafer surface and the interaction with the byproduct can disrupt the equilibrium established before CMP.

Dhane et al [37] have found that the effective concentration of BTA can decrease significantly due to the introduction of copper ions during CMP. The positively charged complex formed between BTA and copper ions has a much greater tendency to adsorb onto negatively charged silica surface. In addition, to aid the transport of polishing debris, the hydroxyl groups on the abrasive particles, especially for silica, have a significant impact on the polishing rate and removal rate selectivity. They also performed a mass-balance study to determine the amount of copper adsorbed onto the abrasives with model CMP slurry. It was found that the amount of copper in the form of oxide adsorbed onto the silica (45%) was approximately five times higher in comparison to alumina (8%).
removal rate of copper, however, was higher with the alumina abrasives, thereby showing a larger impact of the abrasive hardness on the removal rate under the experimental conditions.

In general, silica surface has a higher number of hydroxyl groups (4 per nm²) than alumina, ceria, titania and diamond. Therefore, silica has an advantage in accommodating polishing debris or by-product. This is why the addition of silica particles can help the reduction of surface scratches. This is also consistent with the fact that some abrasive-free solutions (without the benefit of abrasive particles) give more surface scratches than their counterparts that contain the same chemistry except a small amount of extra silica particles.

1.7 Research Need, Objective and Scope of this work

Fundamental studies of copper CMP slurry formulations reported in literature are often limited to blanket copper films. CMP processing of copper patterned test structures using commercial slurries had been reported, but often these commercial slurries have propriety chemical components and hence the formulation details of these slurries are not typically provided. Hence, there is a need to investigate and relate the performance of a copper CMP slurry on 300mm wafer patterned BEOL test structures to the chemical components in the copper CMP slurry formulation used. The work presented here aims to bridge the gap between slurry components and slurry polishing performance of copper structures on device wafers.

In this work, the development and investigation of Cu CMP slurry comprised of four basic components – abrasives (alumina), oxidizer, passivating agent, and complexing
agent is reported. Novel alumina particles of approximately 40-50 nm particle size, suspended in only D.I water were used in this study. The proprietary process which was used to manufacture these alumina particles eliminated the need for any additional chemical components needed for suspension. Thus a direct correlation could be established between the relative concentrations of the basic slurry component, the performance of the slurry with respect to 200mm and 300mm blanket Cu polishing, and the performance of slurry with respect to patterned Cu test structures (dishing, erosion, end pointing, and compatibility with 2nd step barrier CMP) and in turn, the electrical performance in terms of isolated resistance, shorts and opens of the copper test structures on the patterned wafers.

The first objective of this work was to develop a Cu CMP slurry consisting only of the basic chemical components and novel alumina abrasives having removal rates comparable to that of commercial slurries on 200mm & 300mm blanket wafers. The second objective of this work was to isolate, engineer, evaluate and determine the role of four basic components – (i) oxidizing agent - H₂O₂ (ii) complexing agent - Glycine (iii) passivating agent – BTA and (iv) pH concentration in Cu CMP slurry on a 300mm commercial manufacturing platform. The third objective was to contrast and compare the polishing performance of a chemically dominant to a mechanically dominant removal process as a function of the nano-abrasive particle concentration. The interactions of the alumina nano-abrasives with the four basic components of the slurry were also studied. The final objective was to relate the effect of the basic components and the polishing performance to the electrical test data.
1.8 Organization of the Dissertation

This dissertation document is divided into six chapters.

Chapter 1 provides the introduction and discusses the need for this work.

Chapter 2 presents the experimental methodologies used on the 200 mm and 300 mm wafer platform. The metrology and characterization methods used for the 200 mm and 300 mm platforms are also discussed. Finally, the characterization of nano-abrasive particles used in these experiments is discussed.

Chapter 3 presents the pre-development experiments and the subsequent results on copper blanket wafers on the 200 mm platform. Results obtained from experiments to determine static etch rates of the formulations are also discussed.

Chapter 4 presents the results obtained by polishing 300mm M1-patterned wafers and relates the polishing performance in terms of material removal rate, dishing, erosion and subsequent electrical test results to the formulation of the novel alumina ANW slurry that was used to polish these patterned wafers.

Chapter 5 discusses the component role to the performance of slurry with respect to patterned Cu test structures (dishing, erosion, end pointing, and compatibility with second step barrier CMP).

Finally, Chapter 6 provides the conclusions of this work and suggests the direction for the future course of this work.
References


CHAPTER 2

EXPERIMENTAL METHODOLOGY AND CHARACTERIZATION

2.1 Experimental Procedure

As discussed in Chapter 1, this work consisted of evaluating polishing performance of various slurry formulations consisting of basic components and novel abrasive particles (ANW Alumina). For polishing performance, commercial slurries were used to make baseline comparisons. The commercial slurry that was used for reference purposes was Cabot alumina C7092 slurry and JSR copper slurry. Nonabrasive slurries including Cabot slurry are discussed in 2.1.2.

2.1.1 Design of Experiments and Slurry Formulation process

![Flow diagram showing the slurry formulation process for both 200mm and 300mm wafers used in this work.](image)

*Fig 2.1 Flow diagram showing the slurry formulation process for both 200mm and 300mm wafers used in this work.*
Figure 2.1 displays the basis flow diagram for investigation, development, and evaluation of ANW-based slurries for Cu CMP. As shown in the flow diagram, the copper slurry formulation process was developed on both 200 mm and 300 mm tool using a Design-of-Experiments (DOE) approach. Applied Nanoworks (ANW) based slurries employing alumina as the nanoabrasive particles were used for both 200mm and 300mm experiments. The details of all the slurries used in this work are discussed in Chapter 2.2.

As outlined in Fig. 2.1, the preliminary Cu CMP processing for ANW slurry development was performed on a 200mm Strasbaugh 6DS-SP CMP tool in a lab environment. Slurry formulations were then developed using a run table based on an n-type factorial DOE [1], where n is the number of variables. In order to determine the primary slurry candidates for 300mm wafer processing, the CMP was performed on various 200mm blanket wafers based on the run table. The run table and the DOE on 200mm tool are discussed in detail in Chapter 3. The primary slurry formulation candidate was determined based on various mechanical parameters which mirrored the final surface quality and polishing performance of the wafer. The CMP processed wafers should have (i) High Material Removal Rate (MRR) ≥ 5000 Å/min (ii) Low Static Etch Rate (SER) ≤ 500 Å/min and (iii) Minimal RMS Surface Roughness. It is important to note that a good MRR alone is not the sole determining criteria for selecting the primary candidate as the translation from a 200 mm to 300 mm CMP toolset is not straightforward and quite complex. This is also further discussed in detail in Chapter 3.

Once the primary candidate is determined, another set of Design-of-Experiments [1] was performed and the slurry formulations were determined based on a new run table for the 300mm CMP tool. Two different sets of DOEs were performed in two different phases
for 300mm wafer Cu CMP. The first set of DOEs was performed in Phase I where 300mm blanket wafers were used. These formulations for the first DOE set were chosen primarily based on the results obtained from 200mm blanket wafers. Unlike the 200mm CMP results, the process quality determination was primarily made based on the MRR parameter.

The Phase II DOE was primarily carried out for further optimization of the CMP process parameters for the ANW slurry formulations of interest. The DOE and slurry formulations for Phase II were performed on 300mm patterned wafers. The layouts of the patterns were based on IBM’s 90nm BEOL technology and M1 process. The details of the pattern and the layout are discussed at the end of this chapter. In addition to the standard variables, an additional variable based on end point detection were also included for these patterned wafers. This variable is important for optimizing the Cu CMP overpolish time.

Once the CMP process was complete based on the aforementioned DOE-based slurry formulations, the patterned 300mm wafers were subjected again to a secondary barrier (Ta/TaN) CMP step using commercial barrier slurry. Once the process was complete, the polished wafers were sent through CNSE 300mm prototyping line for physical and electrical characterization. The first level of physical characterization was performed using High Resolution Profilometry to determine the amount of dishing and erosion in the 300mm wafer M1 patterned structures. In addition, the MRR was also calculated. The next step was to perform a visual inspection using Leica Optical Microscope in order to determine whether the copper metal was cleared from the barrier layer. Further details regarding post-CMP characterization techniques are discussed in Chapter 2.4. If the post-
CMP results did not meet the required performance or yielded inconsequential results in terms of MRR, dishing or erosion, the formulation was modified (starting, if necessary from 200mm wafer evaluation) and a follow-on set of DOEs was carried out. However, if the results met the required target, the wafers were evaluated with regard to M1 electrical performance. The isolated and nested resistance of M1 BEOL test structures was evaluated using four-point probe methods and tested for opens and shorts using an advanced semiconductor parametric tester and autoprober. The wafer was considered to have met the target performance if it met the nominal MRR value and low dishing and erosion values (≤ 500 Å). Specific experimental results following this development and testing flow are discussed in Chapter 4 of this dissertation.

2.2 Nanoabrasive slurries for copper CMP

Traditionally, CMP slurries were divided into two types according to the materials to be polished, i.e. oxide-polish and metal-polish slurries. Both types of CMP slurries generally incorporate nanoabrasives to abrade the chemically treated surface exposing new material for chemical reaction. Nanoabrasive particles require appropriate surface charge to stay suspended in slurry mixtures, correct hardness to impact the wafer surface, and must be stable in the slurry solution. Materials for oxide-polish generally contain silica or ceria particles dispersed in aqueous alkaline solutions, and are used for interlayer dielectric films. Metal-polish slurries generally contain alumina or silica particles dispersed in acidic aqueous solutions usually with oxidizing agents, metal ion complexing agents, and metal corrosion inhibiting agents. They are used to polish copper, aluminum, tantalum or
semiconductors, such as doped silicon or polysilicon films. Alumina particles have good mechanical strength and give high removal rates, but are difficult to maintain in suspension without chemical additives (required for smaller IC features sizes). Silica is a softer abrasive, stays well suspended and yields a good post-polish surface finish, but often has low material removal rates. In general, it is difficult for single-component nanoabrasive slurries to meet simultaneous demands of polish rates, material selectivity and excellent surface quality.

The oxidizing agents in metal CMP slurry generally form a passivating layer on the metal film to avoid isotropic etching. Metal corrosion inhibiting agents typically form a protective layer in the recessed regions on the metal film to prevent them from being corroded by the slurry, while the protruding regions can still be removed by both mechanical abrasion and chemical dissolution/corrosion. Well-performing slurries for CMP processing exhibit desirable polish rates, good surface quality, local and global film planarity, and optimal selectivity. Table 2.1 gives the hardness and isoelectric point (IEP) values of some commonly used abrasive particles. Since it is difficult to quantitatively measure the hardness of sub-micron particles, the values shown in Table 2.1 are those of micrometer-size particles.

Table 2.1 IEP and hardness of commonly used abrasive particles[2].

| Abrasive       | IEP (pH) | Hardness (GPa) |
|----------------|----------|                |
| Alumina (Al₂O₃) | 9.1      | 19.6           |
| Silica (SiO₂)  | 2.2      | 11.8           |
| Ceria (CeO₂)   | 6.7      | 11.3           |
| Zirconia (ZrO₂)| 6.7      | 12.3           |
| Titania (TiO₂) | 4.7      | 9.8            |
Four types of slurries for Copper CMP are used in this work - (i) Cabot C7092/C5001 slurry (commercial) (ii) JSR Cu slurry (commercial) (iii) ANW alumina slurry (developmental) and (iv) JSR barrier slurry (commercial). The nanoabrasives that were used in each slurry are discussed below.

2.2.1 Cabot C7092/C5001 Slurry

Cabot iCue C7092/C5001 is a family of commercial copper CMP slurries used for 130nm - 45nm technology nodes primarily on the 200 mm wafer CMP tool. 2% hydrogen peroxide (by volume) was added to the slurry (per vendor recommendations). After adding hydrogen peroxide in the slurry, slurry mixing [3] employed a mechanical stirrer at an operating speed of ~350 rpm for 10-15 minutes before the slurry was used for polishing. The slurry composition and physical/chemical properties [4] of the slurry are given below in Table 2.2 and Table 2.3, respectively. The Cu material mean removal rates (MRRs) achieved with this slurry (on the 6DS-SP CMP tool) by mixing different amounts (by volume) of hydrogen peroxide is shown in Fig. 2.9. The Cabot C7092/C5001 commercial Cu slurries [5] contain alumina nanoabrasives as shown in Fig. 2.10. The average size of the nanoabrasive was approximately 70 nm.

Table 2.2 Composition/information on Cabot iCue 7092/5001 Cu slurry ingredients.

<table>
<thead>
<tr>
<th>Component</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum oxide</td>
<td>2-5</td>
</tr>
<tr>
<td>DIW</td>
<td>93-96</td>
</tr>
<tr>
<td>Proprietary ingredients</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
Table 2.3 Physical and chemical properties of Cabot C7092/5001 alumina slurry.

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.027-1.031</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>dispersible</td>
</tr>
<tr>
<td>pH</td>
<td>7.5-7.9</td>
</tr>
<tr>
<td>Boiling point</td>
<td>&gt; 100 C/ 212 F</td>
</tr>
<tr>
<td>Viscosity</td>
<td>3-13</td>
</tr>
</tbody>
</table>

Figure 2.2 Average Cu MRR on circular rings at certain radii of the 200mm Cu wafer as a function of $H_2O_2$ concentration (by volume) mixed with Cabot 7092/5001 slurry. Polishing downforce was 2 psi and wafer was polished on 6DS-SP tool[5].

Figure 2.3 SEM image of alumina nanoabrasives used in Cabot C7092/5001 commercial slurry.
2.2.2 JSR Slurry

While Cabot slurries contain alumina as nanoabrasives, the JSR Cu polishing commercial slurry (which comprised the 300mm blanket/patterned Cu CMP baseline slurry) contains silica as nanoabrasives. The average size of the nanoabrasive was ~50 nm. The SEM images of silica particles from the JSR Cu slurry are shown in Fig. 2.4.

![SEM images of silica nanoabrasives in commercial JSR Cu slurry](Image Courtesy: Iftikhar Ul-Hasan).

The JSR slurry consisted of three components with chemical and nanoabrasive solutions [6]. This slurry required two delivery lines and was mixed at the platen point of use (POU). The slurry mixing procedure (prior to and at POU) is shown in Fig. 2.5. Slurry additives concentrations as well as physical and chemical properties are shown in Table 2.4 and Table 2.5. The final JSR slurry pH was measured in the lab and was found to be ~ 8.3. As shown in Fig 2.6, this slurry provided an average Cu MRR of roughly 400nm/min on 200mm CMP tool.
Figure 2.5 Slurry mixing procedure of JSR silica slurry. wt % concentrations are not shown due to proprietary information [7].

Table 2.4 Composition and information on JSR Cu slurry ingredients.

<table>
<thead>
<tr>
<th>Component</th>
<th>JSR CMP slurry CMS7401</th>
<th>JSR CMP slurry CMS7452</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium hydroxide</td>
<td>1-3%</td>
<td>0.1-3%</td>
</tr>
<tr>
<td>Water</td>
<td>90-99%</td>
<td>75-95%</td>
</tr>
<tr>
<td>Additive</td>
<td>1-10%</td>
<td>1-10%</td>
</tr>
<tr>
<td>Amorphous silica (particles)</td>
<td>-</td>
<td>5-15%</td>
</tr>
</tbody>
</table>

Table 2.5 Physical and chemical properties of JSR CMP silica slurry.

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th>JSR CMP slurry CMS7401</th>
<th>JSR CMP slurry CMS7452</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1~1.1</td>
<td>1~1.1</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Dispersible</td>
<td>Dispersible</td>
</tr>
<tr>
<td>pH</td>
<td>7~10</td>
<td>7~10</td>
</tr>
<tr>
<td>Boiling point</td>
<td>100 C</td>
<td>100 C</td>
</tr>
</tbody>
</table>
Figure 2.6 Average Cu MRR on circular rings at certain radii of the 200mm Cu wafer polished with JSR Cu slurry on 6DS-SP CMP tool. Where, D.F=2 psi, S.F.R=150 ml/min, S.S/T.S=70/60 rpm, B.P=0 psig, R.F=1 psi, P.T=60 secs [6,7].

2.2.3 Applied Nano Works (ANW) Nanoabrasives and Slurry

Applied Nanoworks Inc. (ANW) alumina nanoabrasives (Fig. 2.7) were used to develop in-house slurry for copper CMP for this dissertation. All the custom slurry formulations presented in this work were using these nanoabrasives. The average particle size was approximately 40-50 nm and the alumina particles were suspended in D.I water without the use of any additional chemical components. Using alumina nanoabrasive supplied by ANW the baseline copper slurry was formulated, characterized and evaluated. Properties of the ANW alumina nanoabrasive solution are shown in Table 2.6.
2.2.3.1 Slurry Mixing Procedure for ANW slurry

The slurry mixing procedure to formulate copper baseline slurry with ANW nanoabrasives was as follows – ANW alumina particles suspended in DI water having a tight size distribution (diameter 40-50 nm) were used. The Cu CMP slurry formulation procedure involved the mixing of all four components at predetermined amounts per the DOE. First, the appropriate amount of D.I water necessary to reduce alumina concentration from 5 wt% (as-received) to the desired alumina concentration was calculated. Then calculated amount of BTA to achieve desired concentration was added to DI water. The mixture was then stirred for 3-5 minutes with the help of a mechanical stirrer. Then the required amount of glycine was added to the DI water/BTA mixture and

---

**Figure 2.7** SEM picture of alumina nanoparticles used in ANW alumina slurry.

**Table 2.6** Physical and chemical properties of ANW Cu slurry ingredients[8].

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH range</td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Specific gravity (Water = 1)</td>
</tr>
<tr>
<td>Water solubility</td>
</tr>
</tbody>
</table>

---
stirred again until glycine was fully dissolved. Then the required amount of 5 wt% ANW alumina nano-abrasive was added to the DI water/BTA/glycine mixture. The next step was to add the required amount of hydrogen peroxide to the mixture. Finally, the pH of the solution was checked and adjusted to the required value using KOH.

2.2.4 Second Step Slurry

A proprietary second step slurry - CMS8401 + CMS8452 + H₂O₂ with concentration of 30wt% was used for second step barrier polishing.

2.3 CMP polishing tools

The polishing tools used for CMP obviously play a vital role in the planarization process. The down force and the mechanical motion are imparted to the wafer by the polishing tool [2]. The tools themselves have many variables associated with the polishing process. It is critical that the polishers are properly aligned and calibrated prior to wafer polishing. If these alignments and calibrations are not performed or completed incorrectly, then these tools could drastically affect the results of the polishing process.

Two kinds of polishing tools were used for this work. A Strasbaugh 6DS-SP CMP tool was used for developmental 200mm blanket work. An Ebara F-REX 300S was used to polish 300mm blanket and patterned wafers.

2.3.1. Strasbaugh 6DS-SP CMP Tool (200 mm Blanket Wafer Polishing)

The Strasbaugh 6DS-SP wafer polisher is a fully automated tool for CMP polishing of semiconductor wafers. It can planarize wafers from 100mm to 200mm in diameter and is
suited for materials polishing applications that require repeatability with operational and processing flexibility. The wafer polisher features automatic wafer handling and is capable of polishing two wafers on a single platen [9].

2.3.2. Ebara FREX300 CMP Tool (300mm Blanket & Patterned wafer polishing)

The FREX300 CMP tool is the enhanced version of Ebara’s dry in/dry out integrated clean CMP system [5]. Ebara’s FREX300 has a two-head, two-platen and two-buff station design, which allows for mixed process recipes. The two-head/two platen design with integrated four station cleaning allows for flexibility in serial or parallel operation. The Ebara FREX300 also contains features like 3-step chemical clean, buff stations and four FOUP loader ports. 300mm wafers processed in the Ebara FREX300 for this study followed the same processing protocol as those wafers polished with commercial Cu CMP slurries.
2.3.3 Basic Configuration and Working Procedures of a CMP Tool

The wafer to be polished is placed on a load/unload station on the shuttle of the polishing tool. The shuttle serves as a rinse station as well as a wafer loading platform. The wafer is then picked up by the wafer carrier using a negative back pressure. The carriers are attached to spindles mounted on a bridge assembly which moves from the loading station to the polishing platens. The polishing platen is a circular polished slab (stone or polished metal) ~ 30 inch in diameter. The CMP pad is attached to the platen via a backside adhesive. To polish a wafer, the loaded carrier is transported from the shuttle position to the polishing table. Both the carrier (holding the wafer) and the table (holding CMP pad) are rotated independently with particular angular velocities (as desired by the operator) before lowering the wafer over the CMP pad. The carrier and platen rotational speeds are referred to as the spindle speed (S.S) and the table speed (T.S) respectively. Both platen and carrier can be rotated clockwise or counterclockwise. At the start of the platen rotation, polishing slurry, is continuously supplied with a specific slurry flow rate (S.F.R) to the pad until the end of CMP process.

The rotation of the polishing table distributes the slurry over the CMP pad. This distribution is promoted by the design of the grooves and open pores on the pad surface. The rotating wafer carrier is lowered against the CMP pad. Polishing downforce (mechanical pressure onto polishing pad applied by the spindle) and back pressure (denoted as B.P) are applied during polishing time to the backside of the wafer to promote film removal and to compensate for film non-uniformity. The CMP tool also possesses force ramp and back pressure ramp parameters which can be varied to optimize
a given process. The wafer is polished for a certain amount of time, known as the polishing time.

After each wafer polish on the polishing table, the CMP pad is conditioned, using a diamond studded CMP conditioning wheel. The CMP conditioner is lowered, rotated, and swept on the rotating pad, with desired conditioning parameters, by a robotically controlled conditioning arm. After the polishing is complete, the spindle/carrier lifts up the polished wafer from the pad surface and brings the polished wafer over to either a next step polish (e.g. barrier), a buffing table, or to a cleaning/drying station. After completion, the wafer is transported to the unloading station.

2.3.3.1 End Point Detection

The end of a polishing step is traditionally determined by setting a time limit in the process. Changes in a removal rate due to normal polish pad life cycle, variations in slurry and pad lots, conditioning issues, and a myriad of other potential variables can result in under- or over- polish errors. Additionally, incoming initial oxide or metal layer thickness may fluctuate. Therefore, in-line monitoring and automatic end-point detection of CMP offers many manufacturing advantages such as improved process yields, reduced product variability, closer conformance to target requirements, and higher throughput. There are many potential payoffs; however, in-line monitoring and automatic end-point is difficult to implement due to the complicated nature of CMP.

Numerous approaches have been proposed for in-situ EPD in CMP: They include optical, electrical, thermal, electrochemical method, and so on. Figure 2.9 summarizes the current
EPD approaches and Table 2.8 summarizes the methods. In the table, D means direct, and I, indirect methods, and G refers to global, and L, local sensing. In conventional copper CMP, end-point detection relies on in-situ or local sensors such as eddy current sensors to measure the remaining copper film thickness.

**Table 2.8 Summary of Current EPD Approaches [11].**

<table>
<thead>
<tr>
<th>Physics</th>
<th>D,I</th>
<th>G,L</th>
<th>App</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical</td>
<td>Reflectance, Absorption</td>
<td>D</td>
<td>L</td>
</tr>
<tr>
<td>Thermal</td>
<td>Temperature</td>
<td>I</td>
<td>L</td>
</tr>
<tr>
<td>Electrical</td>
<td>Motor Current</td>
<td>I</td>
<td>G</td>
</tr>
<tr>
<td>Microphone</td>
<td>Sound Waves</td>
<td>D</td>
<td>G</td>
</tr>
<tr>
<td>Force</td>
<td>Friction Force</td>
<td>D/I</td>
<td>G</td>
</tr>
<tr>
<td>Acoustic Emission</td>
<td>Acoustic Waves</td>
<td>D</td>
<td>G</td>
</tr>
</tbody>
</table>

**Figure 2.9(a) Current Methods used for End-Point Detection [11].**
The Ebara FREX300S CMP tool utilized an eddy-current-based approach for Cu CMP endpointing. The approach and representative data is summarized in Figs. 2.9(b-c). As the Cu clears down to the TaN barrier (Fig. 2.9(b)) the average current sensor signals drops (Fig. 2.9(c)). An endpoint protocol is developed based on the rate of change of the eddy current compared to the clearing of the Cu from the barrier layer. In practice, this endpoint may leave some residual Cu. As a result, an overpolish time ranging from a few
seconds to 10’s of seconds is often employed past endpoint to ensure residual Cu is removed. This end pointing approach is used for the 300mm patterned wafer Cu CMP presented here and is correlated with ANW slurry formulation (Chapter 4).

2.4 Tools and techniques used for characterization of post CMP wafers

2.4.1 Copper thickness measurements (200mm & 300mm Blanket/Patterned Wafers)

The thickness of copper on the wafers used to determine MRR was measured using an automated four point probe [12]. The Signatone QuadPro [13] automatic test system used for this work consists of four equally spaced, serially connected collinear probes as shown in Figure 2.10.

A constant current (I) is passed through the two outer probes and the potential drop (V) across the inner two probes is measured using a voltmeter. The sheet resistance (R_s) is calculated using equation 2.1.

\[ R_s = \left( \frac{V}{I} \right) C \]  

(2.1)

where, \( C \) is a correction factor
The correction factor, $C$, depends on the probe spacing ($s$) and the substrate diameter ($D$). For $s<<D$, the value of $C$ is 4.532. From the value of the sheet resistance, film thickness ($t$) is calculated as

$$t = \left( \frac{\rho}{R_s} \right)$$

(2.2)

where, $\rho$ is the resistivity of the metal film.

For the Signatone QuadPro [12] automated four point probe tester (shown in Figure 2.11), the probe spacing was on the order of millimeters (25 mils = 635 µm), the probe tip radius was 1.6 mils = 40.6 µm, while the Cu films (1 µm or less in thickness) were always on an insulator (SiO$_2$) layer deposited on the Si wafer (200mm or 300mm in diameter) substrates. The resistivity value used for copper films was 2.08 x 10$^{-6}$ ohm-cm.

The resistance was measured at 49 points across the diameter of the copper wafer and the thickness was calculated. The reported Cu thickness value was the average of these 49 values. Within wafer non-uniformity (WIWNU) across the wafer was also calculated from the thickness values from the equation

$$WIWNU = \left[ \text{STDEV(Thickness)} / \text{AVERAGE(Thickness)} \right] \times 100$$
2.4.2 Atomic Force Microscopy

A VEECO Dimension [14] 3100 Atomic Force Microscope (shown in Figure 2.12) was used to investigate the surface morphology of the copper blanket wafers before and after polishing. The AFM scans also gave information about the surface quality and surface roughness of the polished wafers. Any scratches on the wafer surface as well as the residual particle information were also obtained via these scans.

AFMs measure the topography of a surface by bringing a sharp probe very close (within angstroms) to the sample surface to detect small forces due to the atoms on the surface instead of passing a current. Figure 2.13 shows the force plotted against the distance from the surface. A strong repulsive force is encountered by the tip at distances very near the surface atoms, due to electrostatic interactions.
**Figure 2.12** *VEECO Dimension 3100 Atomic Force Microscope [14].*

**Figure 2.13** *Diagram of the tip-sample junction and a force curve for the AFM [15].*
An atomic force microscope can be operated either in the contact mode, non-contact mode, or tapping mode. Contact-mode scanning is said to occur when these repulsive forces are used for regulating the tip-to-sample distance [15]. In non-contact mode scanning the tip is moved away from the surface and the long-range attractive force is used for feedback control. The tapping mode uses intermittent contact which is a mixture of these modes which provides the topographic resolution of contact made with the low tip-surface force interaction of the non-contact mode.

A simplified diagram of an AFM is shown in Figure 2.14. Forces between the tip and sample surface are sensed as the probe tip is brought towards the sample surface. The probe-to-sample distance is regulated by maintaining a constant force via a feedback servo-system, once the initial approach has been completed i.e., the surface has been found. The vertical displacement of the cantilever acquired during scanning is then converted into topographic information in all three dimensions [8]. The AFM scans laterally is x and y and has a constant amount of tip-to-sample force maintained in order to obtain images.

![Simplified block diagram of a generalized AFM system](image)

**Figure 2.14** Simplified block diagram of a generalized AFM system [15].
For this work, tapping mode was used to obtain surface morphology and roughness of the polished wafers to evaluate the polishing performance of the slurries. In addition AFM scans of patterned wafers revealed line edge roughness and detected copper residue as well as particles and scratches present on the surface. The cantilevers used for these scans were of 125 µm length, 4 µm thicknesses and had 40 N/m spring constant, with a 300 kHz resonance frequency. The tip was symmetric and consisted of ~10 nm radius and 15-20 µm height. The tip and cantilever were an integrated assembly of single crystal silicon. Various AFM scan sizes were taken at different locations of the wafer. The AFM scan sizes included 10µm × 10µm, 5µm × 5µm and 1µm × 1µm. The scans were taken at center, edge and middle of the wafers. For each scan size, the surface roughness (Ra) values were averaged and a standard deviation was determined to characterize the polished Cu wafer surface roughness. The scan rate was generally very slow, 0.5 Hz and images were collected at a resolution of 512 × 512 data points.

2.4.3 Scanning Electron Microscopy

The scanning electron microscope used for this work was a LEO 1550 SEM [16], as shown in Figure 2.15. The SEM provides a higher resolution than that is possible by the optical microscope and is a very important tool, used in many phases of semiconductor manufacturing for high resolution analysis and inspection. The SEM has a finely focused beam of electrons is moved or scanned from point to point over the specimen surface in a precise square or rectangular pattern called a raster pattern [15].
Figure 2.15 *Leo 1550 Scanning Electron Microscope [17].*

The primary beam electrons originate from an electron source and are accelerated towards the specimen by a voltage usually between 0.2KV and 30KV. The electron beam travels down the column, where it undergoes an electron optical deformation by one or more condenser lenses. This demagnification reduces the diameter of the electron beam to nanometer dimensions. The proper accelerating voltage and amount of condenser lens demagnification is chosen to optimize the image. The electron microscope column of an SEM needs to be in high vacuum, as electrons can not travel for appreciable distances in air [18].

Scanning coils in the microscope precisely deflect the electron beam in a raster pattern controlled by a digital or analog X and Y scan generator. This deflection is synchronized with deflection of the record cathode ray tubes (CRTs) so there is a point-by-point visual representation of the signal being generated by the specimen as it is scanned. The smaller the area on the sample represented by one pixel, the higher the effective magnification.
The interaction of an energetic electron beam with a solid results in a variety of potential ‘signals’ being generated from a finite interaction region of the sample [19], as shown in Figure 2.18. The most commonly used of the SEM signals are the secondary and backscattered electron signals. The electron beam can enter into the sample and form an interaction region from which the signal can originate. The size of the interaction region is related directly to the accelerating voltage of the primary beam, the sample composition, and the sample geometry. The signals that are produced within the interaction region and leave the sample surface can be potentially used for imaging.

The most commonly collected signal in the CD-SEM is the secondary electron (SE). Secondary electrons are generated by the primary electron beam within the first few nanometers of the specimen surface, their escape depth varying with the accelerating voltage and the atomic number of the specimen [8]. The secondary electrons are generated have between 1 and 50 eV of energy. The secondary electrons are the most
commonly detected for low-accelerating voltage inspection due to their relative ease of collection and since the signal is much stronger with these secondary electrons. The backscattered-electron (BSE) signal is also very useful [20]. A fraction of the electrons that undergo elastic scattering at the sample are ultimately directed back out of the specimen as BSE. BSEs carry information about features that are deep below the specimen surface. The images obtained with BSE are principally used to reveal compositional variations. The BSE signal tends to concentrate around the beam axis. Therefore, unlike the SEs, the high energy BSEs can only be collected by placing a detector directly over the top of the specimen where it is likely to be struck with the emitted electrons.

As mentioned earlier, an LEO 1550 SEM was used for imaging throughout this work. Imaging resolution is 1 nm@ 15 KV for the Leo 1550 SEM [16,17]. Primary electron gun voltages of 10 KV and 7 KV were employed for high resolution imaging (at 60-100 Kx magnification). Working distance (WD) for pad samples was selected from 13-17 mm. For slurry nanoabrasive sizing, 4mm WD, 5-15 KV primary electron gun voltage and 100-700 Kx magnification were utilized.

2.4.4 High Resolution Profilometry

The challenges of metal CMP and etch processing can be best met by carefully characterizing process margins during process development and implementing an efficient process-control strategy during full-scale manufacturing. The metrology tool used for these measurements must have the following performance characteristics [21]:
(1) A scan length greater than 50mm; (2) Ability to image 0.25 micron features; (3) Repeatability of better than 1nm on depth measurements; (4) Easy to use and quick time to results. Because a High Resolution Profiler has all these capabilities, it is used predominantly used in the manufacturing flow of all types of chips: ASICs, memory and microprocessors. The HRP has both micro- and macroimaging capabilities: the ability to position the stylus with nanometer resolution and a lateral scan range of up to 300mm[8]. This is accomplished with a dual-stage system as shown in Figure 2.17. The choice of stage depends on the features being measured. Sensor stage scans are limited to 90 micron and smaller, so if the feature is larger than 90 micron, the only option is to use the sample stage.

![HRP dual stage technologies](image)

**Figure 2.17 HRP dual stage technologies [22].**

The sample stage (contact mode) is used to measure large features, such as scribe line test structures, die, and global planarity. Sample stage scans are performed by moving the wafer under the stylus, as shown in the Figure 2.18. The sample stage is resting on an optical flat and when it is combined with the guide bar, motion in the x-direction is stable, smooth and flat. The sample stage is a mechanical stage with a repeatability of 1
micron (1σ). The drive mechanism of the stage is based on a mechanical screw with a pitch of 1mm. The carriage slides on a glass reference flat that constrains the motion of the sample stage to a horizontal plane.

Sensor stage (contact mode) scans are generally used to measure small features using sharp or high aspect ratio tips. The sensor stage generally has better noise performance than the sample stage. The sensor stage, used for micro-imaging, has a range of 90 micron and 1 nm resolution. It consists of piezoelectrics, mounted in a mechanical (flexure) frame. The flexure frame is designed to remove the undesirable bending motions of the piezoelectrics and to only allow the desired x-y rectilinear expansion. The flexure mechanism keeps the piezoelectric bending motions from degrading the HRP’s repeatability. The sensor stage also contains two capacitance sensors, both with resolution of 1nm, which determine the x and y positions of the stage. Positioning accuracy with the sensor stage is better than sample stage accuracy, because the sample

![Diagram](image.png)

*Figure 2.18 Motion of Stylus during Contact Mode scanning [23].*
stage only needs to move to a coordinate and does not require sample stage motion during the scan.

The HRP sensor consists of an electromagnet, a flexure hinge, a linear variable differential capacitor (LVDC) sensor, and a sensor vane as shown in Figure 2.19 [21-23]. In the contact mode, the stylus moves up and down as it lightly scans over the contours of the surface in contact with it [21-23]. The flexure hinge constrains the stylus arm to pivot about the hinge in a seesaw motion and changes the relative position of the sensor vanes between the capacitor plates [21-23]. The capacitance sensor measures the height of the stylus, which is proportional to the separation of the capacitor plates, d. If the variations in the electric field near the edges of the plate are ignored, the relationship between the distance between the plates, d, and the capacitance C is that of an ideal parallel plate capacitor.

By measuring the change in capacitance of the plates, the change in spacing, d, and the change in the height of the surface being scanned, s, can be determined. The sensor design enables tracking vertical changes in the surface topography with better than 0.1% linearity over the entire range of 130 µm. The HRP capacitance sensor can measure the surface height with two range settings. For a range of 13 µm, the resolution is better than 0.01 nm; and for a range of 65 µm, the resolution is better than 0.1 nm.
The other mode of scanning for the HRP is the **dipping mode**. Dipping mode is designed for measurement of high aspect ratio features (greater than 1:1 aspect ratio) that are not possible when using the contact mode. Dipping mode is a scanning mode used to reduce the lateral force applied to the stylus enough to allow the use of a stylus with a small cone angle and tip radius for measurement of high aspect ratio features. In Dipping mode, the stylus moves perpendicularly in and out of features, with all lateral movement occurring when the stylus is clear of the surface. The scanning motions are performed with a z-stage for the perpendicular motion and the sensor stage for lateral motion when the stylus is clear of the wafer surface. This mode of scanning eliminates the lateral force. For each approach to the surface, the capacitive sensor is used to detect when the tip has reached the surface and a data point needs to be recorded. Figure 2.20 illustrates the Dipping Mode scan movement.

![Figure 2.19](image)  
*Figure 2.19 HRP ultralite sensor [22].*
For all the scans reported in this work, the contact mode of the HRP was used. The styli used in the HRP in contact mode are made from bulk diamond, which makes them robust and long lasting. They are available with variety of radii of curvature as appropriate for applications ranging from measuring the recess of submicron tungsten vias to the height of solder bumps [24]. The recommended scan speeds and applied forces for different types of scans are as shown in Table 2.9. The sampling rate, which is the frequency at which data points are collected (number of data points per second), generally set to the default value of 200Hz.

**Table 2.9 Various parameters for Dipping Mode Scanning Motion.**

<table>
<thead>
<tr>
<th>Stylus Tip size</th>
<th>Applied Force</th>
<th>Scan Speed</th>
<th>Related Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 µm</td>
<td>0.20 – 2.00 mg</td>
<td>No Limitations</td>
<td>Normal scans</td>
</tr>
<tr>
<td>2 µm</td>
<td>0.05 – 0.50 mg</td>
<td>Not to exceed 10 µm/s</td>
<td>Soft materials</td>
</tr>
<tr>
<td>Submicron</td>
<td>0.20 – 2.00 mg</td>
<td>No limitations</td>
<td>Normal scans</td>
</tr>
<tr>
<td>Submicron</td>
<td>0.05– 0.50 mg</td>
<td>Not to exceed 10μm/s</td>
<td>Soft materials</td>
</tr>
</tbody>
</table>
A KLA Tencor HRP-240/340CMP system [23] was used for polishing performance evaluation. Dishing and Erosion values were determined from the HRP scan profiles for post polished patterned wafers. The lower the dishing and erosion value, the better was the polishing performance of the slurry that was used to polish the wafer.

The differential removal rate between Cu, barrier, and dielectric leads to dishing of Cu features, as shown in Figure 2.21. Dishing occurs as the metal removal rate is much larger than the dielectric removal rate. Dishing is usually expressed in angstroms (Å). Dishing also leads to erosion of narrow dielectric features. The amount of dielectric removed corresponds to Erosion, which is also expressed in angstroms (Å).

![Figure 2.21 Illustration of Dishing and Erosion.](image-url)
The patterned wafers used for this work were manufactured using IBM’s 90nm node mask. The wafers had inbuilt designated macro’s which were used for measuring dishing and erosion. For evaluation of dishing of large features, dishing of the 100µm×100µm, 250 nm deep copper pad, called ‘Macro’, was measured. Dishing and erosion of smaller features was determined from HRP scans of ‘Site 12’ which had 25 µm, 250 nm deep lines. HRP scans were taken at three different positions on the wafer; center, middle and edge of the wafer and an average of these values was used in evaluation of the polishing performance. Figure 2.22 shows an optical microscope image of these features on the wafer.

**Figure 2.22** Optical Microscope images of features for measurement of dishing and erosion.
An example of an HRP scan as obtained is shown in Figure 2.23.

2.4.5 Leica INS – 3300 Optical Microscope

Optical inspection of the 300mm patterned wafers was carried using a Leica INS-3300 optical microscopy [25] for post-polishing to check for clearing of copper. The microscope is fitted with a camera from which optical images of different features on the wafer can be saved and retrieved, as shown in Figure 2.24.
2.4.6 TEL Prober P12XL and Agilent Parametric Tester 4073

The electrical performance including, testing for isolated resistance and testing for shorts and opens was done using a TEL Prober P12XL and the Agilent Parametric Tester 4073 [26] as showing in Fig 2.25. The Agilent 4073B Ultra Advanced Parametric Tester is designed to perform fast and precise DC measurements and capacitance measurements.
The prober brings the wafer in contact with tiny probes (or needles) where the dies are electrically stimulated or tested with the help of the parametric tester. Wafer probers must ensure XYZ mechanical accuracy and include optics for performing alignment between the probes and the contact pads of each die (bond pads). The map of the dies tested was also provided by the prober. Figure 2.26 shows an example of map of the dies tested. The patterned wafers used in this work had in-built serpentine/comb structures to test for isolated resistance, shorts and opens. Figure 2.28 shows the serpentine/comb structures that are present on the patterned wafers.
Depending on the width $w$, the estimated line resistance is within the range of 30 to 650 $\Omega$, so that $R$ can be easily extracted by an automatic impedance test. For each line, there are two pads at each end that are used as probe contacts during E-test. Four-point probe measurement applies current through the two outer pads and measures the voltage difference between the two inner pads and is employed to measure the resistances of the lines. On the right side of the E-test cell, eight long lines are laid out for scanning electron microscopy (SEM) test, which can provide the cross-sectional view of metal lines after CMP.
Figure 2.27 Serpentine/Comb structures on 300mm patterned wafers.
References


CHAPTER 3

BASELINE ANW ALUMINA SLURRY DEVELOPMENT:
EVALUATION ON 200mm BLANKET Cu WAFERS

3.1 Introduction

Slurries containing the ANW Alumina abrasive and basic chemical components were initially developed using blanket Cu films deposited on 200mm wafers and polished using laboratory 200mm wafer CMP tools, prior to development and evaluation on 300 mm blanket and patterned wafers. The reasons for this were two fold. Firstly, it was cost effective to screen formulations with blanket wafers on the 200mm laboratory tool, before polishing patterned wafers. Secondly, deployment of the experimental slurries on the 300mm polishing tool required initial performance data and reference points for initial process recipes.

Copper-coated blanket Si 200mm wafers (~1000 nm Cu/20 nm TaN/300 nm thermal silicon oxide) were used for initial evaluation of copper material removal rates (MRR), within-wafer-non-uniformity (WIWNU) and static etch rate (SER) values for ANW slurry formulation screening. Each set of ANW slurry formulations was screened with respect to these quantities to evaluate suitability for polishing 300mm patterned wafers.

3.2 ANW Alumina copper slurries for 200mm lab environment

3.2.1 Development for the initial formulation(s) with ANW Alumina Nanoabrasives

Initial values of concentration of the basic chemical components, BTA, Glycine and Hydrogen Peroxide (H$_2$O$_2$), were chosen from literature [1] as shown in Table 3.1. The commercial CMP Cu slurry which was used as a baseline against which to evaluate the
performance of the Applied Nanoworks Slurry was Cabot Microelectronics C7092 Alumina slurry. The concentration of ANW alumina particles was chosen to be 0.44 wt% to coincide with the final weight percent concentration of the alumina abrasives in the cabot C7092 slurry. The pH of the initial ANW Alumina slurry was also chosen to be 8.5 for this reason.

Table 3.1 Polishing parameters for 200mm 6 DS-SP Strasbaugh CMP tool.

<table>
<thead>
<tr>
<th>200mm CMP Tool Polish Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polish Time (P.T.)</td>
<td>60</td>
<td>seconds</td>
</tr>
<tr>
<td>Down Force (D.F)</td>
<td>2</td>
<td>psi</td>
</tr>
<tr>
<td>Slurry Flow Rate (S.F.R)</td>
<td>150</td>
<td>ml/min</td>
</tr>
<tr>
<td>Spindle Speed/Table Speed (S.S/T.S)</td>
<td>70/60</td>
<td>rpm</td>
</tr>
<tr>
<td>Back Pressure (B.P)</td>
<td>0</td>
<td>psig</td>
</tr>
<tr>
<td>Ring Force (R.F)</td>
<td>1</td>
<td>psi</td>
</tr>
</tbody>
</table>

Polishing parameters were estimated from previous copper work done on the 200mm 6 DS-SP Strasbaugh CMP tool. Table 3.1 shows the baseline Cu CMP polish parameters on this 200mm platform. Table 3.2 shows the first set of experimental runs based on $2^n-1$ type factorial DOE. Three variables – BTA, Glycine and $\text{H}_2\text{O}_2$ were chosen for this study providing 7 ($2^3-1$) runs which are captured as wafer splits. The first subset contained 3 wafer splits where the concentration of Glycine was varied from 0.5 to 2 wt%, keeping the molar concentration levels of BTA at 0.005 and levels of $\text{H}_2\text{O}_2$ as 1 wt%. The second subset contained 2 wafer splits where the concentration of $\text{H}_2\text{O}_2$ was varied from 3 to 5.
wt%, keeping levels of BTA at 0.005 M and Glycine levels constant. The third subset contained 2 wafer splits where the molar concentration of BTA was varied from 0 to 0.015 M, keeping levels of H$_2$O$_2$ and Glycine constant. X and Y in the table indicate that the levels were set based on previous trial runs.

**Table 3.2 Slurry formulations for initial set of copper polishing experiments.**

<table>
<thead>
<tr>
<th>Subset</th>
<th>Wafer</th>
<th>Glycine wt %</th>
<th>BTA (M)</th>
<th>H$_2$O$_2$ wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.5</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>X</td>
<td>0.005</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>X</td>
<td>0.005</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>Y</td>
<td>0</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Y</td>
<td>0.015</td>
<td>Y</td>
</tr>
</tbody>
</table>

The copper material removal rates for the first set of blanket wafer polishing experiments are as shown in Figure 3.1. The material removal rates were relatively low even with higher concentrations of the complexing agent glycine (2 wt%).
Figure 3.1 Cu Blanket MRR as a function of glycine concentration (0.005M BTA, 1 wt% H₂O₂, 0.44 wt% ANW Alumina, pH = 8.5).

The low removal rates of copper, even with a high concentration of Glycine, implied the presence of substantial surface passivation. This is associated with the formation of Cu-BTA complexes on the copper surface. Deshpande et al. [2] showed that the inhibition efficiency of BTA increased rapidly with increasing BTA concentration. This is because the passivation film has two key components. The first is a complex layer between BTA and oxidized copper. The second is a hydrophobic layer stacked with BTA molecules as shown in Figure 3.2. The BTA first forms a monolayer that is in direct contact with the copper film and then multilayers assemble on top of the monolayer [3]. This complexing and multilayer stack forms a thick Cu–BTA passivation film thereby effectively reducing the copper dissolution rates, especially in the presence of a high concentration of complexing agent and low concentrations of the ANW alumina abrasives.

The passivation effect of the BTA can be seen in Figure 3.3, where reducing the BTA concentration by half increased the copper removal rate by two times. When there was no BTA present in the solution, the removal rate increased by an average rate of ten times.
But in the absence of a passivating agent, the copper is primarily removed via chemical dissolution. This can be seen from AFM topographs in Fig 3.4 which show the pitting and corrosion present on a copper blanket wafer polished with an ANW Alumina slurry formulation which had no BTA.

**Figure 3.2** Schematic representation of a BTA passivating layer formed on copper.

**Figure 3.3** Cu Blanket MRR as a function of glycine concentration (2 wt% Glycine, 0.44 wt% ANW Alumina, pH=8.5).
Figure 3.4 Pitting and Corrosion on wafer polished with ANW Alumina Slurry formulation with no passivating agent.
For more controlled Cu removal, a passivating layer is necessary to prevent the free dissolution of copper into copper ions. Aksu and Doyle [4] showed that for a glycine slurry system that promotes passivation in the absence of abrasion, regions of the copper surface that are abraded mechanically in CMP will dissolve much faster than those that are not abraded. This is consistent with the increase in the copper material removal rates with the addition of small amounts of BTA observed for ANW slurry screening formulations, as shown in Figure 3.5. The addition of smaller concentrations of BTA promoted the formation of a passivation film, which was thin enough to be abraded by the relatively small concentrations of ANW alumina abrasives present in the slurry solution, but not so thick that abrasive particles were not able to abrade the film.

Figure 3.5 Copper MRR as a function of BTA concentration (2 wt% Glycine, 1 wt% H$_2$O$_2$, 0.44 wt% ANW Alumina, pH=8.5).
The copper removal rates obtained from the commercial Cabot slurry was set as the target removal rate for ANW slurry formulation screening on 200mm copper blanket wafers. The highest copper material removal rate for the ANW screening formulations was achieved when the BTA concentration was as low as 0.0005M. For the first pass ANW slurry developmental work, the other components of the slurry including oxidizing agent, pH and alumina abrasive concentration were kept constant while varying the complexing and passivating agents to evaluate impact on copper material removal rates. Figure 3.6 shows the 200mm blanket CMP copper removal rates as a function of glycine concentration for slurry solutions which had 0.0005M BTA (highest copper removal rate).

![Graph: Copper MRR as a function of Glycine at 0.0005M BTA, 1% wt H₂O₂, 0.44 wt% ANW Alumina, pH=8.5.](image)

As expected in the presence of low BTA passivation of the Cu surface, increased glycine concentration dramatically increased Cu MRR. Hariharaputhiran *et al* [5] reported that
the main role of glycine, as a complexing agent was to form a complex with the Cu$^{2+}$ ions generated during the CMP polishing process. The complex can catalyze the decomposition of hydrogen peroxide leading to the formation of hydroxyl radicals ($^*$OH). The formation kinetics of $^*$OH has also been shown to have a direct correlation with the material removal rate of Cu during the polishing process. Upon the addition of excess Cu$^{2+}$, the material removal rate was further increased as the concentration of $^*$OH was elevated.

At low concentration of the passivating agent BTA, the number of glycine-copper complexes increased as the concentration of the complexing agent increased. This led to an increase in the copper material removal rates shown in Figure 3.6. But, at the point where glycine saturated (or used up) the copper ions from the copper blanket wafer, the copper removal rates no longer increased.

From Figures 3.5 and 3.6, the highest removal rates for copper (> 5000 Å/min) were obtained at a passivating agent concentration of 0.0005M BTA and a complexing agent concentration of 1 to 1.5 wt% glycine. Additional evaluation was carried out to investigate the effect of varying the pH on this first pass slurry formulation. The results are shown in Figure 3.7. The pH of the slurry was adjusted to the required value by using a basic buffering agent, ammonium hydroxide (NH$_4$OH).
As can be seen from Figure 3.7, the copper material removal rates were highest at a pH of 8.5, which is neither very acidic nor very basic. This agrees with the work of Gorantla et al [6]. At pH = 4, the amino acid – copper complex has minimal impact on the formation of hydroxyl radicals and the hydroxyl radicals have minimal impact on the removal rates. This is because at pH = 4, majority of the amino acid (glycine) is protonated and unable to form a copper-amino acid complex. But at pH = 8, the removal rate increased, since at such high pH values, the formation of amino acid – copper complex was relatively efficient, as was its impact on the formation of hydroxyl radicals. Hydroxyl radicals are a strong oxidizing agent, even stronger than hydrogen peroxide and hence causes a significant increase in the copper removal rates, as is evident in the increase in copper removal rate at pH 8.5. (Figure 3.7)

When the pH of the ANW slurry formulation increases beyond 8.5, it is important to note that in BTA-glycine based slurry, the BTA is less protonated at higher pH [2]. So at
higher pH, BTA and BTA-copper clusters have low relatively solubility in water. This often leads to the formation of large particles that cause scratching during polishing and leave organic residues that are difficult to clean. Figure 3.8 shows an AFM topograph of a Cu-coated wafer surface after polished with ANW Alumina copper slurries at pH= 9. Micro-scale scratches visible to the naked eye were evident on the wafer surface, consistent with large particle formation.

![AFM topograph of a Cu-coated wafer surface after polishing with ANW Alumina copper slurries at pH= 9.](image)

**Figure 3.8** Scratches on surface of copper wafer polished with ANW slurry with pH=9.

The first formulation (Formulation 1) thus developed was transferred to 300mm tools and used to polish 300 mm copper blanket and M1 patterned wafers, the results of which are discussed in Chapter 4. Details of Applied Nanowork’s (ANW) Alumina Slurry,
Formulation 1 was: 0.0005M BTA, 1-1.5 wt% Glycine, 0.44 wt% ANW Alumina, 1 wt% H₂O₂ and pH = 8.5.

3.2.2 Static Etch Rate

Although details of the evaluation of ANW Cu slurries on 300mm blanket and patterned wafers are presented in Chapter 4 it is worth noting initial outcomes of the application of ANW Formulation 1 Cu slurry to 300mm wafers. Firstly, the material removal rate of copper on the 300mm CMP tooling was not as high as the MRR obtained on the 200 mm CMP tools. There was a nontrivial discrepancy between the polishing results obtained on the 200mm polishing tools and the 300mm CMP tools with the first pass ANW Alumina slurry. Following a first-pass optimization cycle, the maximum MRR for ANW Formulation 1 was ~ 5000 Å/min on 300mm Cu wafers whereas the MRR obtained on the 200mm CMP tool with this ANW slurry formulation was ~ 10,000 Å/min. The precise causes for this discrepancy (assuming correct calibration of CMP tool parameters) requires further investigation, although it is beyond the scope of the work presented in this dissertation.

A second observation was that the CMP of bulk copper for this formulation exhibited substantial local variations, especially when polishing 300mm patterned wafers. Cu material in damascene trenches was attacked and non-uniform removal across the wafer was observed, including instances of severe dishing and erosion. The copper and underlying material showed evidence of chemical attack. Consequently, experiments were designed to determine the static etch rate (SER) and further polishing experiments were carried out to evaluate ANW slurry formulations with lower SER’s. As noted in
Chapter 2, SER was measured by submerging sections of Cu-coated wafers in ANW slurry solutions for a one minute. The difference between pre and post-immersion thickness yielded the static etch rate values (SER). AFM was also performed on these pieces to determine the presence of pitting and corrosion due to static immersion. AFM scans of the 200mm copper blanket wafers which had been polished with Formulation 1 were also carried out, in order to determine the presence of slurry-related corrosive attack. Figure 3.9 shows AFM micrographs of sections of 200mm post-CMP wafers which have been polished with Formulation 1: 0.0005M BTA, 1-1.5 wt% Glycine, 0.44 wt% ANW Alumina, 1 wt% H₂O₂ and pH = 8.5.

**Figure 3.9(a) Pitting on copper wafer surface polished with ANW Slurry (0.0005M BTA, 1 wt% Glycine, 0.44 wt% ANW Alumina, 1 wt% H₂O₂ and pH = 8.5).**
Figure 3.9(b) Corrosion on copper wafer surface polished with ANW Slurry (0.0005M BTA, 1.5 wt% Glycine, 0.44 wt% ANW Alumina, 1 wt% $\text{H}_2\text{O}_2$ and pH = 8.5).

Corrosion and pitting on the copper wafer surface polished with the ANW slurry shows that there was substantial electrochemical attack by the slurry. Pitting is also a form of copper corrosion, leading to voids on the surface. According to Li et al [7], such electrochemical attack can completely remove the copper from the structures as was noticed on the patterned wafers (discussed in detail in Chapter 4) and occurs when the slurry does not contain enough or effective corrosion inhibitor. This underscores the need to determine the static etch rates of the ANW slurry formulations. Figure 3.10(a) shows the static etch rates (SER) with the ANW slurry formulation containing 0.0005M BTA.
Figure 3.10(b) shows AFM micrographs of copper wafer pieces exposed to the ANW slurry formulation (w/o any polishing).

Figure 3.10(a) Static Etch Rate as a function of Glycine for Formulation 1 (0.0005M BTA, 0.44 wt% ANW Alumina, 1 wt% H₂O₂ and pH = 8.5).

Figure 3.10(b) AFM of copper after etch, 0.0005M BTA & 1 wt% Glycine (0.44 wt% ANW Alumina, 1 wt% H₂O₂ and pH = 8.5).
Figure 3.10(c) AFM of copper after etch, 0.0005M BTA & 1.5 wt% Glycine (0.44 wt% ANW Alumina, 1 wt% H$_2$O$_2$ and pH = 8.5).

Figure 3.10(d) AFM of copper after etch, 0.0005M BTA & 2 wt% Glycine (0.44 wt% ANW Alumina, 1 wt% H$_2$O$_2$ and pH = 8.5).
As apparent in Figures 3.10 (a) and 3.10 (b), the ANW slurry formulations with low amounts of passivating agent (0.0005M BTA) and low abrasive concentration (0.44 wt% ANW Alumina) exhibited very high SER’s (~3500 Å/min). Most of the SER Cu removal was attributed to direct dissolution of copper as evidenced by the increase of the measured SER with glycine concentration. There was also an increase in the amount of copper corrosion with increasing glycine in the ANW slurry formulation. This is apparent in the AFM micrographs (Figs. 3.10(b-d). Figure 3.11(a) shows the decrease in the SER as the concentration of the passivating agent (BTA) increased from 0.0005M BTA to 0.001M BTA (for this plot the concentration of all other chemical components in the slurry remained the same).

![Graph showing SER as a function of BTA concentration](image)

**Figure 3.11(a)** SER as a function of BTA concentration (0.44 wt% ANW Alumina, 1 wt% H₂O₂, 1 wt% Glycine and pH = 8.5).
As shown in Fig 3.11(b), the static etch for the ANW formulation with 0.001M BTA, was much lower than that of the ANW slurry formulation which had 0.0005M BTA. The lowest measured SER was obtained for the formulation which had 0.002M BTA. However, the increase in the concentration of the passivating agent to 0.002M BTA decreased the MRR to ~1700 Å/min. The material removal rate was still below the target MRR (~5000 Å/min), even with an increase in the concentration of the ANW alumina abrasives as shown in Figure 3.12. As discussed later in this thesis, the ANW alumina concentration had to be increased substantially (≥ 1.3 wt %) to see a significant increase in the material removal rates, especially for the ANW formulations which contained higher concentration of the passivating agent, BTA (0.002M BTA).
On the other hand, for the ANW Alumina slurry formulations which had 0.001M BTA and 1wt% Glycine, the material removal rates increased by almost ~700 Å/min with an increase in the ANW alumina abrasive concentration from 0.44 wt% to 0.66 wt%, as shown in Figure 3.13. But the static etch rate remained almost constant.
From Fig. 3.13, it can be noted that the ANW Alumina formulation with 0.001M BTA and 0.66 wt% (1wt% H$_2$O$_2$, 1wt% Glycine and pH=8.5), has nearly an acceptable material removal rate with low static etch rates. Addition of alumina (0.88 wt%) did not increase the material removal rate by a significant amount. Figure 3.14 (a) shows the AFM micrographs of the wafer polished with this formulation.
The AFM micrographs of the wafer polished with this formulation (0.001M BTA, 0.66 wt% ANW Alumina, 1wt% H₂O₂, 1 wt% Glycine and pH = 8.5) shows much less severe corrosion of copper than the wafer which was polished with the formulation containing 0.0005M BTA, 0.44 wt% ANW Alumina, 1wt% H₂O₂ , 1wt% Glycine and pH = 8.5(Figure 3.9). The AFM micrograph of the copper piece etched with the ANW Alumina
formulation containing 0.001M BTA also showed less severe attack of copper, as shown in Figure 3.14(b).

**Figure 3.14 (b)** AFM micrograph of wafer etched with ANW Alumina Slurry Formulation (0.001M BTA, 0.66 wt% ANW Alumina, 1wt% H₂O₂, 1wt% Glycine and pH = 8.5).

### 3.2.3 Development of additional formulation(s) with ANW Alumina nanoabrasives

Based on the SER data shown in Figs. 9-14 a 2nd–pass polish formulation for 300mm Cu wafer CMP was derived. **Formulation 2:** 0.001M BTA, 0.66 wt% ANW Alumina, 1wt% H₂O₂, 1/1.5 wt% Glycine and pH = 8.5. The results from polishing experiments using this and subsequently formulated ANW slurries are discussed in more detail in Chapter 4.
300mm copper patterned wafers polished with Formulation 2 also exhibited unacceptably high dishing and erosion (~1600 Å) compared to the target of ~500 Å. As shown in Figure 3.11 the lowest static etch rate was obtained when the ANW alumina slurries had 0.002M BTA. AFM micrographs of copper wafers subject to CMP polish as well as to static etching with ANW slurries containing 0.002M BTA did not show any sign of severe defectivity (corrosion, pitting) on the copper surface, as shown in Figure 3.15.

**Figure 3.15(a)** *AFM micrograph of wafer polished with ANW Alumina Abrasive formulation (0.002M BTA, 0.88 wt% ANW Alumina, 1wt% H$_2$O$_2$, 1 wt% Glycine and pH = 8.5).*

In order to increase material removal rates of copper and also to study the function of the Applied Nanoworks Alumina abrasives in the removal process, the subsequent set of slurry formulations used to polish 300 mm wafers utilized higher amounts of ANW alumina abrasives (> 1 wt%), along with 0.002M BTA as the passivating agent.
As noted earlier, the MRR values did not translate directly from the 200 mm platform to the 300mm platform, hence no additional experiments were done on the 200 mm platform.

Formulations 3: **0.002M BTA, 0.9/1.5wt% Glycine, 1.3wt% ANW Alumina, 1wt% H₂O₂, and pH = 8.5** & Formulation 4: **0.002M BTA, 0.5wt% Glycine, 1.3/2/3 wt% ANW Alumina, 1wt% H₂O₂, and pH = 8.5** were the next ANW formulations which were used to polish 300mm copper blanket and patterned wafers. The results are discussed in Chapter 4.
References


CHAPTER 4

INVESTIGATION OF PERFORMANCE OF NOVEL ANW ALUMINA NANOABRASIVE BASIC CHEMICAL COMPONENT SLURRY FOR 300MM PATTERNED WAFERS

4.1 Patterned wafer polish with Applied Nanoworks Alumina Slurry (ANW Slurry)

As discussed in Chapter 3, slurries containing Applied Nanoworks Alumina and basic chemical components were developed and evaluated, for acceptable copper material removal rate (MRR ~ 5000 Å/min) and static etch rates (SER < 500 Å/min), on the 200mm CMP lab polishing tools. The optimized slurry formulations were then evaluated through Cu CMP of 300mm patterned wafers. The results of that evaluation are discussed in this chapter. The formulations used to polish 300mm patterned wafers contained only novel alumina nanoabrasive particles (Applied Nanoworks Alumina) and basic chemical components present in copper CMP slurries: a complexing agent (Glycine), an oxidizing agent (Hydrogen Peroxide) and a passivating agent (Benzotriazole). Thus, a direct correlation between the slurry components (novel alumina abrasives, basic chemical components) and the polishing performance (in terms of dishing, erosion and electrical test results) could be established.

The slurry formulations that were used to polish 300mm patterned wafers are listed in Table 4.1. A patterned 300mm wafer was also polished with JSR commercially available slurry. The results obtained from the patterned 300mm wafer polished with the JSR slurry served as a baseline (for comparison) for evaluating the polishing performance of the Applied Nanoworks Alumina slurries.
Table 4.1 Slurry Formulation used to polish 300mm patterned wafers

<table>
<thead>
<tr>
<th>Formulation</th>
<th>SLURRY FORMULATION (1wt% H$_2$O$_2$, pH = 8.5)</th>
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<tr>
<td><strong>Formulation 1</strong></td>
<td>0.0005M BTA, 1wt% Glycine, 0.44wt% ANW Alumina 1(a)</td>
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<tr>
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<td>0.0005M BTA, 1.5wt% Glycine, 0.44wt% ANW Alumina 1(b)</td>
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<tr>
<td><strong>Formulation 2</strong></td>
<td>0.001M BTA, 1wt% Glycine, 0.66wt% ANW Alumina 2(a)</td>
</tr>
<tr>
<td></td>
<td>0.001M BTA, 1.5wt% Glycine, 0.66wt% ANW Alumina 2(b)</td>
</tr>
<tr>
<td><strong>Formulation 3</strong></td>
<td>0.002M BTA, 1.5wt% Glycine, 1.3wt% ANW Alumina 3(a)</td>
</tr>
<tr>
<td></td>
<td>0.002M BTA, 0.9wt% Glycine, 0.9wt% ANW Alumina 3(b)</td>
</tr>
<tr>
<td><strong>Formulation 4</strong></td>
<td>0.002M BTA, 0.5wt% Glycine, 1.3wt% ANW Alumina 4(a)</td>
</tr>
<tr>
<td></td>
<td>0.002M BTA, 0.5wt% Glycine, 2wt% ANW Alumina 4(b)</td>
</tr>
<tr>
<td></td>
<td>0.002M BTA, 0.5wt% Glycine, 3wt% ANW Alumina 4(c)</td>
</tr>
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Table 4.2 Process parameters used to polish 300mm blanket and patterned wafers

<table>
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4.2 Preliminary work on 300mm blanket wafers

As discussed in Chapter 3, the Applied Nanoworks Slurry formulations that were developed and optimized on 200mm laboratory CMP tools were used to polish 300mm copper blanket wafers to test and optimize process parameters for copper material removal rates. The target copper removal was ≥ 5000 Å/min for the slurry to pass qualification. Removal rates substantially lower than this would lead to longer copper endpointing for bulk copper removal on the patterned wafers. This could, in turn, increase the defectivity on the patterned wafers, by galvanic corrosion and copper pitting. Patterned wafers polished with some of the slurry formulation show such behavior which will be discussed later in this chapter. Therefore it becomes important to have background knowledge on corrosion and copper pitting which is described further in detail here.

By way of background, galvanic corrosion is an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte. This can occur when a patterned metalized wafer are exposed to a corrosive electrolyte for extended periods of time [1] and is illustrated in Figure 4.1. The source of such a galvanic potential on the patterned copper surface likely results from contact potential differences between copper interconnect structures and the doped silicon wafer through device contacts. Another possible cause of this type of galvanic potential is related to the barrier material induced metal–metal battery effect. Most copper CMP slurries have been developed for Cu structures with Ta or TaN as a barrier material. In some cases, other metals may also be used in addition to the barrier metal. For example, a metal hard mask could contribute to the galvanic corrosion effects. It is
also possible that some types of copper are more susceptible to corrosion than others. The grain size and mechanical strain in the copper lines can have positive or negative effects on the corrosion.

Another form of copper corrosion is pitting. Copper pitting looks like dark spots under an optical microscope, as shown in Figure 4.2 [2]. Both galvanic corrosion and pitting result in localized copper loss and lead to voids on the surface.

**Figure 4.1** *SEM images showing massive galvanic corrosion in copper [3] [Courtesy: John Wiley & sons Inc].

**Figure 4.2** *SEM images showing heavy pitting on the copper structure [3]. The white circles indicate where these heavy pitting occur in these structures. [Courtesy: John Wiley & sons Inc].*
The 300mm CMP tool process parameters were optimized for the different Applied Nanoworks slurry formulations for maximum Cu removal rates on the 300mm copper blanket wafers. The comparison of copper removal rates between the various formulations is shown in Figure 4.3. The primary Y-axis denoted as bars represent the MRR in Å/min while the secondary Y-axis show the within wafer non-uniformity in percentage and is denoted as circles. The obtained standard deviation values of MRR for the slurries are also shown in the form of error bars. As noted in Table 4.1, all the slurry formulations had a hydrogen peroxide concentration of 1 wt% and a pH of 8.5. It is clear from the data that the averaged Cu RR results from the interplay of the Cu slurry components and is not driven by a single component such as abrasive concentration or passivating agent. Average removal rate was enhanced by increased alumina concentration and increased dissolution (glycine). Average removal rate was inhibited by increased passivating agent (BTA). The maximum removal rate was approximately 7700 Å/min for formulation 3(a).
With the increase in the concentration of BTA, there is the availability of a dedicated passivating agent to protect and harden the softened copper surface. The proper combination of passivating agent and complexing agent along with high concentration of abrasive particles provides low static etch rates (low dissolution rates) and high polishing rates (in the presence of mechanical abrasion from the abrasive particles). For a CMP solution containing glycine and hydrogen peroxide, addition of BTA results in the formation of a Cu-BTA complex on the copper surface, which reduces the static etch rates in turn reducing dishing and defectivity on the copper surface [3].

Figure 4.3 Mean Cu removal rate (MRR) from CMP of 300mm blanket Cu-coated wafers for the formulations shown in Table 1 (red bars) and the JSR POR. Filled blue symbols represent the within-wafer non uniformity (WIWNU) calculated from the same wafers. The values of standard deviation are indicated as vertical lines.
For the formulations which had a higher concentration of BTA, 0.002M (with glycine, hydrogen peroxide & pH constant), the reduction in copper removal rate by passivation was compensated by increase in copper removal by increased mechanical abrasion because of an increase in the alumina abrasive concentration, as can be noticed in Figure 4.3. The WIWNU, which is an indicator of the roughness of the copper wafer surface, was also lower as the removal became a more balanced chemical/mechanical removal rather than direct chemical dissolution. The WIWNU is also an indicator of the uniformity of removal process across the diameter of the wafer.

It should be noted that the more balanced Applied Nanoworks slurry formulations which showed lower WIWNU exhibited Cu MRR’s of approximately 4500 Å/min. While this was below the target of 5000 Å/min it was deemed acceptable for investigation and application to 300mm patterned wafers.

When the concentration of the passivating agent (BTA) and the ANW alumina abrasive concentration was low (e.g for the formulations with BTA = 0.0005M & ANW Alumina = 0.44 wt%), the copper removal was primarily due to rapid chemical dissolution of copper. In this slurry formulation (with small amounts of BTA & alumina abrasives), the material removal is predominantly isotropic [2]. The step height reduction efficiency for this type of formulation would be expected to be practically zero because the softened copper surface could be significantly removed even with the weak mechanical force including the shear force impinged by the fluid flow.

This would be expected to translate to high dishing rates (discussed in more detail in Section 4.5) and to corrosion and pitting of the copper film. This is illustrated in Figure
4.4. Figure 4.4(a) shows a post-CMP micrograph of a patterned Cu wafer using Formulation 1(a). The nonuniformity of the Cu features (apparent as pits or ‘speckle’ on Cu pads) denotes Cu corrosion. After further polishing nearly all Cu was removed from the features (Fig. 4.4(b)). Figure 4.4(c) shows the roughness analysis of a patterned wafer polished with Applied Nanoworks slurry Formulation 1(a). The AFM micrograph of a section of unremoved Cu (Fig. 4.4(c)) clearly shows the pitting that results from the dissolution-based Cu removal.

**Fig 4.4(a)** Post-CMP optical micrograph showing the copper corroded lines (left)

**Fig 4.4(b)** Optical micrograph showing the complete removal of copper (isotropic removal)
Fig 4.4(c) Copper Pitting on wafer surface

Figure 4.4 AFM images showing the roughness analysis of a patterned wafer polished with Applied Nanoworks slurry Formulation 1(a).

4.3 End Point Comparison

As discussed in Chapter 2, end point is the time required for the bulk copper to clear. The end point time is inversely proportional to the material removal rates on copper blanket wafers. The bulk copper removal process on the patterned wafers reflected the copper removal on the blanket wafers, as the different formulations followed the same trend for endpointing as the 300mm blanket removal rates. Figure 4.5 shows the end point time comparison of different formulations with the JSR POR used to polish 300mm patterned wafers. The end polish time is shown in Y-axis as red bars while the overpolish time is shown as blue bars over the top of red bars.
As the copper removal process became predominated by mechanical abrasion of the softened copper film (higher passivation & higher concentration of alumina ≥ 1 wt%), the selectivity of the ANW Alumina slurry formulations also improved. Figure 4.6 shows optical microscope images of the patterned wafers which had been polished with Formulation 2 (low BTA & ANW Alumina) and Formulation 3 (high BTA & ANW Alumina). The optical images were taken immediately after end pointing and overpolishing (extra polish time to remove residual copper on the patterned wafer. As apparent in the images based on the interferometric ‘color’ of the wafers under the optical microscope, the patterned wafers which were polished with Formulation 3 had the barrier material intact in comparison with the wafers polished with Formulation 1, where both the copper and barrier material was completely etched out.

![End Point Time comparison of different formulations with the JSR POR used to polish 300mm patterned wafers. The end polish time is shown as red bars while the overpolish time is shown as blue bars.](image_url)
Figure 4.6 (a) Optical and SEM images of a patterned wafer polished with Formulation 2 (after endpoint + overpolish, no second step). All the material in the lines has been etched out.

Figure 4.6 (b) Optical and SEM images of patterned wafers (i) before and (ii) after second step polishing with slurry Formulation 3.
For these ANW Alumina slurries, the alumina nanoabrasives had an average particle size of 50nm. As the concentration of the alumina abrasives increased, the copper removal rates initially increased and then decreased with increase in particle concentration (> 2 wt% of ANW Alumina, Figure 4.3). This supports the contact area mechanism for copper removal, as indicated by Lu et al. [4]. Even though, there wasn’t a removal rate increase on copper blanket wafers because of increase in the concentration of the alumina abrasives, there was a slight decrease (by a few seconds) in the end point time with increase in the concentration of the ANW alumina abrasive particles. The reason for this decrease requires further investigation to determine whether the decrease is merely a tool/end point mechanism discrepancy or is a reflection of the actual bulk copper removal process on the patterned wafers.

4.4 Dishing with different ANW slurry formulations

For this work, dishing ≤ 500 Å [5] was deemed acceptable in that electrical characteristics, such as resistance values of post-CMP Cu interconnect lines, would be within ranges consistent with design specifications. As discussed in Chapter 2, dishing was measured on two different positions on each die, a 100 µm × 100 µm square copper pad and an array of 25 µm lines. Figure 4.7 shows the dishing performance comparison for the various ANW slurry formulations both “at endpoint” and “at endpoint + overpolish times”. The dishing comparison is performed for both 100µm and 25µm features with the values of standard deviation also shown. All ANW formulations with glycine greater than 0.5 wt% exhibited unacceptably large dishing. ANW formulations with BTA concentrations of 0.0005M resulted in nearly complete removal of Cu
(discussed in more detail below). Dishing consistently below 600 Å was observed for ANW slurry formulations 4(a-c). As noted above, these three slurry formulations exhibited the most balanced removal with respect to chemical and mechanical mechanisms. Note that the relative dishing of 100 µm and 25 µm Cu features was relatively unchanged for formulations 4(a-c) implying that increased abrasive concentration was not promoting differential removal of the Cu vs the barrier/dielectric regions.

![Figure 4.7](image)

**Figure 4.7** Dishing on 100 micron (Red bars) and 25 micron (Blue bars) Cu features on patterned 300mm wafer as a function of Applied Nanoworks slurry formulations (Table 1) and the JSR POR. The values of standard deviation are indicated as vertical lines.

The copper removal by ANW slurries formulated with low passivating agent and low abrasive content (Formulations 1 & 2) was isotropic by way of high Cu dissolution. Hence, there was very little selectivity for copper and all the material in the trenches was attacked and removed. This implies that all the copper has been removed and very little
topography remains on the patterned wafers. It is also consistent with an optical micrograph of the same area (Fig. 4.8(a)) which shows little, if any, residual Cu in the dishing test structure (the color contrast is associated with optical interference due to varying dielectric thickness). In contrast, the HRP profile with the optical micrographs of wafers polished with ANW Formulation 4 (Fig 4.8b) shows uniform metal surfaces over the test structures. The bright regions correspond to Cu. The less bright regions correspond to TaN barrier. Note that all the TaN was removed for the ANW Formulation 1.

**Figure 4.8(a)** HRP and optical microscope images of patterned wafers polished with Formulation 1 (low BTA, low abrasive content).
Figure 4.8(b) HRP & Optical microscope images of patterned wafers polished with Formulation 4 (high BTA, high abrasive content).

HRP scan profile of patterned wafers polished with ANW Formulation 4 showed clear depressions over the Cu test structures associated with dishing (Figure 4.8(b)) which ranged roughly from 550 Å to 250 Å. Evident in the data from the experimental results in Figs 4.6-4.8 is the effect of glycine on the patterned wafer structures. The only change in
components between Formulation 3(a) and Formulation 4(a) is the concentration of the complexing agent, glycine. All other variables (both chemical components and processing parameters) remained constant. The glycine concentration in Formulation 3(a) is three times the glycine concentration in Formulation 4(a). Though the end point time for removal of bulk copper increased by 42 seconds from Formulation 3(a) to Formulation 4(a), the dishing for the 100μm feature decreased by ~1200 Å. The improvement in dishing significantly offset the increase in the end point time in terms of process stability. There was also a marked improvement in defectivity due to the change in the chemical components of the Formulation 4 slurries. The improvement followed the balancing of the Cu removal mechanisms towards mechanical abrasion (by ANW Alumina particles) of the softened copper film, rather than by chemical dissolution by the complexing agent, glycine.

The illustration of crossover in CMP removal mechanisms for these two series of slurry formulations are shown using figures 4.9(a) and 4.9(b). They show the SEM micrographs of 150 nm wide Cu lines on the patterned wafers after polishing with Formulation 3(a) and 4(a), respectively. Both SEM micrographs followed barrier polishing.
Figure 4.9(a) SEM micrograph of patterned wafer polished with Formulation 3(a).

Figure 4.9(b) SEM micrograph of Patterned Wafer polished with Formulation 4(a).
The patterned wafer polished with ANW slurry Formulation 3(a) exhibited trenching at the edge of the copper lines (Figure 4.9(a)). Trenching at the edge of the copper lines is a systematic loss of copper at the Cu/barrier/dielectric interfaces. Trenching results from low Cu selectivity which leads to barrier erosion and loss of dielectric around the copper lines. The micrographs in Fig. 4.9 show that when the concentration of the complexing agent is higher, the selectivity for copper is lower which results in trenching, higher dishing and higher line edge roughness (LER) for the array of the smaller copper lines.

It is also noteworthy that when the copper removal proceeded primarily via copper dissolution (low BTA, low ANW Alumina), any overpolish time increased the dishing of both the 100 µm as well as the 25 µm features. This resulted primarily from the additional exposure of the wafer to the slurry, which induced copper corrosion through slurry chemical reaction [6].

A final point to be noted from the dishing data is that when the copper removal becomes more chemical-mechanical balanced (Formulation 4), the measured dishing was observed to be independent of the line width (for feature sizes ≥ 25 µm) contrary to what has been stated by Paik and Park [7] (Fig 4.10 (a)). Fig 4.10(a) shows that the dishing values increase as a function of line width. In contrast, data generated from this research (Fig 4.10 (b)) shows dishing was not a strong function of line widths for patterned wafers polished with ANW slurries. But it should be noted for the data in Fig. 4.10 (b) that the 25 µm features (line array) possess a 80% pattern density compared to the 100 µm features (a solid copper square) which possess no comparable pattern density. So further investigation is required to establish whether the smaller features (1µm-20µm) actually dish more than larger features (50µm-100µm) for patterned wafers polished with ANW.
slurries, especially for features which are in the 10’s or 100’s of nm range (≤ 1 µm).

SEM inspection of the smallest features (~125 nm) on the patterned wafers (Figure 4.9) revealed that these lines did not exhibit any copper dishing.

Figure 4.10(a) Dishing versus Line Width [7].
4.5 Erosion with different ANW slurry formulations

The thickness reduction of the oxide material (between the metal features) with respect to the oxide material at the edge of a group or array of features is termed as erosion [8]. Figure 4.11 shows the erosion performance measured both on 100 µm features (red bars) as well as on 25 µm features (blue bars) for various slurry formulations including the JSR POR slurry. When the concentration of BTA and ANW Alumina abrasives was very low (0.0005M BTA, 0.44wt% ANW Alumina), there was chemical dissolution of the Cu and the features were etched leading to high removal of the dielectric. Since there was no topography present and the HRP profile was flat, as shown in Figure 4.8(a), erosion of

Figure 4.10(b) Dishing versus ANW alumina concentration for 100 and 25 µm features.
the dielectric could not be assigned a specific value. However, as the amount of passivation on the bulk copper increased, the direct dissolution of the copper and underlying materials by the chemicals present in the slurry decreased and a specific value for dielectric erosion was measured.

Based on the data in Fig. 4.11, as the amount of BTA increased, the increase in the passivation of the copper and underlying material resulted in the slurry exhibiting enhanced selectivity for copper (Formulation 3). For the patterned wafers polished with Formulation 3, the erosion for the 25 µm lines macro was higher than the erosion for the macro having the 100 µm × 100 µm features. This is consistent with work done by Steigerwald et al [9]. They also describe a strong, first order pattern dependence in copper polishing and noted that erosion depends strongly on pattern density. Fayolle and Romagna [10] found that when the oxide space is greater than 100 µm, oxide erosion is slight, but it dramatically increases with oxide space reduction. They also found that for fine oxide spaces, erosion is dependent not only on oxide width, but also on the copper line width of the pattern; in other words, an additional density dependence.
This is consistent with the data shown in Fig. 4.11 for patterned wafers polished with Formulation 3 which exhibited greater erosion in the macro which had 25 µm lines, than the macro which had the 100 µm × 100 µm copper features. As the pattern density increased, there was less dielectric to support the force exerted by the polishing pad. Upon removal of the bulk copper, a recess starts developing in the copper features (large feature sizes) with additional polishing. The pad then deflects into the recess to contact
the recessed metal [11]. Hence the pressure on the recessed area decreases and consequently, the pressure on the adjacent dielectric correspondingly increases. When there is less dielectric area, the erosion of the dielectric is higher. This is also consistent with the observed increase in erosion during the overpolish step, as can be seen in the data in Figure 4.11.

As the copper removal becomes more balanced, with the chemical components present in the slurry softening the copper film and the bulk copper removal driven by the abrasion of the alumina particles, the selectivity of the slurry for copper becomes higher. This is evident in the reduction in erosion below 65 Å for the CMP pattern macros with 100 μm × 100 μm copper features and virtually no erosion in the macro with 25 μm copper lines for the ANW Formulation 4 series. It is worth noting that the erosion for these wafers was even lower than the erosion for the patterned wafer which was polished with the commercial JSR slurry (POR). The minimal amount of erosion (≤ 65 Å) ostensibly results from dielectric removal by mechanical grinding on a large field area. To complement the data shown in Fig 4.11, HRP profiles show the topography of 100 μm and 25 μm features on the patterned wafers polished with Formulation 2(a), (2b) and Formulation 4(a),4(b) in Fig. 4.12(a),b, (b),(c) and (d) respectively.
Figure 4.12(a) HRP profiles showing the topography of 100 µm feature macro polished with Formulation 2(a).

Figure 4.12(b) HRP profiles showing the topography of 25 µm lines feature macro polished with Formulation 2(b).
**Figure 4.12(c)** HRP profiles showing the topography of 100 µm feature macro polished with Formulation 4(a).

**Figure 4.12(d)** HRP profiles showing the topography of 25 µm lines feature macro polished with Formulation 4(a).
4.6 Electrical Testing of patterned wafers polished with different ANW slurry formulations

As introduced in Chapter 2, serpentine contact chains and serpentine comb planar test structures were used to test for isolated line resistance, shorts and opens in the post-CMP patterned wafers. Electrical measurements of these structures were undertaken following CMP to complement the physical metrology data presented above to investigate latent or indirect impact of slurry formulation on Cu interconnect performance. With rapid technology scaling and increasingly tighter design budgets, it is crucial to understand impacts of layout dependent effects like dishing, erosion and surface defects, on slurry formulation and/or abrasive size. The understanding of these effects bridges BEOL technology and interconnect electrical performance [12]. In other words, electrical testing of the patterned wafers is necessary to develop technological solutions on the process side to help in meeting design rules for optimum electrical performance. Figure 4.13 gives the isolated line resistance values of the 300mm patterned wafers that were polished with the different slurry formulations. The lower and upper specification limits of the isolated resistance are also shown.

According to Chang et al. [12], excessive dishing causes a non-planar metal surface and reduces the conductive cross-section. Hence the value of the line resistance increases, as compared to the theoretical value of resistance for a line with a planar surface [12]. But from Figure 4.7 and Figure 4.13, it appears that larger values of dishing in the large features did not translate into higher values of resistance for the serpentine feature. The reason for this are speculated to be two-fold.
Firstly, the removal process with Formulations 1 and Formulation 2 is not uniform across the wafer. Copper and the underlying material are completely etched out in some regions of the wafer and residual copper remains in other areas. Figure 4.14 shows optical microscope images of the same feature on three individual die at different positions on the same wafer.

![Figure 4.13 Isolated Resistance in ohms on 300mm patterned wafers for various slurry formulations. The lower and upper specification limits of the isolated resistance are also shown.](image-url)
This non-uniform removal process resulted in a wide distribution of the isolated resistance values which may have masked the correlation with dishing. A more uniform removal process lead to a tighter distribution of the isolated resistance values as can be noticed from the isolated resistance values of the patterned wafer polished with Formulation 4. An overpolish time slightly increased the isolated resistance values.

Secondly, the wafers which were polished with Formulation 1 & Formulation 2 had copper removal mostly by direct dissolution. For these wafers, dishing was predominant in the large features and the smaller copper lines still had copper intact in some places. Because of this reason, the isolated line resistance value of these wafers is not as high as expected (for high values of dishing).

It is also possible that line edge roughness (LER) of the lines used for isolated resistance measurements may contribute to low values of isolated line resistance, even when the dishing is high. LER consists of an irregular side profile of the metal lines, featuring protrusions and notches with nanometer range amplitude [15]. LER is responsible for a local reduction of the spacing between wires which in turn enhances the electric field locally. The electric field enhancement induced by LER occurs when two protrusions of adjacent wires are facing each other. In addition to the local space reduction between

![Optical microscope images on three different dies at three different positions on the 300mm patterned wafer.](image)
wires, LER protrusions accumulate electric charge at their tips, thus further enhancing the electric field. The patterned wafers that were polished with Formulation 1 & Formulation 2 also had high LER (Figure 4.15). This may have translated into an additional decrease in the isolated resistance values although a specific estimate of this effect is beyond the scope of this work.

In contrast it is highly likely that Line Edge Roughness (LER) was also responsible for shorts between the monitor lines, which decreased the isolated resistance values and increased the leakage current. All the patterned wafers polished with the ANW Alumina slurry had rough line edges and copper metal residue left in between the smaller lines on the wafer.

![Figure 4.15](image)

**Figure 4.15** Line Edge Roughness (LER) on patterned wafers polished with ANW slurry (top) Vs. No LER on patterned wafer polished with JSR slurry (bottom).
An increased over polish window (> 10 seconds) would likely help in improving the line edge roughness as well as removing the copper residues. Figure 4.16 shows the test results for shorts on the 300mm patterned wafers with different slurry formulations. The expected mean, upper and lower specification limits are also shown in the figure.

![Figure 4.16 Test for shorts on patterned wafers polished with different slurry formulations is shown as the measured value of current in the Y-axis. The expected mean, upper and lower specification limits are also shown in the figure.](image)

Fig 4.17 shows the test for opens on 300mm patterned wafers polished with different slurry formulations along with reference slurry. The expected mean, upper and lower specification limits are also shown in the figure. Unlike the test for shorts, the test for opens did not yield any significant information, as there was flow of excess leakage current due to the presence of copper metal residue on these wafers.
Figure 4.17 Test for opens on patterned wafers polished with different slurry formulations is shown as the measured value of current in the Y-axis. The expected mean, upper and lower specification limits are also shown in the figure.
References


CHAPTER 5
INVESTIGATION OF THE ROLE OF BASIC CHEMICAL COMPONENTS ON NOVEL ANW COPPER CMP SLURRY PERFORMANCE

5.1 Introduction

As noted previously, the ANW slurry that has been used contained four components: ANW alumina nanoabrasive, complexing agent (glycine), passivating agent (BTA), and oxidizing agent ($\text{H}_2\text{O}_2$). In Chapter 3, the slurry developmental work and pre-screening experiments carried out on 200mm lab polishing tools was presented which led to the initial Cu slurry formulations that were used to polish 300mm patterned wafers. In Chapter 4, the performance of this basic component slurry with respect to patterned Cu test structures (dishing, end point, and compatibility with 2nd step barrier CMP) was evaluated and the results were discussed.

In this chapter, experimental correlations between the relative concentrations of the basic slurry components and the performance of the ANW Cu slurry with respect to 300mm blanket and patterned wafer test structures were considered. Particular attention will be paid to Cu dishing, end pointing and selectivity for copper.

The nanoabrasive (40-50 nm diameter alumina nanoparticle) concentration used in this study ranged from 0.44 wt% to 3 wt%. The corrosion inhibitor (BTA) concentration ranged from 0.0005M to 0.002M and the complexing agent varied between 0.5 wt% to 1.5 wt%. The concentration of the oxidizing agent, hydrogen peroxide ($\text{H}_2\text{O}_2$) is constant and maintained at 1 wt% throughout the study. The pH was maintained at 8.5.
5.2 Role of chemical components on Material Removal Rate and End Point

5.2.1 Copper Material Removal Rate on 300mm copper blanket wafers

Figure 5.1 shows material removal rate, on the y-axis on 300mm blanket copper wafers plotted as a function of component concentration on the x-axis, i.e., passivating agent (BTA), complexing agent (glycine) and ANW alumina abrasive concentration.

![Figure 5.1 MRR on 300mm blanket wafers as a function of component concentration in Applied Nanoworks alumina copper slurries.](image)

**BTA:** Material removal of copper can either be through direct chemical dissolution of copper or through a balanced CMP process. Though the increase in concentration of the passivating agent decreases the copper dissolution rate, an increase in the material...
removal rates was obtained by increasing the ANW alumina abrasive concentration in the slurry formulation, while maintaining the concentration of all other components (1.5 wt% Glycine, 1wt% H$_2$O$_2$, pH=8.5) constant.

**GLYCINE:** On the 300mm polishing platform, when the BTA concentration was lower (0.001M BTA), increase in the complexing agent, glycine, did not translate into an increase in the copper material removal rate. But for a higher concentration of BTA (0.002M), the material removal rates increased with an increase in the concentration of glycine. This implies an interaction between the complexing and the passivating agents in the slurry and indicates a higher dissolution rate of copper in the presence of a thicker passivating film on the copper wafer surface. The work done by Aksu and Doyle [1] states that a glycine slurry with inhibitors, that promotes passivation is more advantageous, as the regions of the copper surface which are covered with a passivating layer and are then abraded mechanically will dissolve much faster, resulting in higher material removal rates. That observation is consistent with the data presented in Fig. 5.1.

**ANW ALUMINA ABRASIVES:** As the concentration of the alumina abrasive particles increased, the MRR on the 300mm copper blanket wafers also increased, consistent with expectations. But this increase in removal rates was more prominent, when the formulations were optimized. Figure 5.1 shows the removal rate trend as a function of concentration of the abrasives for optimized BTA and glycine concentrations (best formulation). However, as the concentration of the ANW alumina particles increased beyond 1.3 wt%, the material removal rate saturated, indicating that after a specific particle concentration, higher wt% of abrasives does not necessarily lead to higher removal rates. This implies a limit to surface abrasion which may be linked to accessible
Cu surface area or, less likely, a concentration-dependent interaction between the nanoabrasives.

5.2.2 End Point on 300mm patterned wafers

As stated in Chapter 2, the end point time on the 300mm patterned wafers is the time in which the bulk copper on the 300mm patterned wafers is removed. The material removal rates on the 300mm blanket copper wafers seem to approximately reflect the material removal process of the bulk copper on the 300mm patterned wafers. The end point time is inversely proportional to the material removal rates on copper blanket wafers, as shown in Fig. 5.2. Figure 5.2 plots the component concentration on the x-axis and the end point time in seconds on the y-axis.

![Figure 5.2](image)

**Figure 5.2** Endpoint on 300mm patterned wafers as a function of component concentration in Applied Nanoworks alumina copper slurries.
An anomaly was noticed with the end point timing. When the concentration of BTA was lower (0.001M), an increase in glycine concentration did not translate into an increase in material removal rate. But there was a reduction in the end point time by approximately six seconds, indicating that apart from the slurry formulation, various other parameters also play a role in the removal process. In this case, heating of the pad due to frictional forces and lower lubrication might have lead to a higher copper removal rate and consequently faster end point time.

5.3 Role of chemical components on Cu dishing

As discussed earlier in Chapter 2, dishing was measured on 100 micron features and 25 micron features on the patterned wafers.

![Figure 5.3](image_url)

**Figure 5.3** Dishing on 100 micron and 25 micron features on 300mm patterned wafers as a function of component concentration in Applied Nanoworks alumina copper slurries.
The dishing values were measured in Å/min and are plotted as a function of component concentration in Figure 5.3.

**BTA:** When the complexing agent (1.5 wt% Glycine), oxidizing agent (1 wt% H₂O₂) and pH=8.5 remained constant, the dishing on both the 100 micron and 25 micron features decreased with an increase in the passivating agent from 0.0005M to 0.001M, though there was a slight increase in the material removal rate because of an increase in the ANW alumina abrasive concentration.

But when the passivating agent concentration increased to 0.002M BTA, the ANW alumina abrasive concentration had also increased from 0.66 wt% at 0.001M BTA to 1.3 wt% at 0.002M BTA (all other components were constant). This lead to an significant increase in the MRR (~2500 Å/min) and consequently a faster end point time. This resulted in an increase in dishing of approximately 300 Å, which can be attributed to the higher material rate. But overall, an increase in the passivating agent had a significant impact on reducing the dishing, both for 100 micron as well as for 25 micron features.

**GLYCINE:** The effect of the complexing agent, glycine, on the dishing was straightforward. As the amount of glycine in the slurry increased, the dishing increased, irrespective of the line width and other chemical components present in the slurry. Figure 5.3 showed that the dishing increased for formulations containing both 0.002M BTA (1.3 wt% ANW Alumina, 1 wt% H₂O₂, pH=8.5) as well as for 0.001M BTA (0.44 wt% ANW Alumina, 1 wt% H₂O₂, pH=8.5). The higher the glycine concentration, the higher is the rate of dissolution of copper.
ANW ALUMINA ABRASIVES: At low concentration of the ANW Alumina particles, the removal is primarily due to copper dissolution and hence there seems to a trend in the dishing. But this decrease is not due to the abrasive themselves, but rather due to the other components like passivating agent and complexing agent present in the slurry formulations, as indicated by ‘best formulation’, as this represented the optimized formulations at specific values of BTA (0.0005M, 0.001M & 0.002M) and glycine (1w%, 1.5wt%). But when all the chemical components in the formulations were maintained constant (0.002M BTA, 0.5wt% Glycine, 1wt% H₂O₂, pH=8.5), a change in the ANW alumina abrasive concentration had little or no effect on the dishing values, as can be seen from Figure 5.3.

5.4 Role of chemical components on Erosion

Erosion is the amount of dielectric removed by the CMP Cu slurry in a patterned field. It is primarily caused by dishing of Cu features on the patterned wafers. Erosion also depends on the selectivity of the slurry, the higher the selectivity of the slurry for copper, the lower the erosion. Figure 5.4 shows the erosion on both the 100 micron and 25 micron features. In Figure 5.4, erosion is plotted on the y-axis as a function of the component concentration on the x-axis.

BTA: There was not a clear dependence of the erosion on the concentration of the passivating agent. At low concentration of BTA, the dishing values were very high. The material in the trenches and surrounding areas were chemically etched out, making it impossible to measure erosion.
**GLYCINE:** No clear dependence of erosion on glycine could be deduced. When the dishing was very high, it became impossible to detect erosion. Also, the removal of dielectric is a very mechanically dominant process and hence, there might be no dependence on chemical components present in slurries, unless the slurries are chemically very aggressive in which the copper and surrounding material is etched out.

**Figure 5.4** Erosion on 100 micron and 25 micron features on 300mm patterned wafers as a function of component concentration in Applied Nanoworks alumina copper slurries.

**ANW ALUMINA ABRASIVES:** For the formulations which were optimized for BTA and glycine concentrations (indicated by best formulation), the erosion increased with the increase in the ANW Alumina concentration irrespective of the concentration of the other
chemical components in the slurry. As the slurry became more selective for copper (indicated by formulations with 0.002M BTA, 0.5wt% Glycine, 1wt% H₂O₂, pH=8.5), the increase in the abrasive content did not affect the 25 micron features which exhibited no erosion. But the erosion for the 100 micron features increased slightly (~ 50 Å) with an increase in the abrasive concentration. The slight increase in the erosion of the 100 micron structures versus the 25 micron structure may have resulted from the pattern density differential between the two. (The 100 micron features consisted of a simple 100 micron x 100 micron Cu square as opposed to the 25 micron feature which consisted of a line array with an 80% pattern density).

5.5 Summary Comments

The overarching goal of the data and discussion presented above was to draw specific correlations between slurry performance and post-CMP electrical test data. Not surprisingly, such correlations are complicated by the interaction of the various CMP slurry components. In general, the impact of individual chemical components present in CMP slurry on the resultant polishing process cannot be completely isolated but must be characterized through their interactions with the other slurry components and the physical tool parameters associated with the process. The data presented above is clearly consistent with this rule. Expanding the number of screening runs and carrying out full-factorial DOE’s would certainly help elucidate the individual and collective effects of slurry components. However, practical limits of time and effort and, especially, resource limitations associated with wafer processing and tool access limit the feasibility of such approaches for research-scale work. These limitations notwithstanding, the data presented above regarding the transition from a chemically-dominant to a mechanically-dominant
regime elucidates the key dependencies of the CMP process on the individual slurry components and provides a clear, if not altogether complete, guide to the impact of slurry components on post-CMP electrical performance of Cu BEOL test structures.
References:

CHAPTER 6
CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

This work investigated, developed and evaluated Cu CMP slurry formulations based on novel ANW nanoabrasives with three basic chemical components: complexing agent, passivating agent and an oxidizing agent. The work demonstrated that a relatively robust and well-performing Cu CMP slurry formulation could be constructed which exhibited promising performance on 300mm patterned BEOL wafers. Specific interactions between the chemical components and the physical components of the ANW Cu CMP slurry formulation were investigated and a regime for balanced chemical and mechanical Cu CMP removal mechanisms was identified. Furthermore, the polishing performance of the nanoabrasive slurries became more comparable to that of commercial slurry as the concentration of the complexing agent decreased and the concentration of the alumina abrasive increased.

It is concluded that the ANW nanoabrasive monodispersity and reduced particle size lead to better polishing performance of the slurry and the ability to reasonably planarize 300mm patterned CMP test structures with a relatively simple chemical formulation. This better performance in turn translated to good electrical performance of the patterned wafers. The ANW nanoabrasive-dominant slurries also had a better selectivity for copper. Based on this work it is concluded that reduced nanoabrasive particle sizes seem to favor higher relative concentrations, especially for slurries, in which the copper removal was predominantly mechanical.
A direct correlation was established between the basic components including nanoabrasives, complexing and passivating agents in the slurry to the dishing, erosion and electrical performance of the patterned wafers. A reduction in the static etch rate of the ANW slurries correlated with reduction in dishing of the 100 and 25 micron features on the patterned wafers, proving that investigation and understanding of the basic chemical components in a copper CMP slurry is a necessity for optimization of the CMP process. For example, SER data in Chapter 3 showed that when the static etch rates reduced from ~2500 Å/min for the formulation containing 0.0005M BTA to ~500 Å/min for the formulation containing 0.002M BTA, the dishing also reduced from ~ 2200 Å to ~ 500 Å for the 25 micron features.

6.2 Future Directions

6.2.1 Additional 300mm patterned wafer experiments to improve electrical performance

As discussed in Chapter 4, there was residual copper left on the patterned wafers polished with ANW Alumina Slurry, which caused severe shorting. The over-polish time (additionally polishing after end point) for the patterned wafers polished with ANW Alumina slurries was between 10 to 20 seconds, whereas the over-polish time for the patterned wafer polished with JSR slurry (commercial slurry) was 40 seconds. So, additional polishing experiments of patterned wafers, with different end point timings, using ANW Alumina slurries, are necessary to improve the electrical performance and reduce the shorting on these wafers.
6.2.2 Investigate the discrepancy between 200mm and 300mm tools

As was discussed earlier in this work, there was discrepancy in the copper material removal rate values between the 200mm polishing tools and the 300mm polishing tools. The material removal rate values obtained on the 200mm polishing tools did not translate directly to the 300mm polishing tools. Whether this discrepancy is a result of tool configuration or is a function of the nanoabrasive slurries needs to be investigated.

6.2.3 Investigation of the role of nanoabrasive composition on 300mm patterned wafer polishing performance

In this work, the novel nanoabrasive particles which were used to formulate ANW slurries were of a single composition, namely colloidal alumina of average particle size of 50 nm. But single abrasive slurries have difficulty in meeting the often conflicting demands of polish rates, material selectivity and excellent surface quality. If the properties of soft abrasives of silica are somehow combined with hard abrasives like alumina, then the wafers polished with such slurries would have high removal rates as well as good surface quality. An example could be formulating slurries with composite particles having an alumina core with a silica shell. Figure 6.1 shows the schematic of composite particles of a wafer polished with such composite particles.

![Composite particles schematic](image)

**Figure 6.1 Schematic of polishing with slurry containing composite abrasives [1].**
The effect of nanoabrasive particle composition on copper material removal rates, endpointing, dishing and erosion has to be studied and analyzed in order to develop slurries which would give the best polishing performance. So, future experiments should consist of polishing copper blanket and patterned wafers with slurry formulations consisting of nanoabrasives of different sizes and compositions to arrive at a size and composition which gives the best polishing performance and in turn good electrical test results.
References